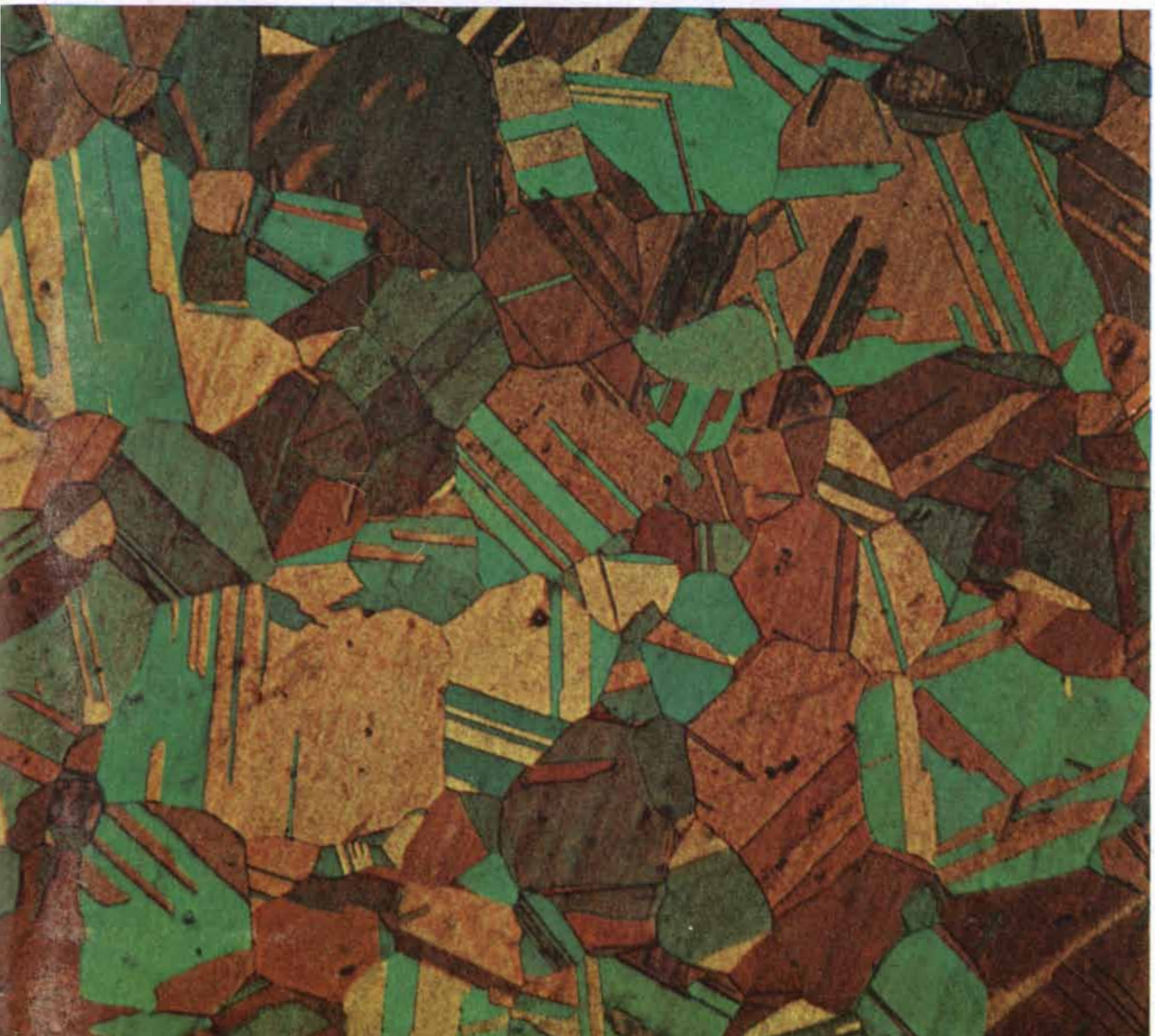
# SCIENTIFIC AMERICAN



MATERIALS

SEVENTY-FIVE CENTS

September 1967

# How First National City Bank helps mining companies to develop financial strategies, conserve their capital, evaluate acquisitions...

## ...and get 9 other services that may give you some ideas for your company.

**1. Develop financial strategies**

Worldwide borrowing: where, when, how, how much? First National City Bank's detailed, up-to-date information about the resources and policies of government and private lenders gives mining company managements an overall strategic view of the financial opportunities open to them in the U.S. and all over the world. And the bank itself acts as a lender in project financing, from drawing-board stage to production.

As a result, mining companies are able to use funds from diverse sources in global, long-range financial planning.

**2. Conserve capital**

Developing new mines, and buying complex new machinery and equipment, has meant sharply increased capital expenditures for mining companies. Citibank has worked out many different types of equipment leasing plans to help these companies conserve capital.

**3. Evaluate acquisitions**

Specialists of Citibank's Minerals and Mining Department analyze financial pros and cons for companies considering acquisition of mining properties or other companies. The bank has designed financing plans and provides substantial funds for such purchases. Where it is secured by the ore reserves acquired, the loan is often on a non-recourse basis to the buyer.

**4. Expedite overseas loans**

Mining companies often make substantial loans to their overseas subsidiaries. Sometimes, however, the bank has been asked to refinance these loans on short notice, and has set up a loan for the subsidiary within hours, repaying the parent company.

**5. Maintain pension trusts**

Citibank is a trustee for pension plans for salaried and hourly employees of several mining companies.

**6. Transportation**

The mining industry has made dramatic improvements in transportation of ore and concentrates. First National City helps finance new and improved bulk carriers, barges, hopper cars and trucks for many companies. We even helped a foreign airline active in serving the mining industry to get aircraft and spare parts.

**7. Transfer stock, etc.**

Citibank is transfer and dividend-paying agent and registrar for the preferred and common stock of many companies in the mining industry.

**8. Find money sources overseas**

Mining is international, and so is First National City. Our unique organization of branches, affiliates and correspondent banks around the world matches the mining industry's need for sources of local information and on-the-scene banking assistance.

For example, a Citibank overseas branch knew that a U.S. company had recently received a large payment in local currency for the sale of a subsidiary. The bank promptly brought together the company and a mining firm that needed funds in the foreign currency.

**9.-12. Important routine services**

Citibank supplies Travelers Checks on consignment; holds company securities in safekeeping; handles foreign exchange; invests company funds in C.D.'s, Treasury Bills, bankers' acceptances, commercial paper, etc.

**We welcome inquiries about the many ways your company can use First National City Bank.**

**FIRST NATIONAL CITY BANK**

399 PARK AVENUE, NEW YORK, N.Y. 10022 · MEMBER FEDERAL DEPOSIT INSURANCE CORPORATION

# Texas Instruments challenges traditional thinking about materials.

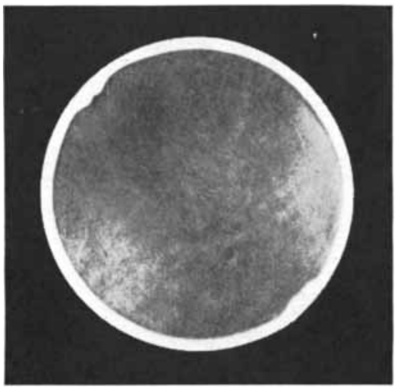
You have an example of our challenge in your pocket. A new dime or 25-cent piece. Take it out and look at it. It's a metal sandwich: cupronickel, a copper core, cupronickel again.

That sandwich is helping ease a major economic problem—the short supply of silver.

And it's only one of TI's new materials systems—combinations of materials that promise to revolutionize the old ways of using monolithic metals.

### Clad vs. monolithic

Ever since man melted copper and tin to make bronze, he has solved materials problems with monolithic alloys. The world's appetite for alloys that use high proportions of strategic metals has caused recurring shortages and higher metals costs.



Copper-clad aluminum wire uses 90% less copper.

But there's another way to combine metals for optimum properties. It's cladding, the metallurgical bonding of two or more metals at the atomic level.

Clad metals have revolutionary advantages. They can be engineered to use just enough critical material—and reduce the use of high-cost metals like gold and silver. They can significantly stretch the utilization of a metal in short supply, like copper. They can even be made to solve costly assembly problems. And they can behave like wholly new materials, with a set of useful properties not otherwise available.

### Markets worth billions

Metal cladding experience at TI goes back 50 years. Now, new technical breakthroughs and expanding facilities allow us to tackle materials markets worth billions. Here are a few examples:

*Copper-clad aluminum wire.* Competitive in the whole spectrum of copper-wire products. Costs less. Joins, runs the same as solid copper, has a comparable flexlife. Can be redrawn on same equipment as solid copper.

*Architectural clad metals.* An entire family of clad metal materials systems; copper-clad stainless steel, stainless steel-clad aluminum, and copper-clad aluminum to replace solid copper and stainless in roofing applications. Also bronze- and brass-clad steel for windows, doors, curtain walls, architectural fittings and lighting fixtures.

*Rotary printing plates.* Zinc-clad aluminum. Combine printing surface of zinc with light-weight and non-stretch properties of aluminum, and cut press stoppages for plate changing.

*Automotive materials.* Stainless-clad aluminum trim, brass-clad steel radiator tanks and fins, clad metal specialty products in electrical and mechanical subsystems.

*Wearing surfaces.* Silicon carbide or titanium carbide on wearing surfaces. Only diamond surpasses these materials in density and hardness.

Clad metal coins stretch world supply of silver.

*Coinage.* New materials for any free-world treasury.

### Potential almost untapped

Texas Instruments is built on new ways to do things better. This one—a way to create new materials—makes us a primary materials supplier with a market potential still almost untapped.

Contact us for the answer to your materials problem. Write Marketing Manager, Materials Division, Texas Instruments Incorporated, Attleboro, Massachusetts 02703.

TEXAS INSTRUMENTS
INCORPORATED

Established 1845 **SCIENTIFIC AMERICAN** September 1967 Volume 217 Number 3

## ARTICLES

## DEPARTMENTS

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## THE COVER

The photomicrograph on the cover symbolizes the theme of this issue of Scientific American: materials, with special reference to their fundamental nature and the properties shared by all of them in various degrees. The photomicrograph shows the grain structure of brass, enlarged some 250 diameters. It was made with the Zeiss camera microscope "Neophot 2."

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# S. D. Warren is looking for a co-inventor.

We don't care who you are: an individual, a company, a non-profit research organization, or a government.

If you have some new thoughts about making something out of paper, we're spending several thousand dollars on this ad to find you.

We can't tell you exactly what we'd be interested in. But maybe this will give you some idea:

S.D. Warren is a paper company that specializes in *coated* papers. We were among the originators of coated printing paper (which is what this magazine is printed on).

But we've also come up with other ways to use coatings:

Coated release papers. Manufacturers spread liquid plastic on them, peel the paper away, and get a very realistic pattern in plastic film.

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Photographic paper. Heat developable, no chemicals needed. Their potentials are in portrait proofing and lithographic plate proofing.

Improved electrostatic papers. These papers use organic photoconductors.

Magnetic coated dictation belts. The standard dictation belts are made of plastic and sell for as much as 65¢. Ours are made of paper and, according to our tests, could sell for about 15¢.

But there must be a hundred things we haven't done, haven't thought of, and probably won't do. Unless somebody comes to us with a proposal.

That's where you come in.

Write the S.D. Warren Co.,
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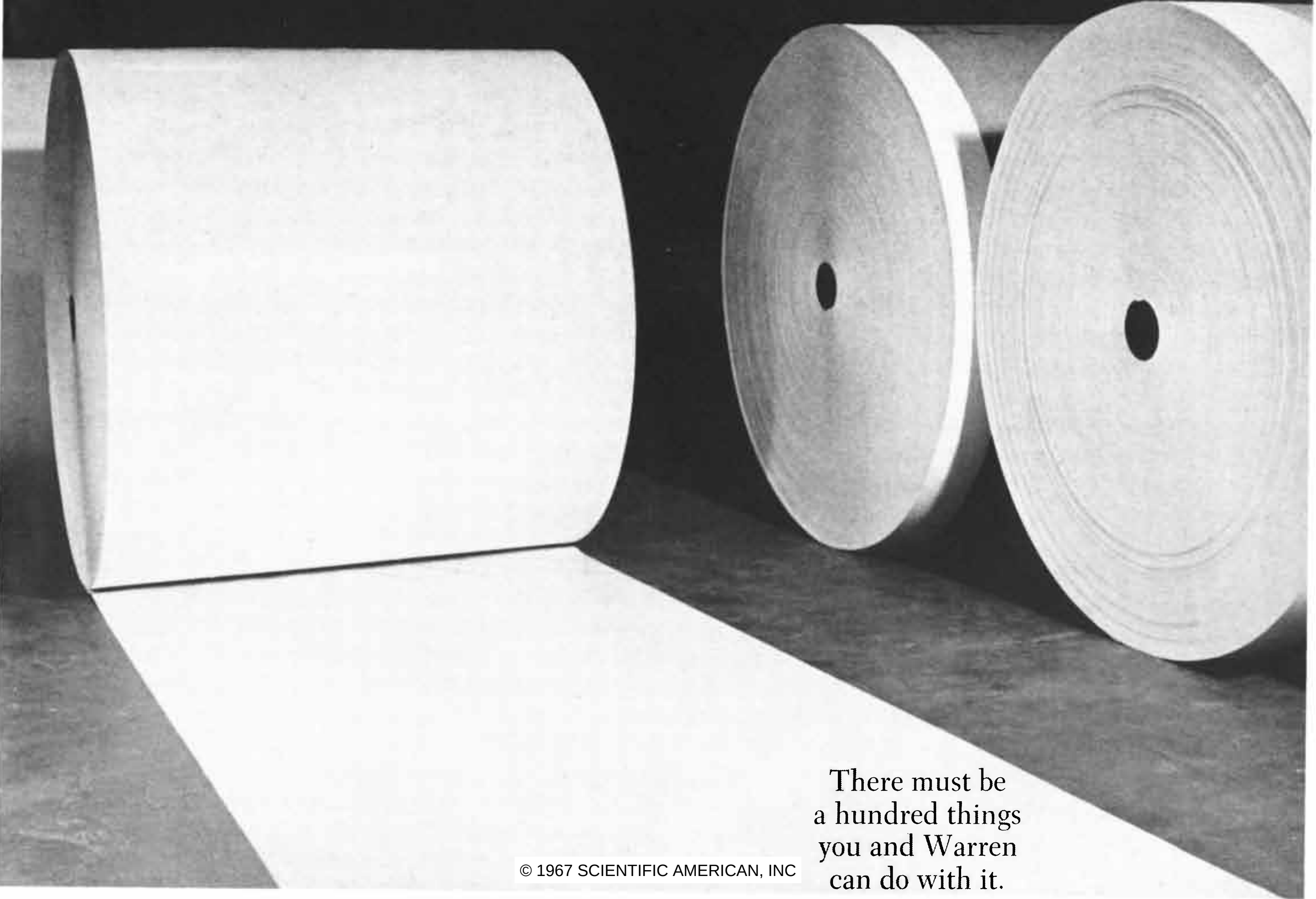
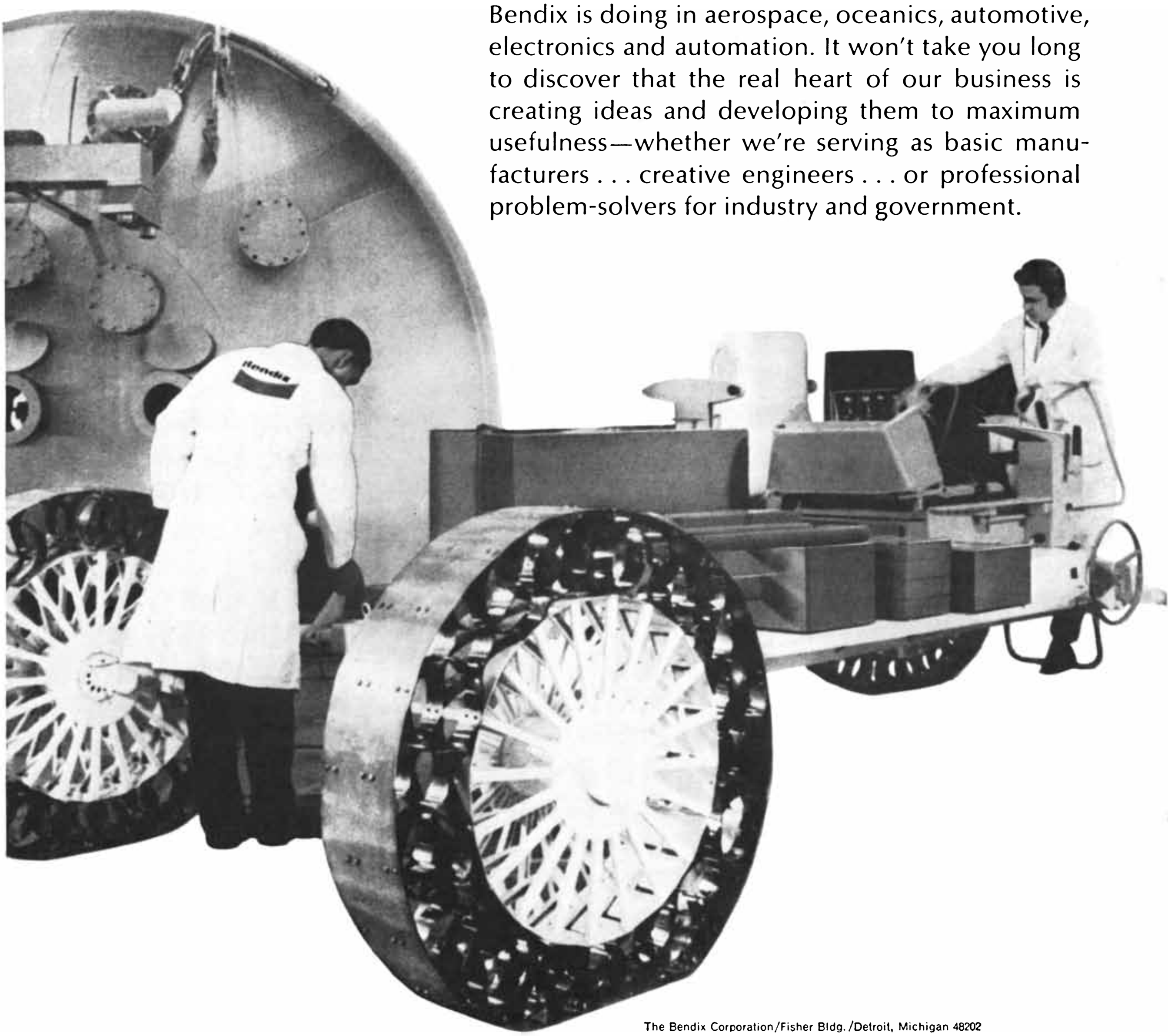
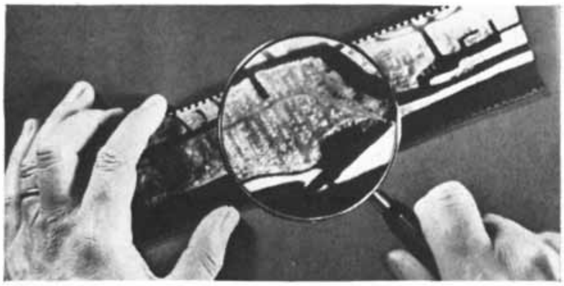
warren

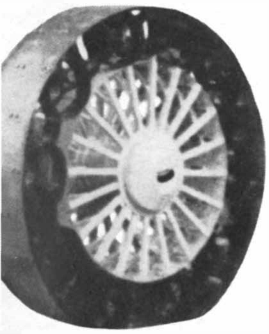


There must be
a hundred things
you and Warren
can do with it.

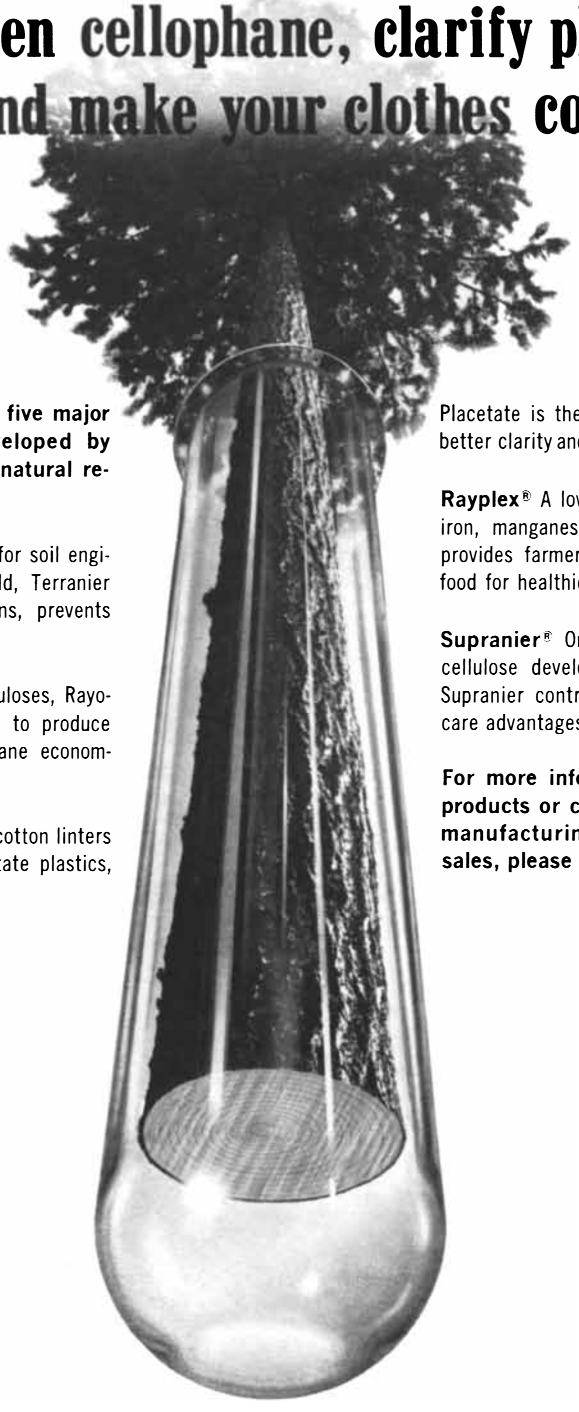

Bendix


FLUIDIC DIGITAL ADDER





After they got the tree
into the test tube,
our chemists discovered how to stabilize soil,
strengthen cellophane, clarify plastics,
aid crops and make your clothes comfortable.



**Take a few minutes to read about five major chemical products recently developed by Rayonier through the diversity of natural resources chemistry.**

**Terranier®** A chemical grouting agent for soil engineering in the heavy construction field, Terranier strengthens unstable ground formations, prevents water seepage, controls erosion.

**Rayofilm®** One of many Rayonier celluloses, Rayofilm enables cellophane manufacturers to produce thinner yet tougher sheets of cellophane economically.

**Placetate®** In direct competition with cotton linters as a basic raw material for clear acetate plastics, Placetate is the new chemical cellulose that offers better clarity and color than previous wood celluloses.

**Rayplex®** A low-cost micronutrient carrier for zinc, iron, manganese, copper and magnesium, Rayplex provides farmers with an economical natural plant food for healthier, more proficient crops.

**Supranier®** One of several specialized grades of cellulose developed for high performance rayons. Supranier contributes to the comfort and ease-of-care advantages important to modern fabrics.

**For more information on Rayonier chemical products or career opportunities in chemical manufacturing, research, engineering and sales, please write.**

RAYONIER

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We made a raincoat
for a bee.

Not just an ordinary raincoat either.

It's a skintight plastic coat so thin you would never know it's there. Yet it covers the bee completely, right down to the individual hairs on the bee's knees. It was done to protect specimens in a natural history museum.

But we didn't spend 12 years on a new plastic just to protect bees. We developed parylene to protect things *like* bees—fragile, complex things so intricate in shape they are next to impossible to coat.

For instance. Each tiny grain of a highly reactive chemical can be protected to provide stability in the presence of gases or moisture. Tiny electronic capacitors, just one-fifth the size of previous types, can be insulated with a coating as thin as eighty-millionths of an inch.

Union Carbide finished the initial development work on parylene in February 1965. Until then, there was no comparable way to encapsulate delicate objects.

Parylene is one of the latest, most sophisticated new plastics to result from the exploring, researching and discovering that is always going on at Union Carbide. The same scientific inventiveness that has put Union Carbide into a greater variety of plastic products than anyone else. Ever.

**UNION CARBIDE**
THE DISCOVERY COMPANY


pad
pad
bad
rap
ram
Pam

# He is learning to read from a computer. Someday a single computer will give individual instruction to scores of students – in a dozen subjects at the same time.

(The steels are ready whenever you are)

The computer will very probably revolutionize teaching – and learning – within a decade. It is already happening in its early stages.

Computerized instruction can practically (and pleasurably) allow each student to learn more, faster, but always at his own pace. Individualized instruction, the ultimate dream of effective education, is well within the range of possibility. And, by spurring students to think experimentally, computers may eventually spark imaginative, independent thinking.

Computerized education will require huge tonnages of steel. In addition to computers themselves, this method of education will necessitate construction of new buildings, special communication systems, new steel furniture, movable interior steel walls and partitions. Required will be improved sheet and bar steels, and untold miles of highly dependable steel pipe and tubing.

Republic Steel has anticipated the steel needs of the future. New mills, new processes, and intensified research and development will assure that the new weight-saving, more durable steels will be ready when needed.

At this moment, the long reach of steel from Republic is probing into every area where man's imagination needs it – from schoolroom to satellite, from the heartbeat of man to the drumbeat of defense. Republic Steel Corporation, Cleveland, Ohio 44101.

**You Can Take the Pulse of Progress at**

**REPUBLIC STEEL**

CLEVELAND, OHIO 44101

Pupil at Brentwood School, East Palo Alto, California, points to the word on right screen that matches picture on left screen. The teacher monitoring 16 pupils' stations has just praised him for his good work.

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# Ford Motor Company research leads to breakthroughs in materials development

## RADIATION-INDUCED POLYMERIZATION

Polymerization initiated by high-energy electrons is being explored by Ford Motor Company scientists. Results reflect the unique mode of interaction between high-intensity, high-energy electrons and organic molecules.

Optimum reaction rates at a given radiation intensity are noted for solutions containing 65% ester (Figure 1). The overall rate depends both on the reactivity of the components and the steric constraints imposed on the system by the rigid network produced. Since the reaction occurs at room temperature, below the glass transition point of the network, the growing chains are not sufficiently mobile to accommodate the configuration predicted by the established copolymerization theory. The structure depends instead on the concentration of double bonds at the instant of radiation.

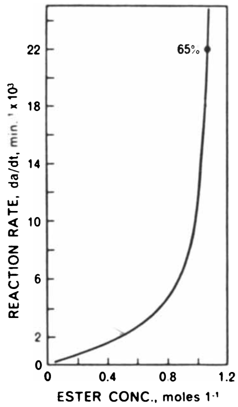


Figure 1. Rate of polymerization as a function of ester concentration; commercially useful systems are in the 65% ester range (Burlant and Hinsch, J. Polymer Science, 2,2135 (1964).)

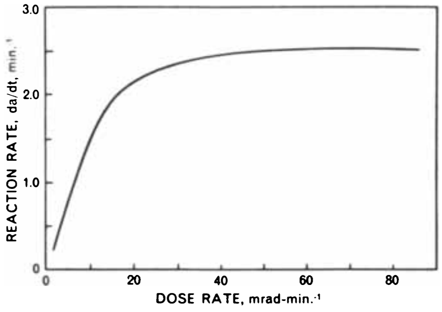


Figure 2. Rate of polymerization as a function of radiation intensity for 65% ester solutions; optimum rate occurs with an electron beam intensity of 40 MRAD-min-1 (Burlant and Hinsch, J. Polymer Science, 3,3587 (1965).)

As the beam intensity becomes greater (Figure 2), the rates increase linearly; network formation occurs within small isolated volume elements swept out by the incident electrons. At higher intensities, volume elements overlap, and efficiency of the reaction is reduced. These studies led to a major innovation in paint-curing technology. Chemical structures exhibiting maximum sensitivity to radiation were designed and synthesized. The result is a coating that cures in seconds. And at room temperature.

## ADVANCED THERMIONIC EMISSION MICROSCOPE

In order to eliminate the mechanical problem associated with thermionic emission microscopy, our Scientific Research Staff designed and built a new thermionic emission microscope. This instrument has two lenses, a combination electrostatic-electromagnetic objective lens and a magnetic projector lens. It is capable of magnifications of from 78 to 6000 diameters with a resolution in the order of 300A over the entire magnification range, and can be used to study reactions in the temperature range of from 450° to 2300°C.

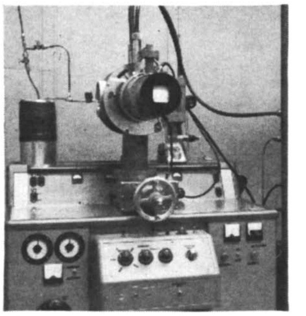


Figure 1. View of the thermionic emission microscope. Console contains the microscope chamber, vacuum system lens power supplies and the high voltage power supply.

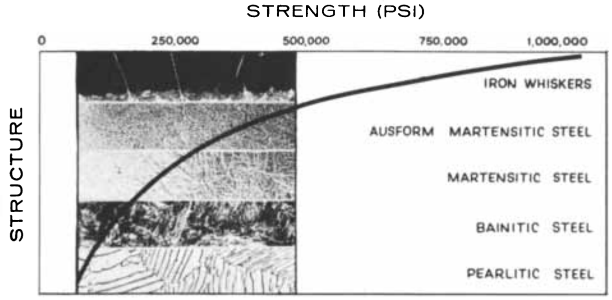
The vacuum system has an ion-getter type of high vacuum pump and is capable of operating at $10^{-8}$torr with the specimen at room temperature and at $10^{-7}$torr with the specimen at 1600°C. Also available is a temperature measurement and control system capable of measuring specimen temperature to better than ±5°C. The specimen at a potential of 50 KV required designing a system which is floating and isolated at this voltage. Specimen movement is controlled electronically and a measuring system devised so that the exact area of the specimen which is being viewed on the microscope can be determined.

With an instrument of this kind, it is possible to study phase transformations, recrystallization and sintering mechanisms, as well as fundamental studies of electron emission.

Studies made with this microscope should lead to a better understanding of the mechanism of the allotropic transformation in steel and should eventually lead to production of better alloys.

## DEVELOPMENT OF AUSFORMED STEELS

Research in strengthening mechanisms resulted in the introduction of ausformed steels. Mechanical working of metastable austenite prior to transformation to martensite resulted in tensile strengths over 450,000 psi with high ductility. The discovery of a stable dispersion of fine alloy carbides in the austenite after deformation was an important contribution to the understanding of the strengthening mechanisms.



Ausform steels, reflecting the fine martensitic grain size, are stronger in bulk samples and have better engineering properties for many applications than conventionally treated steels.

These steps are required in ausforming: 1. Austentize to dissolve carbides; 2. Cool austenite rapidly to 800-1200°F. to avoid transformation; 3. Deform with 50-90% reduction in area by forging, rolling or extrusion; 4. Quench and temper. The process is applicable to any steel with austenite sufficiently stable to allow heavy deformation without transformation. This opens the way to commercial applications and the use of lower alloy, more economical steels.

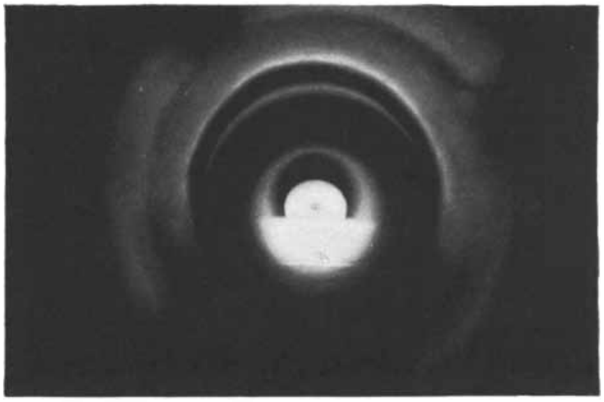
## NEW CUTTING TOOLS WITH 10 TIMES LONGER LIFE

The problem of forming a strong bond between dissimilar materials such as metals and ceramics, led to extensive study of the wettability in liquid-solid systems.

In the case of metal-ceramic composites, wetting is studied at Ford Research by placing a piece of metal on a flat ceramic and heating the combination until the metal melts. When molten, the metal forms a specific drop shape, governed by gravitational and surface forces. The extent to which the liquid will wet the solid is a measure of the adhesion between the two materials.

Working with many metals and ceramics in the course of these wettability studies, Ford scientists developed an exceptional material. This synthetic composite consisted of titanium carbide bonded with nickel and molybdenum.

Further testing and studies showed that this material had a high hardness and strength which seemed very well adapted to use as tool bits for metal cutting.



Bright central area is metal melting on a ceramic base in Sessile Drop Furnace. Photo taken at Ford Research Laboratories.

In comparison with the hardest tool bits previously developed, this new material offered a service life approximately 10 times longer.

## DEVELOPMENT OF NEW TYPE SOLID STATE SPECTROMETER

Physicists from the Scientific Research Staff recently developed a device to demonstrate a new phenomenon in solid state physics.

The device, called a Solid State Spectrometer represents a significant development in our ability to detect microscopic amounts of chemical materials.

The phenomenon, known as inelastic electron tunneling, is capable of seeing minute amounts of molecular material which are in the adsorbed state.

In the experiment, a spectrum was obtained that was characteristic of the particular molecular species. The spectra reflect the internal molecular vibrations.

Traditional methods of obtaining this information have used infrared light of varying wave length to probe the sample. In this new method, electrons take the place of light waves and the voltage applied to drive current through the insulating film takes the place of wave length.

Compared to infrared absorption, electrons are effected more than a thousand times more efficiently in this method, which accounts for its high sensitivity.

Besides providing a new analytical tool, the Solid State Spectrometer permits experimentation on molecules in the adsorbed state, which will be of importance to the field of surface chemistry. It also represents an advance in understanding the basic processes related to electron tunneling in the solid state.

Ford

# PROBING DEEPER FOR BETTER IDEAS

PATENT NO. 3,199,002: SOLID STATE CIRCUITS WITH INSULATED CROSSING LEADS

# LETTERS

Sirs:

In connection with your article "Geological Subsidence" [Scientific American, June] it may interest you to know that in Germany such a subsidence is being induced on purpose. Near the great port of Duisburg-Ruhrort the water level of the Rhine has sunk gradually by several meters because of erosion, so that the level of the water at the port has sunk accordingly. Now, under the port there is a coal mine. By letting the galleries of the mine collapse as they are worked out, the entire port, including its piers and buildings, is being made to sink appropriately.

Wilhelm H. Westphal

Technische Universität
Berlin

Sirs:

You may be interested to hear that the algorithm published in your department "Mathematical Games" [May] for finding the day of week, given the date, has been incorporated into the Federal Aviation Agency's semiautomated air traffic control system.

Previously the computer operator was required to supply the day, along with the date, at start-up time. The simplicity of the algorithm has made it practical to relieve the operator of this small burden.

Henry S. Warren

John E. Mignosa

International Business Machines
Corporation
Atlantic City, N.J.

Sirs:

Billy P. Glass and Bruce C. Heezen are to be warmly congratulated for adding an important new weapon to the geological detective's kit for unraveling the mysteries of Lady Earth's enigmatic past ["Tektites and Geomagnetic Reversals," Scientific American, July]. They present, however, a stratigraphic puzzle of their own, which they leave unanswered. The puzzle is that in four of the five cores of deep-sea sediments they exhibit, the microtektites *all* lie *above* the layer that marks the magnetic reversal—in two of the cores by a considerable distance. Shouldn't this mean that the event that distributed the microtektites occurred *after* the magnetic reversal, perhaps by a period of tens of thousands of years? If the microtektites were deposited in a single event and then subsequently diffused through the sediments, should they not appear to be diffused on both sides of the magnetic reversal layer?

If, on the other hand, the fall of microtektites covered a rather wide range of years, as would appear from the diagrams presented, is it not strongly suggested that they should cover considerably *more* than a tenth of the earth's surface—that, indeed, they should be global in extent? Have similar cores taken, say, from the West Coast of America, or from the Atlantic, failed to show the presence of these intriguing crystal balls? It is clear that the geographical extent of such a field cannot be described entirely by where the samples are found, without also knowing where they are *not* found.

Leo L. Baggerly

Professor of Physics
Texas Christian University
Fort Worth, Tex.

Sirs:

We agree with Professor Baggerly that the occurrence of the microtektite layer

**Scientific American,** September, 1967; Vol. 217, No. 3. Published monthly by Scientific American, Inc., 415 Madison Avenue, New York, N.Y. 10017; Gerard Piel, president; Dennis Flanagan, vice-president; Donald H. Miller, Jr., vice-president and treasurer.

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**Change of address:** please notify us four weeks in advance of change. If available, kindly furnish an address imprint from a recent issue. Be sure to give both old and new addresses, including ZIP-code numbers, if any.

above the reversal does seem to indicate at first glance that the microtektites fell later than the reversal of the geomagnetic field. But if one were to assume that the microtektites did indeed fall later than the reversal, then one would expect the distance between the center of the microtektite layer and the reversal boundary to be a function of sedimentation rate. This is not observed. For example, in core V19–153 from the Wharton Basin the sedimentation rate is nearly three times as great as in core RC8–53 from the Australia Basin; however, the microtektite layer in V19–153 is as close, if not closer, to the reversal as it is in RC8–53. Therefore one must look for another reason to explain the extension of the microtektite layer above the reversal.

The sediments near the sediment-water interface are unconsolidated. Following a reversal of the earth's field the top 10 to 30 centimeters of sediment may acquire a magnetic polarity opposite to that prevailing at the time of deposition. In other words, there is a depth at which the magnetic polarity of the sediment becomes fixed. This causes the entire magnetic stratigraphy to be slightly shifted down in the core by some depth that varies from core to core depending on sedimentation rate, lithology, bottom currents and so on.

There is other evidence for the downward shift in the magnetic stratigraphy. First, the top 10 to 50 centimeters of nearly all cores are unstable. Second, if one plots reversal depth against time of reversal for cores with long magnetic stratigraphies, one finds that the best-fitting line through the points falls short of the origin (zero depth) by about 10 to 50 centimeters, which again indicates that the magnetic stratigraphy is shifted down in the cores.

Professor Baggerly's second comment, that the geographical extent of the microtektite field cannot be determined only by where the microtektites are found without knowing where they are not found, is well taken. More than 30 cores penetrating the 700,000-year-old sediment layer have been examined. Of these only nine contain the microtektites and all nine are within the microtektite field outlined in the illustration on pages 34 and 35 of our article. The remaining cores are from outside this area (from the North Pacific and South Pacific, Indian and Antarctic oceans and the South Atlantic) and do not contain any microtektites near the 700,000-year-old level. The geographical extent of the 700,000-year-old microtektites is therefore fairly well known, although additional cores will

# What's an ad for softwood plywood doing in a magazine full of information on far-out space age materials?

# Maybe it's to remind you of a lot of useful properties you've either forgotten about or never even knew.

Like its ancestor, good old wood, plywood has certain desirable qualities that many plastics and metals lack. Such as: predictable strength under stress. Resistance to chemicals. Natural insulation. Easy fastening. And absolute refusal to rust or corrode.

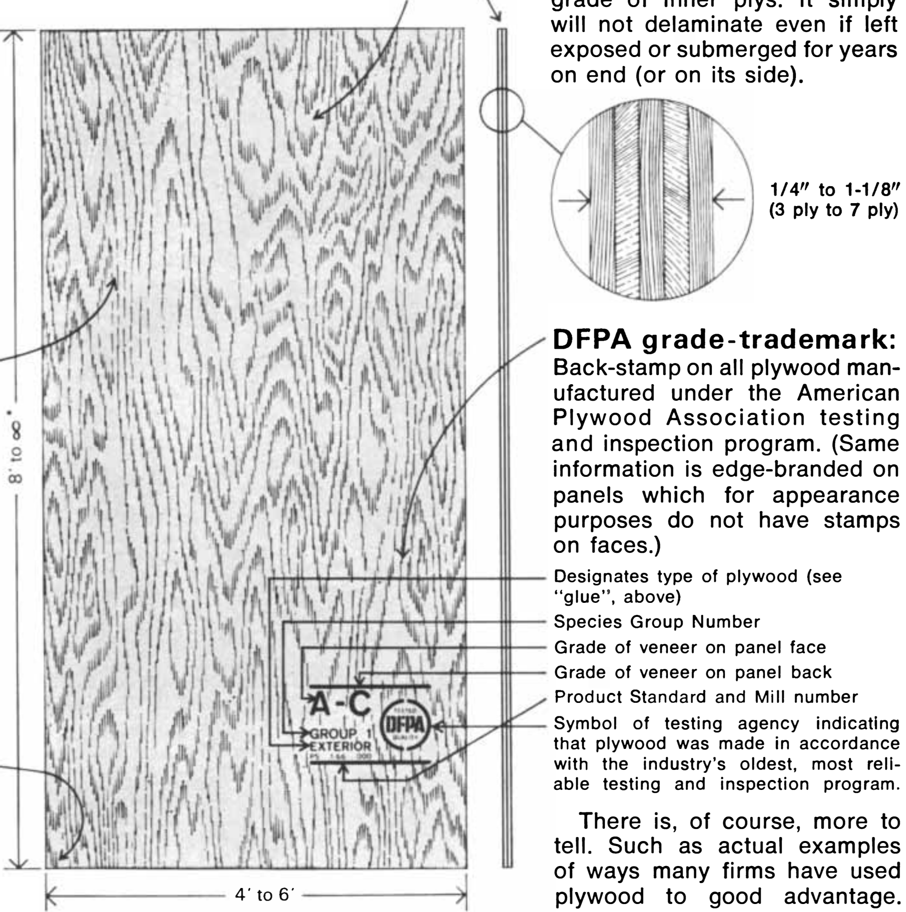
But in plywood, man and technology have improved on nature, to give this surprisingly versatile material its own set of unique advantages. You know the splendid job plywood does in construction. But have you seriously considered its suitability for hundreds of demanding applications in the industrial sector? From acid tanks to mock-ups of the SST, it's worth considering. So, in 345 words, here's plywood:

**Strength:** Astonishing. Pound for pound, actually stronger than steel. Thanks largely to its cross-laminated construction, plywood excels in impact resistance, stiffness, compression and flexural strength. E.g.: ultimate load on a 3/4″ panel, supported on 16″ centers, and through a typical forklift wheel, is 5,200 pounds. For more on plywood's strength and test descriptions, see Product Designer's Guide, offered below.

**Corners:** Square. Everything about plywood is square and true. It's designed by engineers for engineers.

**Standard panel size:** Big. Width, 48″. Length, 96″. Thickness, from 1/4″ to 1-1/8″. Oversized panels to 72″ by 144″ available. Theoretically, a scarfed panel may be made a mile long — if you can figure out how to carry it away.*

**Surface:** Your choice, among some 50 textures, patterns, or special coatings impervious to natural and unnatural hazards. Including: Sanded. Unsanded. Preprimed. Prepainted. Hardboard faced. Medium Density Overlaid (smooth, flat, paintable). High Density Overlaid (hard-surfaced, abrasion-resistant, especially resistant to acids). Aluminum-faced. Vinyl coated. Fiberglassed. Epoxy coated. Polyvinyl fluoride overlaid. And many, many more.



**Species:** Used to be mostly Douglas fir. Now, improved knowledge of wood properties and how to combine and balance them permits use of some 30 species, grouped according to stiffness. (Group number appears on every panel.)

**Glue:** Exterior or Interior. Interior type plywood, made with highly moisture resistant glue, is used where the product won't encounter prolonged dampness or exposure. Exterior type is made with 100% waterproof glue and with a higher grade of inner plys. It simply will not delaminate even if left exposed or submerged for years on end (or on its side).

**DFPA grade-trademark:** Back-stamp on all plywood manufactured under the American Plywood Association testing and inspection program. (Same information is edge-branded on panels which for appearance purposes do not have stamps on faces.)

There is, of course, more to tell. Such as actual examples of ways many firms have used plywood to good advantage. And more on plywood itself: Its gas permeability (low), hygroscopic and thermal changes (minimal), dielectric properties (when dry), chemical resistance (superb). But you'll find it all in these publications: "Guide to Plywood for Product Designers" and "U. S. Product Standard PS 1-66 for Softwood Plywood." Yours by writing us at Tacoma, Washington 98401, Dept. SC.

AMERICAN PLYWOOD ASSOCIATION

Plywood quality-tested by the Division For Product Approval

TESTED DFPA QUALITY

help to determine the details of the distribution.

Bill Glass

Bruce C. Heezen

Lamont Geological Observatory
Palisades, N.Y.

Sirs:

As a computer manufacturer, we read Jan A. Rajchman's article "Integrated Computer Memories" in your July issue with considerable interest. We feel the article is a lucid survey of the computer-memory field, with one notable exception. We were surprised to find in the author's discussion of plated-wire memories no reference to the National Cash Register Company's plated-wire magnetic thin-film rod-memory work.

NCR is a pioneer in the field of cylindrical, that is, "plated wire," thin-film magnetic-memory elements. The first public disclosure of this work was in a technical paper presented to the November 1958 Magnetics Conference in Philadelphia. (See Meier, Donal A. "Millimicrosecond Magnetic Switching and Storage Elements," *Journal of Applied Physics,* Vol. 30, pages 45S–46S; April, 1959.) Coincident with the conference NCR held a press conference on the new rod-memory developments that resulted in widespread national and international publicity. Since then numerous additional technical papers have been published documenting NCR's progress in plated-wire-memory technology.

In September, 1965 (a year prior to the announcement of the rod memory discussed in the article), NCR delivered the first 315 RMC (rod-memory computer) to Rich's department store in Atlanta. This represented a historic first, since the 315 RMC was the first commercial computer to use an all-magnetic thin-film plated-wire internal memory. Since then more than 60 of the 315 RMC systems have been installed in a wide variety of commercial applications domestically and abroad. Obviously the economy of such systems is not open to question, as Dr. Rajchman suggests. Also, in July of 1963 NCR delivered to Raytheon a very-high-performance plated-wire rod memory. This memory was subsequently incorporated into a military system that is in operation today.

Robert G. Chollar

The National Cash Register Company
Dayton, Ohio

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| PROPERTIES | Teabag | Meat Casing | Mimeo Stencil | Wiping | Vinyl Backing | Electrolytic | Vacuum Cleaner Bags | Automotive Oil Filter | Automotive Air Filter | Lens Tissue | Cryogenic Insulation | Absolute Air Filtration | Drapery Heading | Ceiling Tile | Activated Carbon | Adhesive Carrier | Ceramic Fiber Paper | Disposable Clothing | Coffee Filter | Hospital Face Mask | Pad Cover Stock |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | PLIABLE TYPES |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Porosity | ● |  | ● |  |  |  | ● |  | ● |  |  | ● |  | ● | ● | ● | ● | ● | ● | ● | ● |
| Absorbency |  | ● | ● | ● | ● | ● |  |  |  | ● |  |  |  |  | ● | ● |  |  |  |  | ● |
| High Wet Strength | ● | ● |  | ● |  |  | ● | ● | ● | ● |  | ● | ● |  | ● | ● |  | ● | ● |  | ● |
| High Burst Strength |  | ● |  |  |  |  | ● |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |
| High Tear Strength |  | ● |  | ● | ● |  | ● |  |  | ● |  |  | ● |  |  | ● |  | ● |  |  | ● |
| Filtration Capacity |  |  |  |  |  |  | ● | ● | ● |  |  | ● |  |  | ● |  |  |  | ● | ● |  |
| Saturation Capacity |  | ● | ● | ● |  | ● |  |  |  | ● |  |  |  |  | ● | ● |  |  |  |  |  |
| Surface Smoothness |  |  | ● | ● | ● | ● |  |  |  | ● |  |  |  |  |  | ● | ● | ● |  |  | ● |
| Controlled Fiber Orientation | ● | ● | ● |  |  |  | ● |  |  |  |  | ● | ● | ● |  | ● |  | ● |  |  | ● |
| Controlled Filtration Efficiency | ● |  |  |  |  |  | ● | ● | ● |  |  | ● |  |  | ● |  |  |  | ● | ● |  |
| Controlled Flow Rate | ● |  |  |  |  |  |  | ● |  |  |  |  |  |  | ● |  |  |  | ● |  |  |
| Heat Sealability | ● |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |  | ● | ● |  |
| Lint Freeness | ● | ● | ● | ● |  | ● |  |  |  | ● |  |  |  |  |  |  |  | ● |  |  | ● |
| Pleatability |  |  |  |  |  |  |  | ● | ● |  |  | ● | ● |  | ● |  |  |  |  |  |  |
| Flame Retardancy |  |  |  |  |  |  |  |  | ● |  | ● | ● |  | ● |  |  | ● | ● |  |  |  |
| Thermally Insulative |  |  |  |  |  |  |  |  |  |  | ● |  |  |  |  |  | ● |  |  |  |  |
| Sound Dampening |  |  |  |  |  |  |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |
| Bacteriostatic |  |  |  |  | ● |  | ● |  |  |  |  | ● |  |  |  |  |  |  |  | ● | ● |
| Biodegradable |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | ● |
| Impact Resistance |  |  | ● |  |  |  |  | ● |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Chemical Purity |  | ● |  | ● |  | ● |  |  |  | ● | ● |  |  |  | ● |  | ● | ● | ● | ● | ● |
| Corrugatable |  |  |  |  |  |  |  | ● | ● |  |  |  |  |  | ● |  |  |  |  |  |  |
| Thermoformable |  |  |  |  |  |  |  | ● | ● |  |  | ● |  | ● |  |  |  |  |  |  |  |
| Inorganic Fibered |  |  |  |  |  |  |  |  |  |  | ● | ● |  |  | ● |  | ● |  |  | ● |  |
| Stitchability | ● |  |  |  |  |  | ● |  |  |  |  |  | ● |  | ● |  |  | ● | ● |  |  |
| Washability |  |  |  |  |  |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |  |  |
| Adsorbency |  |  |  |  |  |  |  |  |  |  |  |  |  |  | ● |  |  |  |  |  |  |

With every passing day, Dexter's specialty papers and webs—we call them "Pliables*"—are solving more and more unique problems in the industrial world. These "materials systems" are literally designed and manufactured to meet specific design needs . . . to perform precise and critical functions.

Up to the present time, over 1,500 distinctly different Dexter pliables have been engineered and active work is under way on scores of new products. The table above lists only a few of the properties which can be incorporated—in virtually any combination—into specialty paper products. Some of Dexter's current pliables are shown, with their principal properties checked off.

We'd like to try to solve your materials problems, too. We thrive on unique problems because we have the capabilities to make unique materials—quickly and economically.

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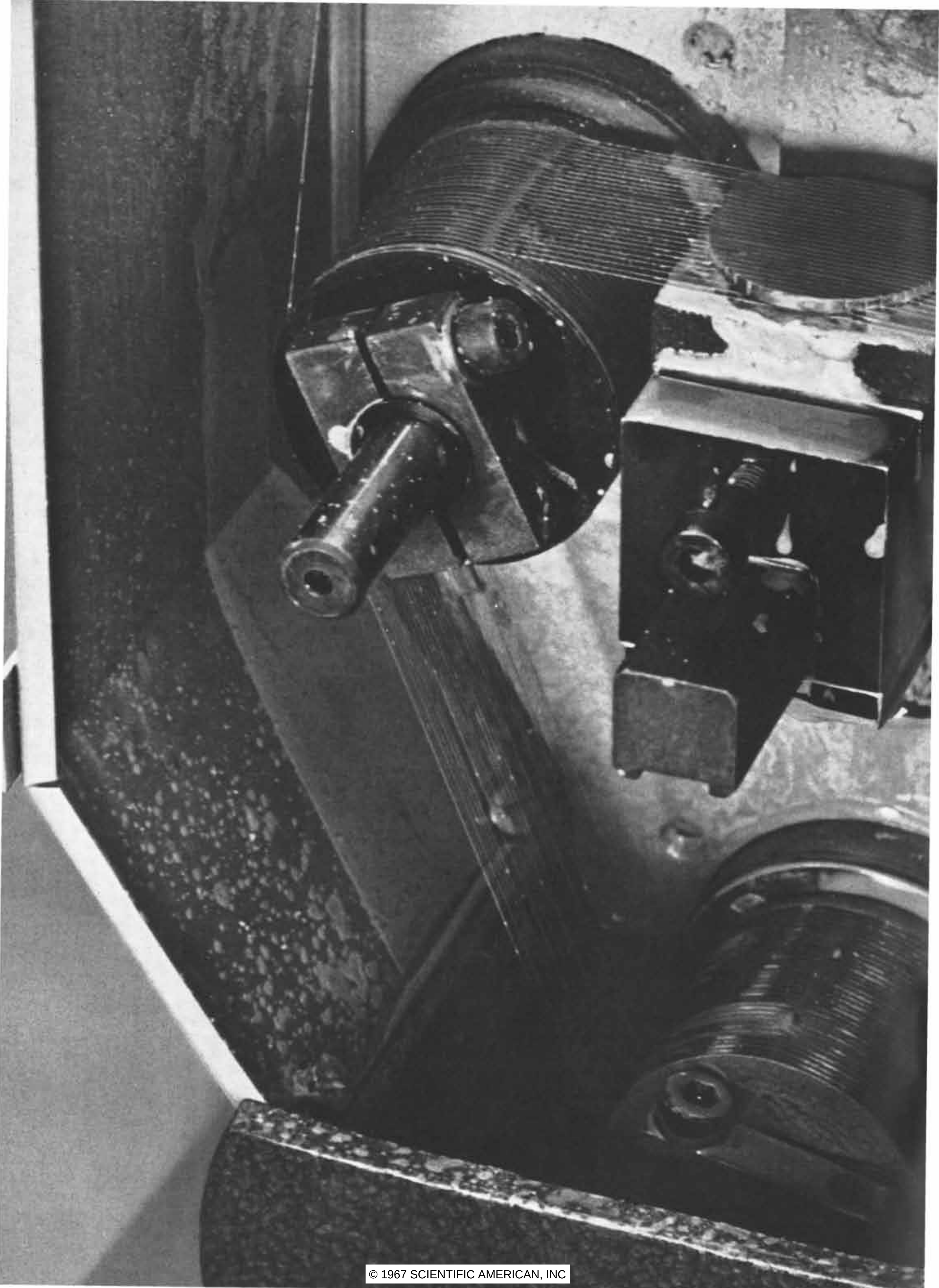

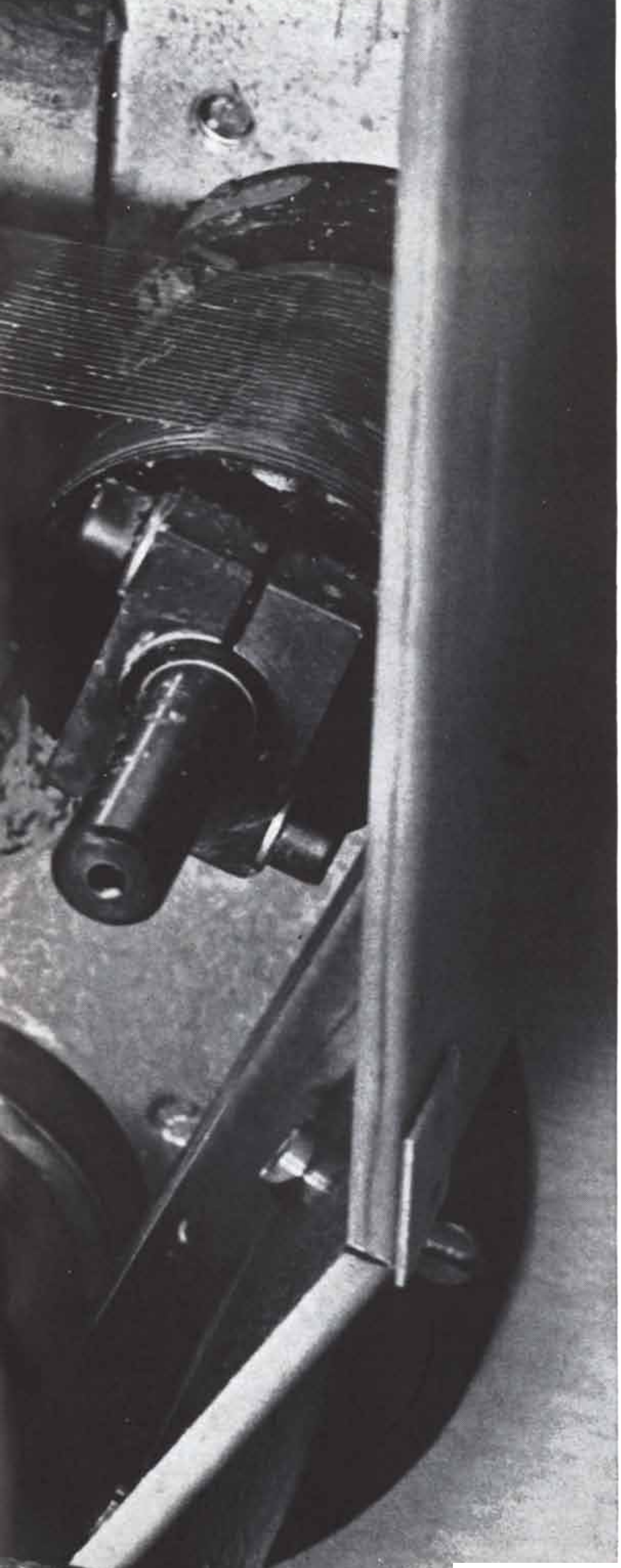

# "Cheese cutter" uses diamond dust to dice silicon wafers

Now the unmachinable can be machined.

You're looking at a device so new it still bears an unpretentious name—the Sea-Saw. Developed by Geoscience Instruments Corporation, Mt. Vernon, New York, the Sea-Saw cuts and laps silicon wafers in one fast operation instead of two slow ones.

Thin tungsten wires seesaw on spools at speeds of 50 inches per second. Through the lower spool, the wires pass through a slurry containing block-shaped diamonds 1 micron in size. The fine diamond paste adheres to the wires and cuts through the ⅛" wafer in minutes, at which point the work is rotated 90° and sawed again into minute dice.

But you don't have to mince the unminceable to take advantage of diamond tools. Manufacturers and metal fabricators all over the world are finding that diamond tools make tough jobs easy, expensive ones cheap. That's why diamond grinding wheels, dressing tools and lapping compounds are being used more and more widely.

Are you frightened by the cost of diamond tools? Forget it. If you cut, sharpen, grind or smooth anything, you can probably use diamond tools profitably. Your tool and wheel maker can show you how.

**"The Industrial Diamond Revolution"—A Technical Conference sponsored by The Industrial Diamond Association of America at Battelle Memorial Institute, Columbus, Ohio, November 13-14-15, 1967.**

**Papers will be presented on applied research, technology, use and new applications of diamonds. For information, write to: "Diamond Conference," 330 S. Wells St., Chicago, Ill. 60606.**

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# The gregarious metal

## Nickel is a friendly metal. Affable. A joiner. A good mixer.

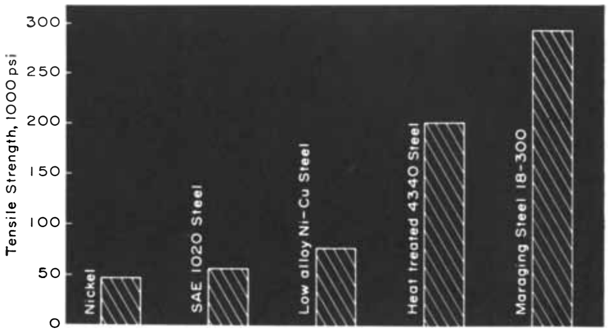
**Although nickel has many important uses in the commercially pure state, it is in association with other metals that it finds its widest application.** In over 3,000 alloys, nickel is used to impart added strength, toughness, resistance to corrosion and abrasion, high-magnetic or non-magnetic characteristics and low or high thermal expansion.

Because of this unusually wide range of useful contributions, nickel is a fundamental alloying element in compositions ranging from cast irons, alloy and stainless steels to non-ferrous copper-nickels, nickel silvers and high-nickel alloys. It is also used extensively for electroplating and other finishing systems. Some of these properties to which nickel contributes are highlighted here:

### MECHANICAL PROPERTIES

Nickel is a widely used alloying element in steel, and is added in amounts ranging from ½ per cent to 20 per cent. The tensile strength of low carbon steel, about 50,000 psi, can be greatly increased by alloying and proper heat treatment. Nickel-containing alloy steels are available with tensile strengths ranging from about 70,000 psi, without heat treatment, to as high as 350,000 psi with proper alloying and heat treatment. Nickel not only contributes to the increased strength but also permits steels to retain toughness and ductility at high strengths. Examples are: the AISI 4300 alloy steels and the 18% nickel maraging steels.

Nickel added to copper also results in increased strength, such as in the 90-10 and 70-30 copper-nickel alloys.



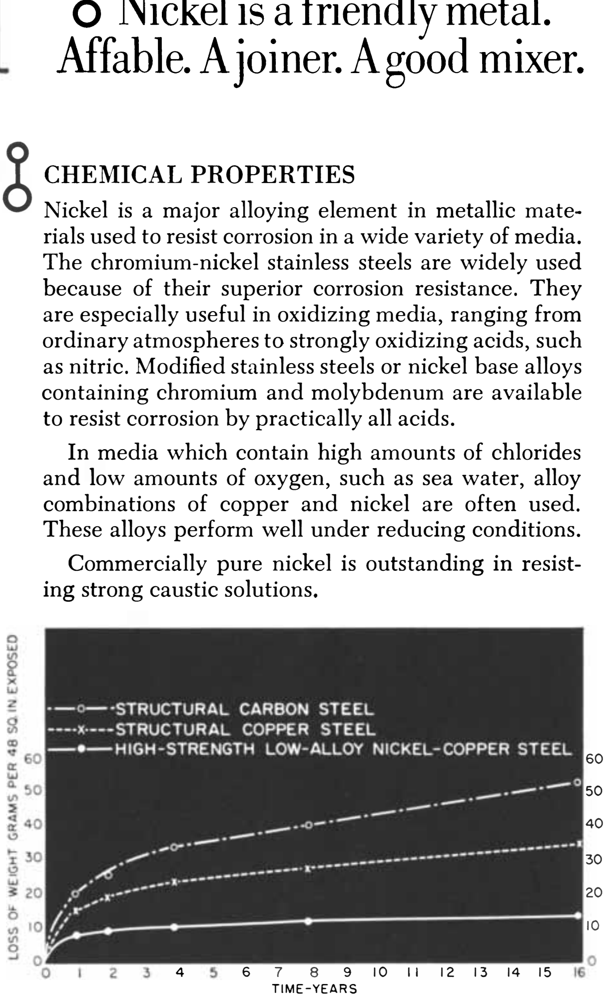
Relative tensile strength of nickel and certain nickel-containing alloys.

### CHEMICAL PROPERTIES

Nickel is a major alloying element in metallic materials used to resist corrosion in a wide variety of media. The chromium-nickel stainless steels are widely used because of their superior corrosion resistance. They are especially useful in oxidizing media, ranging from ordinary atmospheres to strongly oxidizing acids, such as nitric. Modified stainless steels or nickel base alloys containing chromium and molybdenum are available to resist corrosion by practically all acids.

In media which contain high amounts of chlorides and low amounts of oxygen, such as sea water, alloy combinations of copper and nickel are often used. These alloys perform well under reducing conditions.

Commercially pure nickel is outstanding in resisting strong caustic solutions.



Time-corrosion curves of three steels in industrial atmosphere, Kearny, N. J.

### ELECTRICAL PROPERTIES

The most widely used alloys for electrical resistance heating elements are 80 Ni-20 Cr and 60 Ni-16 Cr-bal Fe. These elements are used in appliances because they are efficient, durable and readily fabricated. Commercially pure nickel finds wide use in electronic applications because of its desirable combination of electrical properties, strength and fabricability.

Nickel finds many uses in batteries for such things as hearing aids, rechargeable cordless appliances and industrial applications.

## THERMAL PROPERTIES

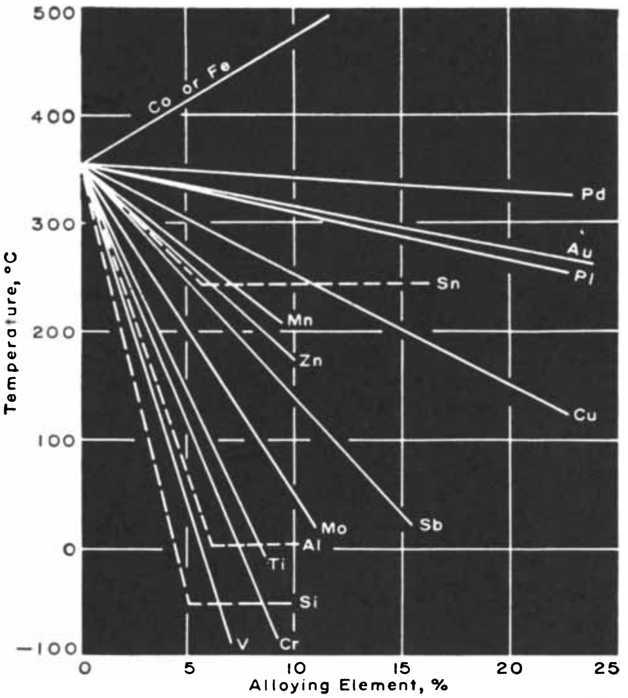
Nickel is the most important metallic element known for developing alloys with controlled thermal expansion characteristics. By the proper additions of nickel to iron, alloys can be produced to match the expansivities of most other materials. Invar (36% Ni-bal Fe) has practically no thermal expansion at ordinary temperatures (0.8 x $10^{-6}$ per degree F.). This is much less than ordinary steel (6.7 x $10^{-6}$ per degree F.) and aluminum (13.1 x $10^{-6}$ per degree F.). Other nickel alloys are available to match the expansivity of various kinds of glass and even to make the high expansion elements in temperature control devices. Nickel is added to steel to prevent brittleness at low temperatures. Even at temperatures approaching absolute zero (−459.6 F.), the chromium-nickel stainless steels are not brittle.

Most of the high temperature-high strength alloys which are used at temperatures up to 2000 F. contain nickel as a major alloying element.

Effect of nickel on the coefficient of linear thermal expansion of iron-nickel alloys (0.4% Mn, 0.1% C) at 20C.

## MAGNETIC PROPERTIES

Among the best permanent magnet materials are the Alnico family of alloys, which contain nickel ranging from 14 to 28 per cent. Many of the magnetically soft alloys contain as much as 79% nickel. The chromium-nickel stainless steels are non-magnetic in the annealed condition and some are slightly magnetic when heavily cold worked. Precipitation hardening stainless steels are ferromagnetic. Nickel itself is ferromagnetic at room temperature and when alloyed with copper can be either non-magnetic or ferromagnetic.



Effect of single alloying elements on the Curie point of nickel.

## OPTICAL PROPERTIES

Nickel is a prime alloying element to whiten other metals such as in copper to produce the nickel silvers, in gold to make white gold and to whiten even aluminum. Sunglasses are frequently made by vapor coating glass with nickel-chromium-iron alloys. This thin coating reflects most of the light and gives the glass the appearance of having been darkened. The thin coating is corrosion resistant and long lasting.

Alloys of nickel and copper exposed to natural atmospheres develop patinas, ranging from brown to blue green. The exact color will depend on the nature of the atmosphere, as well as the alloy composition. Such patinas can produce interesting architectural effects.

Nickel compounds are also used as a coloring agent in the glass industry.

It would be easy to specify a metal for a job if you had to consider only one property . . . but this is seldom the case. The variety of property combinations available in nickel-containing materials is extensive. If you have a problem and would like further data on nickel, its alloys, or compounds, our engineers will be available to discuss it with you personally.

**To meet the world's ever increasing demand for nickel,** International Nickel has been accelerating its mine and plant expansion. Within three years, our annual capacity at Canadian mines will increase by some 100 to 150 million pounds of nickel. Our exploration activities to further increase nickel supplies for industry are being carried out on a worldwide scale. We are active in areas as far afield as Minnesota and Guatemala, Australia and the British Solomon Islands.

As a developer of mineral resources and a leader in metals research, International Nickel is helping to shape tomorrow . . . today.

**INTERNATIONAL NICKEL**

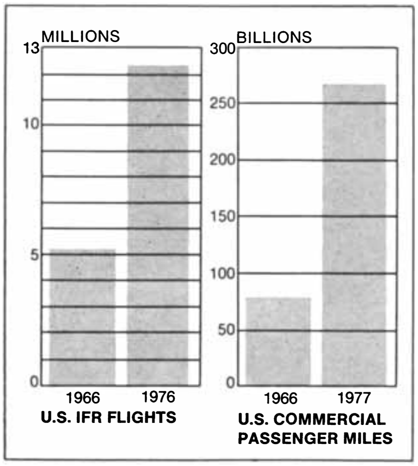
The International Nickel Company, Inc., New York, N. Y. 10005

# Helping the Federal Aviation Administration scuttle its "shrimp boats"

FAA air route traffic controllers continuously monitor all "IFR" aircraft in flight. Radar returns from surveillance radar antennas are displayed on a CRT to indicate the range and bearing of aircraft within a given area. Altitude, now, is determined by radio contact with each flight. Soon, a new display system, developed by Raytheon, will combine this information automatically, giving the controller a "3-dimensional" picture of aircraft under control.

What does it take to control an estimated 9,000 aircraft taxiing, taking off, flying, and landing within the U.S. at any given moment? For the FAA — overseer of all flights operating under instrument flight rules (IFR) in the U.S. — it takes 14,000 highly trained men, extremely sophisticated electronic equipment, and . . . a large supply of small plastic markers called "shrimp boats".

Today, skilled controllers at FAA enroute air traffic centers use these "shrimp boats" to record the altitude and identity of each flight under control. In practice, the controller places a "shrimp boat", with its handwritten information, on his CRT display next to each radar target that represents an "IFR" aircraft. He then must update the information and constantly reposition each "shrimp boat" to match the progress of the flight it identifies.



The FAA, in anticipation of the air traffic control needs of the future (see chart), is rapidly developing its automated National Airspace System (NAS) which will scuttle the "shrimp boats" and free both pilots and controllers from tedious repetitive actions, permitting them to devote most of their attention and energy to their primary tasks — flying the planes and keeping flights safely separated.

### CDC In — "Shrimp Boats" Out

A key element in the NAS is the Computer Display Channel (CDC), being developed and produced by Raytheon, which will provide the interface between the controller and an enormous amount of data being processed by a central computer complex.

The CDC will replace the old fashioned "shrimp boat" markers with electronically-generated alpha-numeric tags that will appear automatically on the controller's CRT display. Most of the vital flight information, formerly recorded manually, will be displayed and updated electronically as each tag follows its target across the scope. The electronic tags can supply the controller with current information about the identity and altitude of each flight, so he will have what amounts to an accurate "3-D" picture of air traffic in his area.

### Greater Information Display Selectivity

The new CDC system gives the controller extraordinary selectivity in the type of information he can extract from the computer and how it is displayed. For example. When traffic is light, a few consoles can be used to display large control sectors. During peak periods, more displays can be brought into action to "zoom-in" on smaller areas for closer surveillance. Because input data is relayed simultaneously to all displays from a common refresh memory (see diagram), information appearing on separate consoles may be compared accurately, regardless of range scales used. In addition, the "electronic" center of each display can be positioned anywhere on the map, allowing the controller to monitor an entire air corridor or to select a particularly dense air traffic area for special attention.

The displays themselves represent a radical improvement over similar equipment in operation today. Because all information is digitally generated, the image is always sharp and flicker-free. Resolution is five times greater than that presently achieved by conventional displays. Each flight with its identifying tag is clearly defined at all times.

### What About Flight "Hand-Offs"?

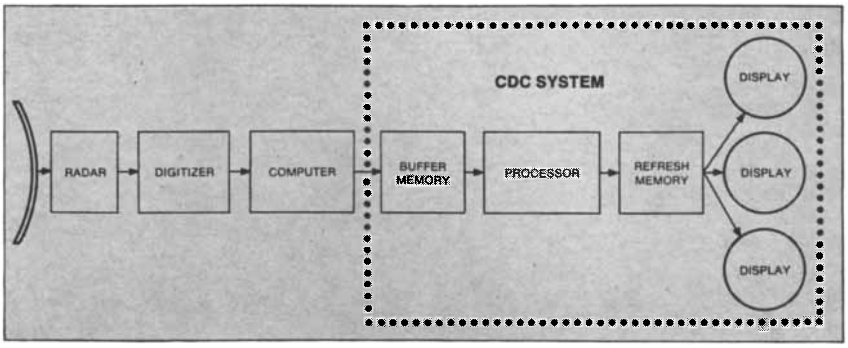
Today, when an aircraft leaves one FAA regional control sector to enter another, the controller "hands-off" the flight to the adjacent area by direct-wire telephone. The receiving controller must make positive identification of the approaching aircraft by radio before clearing the flight to enter. The CDC system, working in conjunction with other NAS equipment, allows this hand-off to be accomplished electronically, without telephone or radio contact, and without delay.

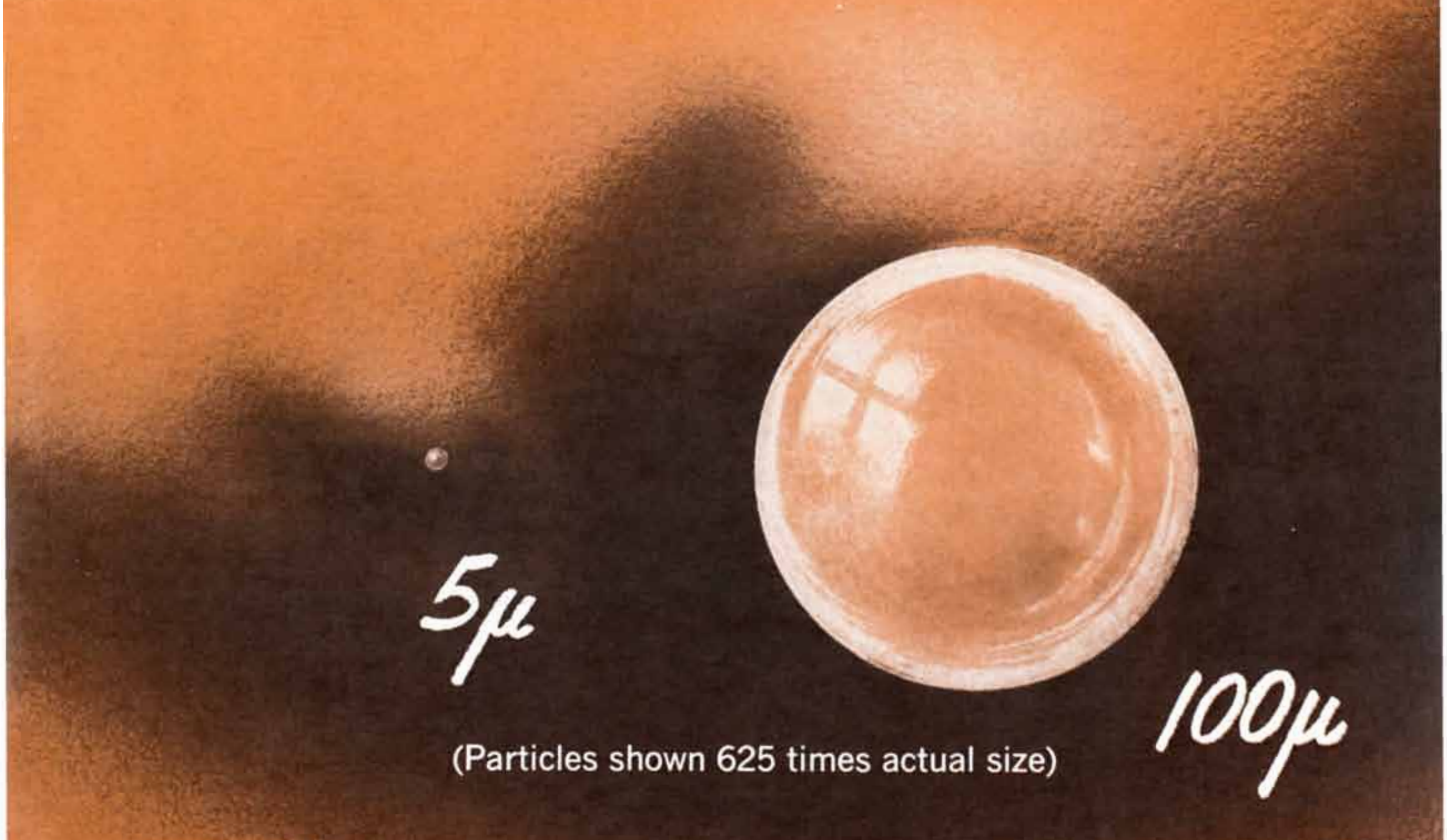
### Applied Systems Management

The ultra-modern CDC equipment is being produced by Raytheon under the largest contract ($44 million) ever awarded by the FAA for air traffic control equipment. The system will utilize the very latest advances in electronic technology, including monolithic integrated circuits and high-speed core memories developed by Raytheon to help insure greater accuracy and reliability. Result: a highly efficient and effective system requiring less space and less power at lower cost.

Solving complex problems by "systematic" thinking and utilization of the company's wide range of technical skills is typical of the way Raytheon works to assure complete customer satisfaction . . . in defense and other government systems and in such commercial markets as education, home appliances, natural resources development, electronic components, marine products and communications. Raytheon Company, Lexington, Mass.

**RAYTHEON**





(Particles shown 625 times actual size)

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# Super stamp

It's just an ordinary airmail stamp. Until you put it under ultraviolet light. Then it turns into a glowing super stamp that lets the Post Office sort 30,000 letters an hour!

Sylvania phosphors did the trick. After seven years of research. Several thousand were tested before two were selected from Sylvania.

Now, the phosphors are simply added into the stamp ink. A red-orange for airmail, a green for the rest. When the letters come in, they are fed through special electronic equipment that cancels and sorts them automatically.

Sounds simple, but it took some doing. The phosphors not only had to luminesce brightly under ultraviolet, but had to be as fine as confectioner's sugar (normally antagonistic characteristics).

Altogether, we offer hundreds of different phosphors. Some detect counterfeiting, some illuminate safety devices, some coat fluorescent tubes, some trace air currents, some make plastics glow, some brighten your TV picture.

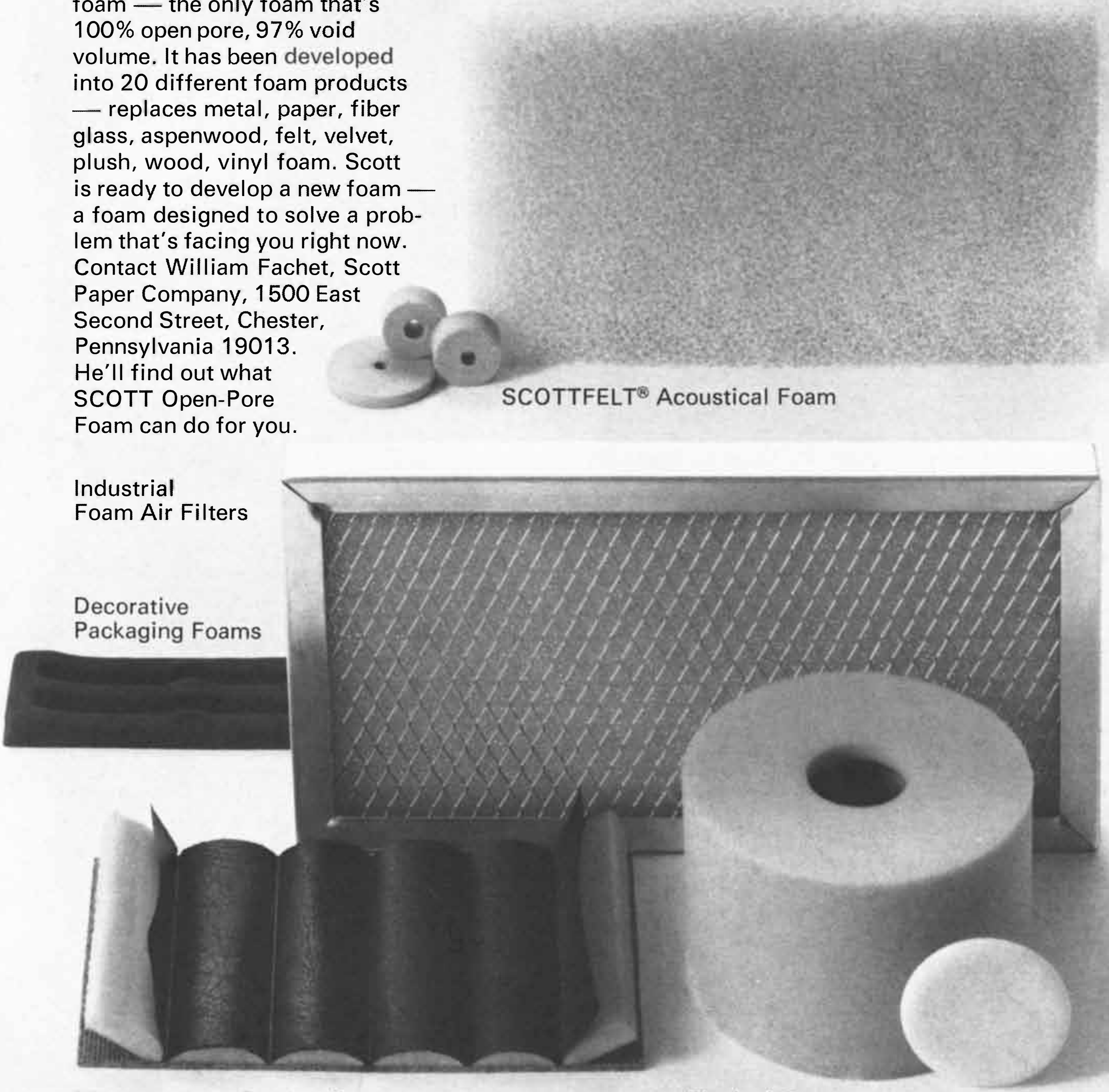
Maybe we can solve your materials problems too. After all, we've been a leading phosphor producer for over 25 years. We're also a leader in tungsten, molybdenum, specialty industrial inorganic chemicals, and semiconductors.

For information, write to Sylvania Electric Products Inc., Chemical & Metallurgical Division, Towanda, Pennsylvania 18848.

**SYLVANIA**
A SUBSIDIARY OF
GENERAL TELEPHONE & ELECTRONICS

# Don't think of SCOTT Open-Pore Foam only as foam. It limits your thinking.

Don't think in terms of foams you know. SCOTT Open-Pore Foam is something else. It's the creative foam — the only foam that's 100% open pore, 97% void volume. It has been developed into 20 different foam products — replaces metal, paper, fiber glass, aspenwood, felt, velvet, plush, wood, vinyl foam. Scott is ready to develop a new foam — a foam designed to solve a problem that's facing you right now. Contact William Fachet, Scott Paper Company, 1500 East Second Street, Chester, Pennsylvania 19013. He'll find out what SCOTT Open-Pore Foam can do for you.



SPECIALISTS IN URETHANE FOAM TECHNOLOGY

SCOTT

# 50 AND 100 YEARS AGO

SCIENTIFIC AMERICAN

SEPTEMBER, 1917: "Possibly no fortified place in history has ever exacted the number of human lives from the assailants and defenders that Verdun has in the past 18 months. It is believed that not less than one million men have been killed, wounded or captured since the assaults on Verdun began in February, 1916."

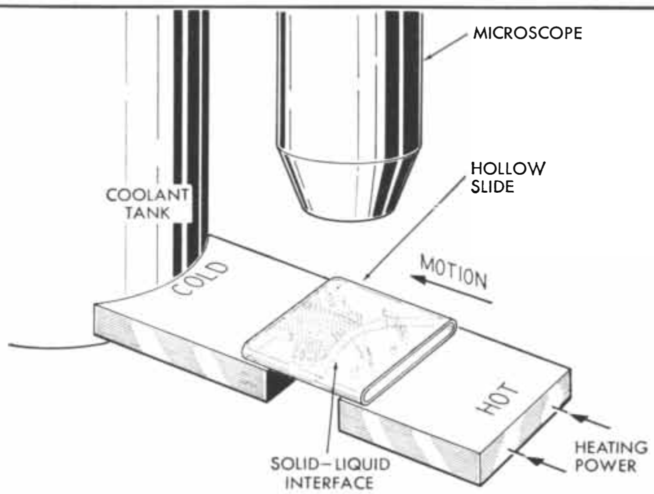
"So much has been written of French, English and German progress in the air that the work of Italy in aeronautics has been overshadowed, believes *Aviation*. Reports now reaching this country indicate that Italy has produced the fastest aeroplane, the best climber, the largest machine and a fleet of dirigibles that have performed marvelous work along the seacoast. The secret of Italy's success in aviation is the powerful and reliable engines that have been developed. It is asserted that the large Italian engines of 500–700 horse-power have proved that larger aeroplanes than have been thought possible from an engineering standpoint can be built and flown successfully. To demonstrate this point there is under construction an aeroplane using 3,000 horse-power and designed to carry 50 passengers."

"The many speculations that have been published concerning the origin of life on the earth and on any other bodies in the universe where it may possibly exist usually assume that, in some way or other, 'life germs' are transported across the gulfs of space from one planet to another. Thus it has been suggested that life may have been brought to the earth in meteors. One of the most recent suggestions is that minute 'life germs' may escape from the atmosphere of a planet in which life exists, just as molecules of the atmospheric gases are believed to escape from our terrestrial atmosphere, and may be driven by light-pressure to some world where physical conditions have become suitable to support life. While there is nothing essentially absurd in these hypotheses, it is not clear why their au-

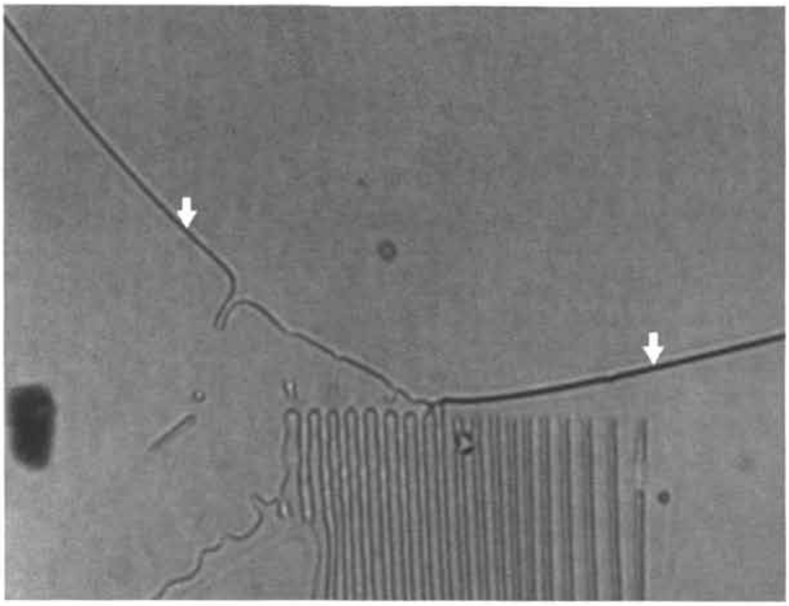
Report from

**BELL LABORATORIES**

# Inside Solidifying Metals



**Experimental setup in which photographs such as that below were taken. The glass slide or cell—containing a liquid which freezes like a metal—is placed between hot and cold blocks of brass. This produces a temperature difference along the slide. A solid-liquid interface then forms between the two blocks. By moving the slide toward the cold block at a constant rate, one can observe the steady growth of the crystal under the microscope.**



**Bell Laboratories' model (200x) permits physical simulation of a eutectic phase diagram for an alloy such as lead-tin. Diagram relates liquid proportions (horizontal scale) to temperature (vertical).**

**Two different liquids were put into a single slide . . . hexachloroethane on the left and carbon tetrabromide on the right. After a brief period, the liquids formed a graded mixture, from 100% of one at the left to 100% of the other at the right. The mixture was partially frozen, then photographed with the slide stationary. The solid-liquid interface (arrows) then showed the freezing point for every possible composition.**

**The "grid" under the solid-liquid interface is made up of alternate solid layers of the two chemicals (the eutectic region).**

As one facet of the materials research going on at Bell Telephone Laboratories, metallurgist Kenneth A. Jackson has devised transparent models of solidifying molten metals. With these models, we can now study what happens inside a metal as it freezes. This gives us a tool which promises to improve existing alloys and will perhaps help us find new and better ones.

The models are hollow microscope slides (diagram) containing such organic liquids as camphor or carbon tetrabromide. These compounds are among the few transparent substances whose molecules freeze without having to rotate into a specific orientation. Metal atoms act the same way, hence the similarity in freezing behavior.

Various modes of metal-crystal growth—planar, dendritic (tree-like branching) and cellular—have been studied in detail with this technique. Also, the solidification of alloys has been simulated (photo). To do this, liquids with freezing characteristics corresponding to those of two metals are mixed and cooled. With this procedure, Jackson and J. D. Hunt (now at the University of Oxford) observed, for the first time, the process by which the "equiaxed" zone forms in alloy castings. This is a zone of relatively small crystals, usually found in the center of an alloy casting. The new technique shows that the equiaxed zone results from "branches" melted from dendritic crystals. As the alloy cools, freezing begins at the outer surface, producing dendrites which project inward toward the hotter, liquid center. Branches, melted from these growing dendrites, are carried to the center of the casting to form the crystals of the equiaxed zone.

Until now, the only methods for studying metal freezing were laborious . . . cutting, polishing and etching, for instance. The new technique is not only simpler but also reveals hitherto unknown details of crystal growth.

**Bell Telephone Laboratories**
**Research and Development Unit of the Bell System**

thors should take it for granted that life cannot originate *de novo* on a cooling planet."

"A practical application of anthropology is noted in the last annual report of the U.S. National Museum. Dr. Aleš Hrdlička, curator of physical anthropology, was employed for three months by the Department of Justice in making an examination of Chippewa Indians for the purpose of determining which shall be classified as full-bloods. The undertaking was noteworthy from a scientific point of view because it definitely puts on record the present racial status of the Chippewa. This people, which is historically important and still very numerous, will before long be composed entirely of mixed bloods and will no longer afford the material for such investigations as those just made by Dr. Hrdlička."

Scientific American.

SEPTEMBER, 1867: "A cable dispatch announces the death of Michael Faraday on the 25th of August. For nearly half a century Faraday has been one of the most eminent of men devoted to science. Learned societies and sovereigns vied with each other to do him honor. He bore his great eminence with childlike gracefulness. In his intercourse with men his artlessness and his love of truth won the admiration and esteem of all. No one ever felt jealous of his reputation, and no one ever disputed his title to his discoveries. As a lecturer he was charming by his earnest simplicity of action and expression. His weekly lectures were one of the most attractive features of the London winter season. Faraday has left an impress on human affairs that will endure forever. When our kings and presidents are forgotten, his name may still be a household word, for he has a place in history with Archimedes, Newton and Franklin."

"Mr. McCormick having accepted an invitation from Emperor Napoleon to give a private exhibition of the working of his reaping machine, a trial was made a short time since on the Imperial farm near Châlons. The trial was a complete success and gave so much satisfaction to the Emperor that he immediately gave orders for the purchase of three of the machines for use on his private farms and earnestly expressed the intention of encouraging the adop-

# SCIENCE/SCOPE

Survivability of materials in outer space is being studied at Hughes under a NASA contract. A special environmental chamber was designed to investigate the effects of high vacuum, extreme temperatures, and radiation on typical space-vehicle materials. Up to 25 specimens at a time can be mounted on its "Lazy Susan" turntable, and special experiments can be made to discover the "failure mechanism" when damage occurs.

A major breakthrough in ablative polymers for spacecraft heat shields is the recent development of a thermosetting polyphenylene resin that is stable at 500°C and retains 80 percent of its initial weight at 1000°C. Hughes chemists are continuing their ultra-stability search among the pyrrone, quinoxaline, and ferrocene polymers.

Two new dielectric materials for encapsulating repairable high-voltage electronic components in spacecraft have been developed by Hughes. One is a lightweight polyurethane foam-in-place that has proved its long dielectric life aboard Hughes communications satellites. The other is a granular, ceramic-filled polymer with a very high filler-to-binder ratio. It is especially useful for high-voltage space and airborne networks that require dissipation of high thermal energy.

Career opportunities at Hughes include immediate openings for magnetic components and electro-optical engineers, circuit designers, and weapon systems analysts. Requirements: at least two years of applicable experience, accredited engineering or scientific degree, U.S. citizenship. Please send your resume to: Mr. J.C. Cox, Hughes Aircraft Company, Culver City, California. Hughes is an equal opportunity employer.

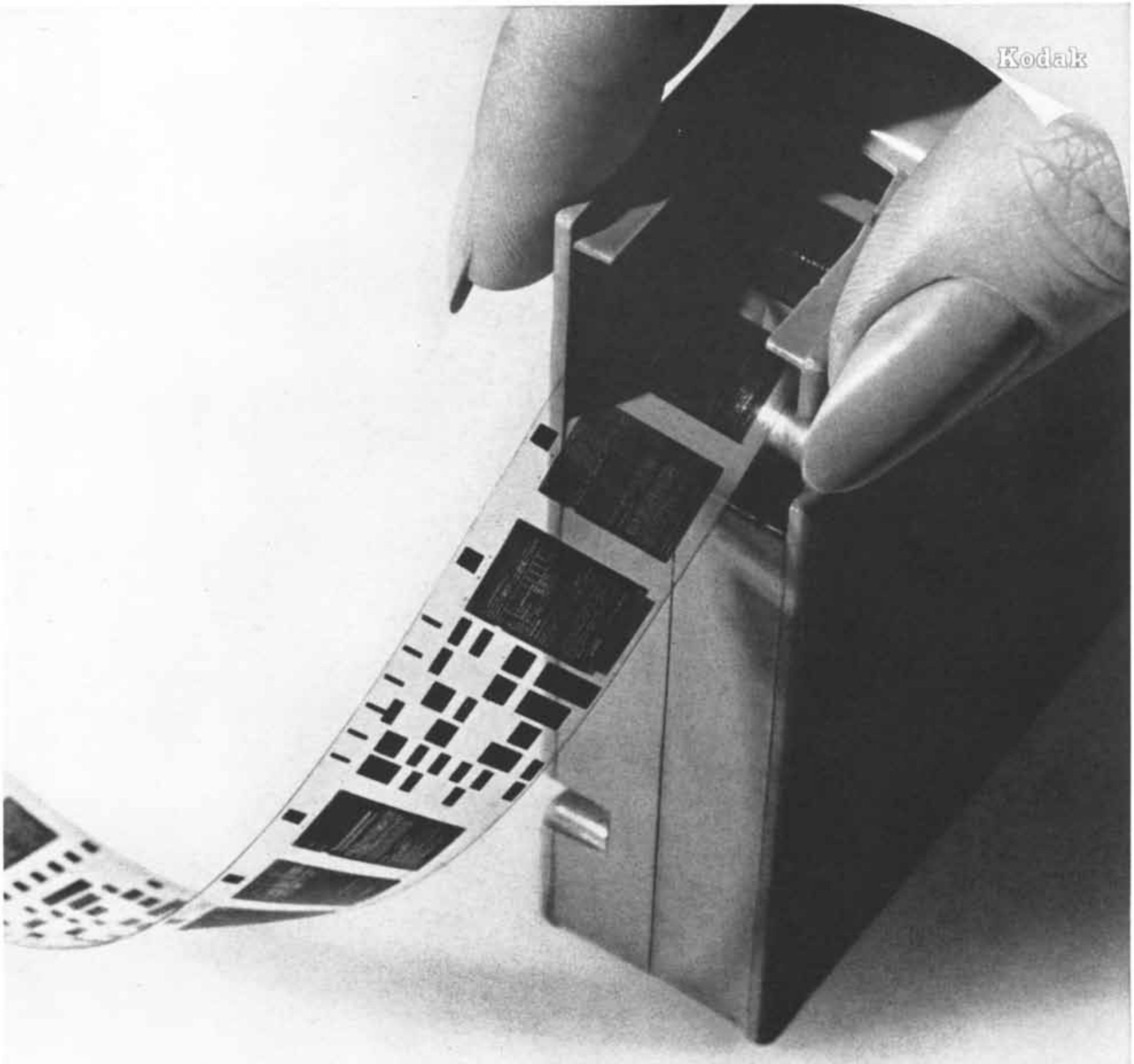
Large, ultra lightweight structures for space are getting special attention at Hughes. Structures would be compactly packaged for stowage in the launch vehicle. In space, they'd be unfurled and inflated, then chemically rigidized. Hughes chemists have developed vapor-catalyzed and ultraviolet- and infrared-activated systems. One particularly promising system uses the vacuum of space to cause automatic rigidization of fiber-reinforced structures that have been impregnated with gelatin -- such as precision antenna parts, gravity gradient booms, radomes, parabolas. System is reversible: structures can be erected on the ground (preferably in a dry climate), tested, and then softened and repackaged.

A new photographic technique developed by Hughes scientists is based on light-induced polymerization. Photopolymer pictures can be taken, developed, fixed, and projected in 1/2-second. The continuous tone photographs have excellent contrast and high resolution. Process uses only light or light and heat...needs no developing or fixing solutions. Potential uses: data-storage and large-screen displays.

*Creating a new world with electronics*

**HUGHES**

HUGHES AIRCRAFT COMPANY


Kodak

tion of the invention throughout France, on account of its great labor-saving properties."

"The first practical example of the Pneumatic Railroad ever constructed in this country has just been completed by the Holske Machine Company and will form one of the prominent features at the exhibition of the American Institute in this city, now just opening. The pneumatic tube is six feet in diameter, composed of 15 thicknesses of wood veneers, wound and cemented one on the other in alternate spirals. The blowing apparatus consists of a wheel 10 feet in diameter, made on the principle of the screw propeller. The pneumatic car consists of an open vehicle with a valve or disk at one end, which fits the tube. The car seats 12 passengers. The tube is over 100 feet long. The railroad is made from designs by Mr. A. E. Beach of SCIENTIFIC AMERICAN."

"At the 16th annual meeting of the American Association for the Advancement of Science, held this year in Burlington, Vt., Prof. Newcomb read a paper on a new determination of the distance of the sun, the calculations having been made at the Naval Observatory in Washington. Ten years ago astronomers began to suspect that the value of the sun's distance found by Encke from the transits of Venus observed in 1761 and 1769 was largely in error. This distance, 95,300,000 miles, had long been received as the standard. But all the modern tests that could be applied to it indicated that it was about three millions of miles too great. In the year 1862 circulars were issued independently from the observatories in Washington and Pulkowa (the Russian national observatory) inviting the cooperation of astronomers everywhere in a general attempt to determine the parallax of Mars at opposition that year. Through the pressure of other duties and the illness of the astronomer who had proposed the work, the Pulkowa observatory had not been able to undertake the discussion of this great mass of observations, so that for five years their result remained unknown. Last winter an arrangement was made between the observatories in Washington and Pulkowa, by which this discussion was placed in possession of the speaker, to be executed and published by authority of the Naval Observatory. It is now complete, and the sun's distance is determined to be 92,340,000 miles, and the velocity of light is thus reduced to 185,500 miles per second."

# Teaching materials to carry bigger payloads.

**New beryllium-aluminum alloys cut weight 50% over magnesium • Superplasticity is opening new avenues of high-strength metal fabrication • An advanced helicopter rotor hub gains performance from composite construction • A way to toughen ceramics may lead to structural applications • Graphite fibers can add greatly to strength of metals.**

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Knowledge being gained from Lockheed's search for ways to increase payloads—of air, space and even undersea vehicles—promises to produce "educated" new materials with higher strength- or stiffness-to-weight ratios.

Here are a few of the materials programs presently under way at Lockheed.

**New lightweight beryllium-aluminum alloys.** Solving a long-elusive problem, Lockheed scientists recently have succeeded in developing a practical beryllium-aluminum alloy suitable for aerospace applications. By carefully controlling microstructure, fine dispersions of aluminum in beryllium have been achieved, providing a series of workable, serviceable alloys. These possess extreme lightness without the brittleness characteristic of unalloyed beryllium. One, a 62%Be-38%Al material called Lockalloy, is now being produced commercially. It provides a 50% weight saving over commonly used magnesium alloys, while having three times the strength and four times the ductility of earlier developed beryllium-aluminum alloys.

**Superplasticity.** Generally, increases in strength of metals are obtained at the expense of ductility, making fabrication into complex shapes much more difficult.

To solve this problem, Lockheed is researching an unusual method of deformation called superplasticity. Both basic and applied studies are being conducted involving aluminum and titanium alloys. With one alloy, using the proper applications of thermal-mechanical treatment, elongations of 1400% have been achieved.

Defined as "an enhanced ductility associated with a microstructural change during application of stress," superplasticity, as far as the actual mechanism of deformation is concerned, is not yet fully understood. It appears to be associated with a fine, interlocked 2-phase microstructure where there is pronounced curvature of the interphase boundaries. Surprisingly, even when certain alloys are elongated enormously, there is no evidence

**LOCKHEED**

**LOCKHEED AIRCRAFT CORPORATION**

*This schematic representation shows the types of phase changes associated with superplastic effects.*

of directionality in the microstructure. Transmission electron microscopy reveals it to be remarkably free of dislocations. None of the usual dislocation networks or tangles in plastically deformed metals can be detected. These results suggest that diffusional processes operate during superplastic deformation. Possibly, the key to the mechanism involved lies in a unique process of vacancy formation and migration inside the metal during stress.

Current investigations include commercial titanium alloys. Some, for example, Ti-8Al-1Mo-IV, can be elongated 400% at very low loads when kept within narrow temperature ranges.

Methods of deformation such as superplasticity may see extensive use in the next generation of aircraft.

**Composites for Rigid Rotor helicopter hub.** The recently developed Lockheed Rigid Rotor helicopter, because of its unique design, also presents some unique materials requirements. For example, the rotor hub. The hub arms must be flexible enough to provide proper dynamic characteristics, yet flexibility must be confined within narrow limits to avoid degrading the Rigid Rotor's outstanding stability and control qualities.

Today, titanium meets these exacting design conditions. But within a few years, composite materials now under development by Lockheed may offer signal advantages over metals in fulfilling the needs of new generations of rotary-wing vehicles. This is because a composite construction made with large-filament glass or metal fibers in a nonmetallic matrix permits superior control of flexibility due to a directionality of stiffness. A rotor hub made of such composites also meets fatigue life specifications while affording a high level of damage tolerance. A material of this type resists small nicks or scratches and is almost completely corrosion-resistant, providing long, safe, trouble-free service life. In addition, it is substantially lighter than a metal hub material and would further increase the helicopter's performance.

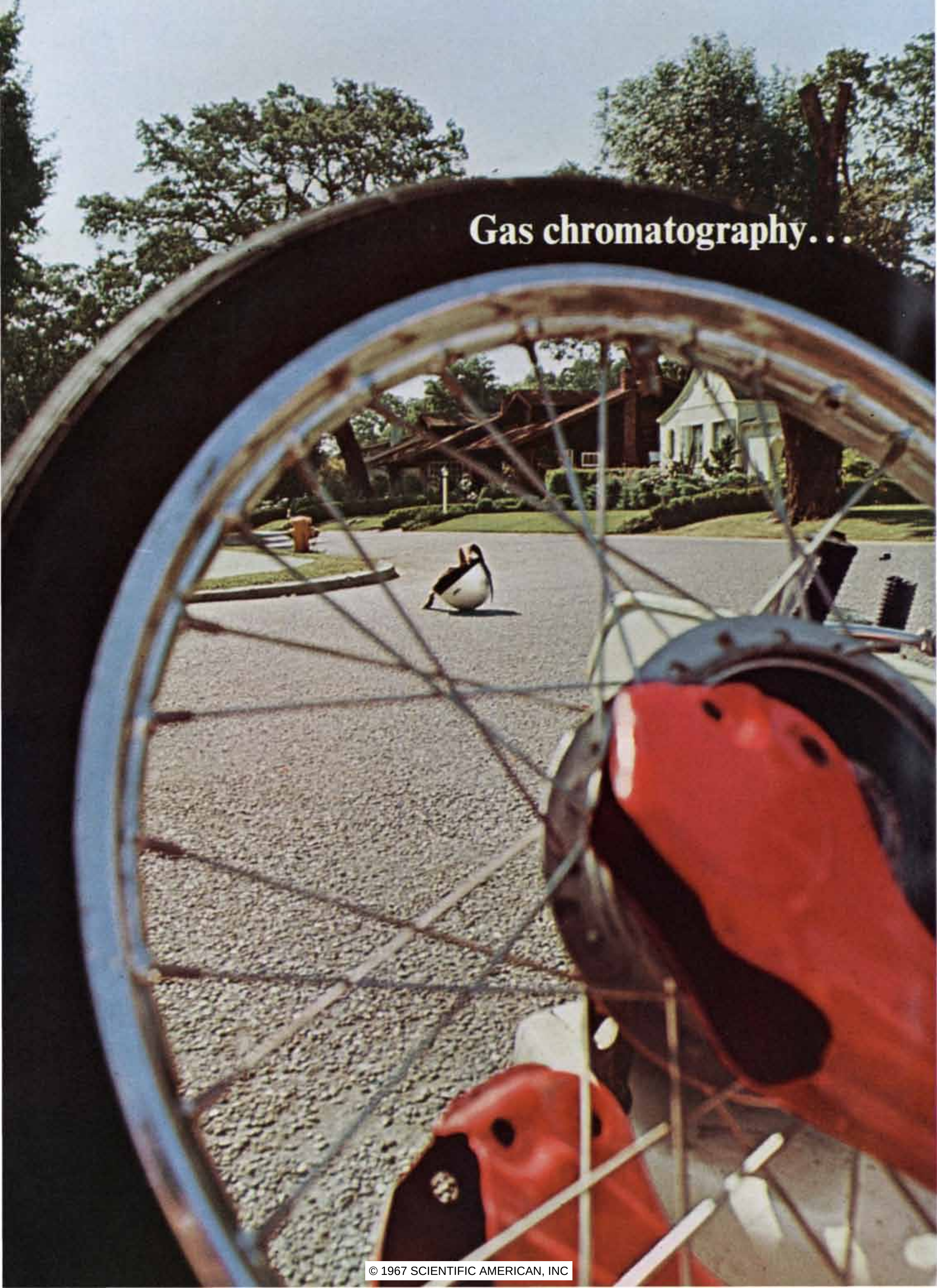
**Ceramic composites.** Ceramics have been tempting as materials to meet high strength-to-weight, temperature-resistance and corrosion-resistance requirements. But the inherent brittleness of ceramics has led to their rejection in previous investigations. New research at Lockheed, however, promises a solution. Using an unusual process involving special techniques and equipment, composite ceramics are being grown from the melt. The resulting laboratory product is a conventional ceramic matrix in which ultra-high-strength single-crystal fibers of either metal or ceramic material are imbedded. Presence of these fibers considerably toughens ceramics—to where they may find application as vehicle fabrication materials.

**Graphite fibers in metal matrices.** Graphite fibers recently have been developed with tensile strengths over 250,000 psi and moduli over 60 x $10^6$ psi. Lockheed currently is investigating the compatibility of these high-modulus carbon fibers with metal matrices. Studies involve the temperatures and times required for composite preparation as well as potential fabrication applications. Compatibility is being tested by determining the wetting behavior of liquid-state metal matrix materials on the graphite substrate. Also, kinetic parameters are being established corresponding to possible interface reactions between fiber and matrix.

Because of their low density, graphite fibers are expected to play a significant role in developing lightweight, high-strength composites for many aerospace applications.

*A longitudinal section of sapphire fibers in an aluminum titanate matrix. This section was produced by electron beam zone melting.*

The activities described here are only a few of Lockheed's current R&D projects in materials. If you are an engineer or scientist interested in this field of work, either in California or Georgia, Lockheed invites your inquiry. Write: K. R. Kiddoo, Lockheed Aircraft Corporation, Burbank, California. An equal opportunity employer.


Gas chromatography...

# can help develop a better material, improve our physical well-being... and catch a hit-run killer.

A motorcyclist was killed by a hit-run driver, a suspect car located. Police found traces of grey and red plastic on its bumper. The problem: how to establish whether the plastic on the automobile came from the motorcycle. Gas chromatography was used to analyze the scrapings from the suspect car and the wrecked motorcycle. The chromatograms, showing exact chemical composition of the plastics, provided comparable chemical "fingerprints" of the two samples. They matched... and these "fingerprints" were used as admissible evidence in court to establish the car's role in the accident.

**How it works:** Gas chromatography (GC) is a process whereby a vaporized material is separated into its constituent compounds as it passes through an adsorptive column. The output of sensitive detectors at the end of the column provides a graph, or chromatogram, showing both the identity and exact quantity of the separated compounds. This efficient analytical tool, combining quantitative analysis with qualitative identification, makes a positive contribution to our lives today... from the purity of the water we drink to the ability of our automobile to stop quickly and safely.

**Health-guard:** By developing the temperature-programmed gas chromatograph, Hewlett-Packard made practical the detection of harmful pesticide residues in foodstuffs ranging from human milk to raspberry preserves. HP GC instrumentation can detect the presence of as little as a picogram ($10^{-12}$ gram) of a pesticide. Because of the toxicity of these chemicals, this 1000-time improvement in sensitivity is of significant importance to pesticide manufacturers, biomedical researchers, and government agencies concerned with public health.

**GC in laboratory and factory:** In industrial research, GC is an important tool for improving both product quality and manufacturing economy. As an example, brake lining material, by design highly resistant to decomposition, was analyzed by combining two HP-developed techniques: pyrolysis GC (where the sample is burned to obtain the test gas) and temperature-programmed GC (allowing separation from a mixture of compounds with widely separated boiling points). Several brake lining formulations were analyzed; their chromatograms showed a direct correlation between the presence of a new compound formed during curing and the actual stopping-ability of the linings. A new brake lining formulation was devised that improved performance with less cost. GC became the quality control specification test for this manufacturer to assure consistency of formulation and, thus, the stopping-ability of the brake lining.

**Making pure chemicals:** Beyond the analysis of small samples, gas chromatography has proved to be a uniquely efficient technique for producing useful liter-quantities of highly pure chemicals. By increasing the volume capacity of "preparative" GC more than 100 times, Hewlett-Packard has added further to the practicability of preparative gas chromatography for industrial use.

**Other Hewlett-Packard analytical instruments:**
Vapor pressure osmometers, $2800.
Membrane osmometers, $4225 to $5550.
CHN analyzers, $6000.
Microwave spectrometers, $40,000 to $60,000.
Gas chromatographs, $1095 to $5400.

Hewlett-Packard laboratories are at work in applied electronics, solid-state physics and physical electronics to develop new analytical techniques, while contributing to the automatic operation and increased efficiency of present techniques.

**Software behind the hardware:** Analytical instruments are among the more than 1500 Hewlett-Packard instruments for chemical, electronic and medical applications. From Hewlett-Packard sales and service offices our engineers and specialists provide customers with help in application, installation and maintenance of these instruments. Through these 107 offices extensive customer training programs and a continuing flow of helpful information are available—on a local basis—to meet the immediate and long-term needs of those whose progress depends on measurement.

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*Measuring instruments for science and industry*

00714

# Traveling can take the fun out of going anyplace.

For 44 years now, we've been watching the frazzled traveler drag himself in and out of cars and trains and planes.

We've seen him arrive in his itchy tweeds when the temperature was pushing 80 degrees.

We've seen him without a hotel room to call his own.

We've seen him looking a little green from something he ate.

We've seen him broke, wet, lost, and befuddled.

And if nothing else, we've sympathized with him. At least our girls at the counters have. So much so, in fact, that an unwritten and slightly haphazard company policy has developed here at Hertz.

It sort of says, "Give the poor guy a break." If he doesn't have a place to sleep, help him find one. If he doesn't know his way around the area, give him a map and show him the way. If he's in a hurry, help him hurry.

What all this has resulted in is that our customers find traveling a little less miserable. Our girls find their jobs considerably more interesting. And we as a company find ourselves doing alright too.

Now it struck us that if our girls could give you all this help pretty much on their own, they could do a lot more if we gave them some tools to do it with. Which we have now done.

From now on when you come up to a Hertz counter in any large city, you can expect to get more than a set of keys.

If you're a stranger in any one of America's 28 largest cities, we'll give you the world's most complete guide on how to survive in that city. It not only tells you where to eat and sleep, it also tells you where to get a haircut, pawn your watch, and have a night on the town.

If you know where you're going, but don't know how to get there, we'll give you a special map of the area and diagram it to make it absolutely clear.

If you run out of money and you have a Hertz charge card, we'll give you $10 cash on your IOU, and tack it on to your rental.

If you know you're going to be late getting to your hotel, we'll call and tell them you're coming and to hold your room.

If it's raining and you left your raincoat home because the weatherman told you it was going to be sunny, we'll give you a raincoat.

If you're running to catch a plane, we won't make you stand in line behind people who aren't. Starting now—if you're charging your car—all you have to do is stuff your keys inside your rental envelope, write your mileage on the back, drop it on the counter and take off.

If you're going on vacation, we'll give you tour maps that describe the most interesting places to see and the most interesting things to do along the way.

Now all this is not to say that we're overlooking the main reason we're in business. To give you a Ford or another good car with a minimum of nonsense.

We'll still let you pick up a regular sedan at any Hertz office and drop it off at any other Hertz office—in practically any major city in the United States—with no drop-off charge.

We'll still give you a choice of more different kinds of cars than any other rent a car company. (If you ever get bored renting plain four-door sedans, that's a nice thing to know.)

We'll still have our yellow Hertz phones in the lobbies of most major hotels and motels. They're direct lines, so you don't have to spend a dime to get a car.

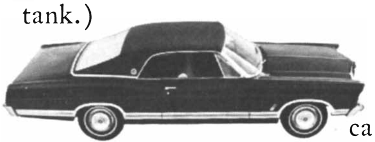
We'll still pay for all the gas you use. (Unless you're getting one of our special rates, in which case we'll still buy the first tank.)

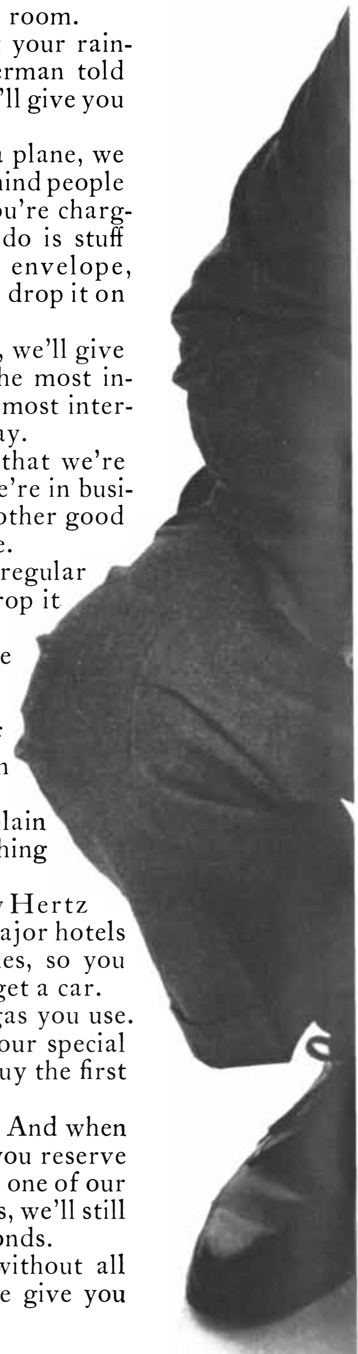
And when you reserve one of our cars, we'll still confirm your reservation in seconds.

After all, we know that without all these things, the extra help we give you wouldn't help.

**Hertz**

We can help a little.





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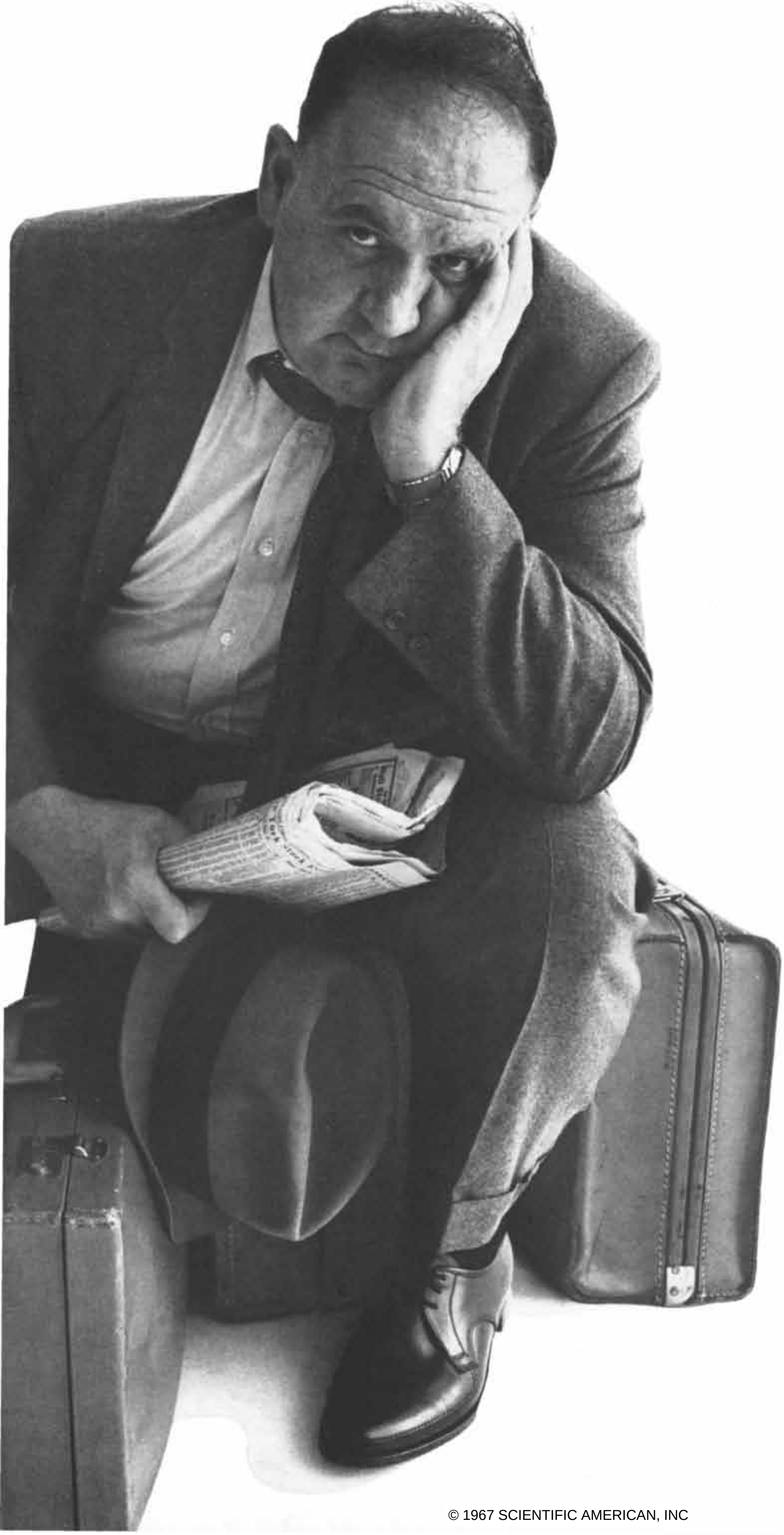
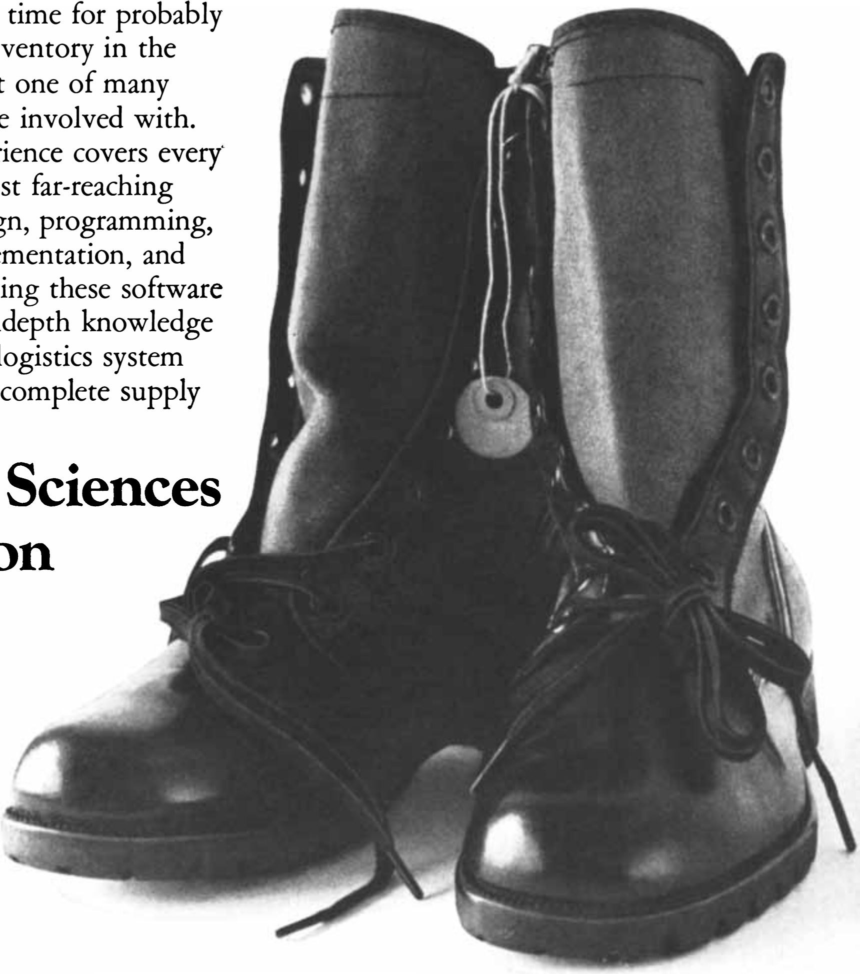


# What's a sophisticated software firm like us doing in the shoe business?

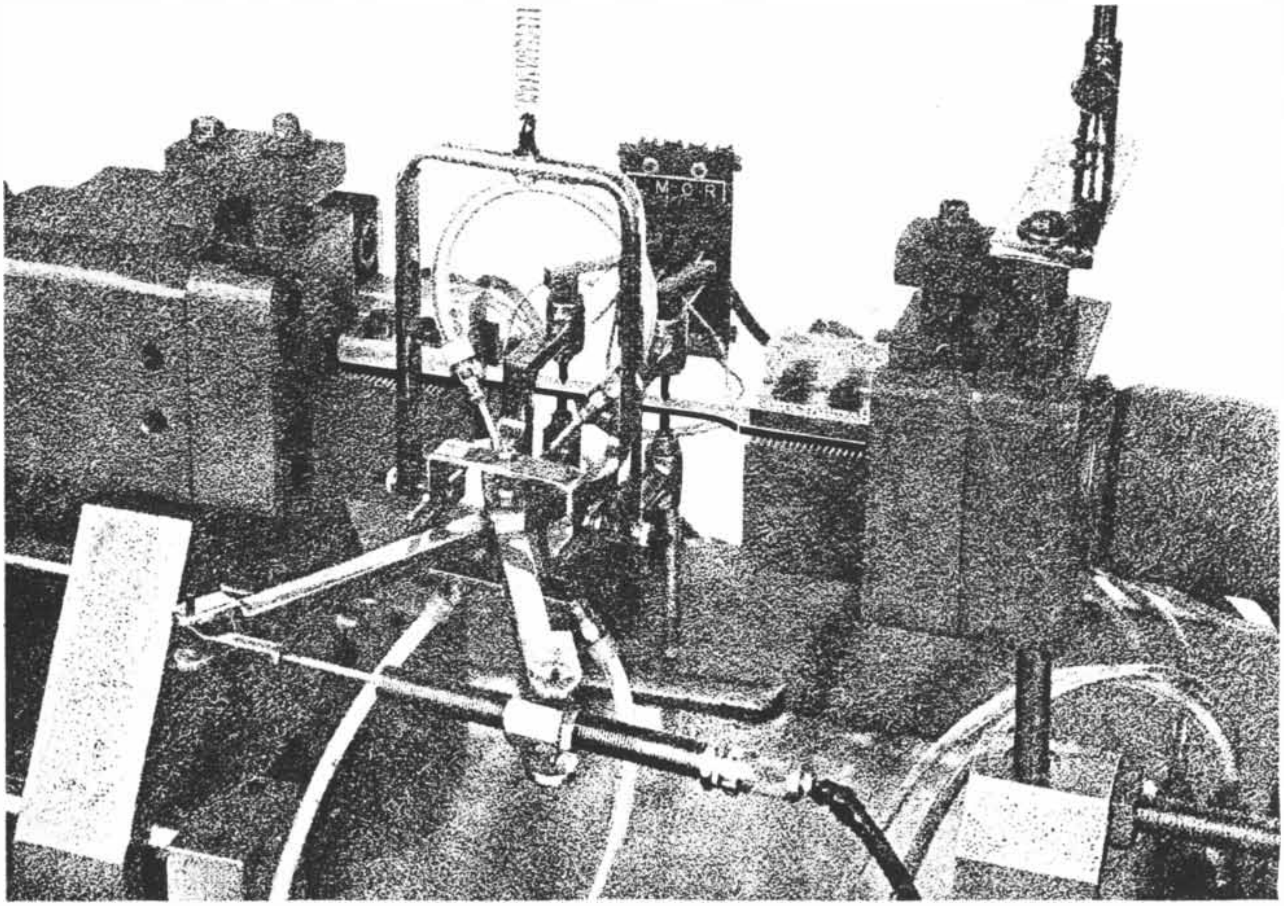
We've been in it since last November when we got together with USARPAC to help refine that command's logistic system. It serves a network of major Army sub-commands throughout Southeast Asia across a 10,000 mile supply line.
We're working closely with the Army in the overhaul of data processing procedures to increase supply system efficiency and speed up turn-around time for probably the largest military inventory in the world. But this is just one of many logistics systems we're involved with.

Our depth of experience covers every phase of even the most far-reaching system; analysis, design, programming, documentation, implementation, and operation. By combining these software techniques with an indepth knowledge of advanced military logistics system concepts, we provide complete supply system know-how, from manufacturer to field user—and back through the loop.

Being in the shoe business has really kept us on our toes. So if you've got a logistics problem, write and tell us. We'll let you know how we can help you solve it. Computer Sciences Corporation, 650 North Sepulveda Boulevard, El Segundo, California 90245.



**Computer Sciences Corporation**



### Historic moon-spectaculars, shot close-up by

# Lunar Orbiter I

The Lunar Orbiter spacecraft is a flying laboratory designed to photograph the moon's surface. Its dual mission: help NASA select the best landing sites for America's Apollo astronauts, and provide new scientific information about the moon and its origin. Four Orbiters have already made flights to and around the moon. While in lunar orbit, these spacecraft respond to commands from earth—240,000 miles distant—with remarkable precision. Orbiter II's path, for example, was within two-tenths of a mile of its planned perilune (low point). Lunar Orbiters have provided NASA scientists with vast new knowledge of the earth's only natural satellite. They have also scored a number of historic firsts. Lunar Orbiter I was the first U.S. spacecraft to orbit the moon, to photograph the earth from the vicinity of the moon, and to photograph the far side of the moon. Boeing scientists, working with NASA personnel, controlled the Lunar Orbiter flights. NASA's Langley Research Center manages the Lunar Orbiter program.

## Designed and built for NASA by Boeing.

Dark areas above indicate potential lunar landing sites explored photographically by Lunar Orbiter I. Texas outline gives scale. Orbiter I transmitted to earth photographs of 150,000 square miles of moon's near side, plus 2 million square miles of moon's far side.

Historic picture below is first view of earth from vicinity of the moon. Picture below it is first U.S. photo of the far side of the moon. Astronomers report that during its first week in orbit, Lunar Orbiter I sent back more information on the moon than had been learned in the past 50 years. Besides photos of surface, Orbiter I measured radiation levels in moon's vicinity and helped determine moon's exact gravitational characteristics.

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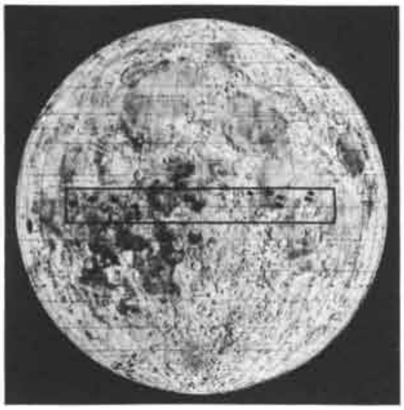
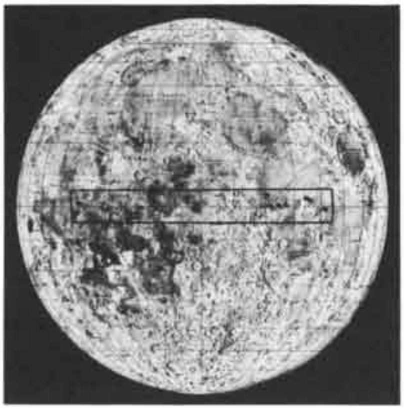


In outline above are the 13 primary targets scouted by Lunar Orbiter II. In addition, Orbiter II photographed 17 areas of secondary interest. Shooting from 28-mile altitude, Orbiter's telephoto shots show objects three feet in diameter —exceeding mission requirements.

# II

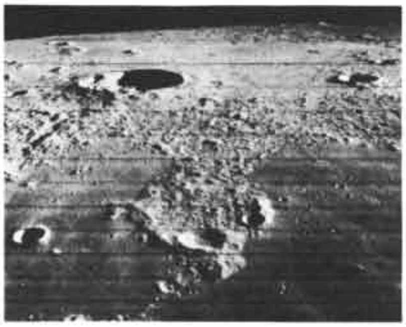
"Photo of century" below is man's historic first look into crater Copernicus. Picture shows 17-mile wide section, with 1000-foot mountains rising from crater floor. Analysts have found evidence of erosion, quakes and volcanic-type activity in picture. Photo below Copernicus pictures crater Marius, and, for first time in detail, nearby lunar domes (1000 to 1500 feet high). Domes confirm the moon's long history of volcanic activity.

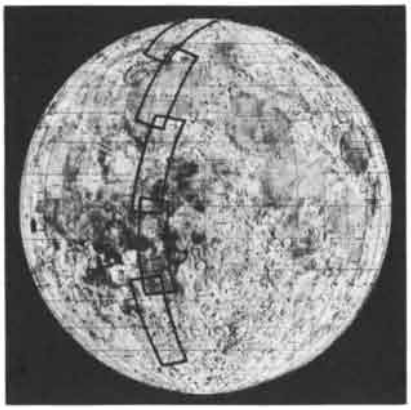


Orbiter III's NASA assignment was confirmation of 12 primary and 32 secondary Apollo sites. Orbiter III sent back telephoto coverage of 2,200 square miles and 11,500 square miles of wide angle coverage. Photos also pinpointed location of Surveyor I on moon.

# III

Orbiter III's spectacular shots included, below, crater Hyginus (about 6½ miles in diameter) centered in branches of its valley. Picture below Hyginus shows crater Kepler, about 20 miles in diameter, located in Ocean of Storms. Smaller crater, right, is Kepler A, about 9 miles across and ½ mile deep. First three Orbiters, NASA reported, met all primary Apollo requirements for photographic information from orbiting spacecraft.

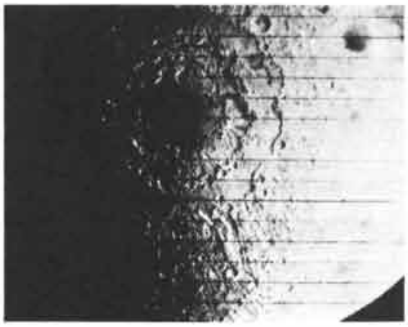




Lunar Orbiter IV's mission was acquisition of scientific knowledge. From near-polar orbit, Orbiter IV shot lunar surface on near and far side using both telephoto and wide-angle systems. Rectangles indicate size and shape of areas shot by telephoto system during each photo pass.

# IV

Orientale Basin, below, pictured for first time from overhead. Cordillera Mountains, ringing Basin, rise as high as 20,000 feet. Picture at bottom revealed, for first time, a 150-mile trough, on hidden side of moon near south pole. Altogether, Lunar Orbiters photographed 99% of the moon's near side, and more than 75% of the far side...a picture survey described as "THE definitive source of lunar surface information for many years."



# THE AUTHORS

CYRIL STANLEY SMITH ("Materials") is Institute Professor at the Massachusetts Institute of Technology, attached to both the department of metallurgy and the department of humanities. Born and educated in Birmingham, England, he came to the U.S. in 1924 as a graduate student and received a doctoral degree from M.I.T. in 1926. From 1927 to 1942 he was research metallurgist with the American Brass Company. In 1946, after three years at the Los Alamos Scientific Laboratory, he went to the University of Chicago to establish the Institute for the Study of Metals, which was the first academic laboratory for interdisciplinary research on materials in the U.S. He took his present position in 1961. Smith was an original member of the General Advisory Committee of the Atomic Energy Commission and has served on the President's Science Advisory Committee. He writes that his "main interests are structure, of all things at all levels, and the history of technology and science."

SIR NEVILL MOTT ("The Solid State") is Cavendish Professor of Experimental Physics at the University of Cambridge and a Fellow of the Royal Society. A Cambridge graduate, he began his academic career as a lecturer at the University of Manchester in 1929. From 1930 to 1933, after a period of work with Niels Bohr, he was a lecturer at Cambridge; for 21 years after that he was professor at the University of Bristol. His appointment as Cavendish Professor at Cambridge took place in 1954. In addition to his work at the Cavendish Laboratory he served from 1959 to 1966 as Master of Gonville and Caius College at Cambridge. Sir Nevill writes: "My research interests were in nuclear physics before I went to Bristol and since then they have been in solid state, particularly in the physics of metals and semiconductors and in the theory of photographic emulsions. My present research interest is in electrical conduction in noncrystalline solids, a subject that is rapidly opening up." Sir Nevill has served on various committees concerned with science education and is now chairman of a committee set up by the Nuffield Foundation to frame new methods of teaching physics and chemistry to students between the ages of 15 and 18. He adds: "I am also interested in disarmament and strategic studies and have been present at some of the Pugwash conferences on science and world affairs."

A. H. COTTRELL ("The Nature of Metals") is Chief Scientific Adviser (Studies) in the British Ministry of Defence. He writes: "Most of my work on the theory of dislocations in metals was done at the University of Birmingham, of which I am a graduate and where I was professor of physical metallurgy. After 1955, when I moved to the Atomic Energy Research Establishment at Harwell, my interests turned toward problems of nuclear radiation damage in solids and later to the theory of fracture, a subject that I continued when I moved to the University of Cambridge in 1958 as the Goldsmiths' Professor of Metallurgy. I have become increasingly interested in recent years in the role of science in national affairs." That interest has led Cottrell successively to membership on the United Kingdom Atomic Energy Authority and the Advisory Council for Scientific Policy, to the Ministry of Defence and to membership on the recently formed Central Advisory Council for Science and Technology.

JOHN J. GILMAN ("The Nature of Ceramics") is professor of physics and metallurgy at the University of Illinois. He took bachelor's and master's degrees at the Illinois Institute of Technology in 1946 and 1948 respectively and received a Ph.D. from Columbia University in 1951. He worked in industry until 1960 and then spent three years as professor of engineering at Brown University before taking up his present work. His research centers on the mechanical behavior of solids; he writes that he "had the good fortune to be the first (together with my then colleague W. G. Johnston) to devise methods for measuring the velocities of dislocations in crystals."

R. J. CHARLES ("The Nature of Glasses") is at the General Electric Research and Development Center in Schenectady. He writes: "Originally a Canadian, I was attracted by the open life of the mining engineer and took a B.S. in mining in 1948 and an M.S. in metallurgy in 1949, both at the University of British Columbia. Astonished by the total disaster of a gold-mining venture I subsequently embarked on, I returned to my long-standing interest in metals and minerals." He did further graduate work at the Massachusetts Institute of Technology, where he received a doctorate in 1954 and served on the faculty until join-

*Albrecht Dürer*
*(1471-1528)*

*Woodcarving by William Ransom*
*Photographed by Max Yavno*

"Dürer's *Unterweisung der Messung,* published in Latin in 1532, served, so to speak, as a revolving door between the temple of mathematics and the market square. While it familiarized the coopers and cabinetmakers with Euclid and Ptolemy, it also familiarized the professional mathematicians with what may be called 'workshop geometry.' It is largely due to its influence that constructions 'with the opening of the compass unchanged' became a kind of obsession with the Italian geometricians of the later sixteenth century, and Dürer's construction of the pentagon was to stimulate the imaginations of men like Cardano, Tartaglia, Benedetti, Galileo [and] Kepler...."[1]

---

[1] Wilhelm Waltzoldt, *Dürer and His Times,* trans. R. H. Boothroyd, London, Phaidon Press Limited, 1950, p. 257.

# INTERACTIONS OF DIVERSE DISCIPLINES

Dürer applied his knowledge of geometry to problems of perspective in his engravings. This use of one discipline to reinforce another has applications today to the profit potential of business.

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ing General Electric in 1956. He writes: "By personal choice my research interests are divided between a long-term interest in theoretical aspects of silicate and oxide systems and shorter-term pursuits selected from an overflowing reservoir of industrial scientific problems." Charles, now a U.S. citizen, says his major outside interest is "the experimental and computer analysis of two-fluid locomotion (sailing)."

HERMAN F. MARK ("The Nature of Polymeric Materials") is director emeritus of the Polymer Research Institute at the Polytechnic Institute of Brooklyn. He has long been a leading figure in the field of polymer chemistry, which he entered more than 40 years ago at the Kaiser Wilhelm Institute for Fiber Chemistry in Germany. Mark was born in Vienna and distinguished himself as an athlete as well as a scholar; he played in the Austrian national soccer league as a young man and also was an excellent skier. In 1921 he received a Ph.D. *summa cum laude* from the University of Vienna. He taught at the University of Berlin for a year before going to the Kaiser Wilhelm Institute; in 1926 he joined the research laboratories of I. G. Farbenindustrie, where he worked on studies of cellulose and other polymeric materials. He resigned from the firm when the Nazis took power; leaving Germany, he became director of the First Chemical Institute of the University of Vienna. When the Nazis invaded Austria, he left Europe and worked for two years with a Canadian pulp company before going to the Polytechnic Institute of Brooklyn. Mark wishes to acknowledge the collaboration on his article of his colleague and successor as director of the Polymer Research Institute, Murray Goodman.

ANTHONY KELLY ("The Nature of Composite Materials") has been a lecturer in metallurgy at the University of Cambridge for the past eight years; in October he will join the National Physical Laboratory as superintendent of a new division concerned with inorganic and metallic materials. Kelly was graduated from the University of Reading in 1949 and obtained a Ph.D. from Cambridge in 1953. Although most of his work has been done in Britain, he has had several associations in the U.S. He was at the University of Illinois from 1953 to 1955 and at Northwestern University from 1956 to 1959; earlier this year he was for a time at the Carnegie Institute of Technology. He often spends summers working in industrial and gov-

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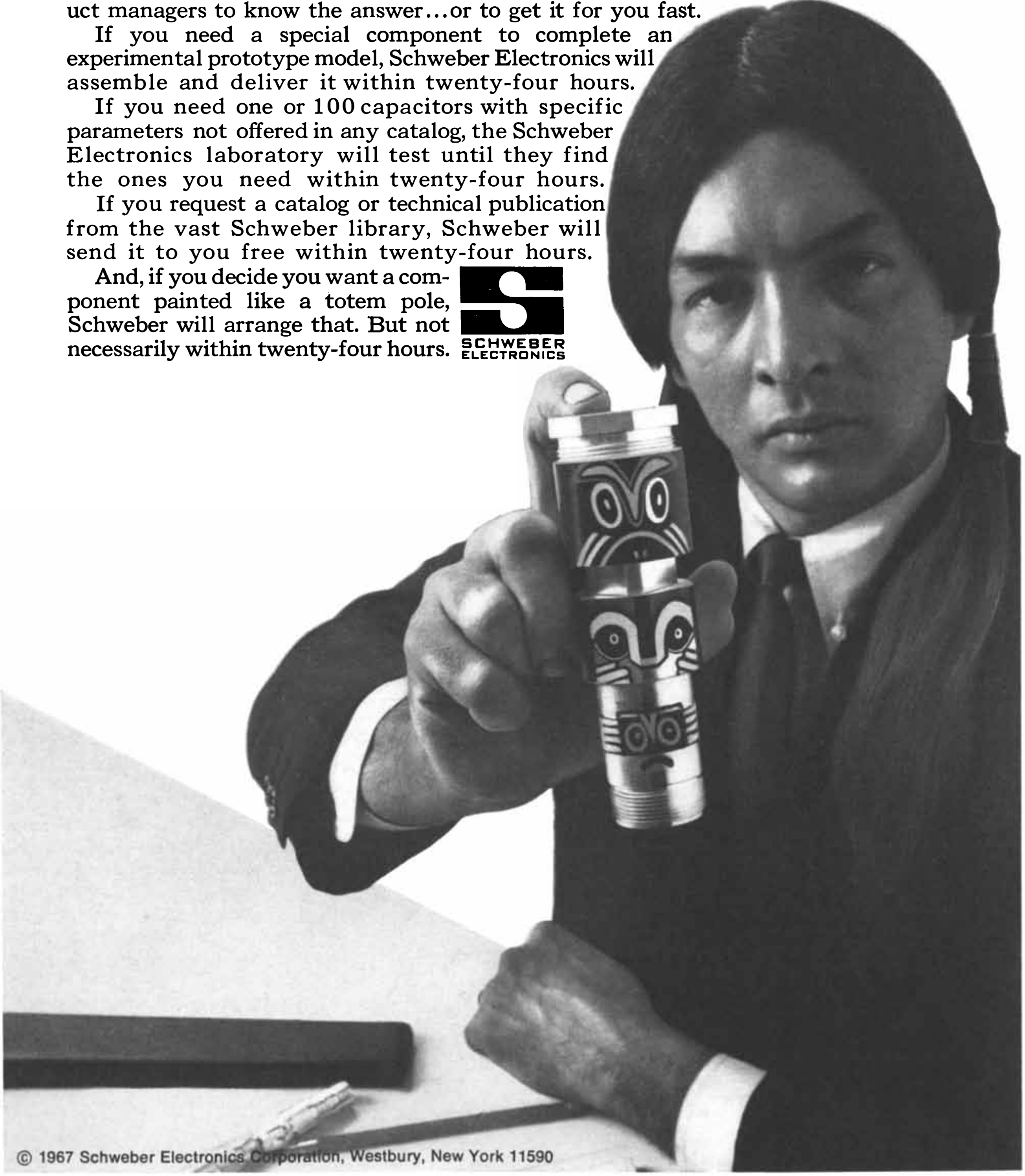

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ernment laboratories; he says he thinks that "is an ideal way to learn what applied science means."

JOHN ZIMAN ("The Thermal Properties of Materials") is professor of theoretical physics at the University of Bristol. Although he was born in England, he lived for many years in New Zealand and received much of his education there. Returning to England for graduate study, he obtained a doctorate from the University of Oxford. In 1954 he became a lecturer at the Cavendish Laboratory of the University of Cambridge. Since going to the University of Bristol three years ago he has been concerned mainly with the theory of the electronic structure of solid and liquid metals. Ziman was recently elected a Fellow of the Royal Society.

HENRY EHRENREICH ("The Electrical Properties of Materials") is Gordon McKay Professor of Applied Physics at Harvard University. Born in Germany, he came to the U.S. in 1940 and did all his college work at Cornell University, from which he received a Ph.D. in 1955. From then until 1963 he was at the General Electric Research Laboratory in Schenectady. His research activities have involved electron systems, transport properties of semiconductors, optical properties of solids, and the band structure and magnetic properties of noble and transition metals.

HOWARD REISS ("The Chemical Properties of Materials") is director of the North American Aviation Science Center in Thousand Oaks, Calif., and a vice-president of North American Aviation, Inc. After being graduated from New York University in 1943 he worked for two years in the Manhattan project. He then began graduate work in chemistry at Columbia University, from which he received a Ph.D. in 1949. Among his associations since then are Boston University, where he was a member of the faculty for two years; the Bell Telephone Laboratories, where he was a member of the technical staff from 1952 to 1960, and Atomics International, a division of North American Aviation, Inc., where he was successively associate director and director of the research division before taking his present position in 1962.

FREDERIC KEFFER ("The Magnetic Properties of Materials") is professor of physics and chairman of the department of physics at the University of Pittsburgh. He did his undergraduate work

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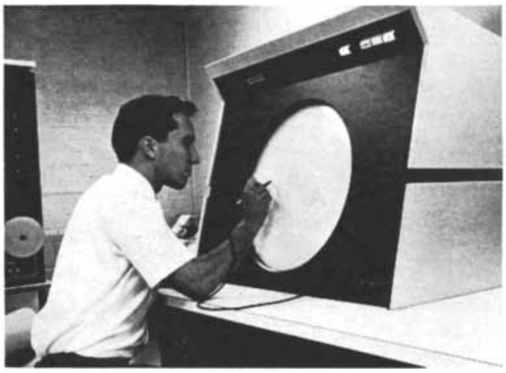
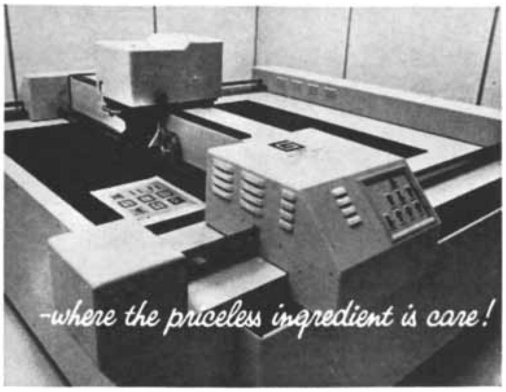


Engineer Optimizes Preliminary Display

Computer Makes Corresponding Changes

Automatic Pen Produces Intricate Final Integrated Circuit Mask



Today, virtually every field of economics and technology depends heavily on the computer to expand its present rate of progress — and at Motorola's Semiconductor Products Division, engineers and computers are teaming up to design the very complex integrated circuits that will make future computers infinitely smarter and more versatile.

How smart can computers get? That depends on how much circuitry can be crammed into a practical amount of space and on how much money we can afford to spend. With a large enough memory and logic system, computers will not only be able to solve problems but they'll be able to figure out the methodology for solving complex problems and to direct their own activities.

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Into the labyrinth of a computer memory is fed all of the electrical and topographical data for many of the simpler integrated circuits which we can already make with high production yields. This information is supplemented with instructions that will permit the computer to call forth and display, in any desired sequence and position, any required number and types of simpler circuits to form a more complex array. Basically, the engineer determines what kind of array he wants; the computer assembles it from the information stored in its infallible memory and displays it on an associated cathode-ray-tube screen.

The engineer now has the option to make changes, additions and deletions in the array, and the computer will make corresponding changes in its own program. And when the engineer is satisfied with the final design, he presses a button and walks away.

Now the computer takes over completely—with a sequential series of electrical impulses, unerringly and tirelessly guides the pen of an automatic drafting machine to produce the mask master for the desired array. It does so with an accuracy unchallenged by the most experienced draftsman and in a compressed time span so vital to the practical implementation of the LSI concept.

At Motorola, millions of dollars have already been invested to initiate the computerized design system. Millions more will be required to work out the details. But the groundwork has been solidly established and in an era where breakthroughs have become routine, the advent of LSI promises to become one of the most significant.

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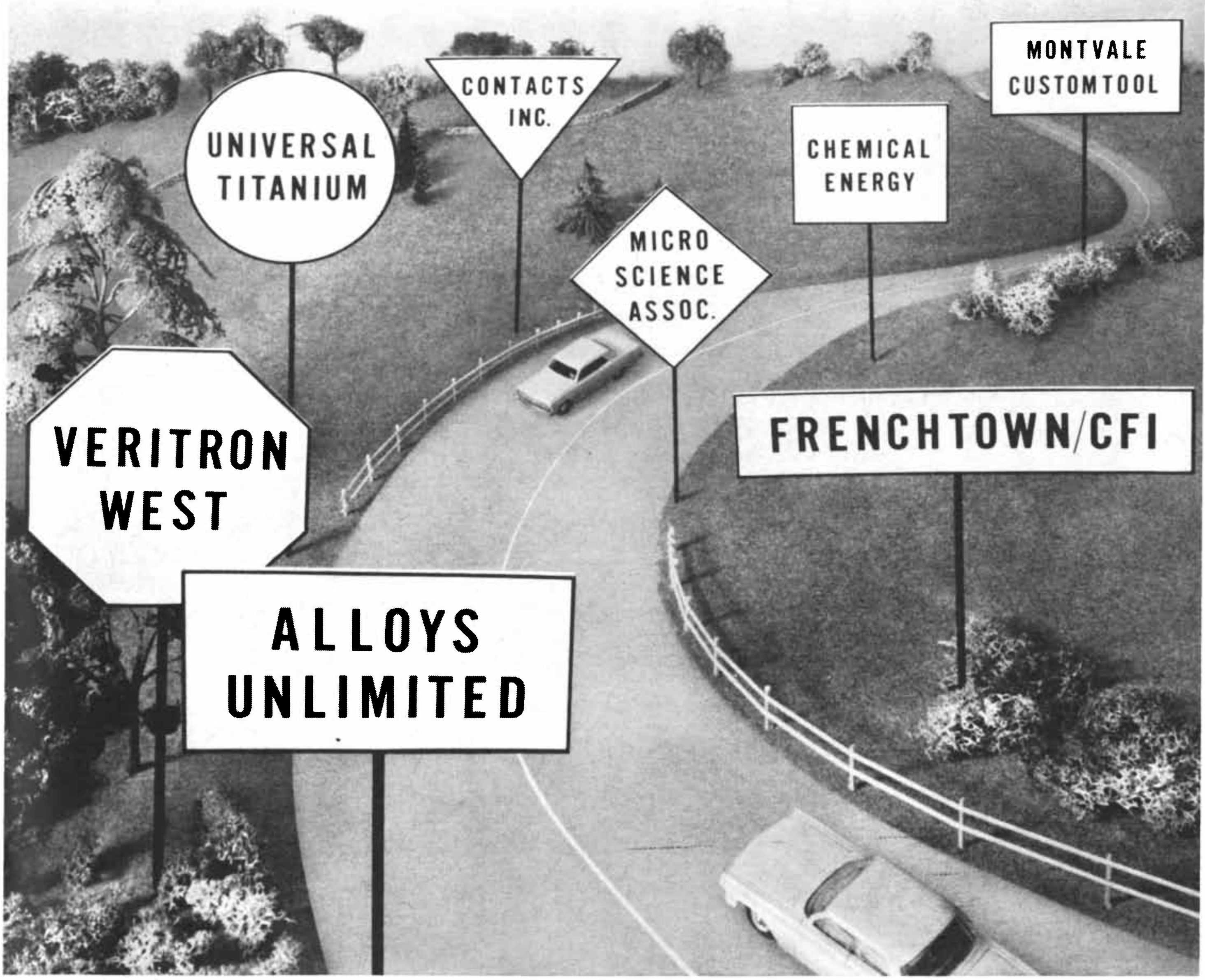
5005 EAST McDOWELL ROAD, PHOENIX, ARIZONA 85008 at the State College of Washington, which is now Washington State University; he writes that "between my desultory senior year in 1939–1940 and the award by the college of a B.S. in 1945 I served for five years in the infantry, touring Europe from Brittany to Leipzig with the Sixth Armored Division." Keffer obtained a Ph.D. from the University of California at Berkeley in 1952 and since then has been at Pittsburgh. His research, he says, "has centered on the theory of magnetism and has included studies of microwave resonance absorption by ferromagnets, ferrimagnets and antiferromagnets; relaxation processes; magnetocrystalline anisotropy; the nature of the short-range coupling force, and types of magnetic ordering."

ALI JAVAN ("The Optical Properties of Materials") is professor of physics at the Massachusetts Institute of Technology. A native of Iran, now a U.S. citizen, he received a Ph.D. in physics from Columbia University in 1954 and remained at Columbia for five years as a research associate. From 1958 to 1961, when he went to M.I.T., he was a member of the technical staff of the Bell Telephone Laboratories.

W. O. ALEXANDER ("The Competition of Materials") is professor of metallurgy and head of the department of metallurgy at the University of Aston in Birmingham, England. He is a graduate of the University of Birmingham, where he studied metallurgy from 1928 to 1937. From 1937 to 1961 he was engaged in metallurgical work at Imperial Chemical Industries. He writes: "So far as my leisure-time pursuits go, I suppose I can be considered first of all a sportsman since I played Rugby football for some 15 years and in my early days played a lot of tennis and in more recent years have swum regularly." He is also interested in the organization of various types of amateur sport. These activities, he says, "only leave me time to take a reasonably intelligent interest in drama and painting and whenever possible the wide-open spaces." The principal content of Alexander's article was originally presented in *Contemporary Physics;* the permission of that journal to repeat it in SCIENTIFIC AMERICAN is gratefully acknowledged.

DENNIS SCIAMA, who in this issue reviews *The Measure of the Universe,* by J. D. North, is lecturer in applied mathematics and theoretical physics at the University of Cambridge.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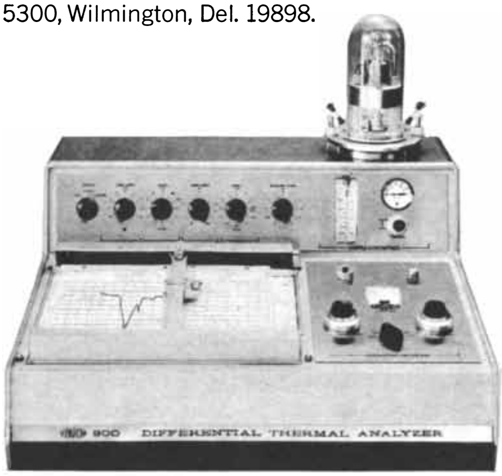
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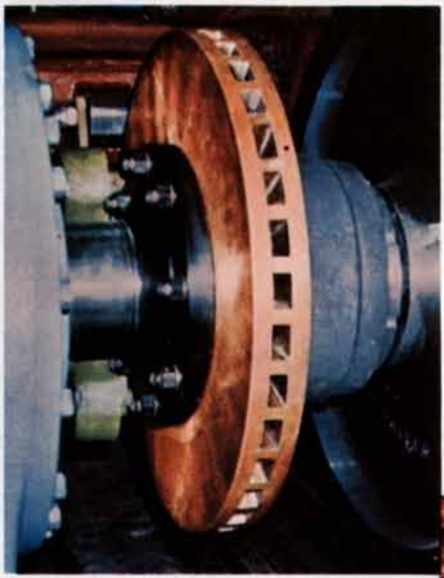
## copper developments



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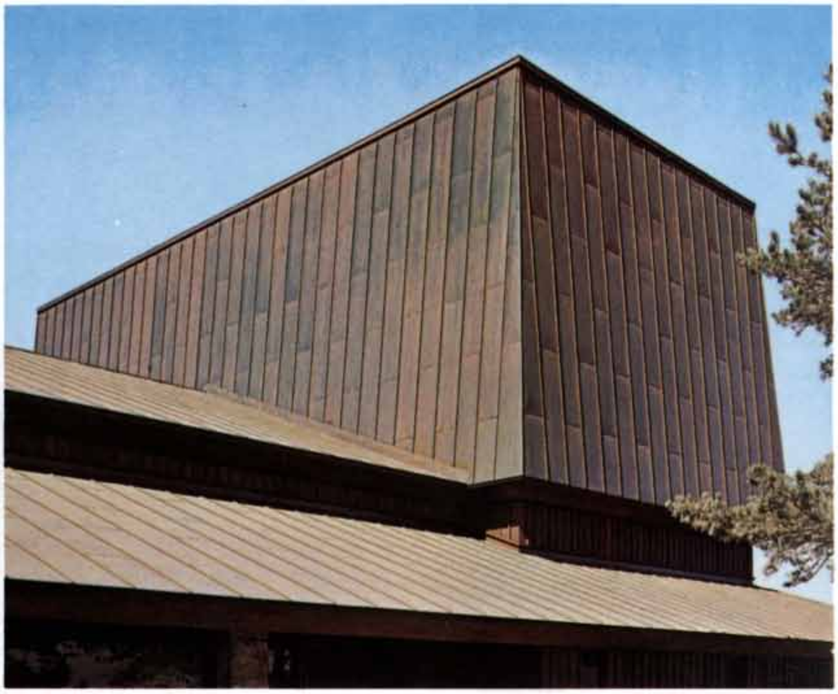

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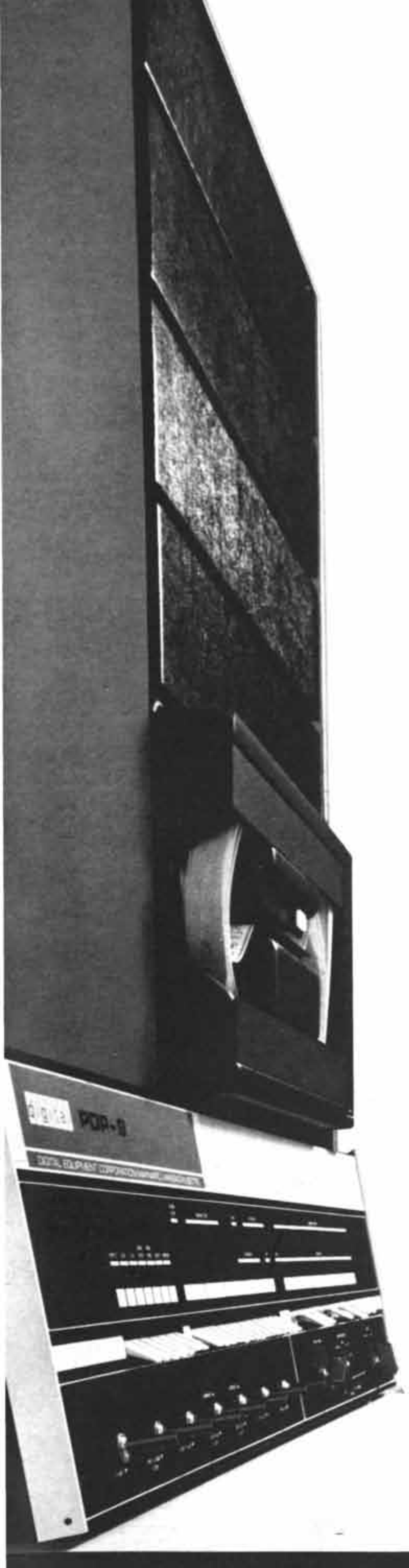

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Second, they used it for fast takeoff. The extra power gets Gulfstream II into the air quickly. It can use local airports.

Third, they used it for fast climb. Gulfstream II takes just 15 minutes to get up to 40,000 feet, far above the weather.

Fourth, they used it for range. Gulfstream II can fly nonstop from coast to coast. New York to Los Angeles, for example, in just 5 hours—with 90 mph headwinds all the way.

And last but not least, they used it for speed. Gulfstream II can cruise at 585 mph—making it the fastest corporate jet in the world.

So far, 70 orders have been placed for Gulfstream II, even though deliveries have just begun.

### In good company

Grumman Aircraft is not the only manufacturer to put the Spey to work. It powers the BAC One-Eleven used by American, Braniff, Mohawk and Aloha Airlines. It substantially improves the performance of the McDonnell Douglas F-4 Phantom ordered by the British Government for the Royal Navy and Royal Air Force. Versions of the Spey also power the Hawker Siddeley Trident, the Fokker F-28, the U.S. Air Force's new A-7D and the Royal Navy's Hawker Siddeley Buccaneer.

All in all, the Spey powers more different aircraft than any other fan-jet engine. The Grumman Gulfstream II couldn't be in better company.

### Look who else is driving a Rolls-Royce

Most people think of the Rolls-Royce Silver Shadow as the ultimate motor car.

But did you know that Rolls-Royce also builds the diesel engine that powers this heavy-duty excavator?

That Rolls-Royce industrial engines generate electricity, pump gas, power hydrofoils and run chemical processing plants?

That Rolls-Royce reactor cores power all of Britain's nuclear submarines?

That Rolls-Royce builds multifuel engines that run equally well on gasoline, kerosene, jet fuel or diesel fuel?

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# *Ever wonder about what a steel research man wonders about?*

## *Some notes on work in progress or recently completed in the research labs of one of the big steel companies.*

By Dr. Karl L. Fetters
Vice President, Research and Development for
Youngstown Sheet and Tube Co.

The curious cats in the research department of our company are continually on the prowl in examination of the thousands of problems and opportunities that surround steel—the most basic of all the basic commodities.

Simply to show you the range of our research activities I have set down here a dozen headings under which we are making investigations, with a few words about what's happening in each.

### Beneficiation and Iron Making

*Sinter Studies.* Sinter mixes consisting of varying proportions of concentrates, fines, and mill scale with and without flux additions, are being tested to determine the conditions for making high iron, low silica sinter having a high bulk density suitable for use in the open hearth.

### Carbonization

*Petrographic Studies of Coal.* Float-sink studies have been initiated on column samples of coal to determine the response to gravity separation of pyrite associated with light and heavy gravity petrographic entitles. The results will be used to develop data whereby predictions can be made on the washability characteristics of the coal by petrographic association analyses.

### Melting

*Study of the Effect of Ingot Mold Size and Steelmaking Practices on the Quality of Rimming and Bottle Top Steels.* A program has been established to investigate the quality of rimming and bottle top steels. This program includes a study of deoxidation practices, teeming speeds, and mold practices.

### Refractories

*Pouring Pit Refractories.* Work continues with ladle nozzle inserts. Initial trials of several inserts looked very promising. Work in progress now is in new nozzle sizes.

### Processing

*Continuous Casting.* Samples of blanks from an AK concast steel run have now been sheared into tensile specimens for evaluation of detailed mechanical properties of cold strip rolled from AK concast steel. Work continues on the determination of oxygen in AK concast steel at various locations in the slabs.

### Corrosion

*Corrosion of Carbonated Beverage Plate.* Results of a blue dye test on nitrogen annealed tin plate from experimental ingots containing varying sulfur concentrations to determine relationship between corrosion resistance and sulfur content.

### Coatings

*Corrosion Resistant Tin Plate.* To determine the extent of improvement in corrosion resistance of tin plate attainable by duplex plating, experiments were conducted on the halogen line by initially depositing tin coatings of .01 and .09 lb./BB; alloying same to FeSn or FeSn$_2$; and subsequently recoating both FeSn and FeSn$_2$ coatings to .25 lb./BB, .50 lb./BB, and 1.35 lb./BB tin.

Laboratory tests will compare corrosion resistance of this material with conventional tin plate of equivalent tin coating weight.

### Physical Metallurgy

*Experimental Tin Plate — Properties of Quenched and Tempered Low Carbon Strip.* Several coils of .0088″ black plate were processed with electron beam guns mainly for setting up the beam gun parameters. And to adapt the equipment to specific tests on quenched and tempered low carbon strip for experimental tin plate.

### Mechanical Metallurgy

*Formability.* Inverse pole figure determinations were carried out on the low-carbon al-killed steel given various per cent cold reduction. Studies have been conducted in the presence of recrystallization components leading to low and high R$_0$ and R$_{90}$ and Maximum R values at 45° directions.

### Operations Research and Applied Mathematics

*Seamless Round Yield Analysis.* To help analyze seamless round yield data on 5,000 keypunch cards, computer programs have been written and run to summarize and group the data in any manner desired. The purpose of the analysis is to determine the effect various factors such as conditioning practice, ingot type, size, have on the yield of seamless rounds.

### Research Services

*Boron Steel.* Forgings have been made of a heat of boron steel, grade AISI 10B48 and these are being tested for automotive application. This steel would be used as a replacement for 5150 steel.

### Research Laboratory Services

*Impact Properties of Tempered and Untempered Weld Zone.* Samples of 20-inch O. D. by 0.234″ wall, Grade X-60 electric weld pipe are being tested. These samples consisted of one which was processed normally, and two which had the weld zone left untempered. The impact properties are being determined and compared.

This is the first of a series of articles in which we'll bring you news of what's going on in steel research at Youngstown.

It is a fact that almost all of our research is "inspired" or motivated by customers' needs and we make quite a thing of offering our research knowledge to the service of our customers. It's all part of a new spirit at Youngstown, expressed in the word Steelability.

Steelability simply stated is Youngstown's capacity plus desire to meet the most strenuous demands of our customers. Research across a wide range and in depth, is a part of Steelability. If you think our researchers might be able to help you, give us a call or Write Dept. 251A6.

**Youngstown Steel**
THE YOUNGSTOWN SHEET AND TUBE COMPANY · YOUNGSTOWN, OHIO 44501

# Living Under the Sea: A report from General Dynamics

The public address speaker screams, "Dive, dive!" In the flickering light of a dank interior, sweaty bearded sailors tumble to battle stations. . . .

This Hollywood image of a submariner's life was, even during World War II, largely stereotype. It is a far cry from life in today's United States Navy nuclear submarines.

Even though about three-fourths of the ship's interior is taken up by machinery, weapons and stores, there's also room for up to 136 men to eat, sleep, relax, work efficiently and remain alert. The sailors who man these submarines on continuously submerged patrols for two months at a time lead a surprisingly comfortable life.

Here's a fairly typical day for nuclear submariner Bill Reilly, Electronic Technician Third-Class.

0700 hours. ET/3 Reilly is awakened by a shipmate. Along his bunk's 6′6″ length—long, wide and deep enough for comfortable sleep—recessed fluorescent fixtures dispel the night. Another "day" has begun.

## 30,000 meals:

0715 hours. Reilly's baritone bounces around the private stall shower. He need not worry about quick sudsing and rinsing; nuclear submarines can distill an ample supply of fresh water.

0730 hours. Breakfast time. More than 30,000 individual meals will be served during the ship's extended patrol—prepared in a galley smaller than the kitchen of an average suburban home. The galley has been laid out to a careful time-space-motion plan. Provisions are stored for easy accessibility in planned sequence. Meat is pre-trimmed; chicken deboned to save precious space. Ice cream cones—by the thousands—are tucked into odd crannies.

0800 hours. Reilly's first four-hour watch begins. His job: monitoring a navigation computer.

All around him the ship stirs with action as crew members go about daily chores (just as Reilly will between his regular watches)—inspecting, cleaning, maintaining.

## "Scrub, burn and filter":

Nuclear submarines do not need to surface to get air for their engines, but Reilly's still a deep breather. Carbon dioxide, exhaled by the crew at the rate of 110 cubic feet each hour, is removed by "scrubbers" before it can build into a dangerous concentration. Oxygen, manufactured by water electrolysis, is fed back to the ship's atmosphere. Over 300 potential contaminants are removed by filtration, electrostatic precipitation or catalytic burning.

Revitalized air, purer than that breathed by city dwellers, is recirculated throughout the submarine, conditioned to a comfortable humidity and 70° temperature.

1200 hours. Lunch. On today's menu: chicken cacciatore.

## Off-watch:

1250 hours. At the ship's laundromat, Reilly drops off his coveralls, made of lint-free polyester to eliminate one potential irritant from the atmosphere; he stops at the 2,000-volume library to pick up an electronics textbook he's studying for college credit.

1315 hours. Alarm signal! Reilly double-times to his duty station. This time it's a fire drill. It might have indicated a potential enemy's presence or a dozen other contingencies. Alarms are sounded at unscheduled times, day or night, throughout the patrol to keep the crew on its toes.

1415 hours. He routinely checks one of his alternate drill stations, then works off some lunch calories with a session on the exercise bicycle.

1600 hours. Reilly spends the next hour making some minor adjustments to one navigation computer that is temporarily "down." Each man on a nuclear submarine is responsible for the performance and maintenance of the equipment that he operates.

As he moves about the ship he continues to study its 110 miles of complex wiring, a requirement for many crew members so a fault can be quickly traced if necessary.

## Versatile mess:

1700 hours. At one end of the mess, a checkers tournament is going on. At the other, Reilly—with one shipmate posing and two others kibitzing—is finishing off a watercolor.

The mess is the most versatile room on the submarine. At various times it becomes movie theater, gym, game room, lecture hall and music room. Two days from now, Sunday, it will become a chapel.

1800 hours. Dinner; lobster—a reminder that today is Friday. Last night the cooks surprised everyone with a Hawaiian luau. The night before, it was roast beef. Food on a submarine is a major morale factor for the crew.

Leftovers are inevitable. Garbage is compacted into a container, weighted, and blown into the sea, where it sinks to the bottom.

1900 hours. The mess has now become a movie theater—tonight Reilly and some of his shipmates enjoy a new James Bond picture, well before it's been released to the general public.

In the unseen world above the surface it is dusk. On extended submerged patrol, every effort is made to make life as comparable as possible to surface duty. The control room is "rigged for red," that is, switched to a dull red illumination; ordinary lights are dimmed to remind the crew that another day is passing into night.

## Shhh!:

Despite 007's noisy battles—or later the sound of hi-fi music—nuclear submariners live in a quiet world. Sounds are muted by vinyl tile decks and acoustic tile overheads. Vibrations are minimized. Turbines, fans and other moving equipment are surrounded by special sound-deadening material.

2000 hours. Bill Reilly begins his second four-hour watch. Others, who are now off-watch, are relaxing, reading, getting ready to bunk down—and some are still sleeping before being awakened later.

2400 hours. Midnight. The ship is quiet. His watch over, Reilly bunks down, draws the curtains for privacy, turns on the overhead fluorescent and reads for a while. He yawns, adjusts the air vent at the head of his bunk, switches off the light. He is asleep.

In building almost 300 submersibles—including the prototypes of most American nuclear submarines—habitability has been a prime concern of General Dynamics designers and engineers since 1900 when the company delivered the United States Navy's first.

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*General Dynamics* is a company of scientists, engineers and skilled workers whose interests cover every major field of technology, and who produce: aircraft; marine, space and missile systems; tactical support equipment; nuclear, electronic, and communications systems; machinery; building supplies; coal, gases.

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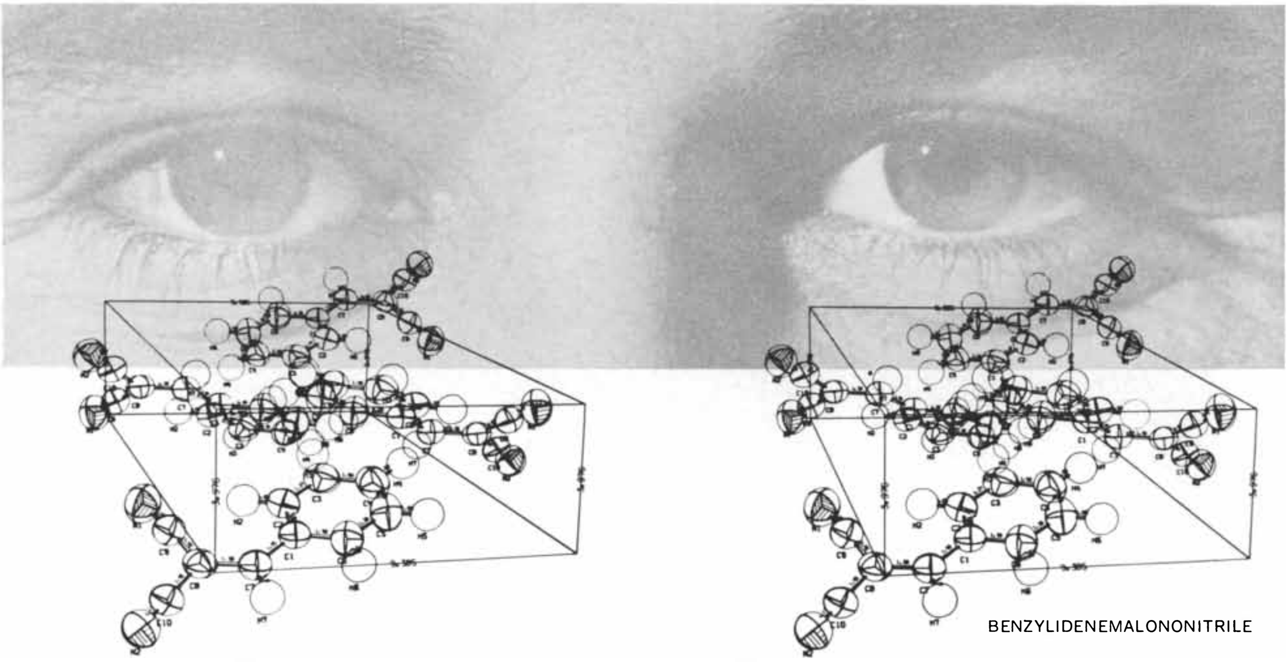


BENZYLIDENEMALONONITRILE

# 3-D Diagrams now produced automatically by computer-plotter

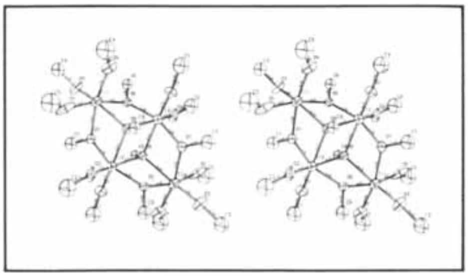
Crystal structure analysis picks up a lot of speed with the use of the computer-plotter combination to turn out 3-dimension diagrams automatically.

These three diagrams were prepared with the CalComp Plotter for the Defence Standards Laboratories, Victoria, Australia.

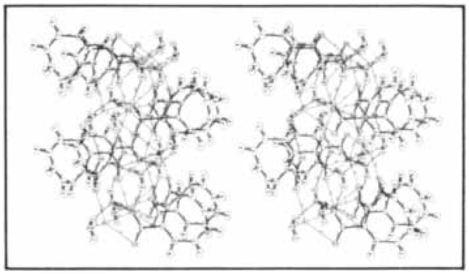
D. A. Wright of DSL reports:

> *"The three crystal structures plotted in 3-dimension diagrams are (1) Hydrogen Bond (2) Titanium Tetramethoxide, and (3) Benzylidenemalononitrile.*
>
> *"They will be used as illustrations to papers in Acta Crystallographica to be published shortly.*
>
> *"All the plots look superb when viewed through prisms."*

For information on the CalComp Plotting Systems available for this and similar scientific analysis, write: Dept. N-9, California Computer Products, Inc., 305 Muller, Anaheim, California 92803. Phone (714) 774-9141.



TITANIUM TETRAMETHOXIDE



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# The men of steel are winning

You are about to find yourself on the right side of radical changes in steelmaking. Tomorrow's steels will take new shapes, do new jobs, last longer, cost less. This year the steel industry is investing $2 billion to revolutionize steelmaking. By 1970 they will have committed nearly $10 billion in all, to the growing struggle for world markets.

The weapons in this steelmaking revolution are new technologies. Basic oxygen furnaces — ore concentration — automated kilns — continuous casting — computerized rolling mills. New ways of doing things that will alter the industry beyond recognition.

Allis-Chalmers part in creating the new world of steel extends from the mine to the mill. Allis-Chalmers construction, electrical, and process equipment helps cut the cost of wresting ore from the ground. Allis-Chalmers automated rolling stands shape and finish it more efficiently.

Surprising to find this unique combination of capabilities in a single company? Expect it when you're working with Allis-Chalmers. This is just one more example of how progress-making combinations of Allis-Chalmers skills are working world wide in industry, agriculture, construction and space exploration. Allis-Chalmers General Offices, Milwaukee, Wisconsin 53201.

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Established 1845 SCIENTIFIC AMERICAN September 1967 Volume 217 Number 3

# Materials

## *Presenting an issue on materials in two aspects: (1) the fundamental nature of metals, ceramics, glasses, polymers and composite materials and (2) the properties that all materials possess in varying degrees*

by Cyril Stanley Smith

In acknowledging the importance of materials in human culture (and conceding that earlier times must have been better than the present) the Greeks posited four ages of man—Gold, Silver, Bronze and Heroic—before their own Iron Age. For all that, materials have been pretty much taken for granted, and their diversity and adaptability has rarely been consciously considered. This lack of interest came about, I believe, mainly because man discovered at an early period a variety of balanced materials that were available without further study for a wide range of uses. The designer simply did not think of applications that required more than stone, fired clay, cement, the common biological materials and the alloys of the ancient seven metals. Moreover, although the philosophy and science of matter is virtually coeval with philosophy and science in general, the science of materials is quite recent. The most useful properties are the structure-sensitive ones with which the classical physicist was utterly incapable of dealing and therefore did not consider to be physics.

In a way it is the merging of two opposing schools of Greek philosophy of matter that gave rise to the modern science of materials. The elemental qualities of Aristotle are seen to arise in the geometric forms of the Pythagoreans. Now that the ultimate structure and gross properties can be related fundamentally, it is seen that there is less difference between different kinds of materials than had been supposed when they were the basis of totally separate crafts and industries. Properties can now be designed, not just selected. With each new design, however, the materials scientist and the engineer must still seek the optimum compromise between workability in the shop and durability in use.

One of the great stages in man's development was the discovery that he could change the very nature of materials. It must have given early man an almost godlike feeling of control over nature as he turned clay to stone by heating it. The nearly unlimited formability in one state is replaced by high stability in the other because of changes in the complicated relation (on both the atomic scale and a larger one) between the microcrystals of the clay substance and water, and the chemical change and complete recrystallization that occurs on firing above a red heat.

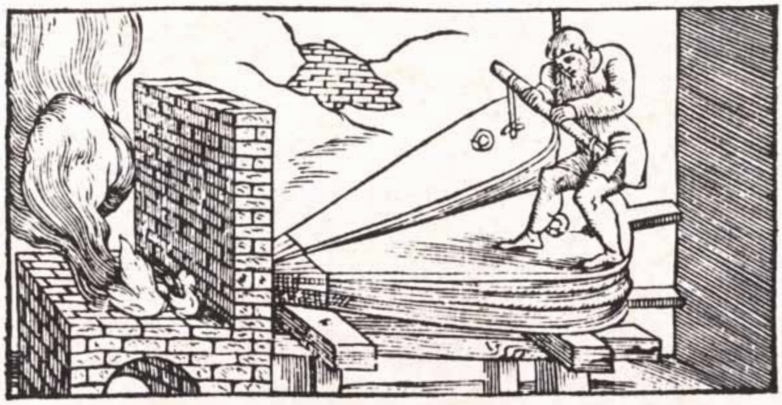
Ceramics, the earliest inorganic materials to be structurally modified by man, exemplify the diversity of structure-related properties better than any other. Except for electrical and magnetic effects, almost all the properties of solids that are the concern of modern solid-state physicists were exploited by early ceramists. Shaping involved moisture-dependent plasticity and thixotropy; decorative textures were derived from vitrification and devitrification, the nucleation of various gaseous and crystalline phases, and local variations of expansivity, viscosity and surface tension; colors depended on various states of oxidation, on abnormal ionic states, on excitons and on structural imperfections in crystals. All these phenomena were discovered for sheer aesthetic pleasure, not utility.

The earliest glazing technique is in many ways the most interesting. This was a Sumerian invention made famous after 4000 B.C. as Egyptian blue faïence. It was not, like later glazes, a melted premix of glass-forming materials but was made in a kind of cementation proc-

**IRANIAN JEWEL BOX is decorated by *hatam-bandi,* an ancient technique of inlaying that has been kept alive by the Islamic fondness for intricate geometric patterns. The inlay worker began with hand-drawn brass wire hammered into a triangular cross section in a grooved block, and with strips of camel bone and colored woods sawed to the desired section and dressed by filing in grooved blocks. The wire and the strips were glued together into composite rods in five separate stages of assembly, pressed into rectangular blocks and finally sawed transversely into slices. The detail of *hatam-bandi* work on the opposite page is enlarged four times. There are more than 400 pieces per square inch in work of average quality. The beauty of the pattern arises not only from geometry but also from the implication of a sectioned three-dimensional structure. In this respect the *hatam-bandi* pattern resembles the microscopic cross sections that illustrate many of the other articles in this issue.**

ess during which potash was drawn by capillarity to react with the surface of a preformed body of siliceous particles to form a glassy coat of copper-colored eutectic silicate that did not "wet" the powder in which it was embedded. The process is still in use in Iran, where it was recently discovered by Hans E. Wulff of the University of New South Wales. Its implications for the history of sand-cored glass-vessel technology and in various metallurgical cementation processes have yet to be explored.

The earliest use of metal followed not long after the first wide use of fire-hardened clay. Metals owe their main utility to the fact that they are rigid below a certain stress (high enough for most service uses) but become quite plastic above a certain stress (low enough to be surpassed locally by the concentrated action of a tool). Above a certain temperature they become liquid and can be shaped by casting.



**BELLOWS ARE WORKED** at a large smith's hearth in Vannoccio Biringuccio's *Pirotechnia*. This book, which was published in Italy in 1540, was a pioneering work on materials.

**CAKES OF COPPER-LEAD ALLOY ARE HEATED** to get silver from copper in a book by Lazarus Ercker published in Prague in 1574. Silver was contained in molten lead (*center*).

Metals began, as did ceramics and many other technological innovations, somewhere in the region that today comprises eastern Turkey, northern Iraq and northwestern Iran. Hammered copper objects in the form of dress ornaments, necklace beads and the like are known from the eighth millennium B.C. They are made of unmelted, unannealed native copper, simply hammered and cut to shape. Native copper seems to have been used in the Middle East mainly for decorative purposes, and no large pieces were fabricated. Conversely, the artisans of the Old Copper Culture in the Great Lakes region of North America (3000–1000 B.C.) hammered sizable pieces of native metal into knives, spears and agricultural implements. The microstructure of these objects shows that the metal had been worked hot or frequently annealed at a red heat in the course of the shaping operation.

In the Middle East cold-hammered native metal was largely displaced around 4000 B.C. by copper smelted from ores. Because copper ores are far more abundant than the native metal, this was a development of vast economic significance. Alloying soon followed. The first copper alloys came from the smelting of ores that contained arsenic and antimony as naturally occurring impurities. These alloys not only are harder than pure copper but also have a lower melting point and give castings with a much better surface and internal soundness. About 3000 B.C. came the bronzes. For two millenniums thereafter the alloys of copper and tin dominated metallurgy in spite of the scarcity of the ores of tin; they combined ease of shaping, beauty and general serviceability better than any other metallic material.

Melting was probably first used to convert copper scrap into lumps that could be hammered into shape, then for casting shaped objects directly. Artisans first used open molds of clay or stone, then molds in two or more pieces assembled to produce objects with more complicated shapes, and eventually clay molds made around a wax pattern that could be burned out, and so removed most restraints in design.

By the time bronze was discovered, elaborate methods of shaping and joining the precious metals—gold and silver—had appeared. Jewelry from the royal graves at Ur in Mesopotamia (around 2600 B.C.) exhibits higher standards, both aesthetic and technical, than most objects made today, and shows that their makers could reproducibly exploit most of the properties of metals that only now are being scientifically explained.

It was economics rather than the inherent qualities of the metal that gave rise to the Iron Age. Unless iron is alloyed with carbon to make steel and is then hardened by heat treatment (for some curious reason it was rarely hardened by cold work) it is weaker and in every way inferior to cold-worked bronze. It is also more difficult to make and more variable in its properties. But iron ores are far more common, and 1,000 inferior iron swords would outweigh 10 good swords of bronze.

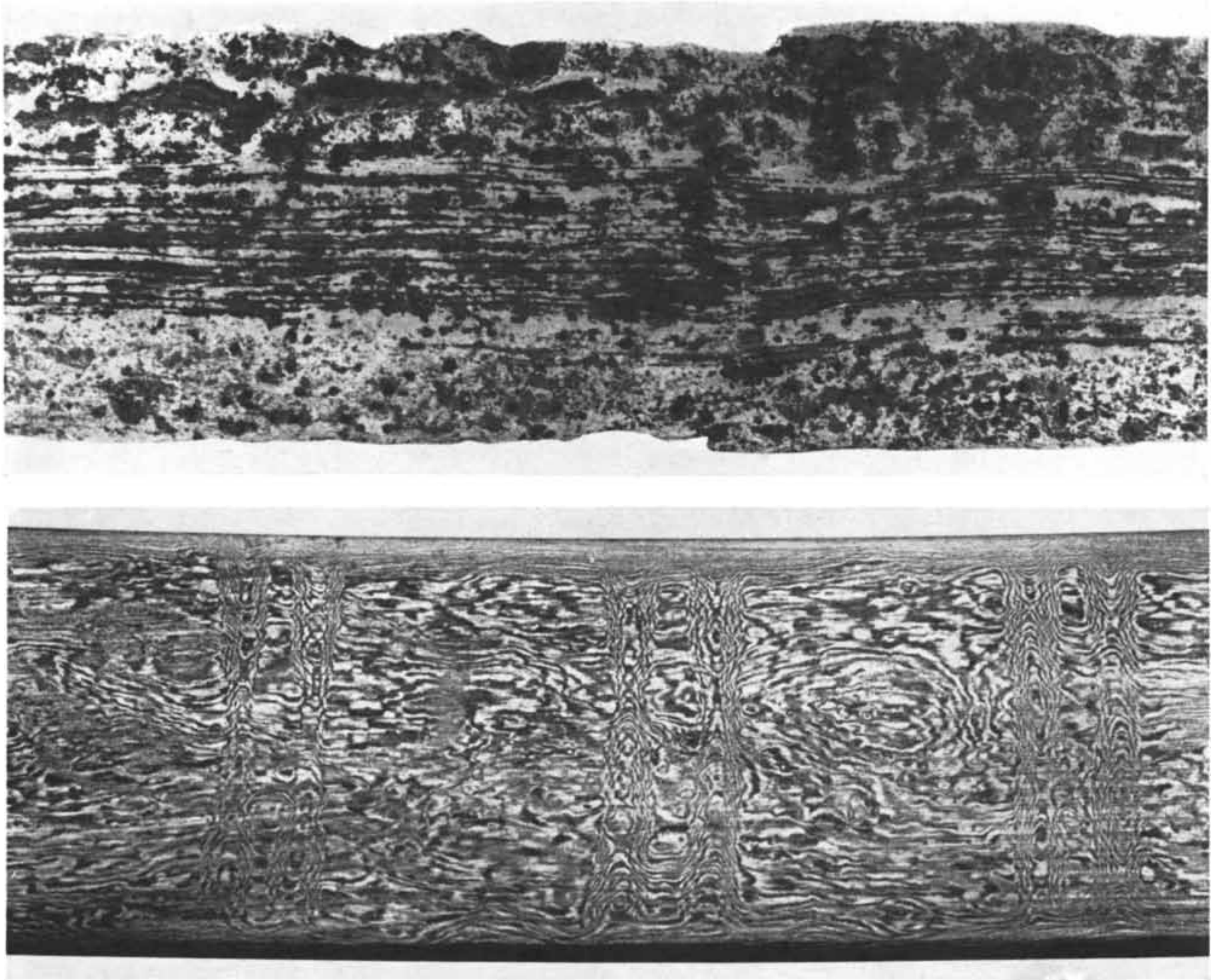
Once steel could be reproducibly heat-treated, of course it became supreme. The early metallurgy of iron was quite different from that of copper. Pure iron was unmeltable in any furnace available prior to the 19th century. If iron is heated in a fire long enough to absorb carbon from the charcoal fuel, it changes its properties greatly, becoming first steel, then cast iron, which is not much more difficult to melt than copper. The cast product, however, is relatively brittle. Before A.D. 1400 it was little appreciated except in China, where it was early used for making agricultural tools, stoves and minor works of art. Farther west iron remained for millenniums the smith's metal. The iron sponge resulting from the reduction of a pure ore with charcoal in a hearth was unmeltable, but it was malleable and easily consolidated by hammering when white-hot. Shaping was done entirely by the skillful use of the hammer. Such "wrought iron" always contained residual inclusions of slag and rocky matter that greatly weakened it.

**GLASS IS MADE in Georgius Agricola's *De Re Metallica*, published in Germany in 1556. The men around the beehive-shaped furnace are holding blowpipes for blowing the glass.**

Steel was easy to discover, but the recognition that it was an alloy was long delayed. Unlike bronze, which was consciously made by mixing things, the alloying of carbon with iron occurred invisibly as it was absorbed incidentally to the processing of the metal. The all-important presence of carbon in steel and cast iron was not discovered until 1774, the same year the chemical role of atmospheric oxygen was discovered. Before this both philosophers and blacksmiths had thought that steel was a purer form of iron—not illogically, because iron turned to steel after prolonged heating in a fire that did purify most things.

Heat treatment is, after work-hardening and alloying, the third basic way of modifying the properties of a metal. Heating most nonferrous metals removes the strain-hardening that results from cold work and causes recrystallization, which puts the metal into a soft state ready for further deformation. In steel the effect is more drastic. At a certain critical "transition" temperature the crystal form of iron changes, and carbon can go into solid solution in the crystal lattice of the iron. On cooling iron rapidly, as by quenching in cold water, an intensely hard metastable phase results.

The date by which men had learned to control the heat treatment of steel reasonably well is still uncertain. The best of the ancient smiths were those of Luristan, in the ninth and eighth centuries B.C. Yet their beautifully forged swords have a microstructure clearly

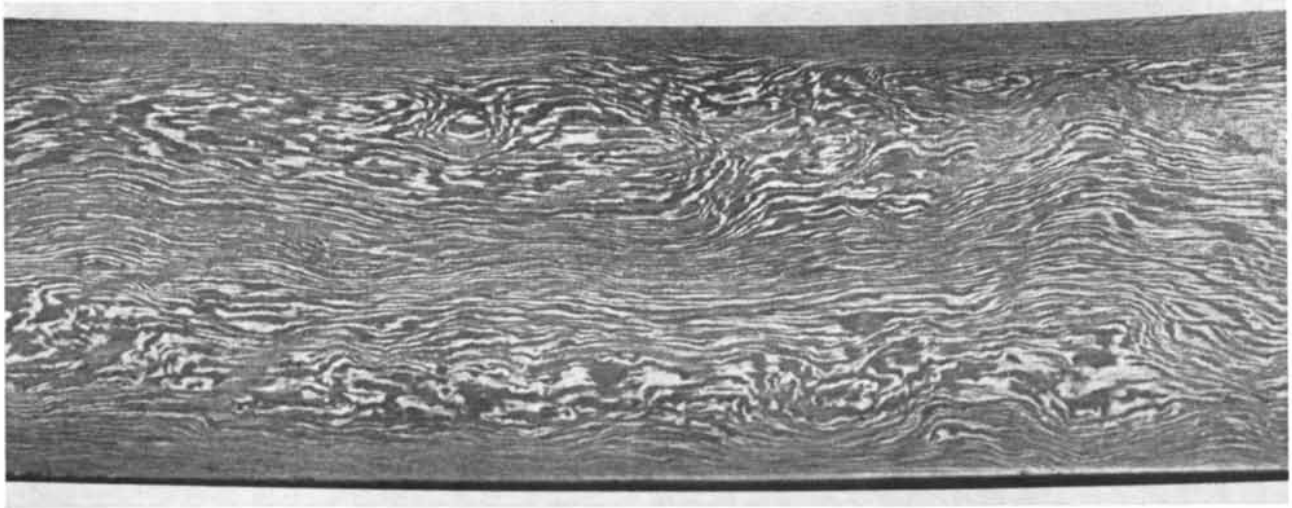


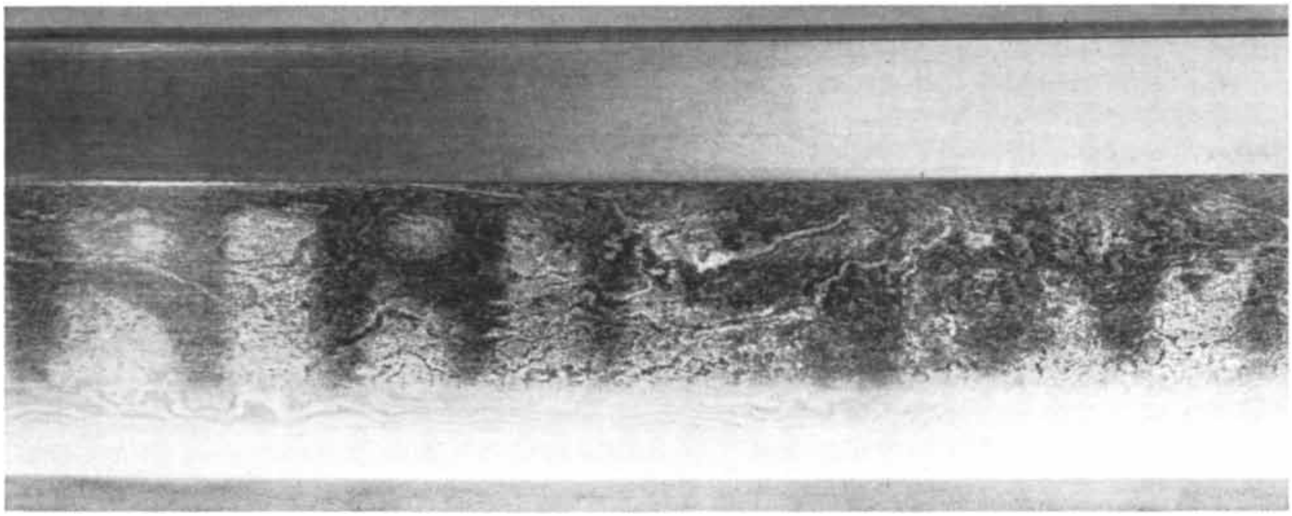
**FOUR SWORD BLADES in New York's Metropolitan Museum of Art reflect three stratagems used by medieval smiths to improve the properties of iron. At top left is an eighth-century-A.D. Carolingian blade. The laminations running down the middle arise from a complex hammer-welding and forging operation that served to break up slag inclusions and give a composite metal that was both tough and decorative. At top right is a Turkish "Damascus" blade. It was forged from a cast high-carbon steel ingot that had been slowly cooled to precipitate iron carbide in a form that remains visible after intensive forging. The curly pattern on the surface is produced**

showing that the metal, usually fairly high in carbon, was hot-worked at a temperature indiscriminately above and below the transition temperature and was not quenched. The weapons of the Greeks and the Romans were sometimes quench-hardened, but rarely and under poor control. To achieve the desired temper directly by quenching was a critical and difficult operation, particularly when failure could as often be due to a wrong carbon content as to a wrong cooling rate. There was no way to measure either. The modern two-stage process—quenching followed by low-temperature reheating to let down the hardness to an appropriate degree—is much easier to control. It is small wonder that the few sword blades of antiquity that were perfectly heat-treated became legendary.

Yet the early Near Eastern empirical discoverers of materials did their work well. They found nearly all alloy compositions that could have been made by charcoal reduction from recognizable natural minerals and that were fit for general service. The tools, guns, gadgets and cathedrals of the Middle Ages, the instruments for the rise of modern science, the machines and structures of the 19th-century engineers—all were made of materials that had been known centuries before the rise of Greece. Metallurgists had been busy in the interim, increasing the scale and the economy of production and the reliability of the products, but neither they nor the user-smiths felt the need for new compositions. Development much beyond the old required new attitudes, new knowledge and new needs, all of which came together not much before the beginning of the 20th century.

The earliest recorded speculations on the nature of matter are those of the Greek philosophers, whose writings reflect appreciable contact with the artisan's knowledge of the behavior of matter. The atomism of Democritus was a natural—almost inevitable—deduction from an examination of the graded textures of stones and ceramics and from the obvious relation between the properties of bronze and steel variously treated and the texture on the fractured surface of a broken piece. Aristotle could specify in a litany of 18 opposites the qualities that a craftsman would observe and exploit: meltable or unmeltable, viscous or friable, combustible or incom-



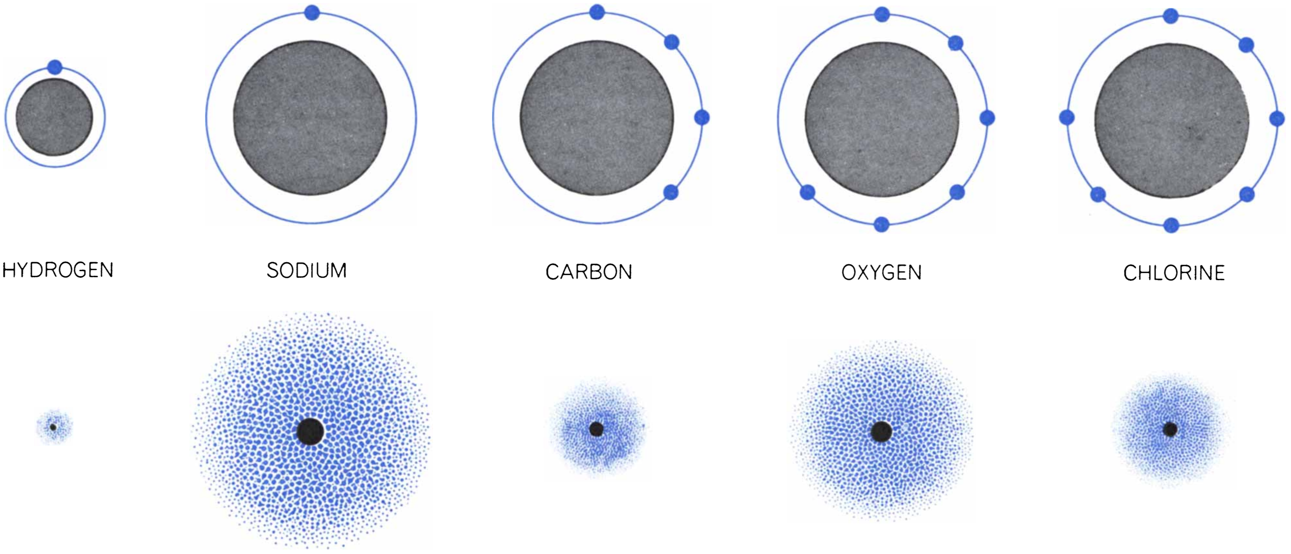


**by local variations in deformation. At bottom left is a Persian scimitar, also made of forged high-carbon steel. The regular vertical markings were made by local hammering that distorted the grain of the metal. At bottom right is a Japanese blade. Part of its pattern is the forged-in grain of mechanically heterogeneous metal. The whitish areas are the result of differential heat treatment. The blade was coated with a refractory material that was locally removed to expose the blade and other parts that were to be hardened; the whole blade was then heated and quenched in water. This procedure was unique with Japanese blades, which excel all others.**

bustible and so on. The three familiar states of the aggregation of matter and their relation to energy gave him his four elements: earth, water, air and fire. This was, in a way, good physics, but the "chemistry" that arose in the attempt to account for various substances by the combination of the associated qualities ended in nonsense.

The alchemists sought a relation between the qualities of matter and the principles of the universe. One of their goals—transmutation—was to change the association of qualities in natural bodies. In the days before the chemical elements had been identified it was a perfectly sensible aim. What more proof of the validity of transmutation does one need than the change in the quality of steel reproducibly effected by fire and water? Or the transmutation of ash and sand into a brilliant glass gem, or mud into a glorious Attic vase or Sung celadon pot? Or the conversion of copper into golden brass? Of course today we know that it is impossible to duplicate simultaneously all the properties of gold in the absence of atomic nuclei having a positive charge 79. One way to secure a desired property is still to select the chemical entities involved, but much can also be done by changing the structure of the substance. Modern alchemy is more solid-state physics than it is chemistry, but it could not have appeared until chemists had unraveled the nature and number of the elements.

In the 16th century the principles of Paracelsus—salt, sulfur and mercury—displaced the elemental qualities of Aristotle, expressing an intuitive awareness of the distinctly different properties associated with ionic, molecular and metallic bonds, but this was soon displaced by a chemistry based solely on analytically determined composition. For two centuries chemists were relatively uninterested in properties. The overthrow of caloric and phlogiston in the 18th century represented a similar turning away from physical concepts to a more precise chemistry. Chemists were rightly excited by the demonstration that the reduction of copper or iron from these ores represented the subtraction of oxygen, not the addition of phlogiston. Nevertheless, in today's quantum theory of solids the reduction of a metal can be considered as the boosting of a valence electron into



**ATOMS ARE REPRESENTED** schematically (*top*) and more realistically (*bottom*). In the schematic representation the dots are the valence, or outer, electrons. The gray area is the inner-electron "core." In the more realistic representation the electrons are shown as a cloud around a nucleus (*black*). The atoms at bottom are drawn to scale according to their size when they are electrically neutral.

the conduction band. The electron is a small thing, as insubstantial as phlogiston itself, yet it is the return of the electron from the oxygen ion to the metal that confers all the properties that make metals interesting or useful. In a way the phlogistonists were right, and the very real advance that came with the chemical revolution was paid for by the loss of an important viewpoint.

In physics the situation was somewhat the same. The great advances of the 17th century concerned mainly mass and other aspects of matter that were not sensitive to structure. The corpuscular philosophers, both the Cartesians and their rival atomists, spelled out explanations of plasticity, ductility and strength based on *ad hoc* assumptions about the manner in which particles were shaped and stacked in contact with one another, to slide, distort and change neighbors under mechanical stress or change in the chemical environment. These were ingenious and often right (if the corpuscles are appropriately and flexibly interpreted) but quite incalculable. Such corpuscular philosophical speculation vanished under the impact of Newton's mathematical methods, and physics could not seriously return to questions about the solid state until our own time.

The first three significant printed books on materials summarized a substantial accumulation of empirical knowledge. Vannoccio Biringuccio's *Pirotechnia* (1540) presents a comprehensive account of the operations of the foundryman and the smith in alloying and shaping materials for diverse end uses. Georgius Agricola's *De Re Metallica* (1556) gives superb detail on the mining of ore and smelting of ores, with disproportionate emphasis on the nonferrous metals and near neglect of iron. Lazarus Ercker's book of 1574 (with the resounding title *Beschreibung Allerfürnemisten Mineralischen Ertzt unnd Berckwercksarten*) presents the quantitative laboratory approach of the assayer.

These three approaches to metals—production, utilization and analysis—have moved forward but have remained somewhat distinct ever since. For geological and economic reasons the production of metals has been conducted on a large scale, whereas end-product fabrication was the work of multifarious smiths and small enterprises. Something approaching professional metallurgy developed, therefore, first in the service of the princely capitalists or others who controlled the large mines and smelters.

The production of materials other than the metals contributed rather little to the growth of their science. Producers of stone, cement and wood operated on too small and local a scale. For a while, early in the 18th century, the desire of European potters to duplicate Oriental ceramics gave drive to the beginnings of analytical chemistry, but thereafter the science of ceramics lagged; the successful ceramic body had too fine a structure to be seen microscopically and was too complex in composition to yield to simple analysis.

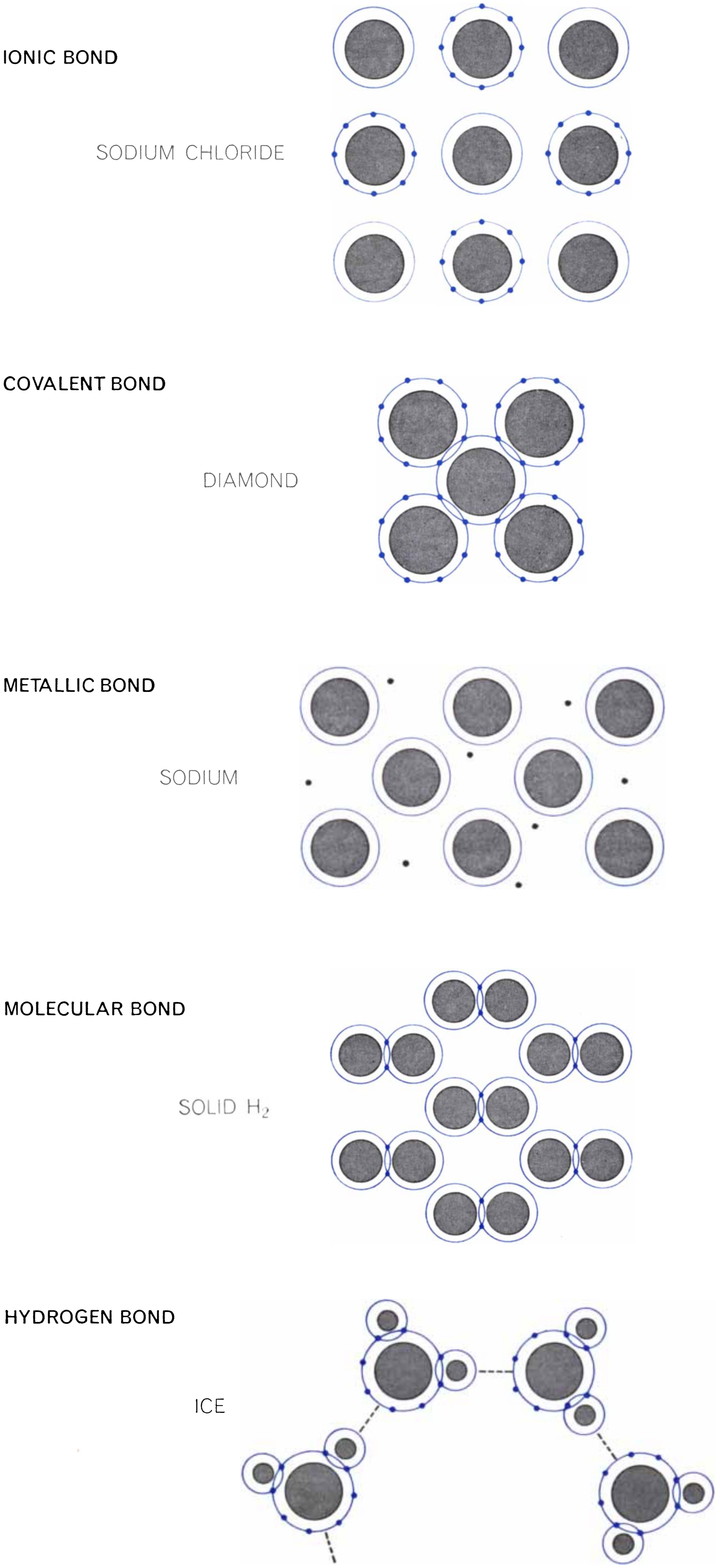
Analytical chemistry owes its origins largely to the methods of the assayer. Economics inspired him to develop ways to recover trace amounts of gold from ores and alloys. He did this quantitatively, exploiting his knowledge that the mass and identity of the metals were preserved through many stages of solution, partition and precipitation in a variety of solvents, mostly nonaqueous ones. The first table of chemical affinity, laid out by Étienne François Geoffroy in 1718, was essentially a putting in order of the separatory reactions long known to the assayer. Assayers knew a lot about oxides, although they did not know oxygen. They had measured the increase in weight that occurred when lead was turned into litharge to leave behind the shiny bead of gold or silver on their cupels, but to see the theoretical significance of this needed a different kind of curiosity.

The structural side of the science of materials, in spite of its early start in fracture tests and corpuscular philosophy, was slower to blossom. In 1772 Réné Ferchault de Réaumur published an outstanding work on iron, based on observed and hypothetical changes of structure on the level that today we associate with the microstructure. In the best scientific tradition he designed laboratory experiments aimed at checking and improving the theory, and from these he developed an important industrial material, malleable cast iron. His work came, however, at the very end of the period during which Cartesian corpuscular theories could be taken seriously by scientists. Newtonian rigor displaced this kind of structural speculation; microcrystalline grains came back into science only at the end of the 19th century, following the discoveries of the microstructure of steel by Henry Clifton Sorby in 1864.

Mineralogists meanwhile had been studying the symmetries of the external shapes of crystals, and the mathematics of the crystal lattice had been developed without the nature of the units being generally recognized: Johannes Kepler's and Robert Hooke's insight showing how the stacking of spheres in contact gave rise to crystalline polyhedrons was forgotten, and the unit had become prismatic boxes in which molecules were placed. Molecular composition rather than crystal structure was the basis of almost all 19th-century physical and chemical discussions of solids. The dominance of the molecule (so supremely justified in organic chemistry and in the kinetic theory of gases) was replaced by today's structural-atomistic viewpoint largely as a result of a new experimental technique.

In 1912 X-ray diffraction was discovered and soon applied to the study of the structure of solids by Lawrence Bragg and his followers. It at once gave a measurable physical meaning to structure on an atomic scale, and made this as real as the larger-scale structures that had been revealed by Sorby's microscopic methods half a century earlier. It was a physicist's method par excellence, and a fundamental one, which served to relate much of the unconnected data of the chemist and metallurgist.

For a time the X-ray-diffraction results led to the construction of too idealized a picture. Then the role of imperfections was perceived, first chemical, then electrical, then mechanical errors in the



**FIVE TYPES OF BOND** that hold all materials together are shown schematically. In the ionic bond the atoms have either lost an electron or gained one, so that their outer electron shell is complete. Thus they cannot share electrons, but since they are electrically charged by virtue of having gained or lost an electron they are attracted to atoms of the opposite charge. In the covalent bond pairs of atoms share their outer electrons in filling their outer shells. In the metallic bond all the atoms share all the valence electrons. The molecular bond, also known as the van der Waals bond, arises from the displacement of charge within electrically neutral atoms or molecules, which produces a weak attraction between them as they approach each other. The hydrogen bond, also a weak one, is mediated by the hydrogen atom and is possible only because of the atom's small size and the ease with which its charge can be displaced. All these bonds are idealized; most materials involve some combination of them.

building of crystals. The last served to explain the deformability of metals as well as the nature of the interface between crystal grains, the old grain boundary about which practical metallurgists had long speculated because of its great practical importance.

Although still dominant, metals thereafter lost their unique position in scientific studies of materials. Ceramics combined all the interesting crystalline complexity of metals with the electrical interest of semiconductors. Organic chemistry had been developing rapidly in the 19th century as analytical methods became available. The awareness that many compounds with the same composition have different properties engendered the organic chemist's particularly fertile concept of structure. Molecular architecture began almost as a notational device but soon became a central part of organic chemistry and was ready to join with X-ray crystallography in guiding the development of the complicated structures that endow synthetic polymers with their properties.

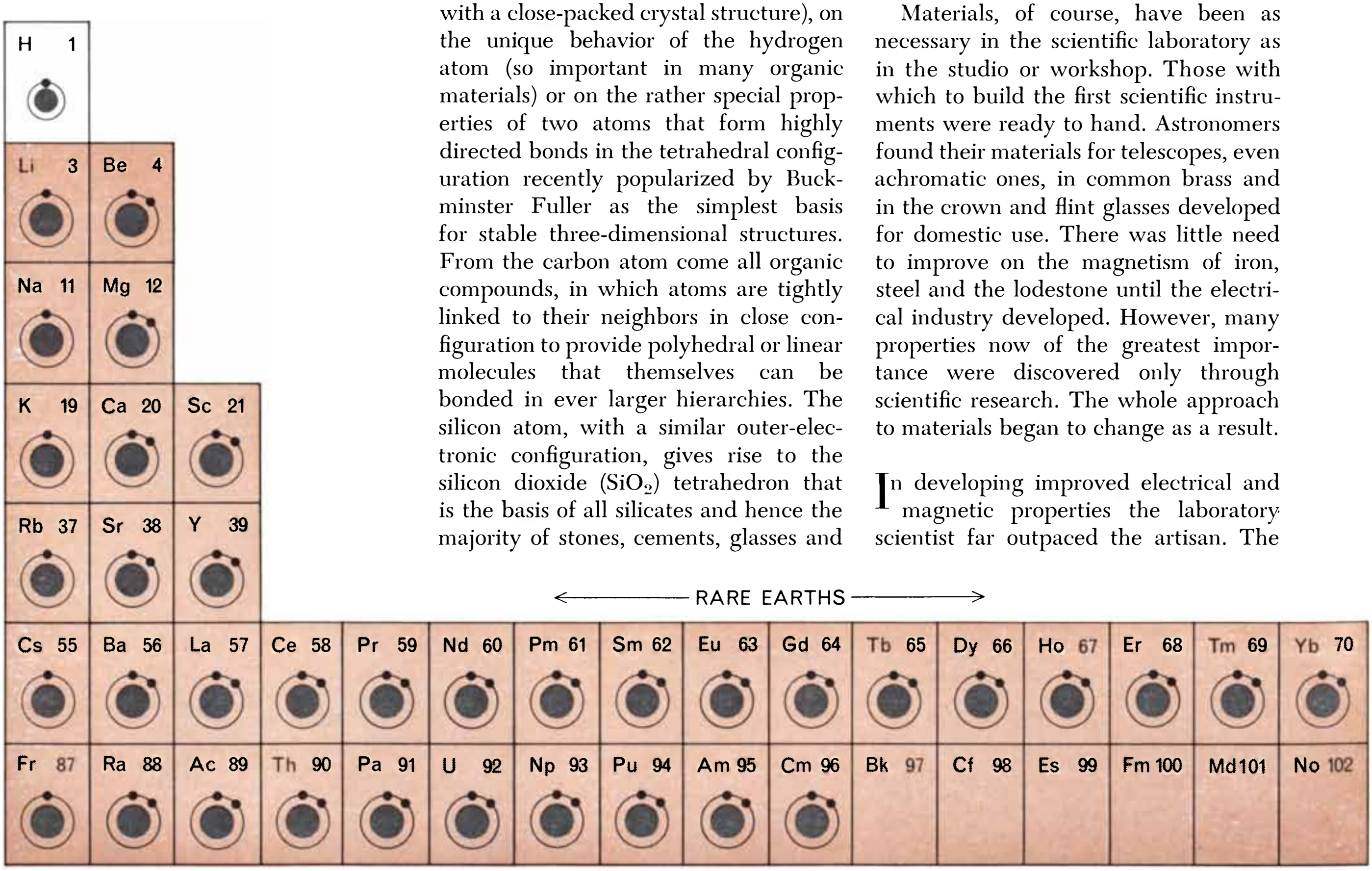
Foremost in the new understanding of materials is the realization that the properties of all types of material arise from their structure, from the manner in which their constituent atoms aggregate into hierarchies of molecular or crystalline order or into disordered amorphous structures. Moreover, the properties of bulk matter of all kinds depend strongly on the structure of imperfections, either purely architectural or chemical, in the main array. Most of the properties observed and exploited in materials are cooperative properties of the aggregate rather than of the constituent atoms and simple molecules that had perforce been overemphasized by 19th-century investigators. It is the arrangements of the outer electrons of the atoms that are of prime importance, and these are strongly modified by the configuration of neighboring ones.

The 93 species of stable atoms, or even the 10 most common ones in the earth's crust, allow for almost innumerable combinations. All materials depend on the five types of bonding in solid-state physics [see "The Solid State," by Sir Nevill Mott, page 80]. Each bond type is in essence a specific structural framework for electron interaction. The commonest structural materials depend either on the behavior of the valence electron in a relatively free state in a crystal (which accounts for all metals with a close-packed crystal structure), on the unique behavior of the hydrogen atom (so important in many organic materials) or on the rather special properties of two atoms that form highly directed bonds in the tetrahedral configuration recently popularized by Buckminster Fuller as the simplest basis for stable three-dimensional structures. From the carbon atom come all organic compounds, in which atoms are tightly linked to their neighbors in close configuration to provide polyhedral or linear molecules that themselves can be bonded in ever larger hierarchies. The silicon atom, with a similar outer-electronic configuration, gives rise to the silicon dioxide ($SiO_2$) tetrahedron that is the basis of all silicates and hence the majority of stones, cements, glasses and ceramics. It is indeed a fortunate circumstance that these two elements, which happen to be present on the earth in great abundance because of their nuclear and geochemical properties, should have the configurational requirements of their outer electrons such that they give rise to such interesting effects.

If today there is a distinguishable materials science and engineering, it is partly owing to the users' preoccupation with physical properties rather than chemical constitution. But it is even more owing to the fact that there is unity in the rules by which atoms and molecules join together in groups and groups of groups. Once the principles of interaction and the possible aggregative geometries have been outlined they will seem to be almost universally applicable. This understanding is not only effective in guiding the development of useful materials; it is also curiously satisfying to the scientist, because it makes him at home in strange landscapes. Of all approaches to nature, a science based on structure seems most able to unite the microscopic and the macroscopic, theory and practice, intuition and logic, beauty and utility. Perhaps it was not chance that involved aesthetics in the early discovery of materials.

Materials, of course, have been as necessary in the scientific laboratory as in the studio or workshop. Those with which to build the first scientific instruments were ready to hand. Astronomers found their materials for telescopes, even achromatic ones, in common brass and in the crown and flint glasses developed for domestic use. There was little need to improve on the magnetism of iron, steel and the lodestone until the electrical industry developed. However, many properties now of the greatest importance were discovered only through scientific research. The whole approach to materials began to change as a result.

In developing improved electrical and magnetic properties the laboratory scientist far outpaced the artisan. The



**PERIODIC TABLE** lists the chemical elements from hydrogen (*H*) to lawrencium (*Lw*). The key to the abbreviations is at top right. In this table the metals are in color and the nonmetals in white. The light-colored elements can be regarded as metals in some only practical precursors to the discovery of voltaic electricity were some electrochemical replacement reactions (the assayer's recovery of silver from spent parting acids, and the large-scale winning of copper from mine waters with iron) and the observation of the accelerated corrosion of iron rudder brackets on ships sheathed with lead. A great impetus to the study of electrical properties of materials came in 1857, when it was found that some good Spanish copper used in the transatlantic telegraph cable had a conductivity only 14 percent that of the best copper available. Thereafter measurements of resistivity became one of the principal tools in the study of materials of all types. The later discovery of the electron not only led to theories of conductivity, but also when seen in the light of quantum mechanics it became the very cause of the aggregation of matter and the basis of all its properties.

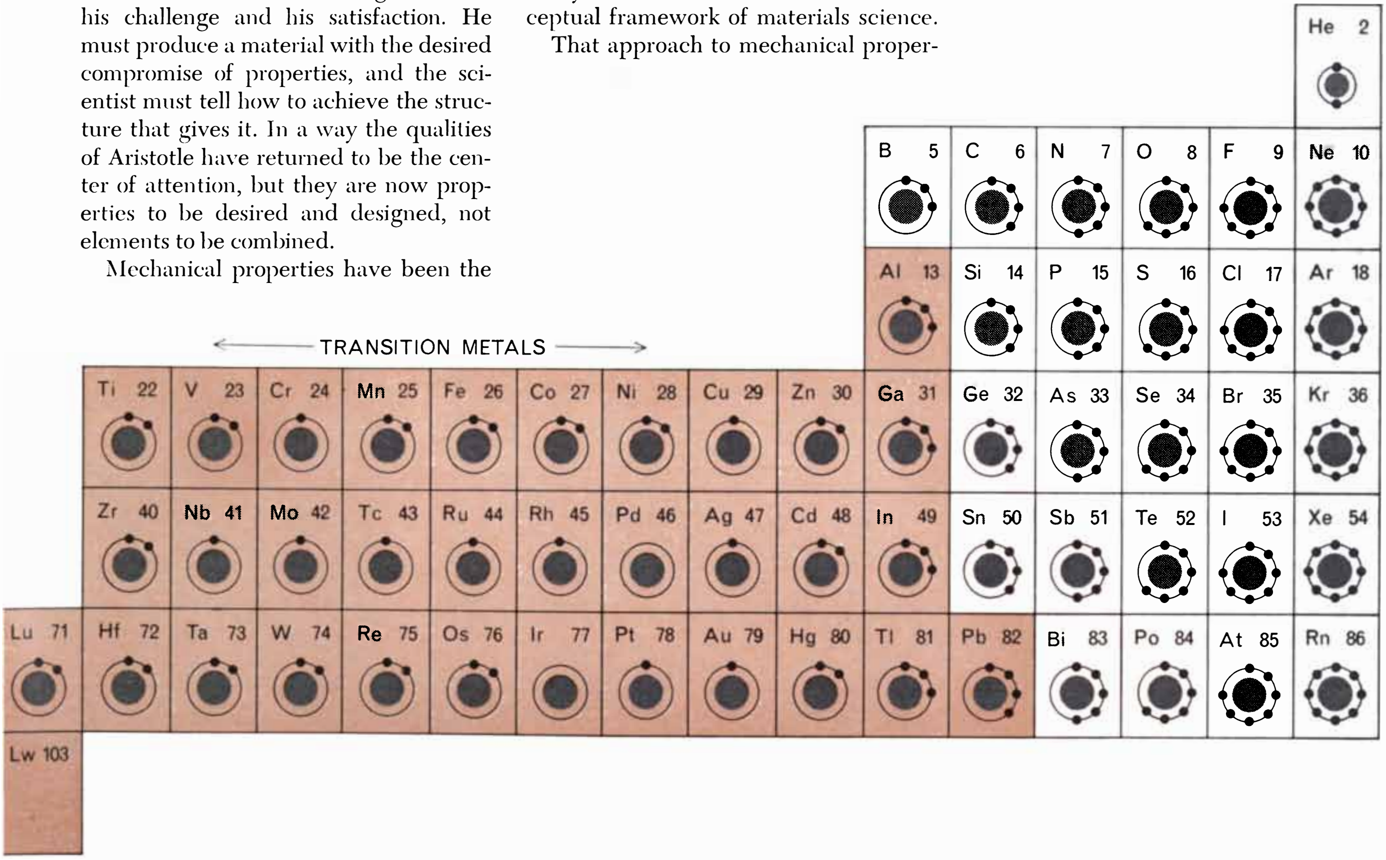
Every use of materials, however trivial, involves selection. It is possible through understanding or experiment to maximize any one property but—and this cannot be overemphasized—in no application is it possible to select a material for one property alone. It is precisely in the balance of one factor against another that the materials engineer finds his challenge and his satisfaction. He must produce a material with the desired compromise of properties, and the scientist must tell how to achieve the structure that gives it. In a way the qualities of Aristotle have returned to be the center of attention, but they are now properties to be desired and designed, not elements to be combined.

Mechanical properties have been the main criterion for the selection of materials from the first use of sticks, and they still limit the size of a building and the cost of an automobile. To understand the basis of strength and ductility was long the main aim of the scientific metallurgist. For many centuries steel has provided the standard of strength. The development of heat-treatable alloy steels that enable high strengths to be achieved in large sections coincided with their need in the first automobiles, and incited a new wave of metallurgical research that is not yet over.

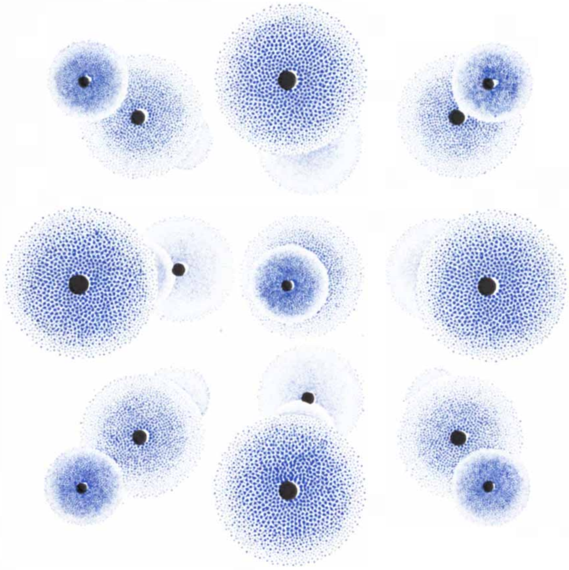
In recent years an increasing diversity of materials has come into competition with steel in satisfaction of mechanical requirements set by the entire framework of the economy of production and use. The electric-power and communications industries in particular have set up a constant pressure of innovative demand. It is not only that designers in these industries are interested in a whole new range of electrical, magnetic and optical properties formerly only of laboratory interest; they have also approached their tasks with little ingrained bias toward one or another class of materials in service. Unlike traditional metallurgists, who perforce concentrated on the perfection of one material, they were ready to see all materials in the new conceptual framework of materials science.

That approach to mechanical proper-

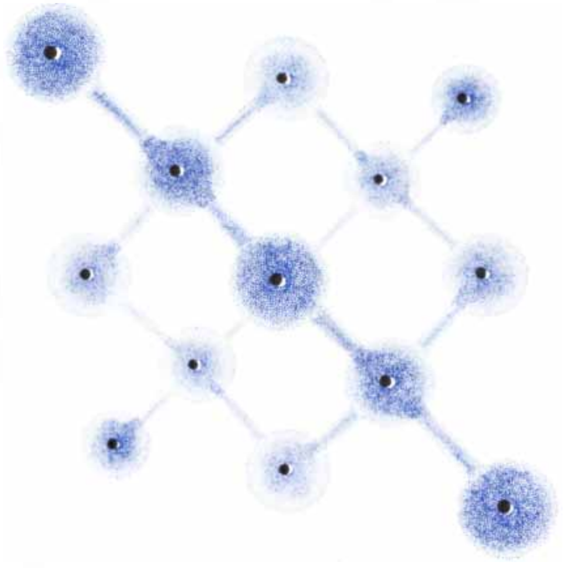
| | | | |
|---|---|---|---|
| H | HYDROGEN | I | IODINE |
| He | HELIUM | Xe | XENON |
| Li | LITHIUM | Cs | CESIUM |
| Be | BERYLLIUM | Ba | BARIUM |
| B | BORON | La | LANTHANUM |
| C | CARBON | Ce | CERIUM |
| N | NITROGEN | Pr | PRASEODYMIUM |
| O | OXYGEN | Nd | NEODYMIUM |
| F | FLUORINE | Pm | PROMETHIUM |
| Ne | NEON | Sm | SAMARIUM |
| Na | SODIUM | Eu | EUROPIUM |
| Mg | MAGNESIUM | Gd | GADOLINIUM |
| Al | ALUMINUM | Tb | TERBIUM |
| Si | SILICON | Dy | DYSPROSIUM |
| P | PHOSPHORUS | Ho | HOLMIUM |
| S | SULFUR | Er | ERBIUM |
| Cl | CHLORINE | Tm | THULIUM |
| Ar | ARGON | Yb | YTTERBIUM |
| K | POTASSIUM | Lu | LUTETIUM |
| Ca | CALCIUM | Hf | HAFNIUM |
| Sc | SCANDIUM | Ta | TANTALUM |
| Ti | TITANIUM | W | TUNGSTEN |
| V | VANADIUM | Re | RHENIUM |
| Cr | CHROMIUM | Os | OSMIUM |
| Mn | MANGANESE | Ir | IRIDIUM |
| Fe | IRON | Pt | PLATINUM |
| Co | COBALT | Au | GOLD |
| Ni | NICKEL | Hg | MERCURY |
| Cu | COPPER | Tl | THALLIUM |
| Zn | ZINC | Pb | LEAD |
| Ga | GALLIUM | Bi | BISMUTH |
| Ge | GERMANIUM | Po | POLONIUM |
| As | ARSENIC | At | ASTATINE |
| Se | SELENIUM | Rn | RADON |
| Br | BROMINE | Fr | FRANCIUM |
| Kr | KRYPTON | Ra | RADIUM |
| Rb | RUBIDIUM | Ac | ACTINIUM |
| Sr | STRONTIUM | Th | THORIUM |
| Y | YTTRIUM | Pa | PROTACTINIUM |
| Zr | ZIRCONIUM | U | URANIUM |
| Nb | NIOBIUM | Np | NEPTUNIUM |
| Mo | MOLYBDENUM | Pu | PLUTONIUM |
| Tc | TECHNETIUM | Am | AMERICIUM |
| Ru | RUTHENIUM | Cm | CURIUM |
| Rh | RHODIUM | Bk | BERKELIUM |
| Pd | PALLADIUM | Cf | CALIFORNIUM |
| Ag | SILVER | Es | EINSTEINIUM |
| Cd | CADMIUM | Fm | FERMIUM |
| In | INDIUM | Md | MENDELEVIUM |
| Sn | TIN | No | NOBELIUM |
| Sb | ANTIMONY | Lw | LAWRENCIUM |
| Te | TELLURIUM | | |



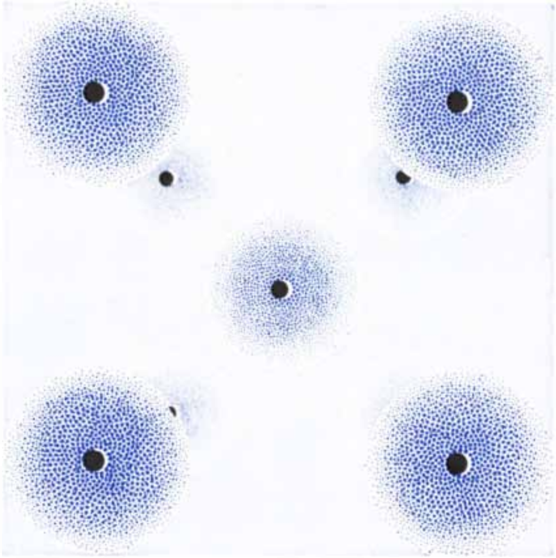
circumstances and nonmetals in others. The inert gases (*far right*) are shown in gray. Here again the valence electrons of each element are dots, and the gray area is the inner-electron core. The valence electrons of the last seven elements listed are not definitely known.



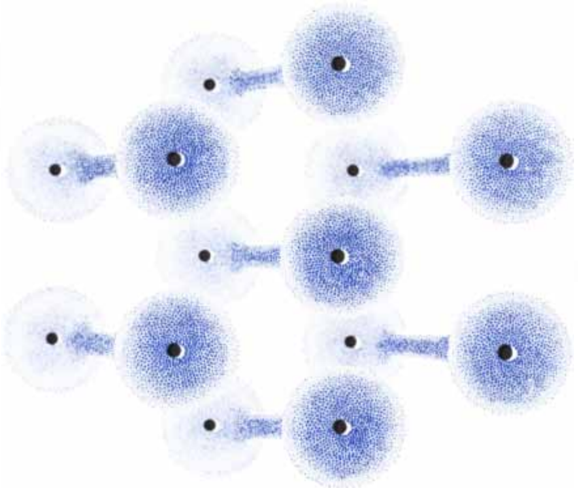
SODIUM CHLORIDE



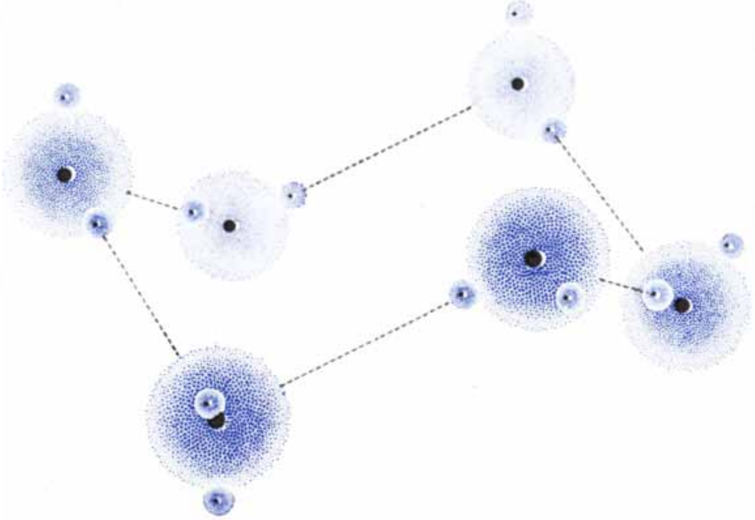
DIAMOND



SODIUM



SOLID $H_2$



ICE

ties is evidenced in the articles that describe the major present classes of materials in this issue of SCIENTIFIC AMERICAN. It is in itself a compelling indication of recent progress in materials science and technology that these articles should be five in number, because two of them deal with kinds of material hardly known before the beginning of this century. Yet Herman Mark shows how the designers of high polymers are now mounting campaigns of research and development on two major markets of the steelmaker, the construction and automobile industries. And Anthony Kelly describes composite materials that harness the high strengths of perfect crystals found in metals and ceramic "whiskers."

The realization of mechanical properties is perhaps the central line of materials development. It is wrong, however, to overemphasize it, because other properties have been equally improved once the need for them was recognized. As the articles in this issue devoted to these properties show, each of them may be sought and developed effectively in more than one of the major families of materials.

Excellent electrical conductors were found even in the days of frictional electricity by testing the common metals, but years of development were necessary to achieve the oxidation resistance needed for high-temperature electrical service. (The nickel-chromium alloys so developed contributed to the development of high-temperature materials for mechanical service.) The development of ductile tungsten filaments needed for the incandescent lamp led in turn to more fruitful studies of grain-boundary behavior than had any scientifically inspired research beforehand. Alloying invariably increases the resistance of a metal at ordinary temperatures; superconductivity has changed all of this and has opened a whole new field of compounds.

The discovery of a wide range of materials for "solid state" electronic devices involved a fine mixture of technology and science. First the scientific but empirical discovery of the photoconductivity of selenium, then the electric lamp to exploit the properties of carbon, then the early crystal-and-whisker radio sets and at last radar to bring out that prince of semiconductors, silicon. This was followed by the invention of the transistor, which forced the development of both better theory and better practical schemes for producing materials of fantastic purity and controlled impurity. Only slightly less glamorous is the story of the development of new magnetic materials, both "hard" and "soft."

Although every engineering decision adds up to an economic choice, economics often enters on its own as an independent variable. An attractive surface quality may disproportionately increase sales; a slightly greater working stress may win an entirely new market. Even the old property of strength is no longer evaluated straightforwardly; instead of overdesign to ensure permanently against failure, design is now for an expected life.

The demand for different kinds of performance by the various parts of a device or structure is usually met by the use of members made of different materials, each doing the best for its local function: a hard steel journal and a bronze bushing in a wooden machine, paint on the surface for corrosion resistance, drawn and heat-treated steel wire combined with a cast-steel shoe in a suspension bridge, a resistor welded to a conductor, a wooden handle on a silver teapot. Some of the more interesting ancient objects, however, are those in which the properties are made to vary from one part to the other within a single continuous mass. Glazed ceramics provide the earliest examples, but the most notable are steel objects with a variable carbon content and variable hardness in different parts. In the old Japanese sword differential heat treatment produced extreme hardness on the cutting edge backed, by means of a graded interface, by the toughness and mass of the unhardened steel in the body of the blade.

Damascus steel had an overall heterogeneity on a scale just visible to the unaided eye. All materials have some microscopic or submicroscopic heterogeneity that is more or less natural to them. An exciting new field is the production of composite materials with synthetic heterogeneity.

Without chemical stability in the environment no other property of a material can be utilized. From the first use of gourds and clay pots as cooking vessels to the latest reactor of stabilized stainless steel, the chemical industry has grown symbiotically with the discovery of new corrosion-resistant materials. These are effectively homogeneous on the scale at which they are used. Perhaps the next stage will be to make large members or entire structures with heterogeneity locally responsive to the different service requirements. The engineer will design the local microstructure of the material at the same time that he designs the machine; the whole will be intricately interwoven with no sharp interface between the corrosion-resistant surface and the stress-resisting inside, with variations of elastic modulus between the ends of the beams and the middle, with gradual transitions from parts made of material so that they can easily be welded to others designed for maximum strength. Electrical circuits designed and assembled from separate units are already being challenged by semiconductor microcircuits in which the resistor, capacitor, rectifier and magnet are hardly distinguishable from one another. Such circuits are at present hard to design but not difficult to make, and they are very easy to use.

The habits of thought engendered by these developments may prove to be more important than the devices themselves. It is the limitations of our past unitary scientific theory that has forced the conceptual separation of functions. There is no reason why this should always be so. In a biological organism it is hardly possible to separate the materials of structural function from the materials of electrical and chemical ones. In such an approach lies, I think, the advancing forefront of materials science in the future.

There is a continuous hierarchy of structures and interactions. Nucleons, nuclei, atoms, molecules, crystals, cells, rocks, plants and animals, societies, mountains, continents, planets, stars, universes. Each has its recognizable structure. For study we divide them down into simple categories, one scale at a time, yet the validity of all lies in the fact that there is interplay between scales. As desirable properties are seen to come from the structure as well as from the unit, new methods of thinking will inevitably develop. In the past almost all advance has been in terms of analysis to find units that could be exactly specified; synthesis has been rudimentary. The alchemist's crucible with its complex compositions of matter and changes of structure and qualities was indeed to some degree a symbolic model of the complex structure and action of the universe. If the principles of hierarchical structure can be adequately developed to aid the science of materials, they may in some degree apply also to biological organisms and even to human society.

**MORE REALISTIC PICTURE, based on quantum mechanics, of the five types of chemical bond on page 75 shows the electrons as clouds around and between atoms.**

# THE SOLID STATE

## Materials are solids, and solids are divided into two general categories: crystalline, in which the atoms are stacked in more or less regular arrays, and amorphous, in which they are not

by Sir Nevill Mott

If you take a paper clip and bend it, it stays bent; it doesn't spring back and it doesn't break. The metal of which the clip is made is said to be ductile. Some other materials are not ductile at all. If you try to bend a glass rod (unless you are holding it in a flame), it will simply break. It is said to be brittle. In this respect, as in many others, glass behaves quite differently from a metal. The difference must lie either in the particular atoms of which metals and glass are made up or in the way they are put together—probably both. There are of course many other differences between metals and glass. Metals conduct electricity and are therefore used for electrical transmission lines; glass hardly conducts electricity at all and can serve as an insulator. Glass is transparent and is used in windows, whereas a sheet of metal more than a millionth of an inch thick is quite opaque.

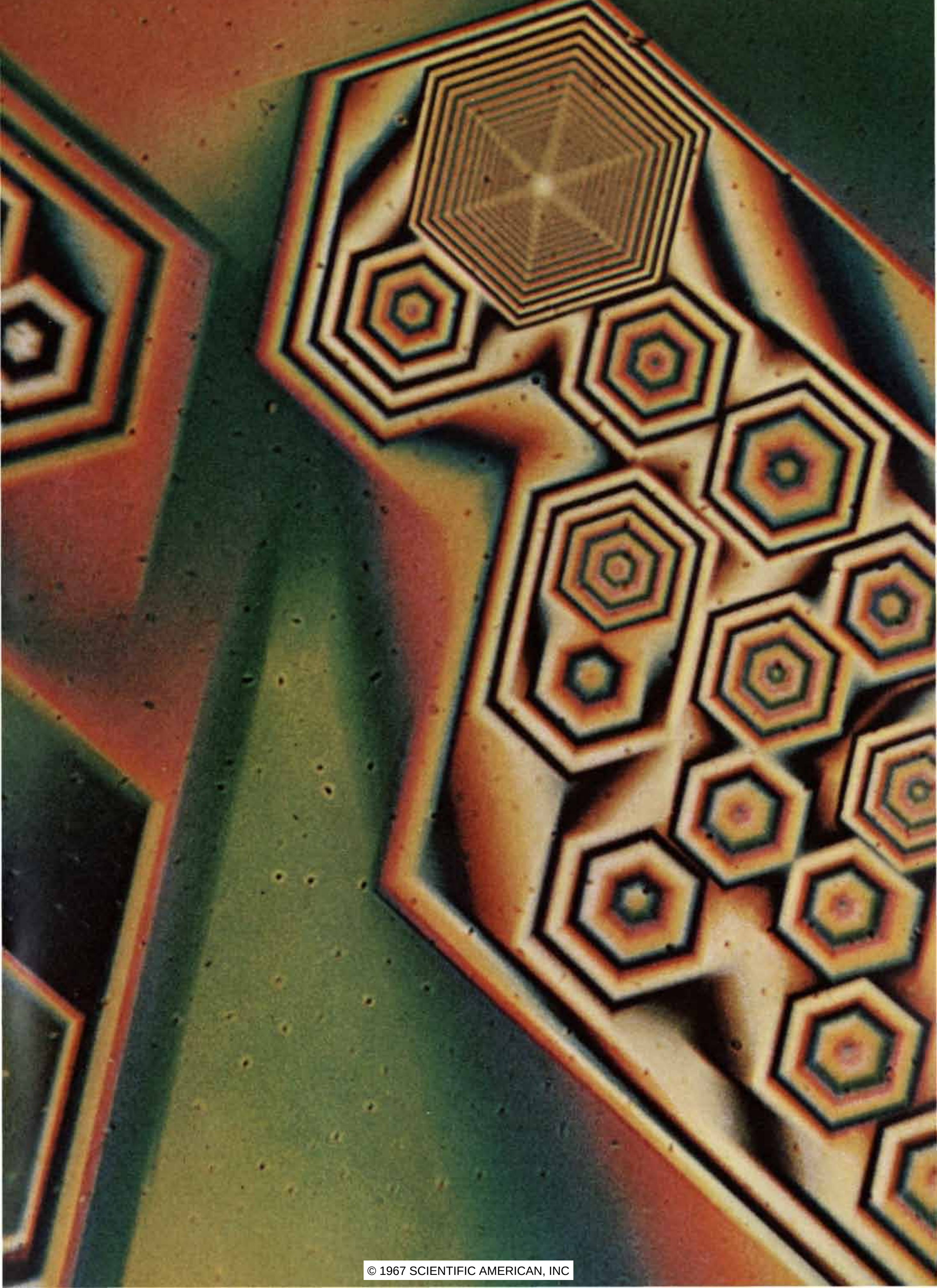
Students of such matters naturally want to understand the reasons for these differences in behavior. They want to study in detail the mechanical, electrical and optical properties of every kind of solid, and many other properties as well. Moreover, they want to provide the basis for choosing materials with desired properties in every branch of technology. During the past 20 years studies of this kind have been called solid-state physics, or sometimes, since the subject includes a great deal of chemistry, just "solid state." It is a major branch of science that has revealed new and previously unsuspected properties in materials. An example is the properties of semiconductors, knowledge of which has given rise to a flood of technological devices such as the transistor. Indeed, solid-state physics has become one of the most important branches of technology. Today engineers freely use expressions such as "valence band" and "conduction band," which are terms of quantum mechanics as it is applied to solids. In solid state perhaps more than anywhere else quantum mechanics has ceased to be restricted to pure science and has become a working tool of technology.

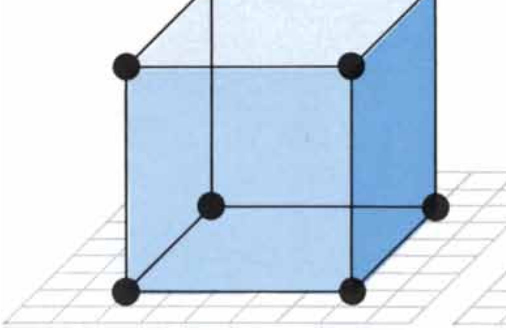
Of course, solids were the subject of experimental investigation long before quantum mechanics was invented. I shall begin with the fact—known since the earliest studies of electric currents—that metals conduct electricity well and most other materials do not. With the discovery of the electron at the beginning of this century and the realization that it was a universal constituent of matter, it was assumed that in metals some or all of the atoms had lost an electron and that in insulators such as glass they had not. The electrons in a metal were thus free to move about and conduct electricity, whereas the electrons in an insulator were not.

Why this happened in metals had to await the discovery of quantum mechanics, and even now the answer is not quite clear. It has been known for some time, however, how to find the number of free electrons in a metal. The simplest way is based on the Hall effect: in the vicinity of a magnet the electrons carrying a current in a wire are pushed sideways, so that a voltage—the Hall voltage—is set up across the wire. This voltage can be measured, and since it depends only on the speed with which each electron is moving down the wire, whereas the current depends both on the speed and on how many electrons there are, the measurement of both Hall voltage and current enables us to estimate the number of free electrons in a wire. It turns out that in a good conductor such as copper each atom has lost just about one electron. There must be in the metal a very dense gas of electrons, more than $10^{22}$ of them in a cubic centimeter.

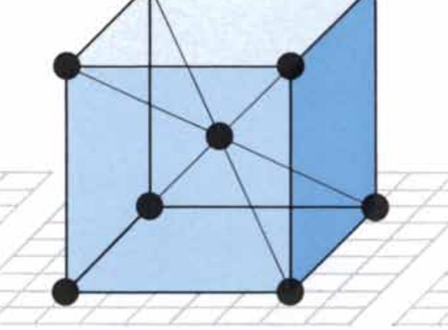
The next question is: How are the atoms themselves arranged? Since the introduction of X-ray crystallography by William Bragg and his son Lawrence in 1911, this has been known for the simpler materials. Solids can be divided into two classes: crystalline and amorphous. In the crystalline group, which is the largest and includes the metals and most minerals, the atoms are arranged in a regular way; in many metals (for instance copper and nickel) they are packed together just as one would pack tennis balls into a box if one wanted to squash in as many as possible. In other metals (for instance iron) the structure is called body-centered cubic; there are four atoms at the corners of a

**ETCH PITS IN CADMIUM SULFIDE, a semiconductor widely used in photocells, are shaped like hexagons, reflecting the geometric pattern of the atoms that compose the material. In this photomicrograph the etched surface of a single crystal is viewed along the hexagonal axis. The colors arise from the interference of incident and reflected light. The concentric hexagons provide a contour map of the pyramidal pits and can be used to calculate their depth. The pit with most concentric bands (*top*) is the deepest. It is depressed about 10,000 atomic layers and measures about 100,000 atoms across. Such pits are formed by treatment of the material with hydrochloric acid. The pits mark defects in the crystalline structure of the material. The photomicrograph was made by Carl E. Bleil and Harry W. Sturner of the General Motors Research Laboratories. The magnification is approximately 800 diameters.**

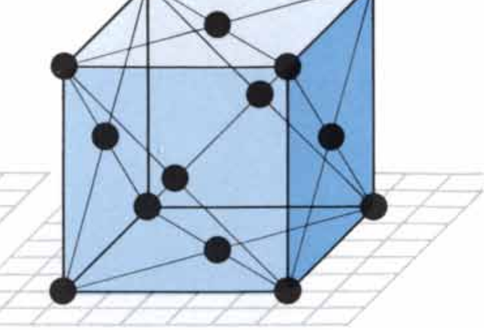




SIMPLE CUBIC



BODY-CENTERED CUBIC



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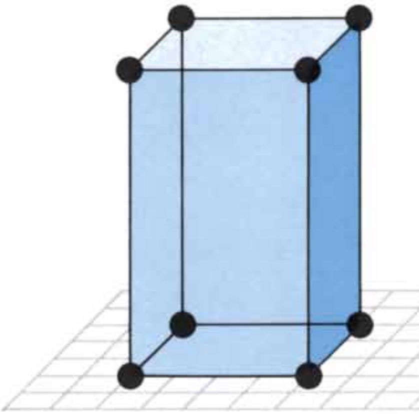
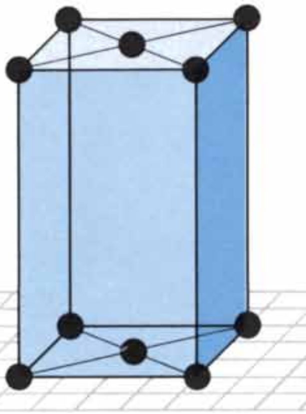


SIMPLE
ORTHORHOMBIC



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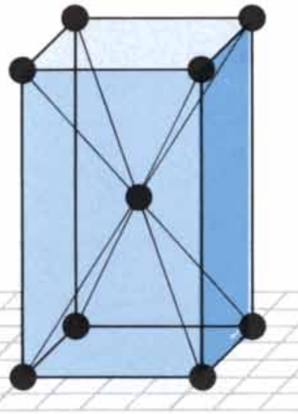

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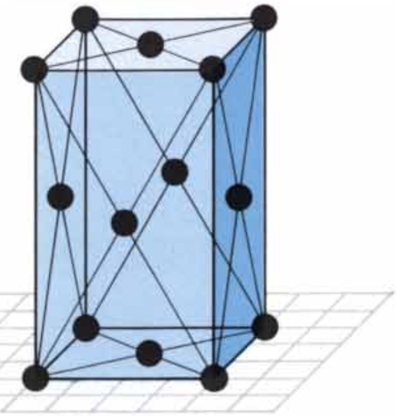

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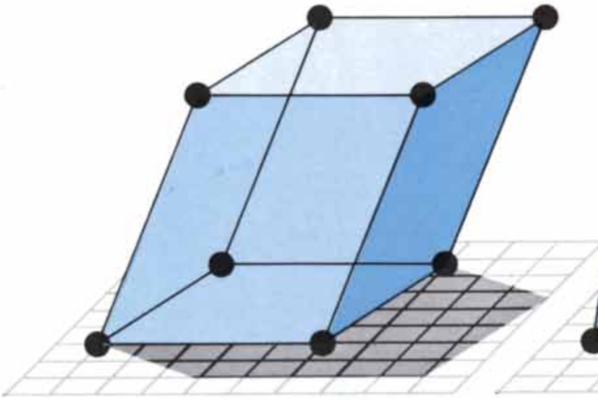

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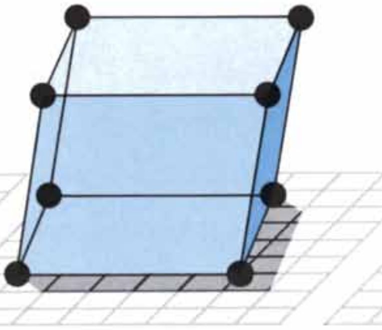
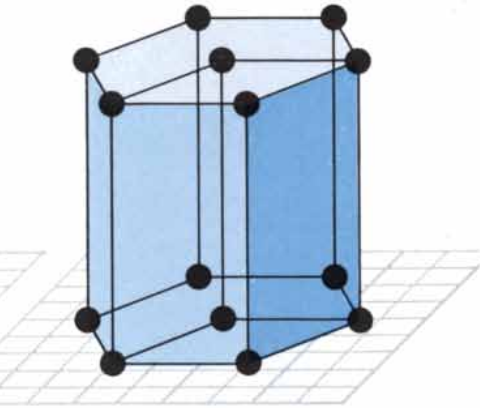
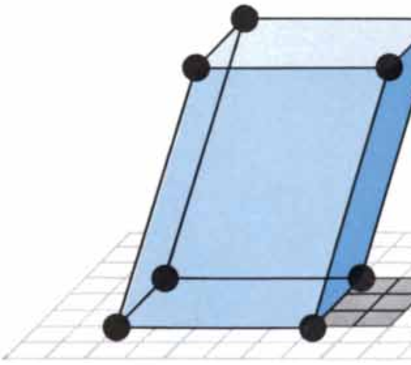


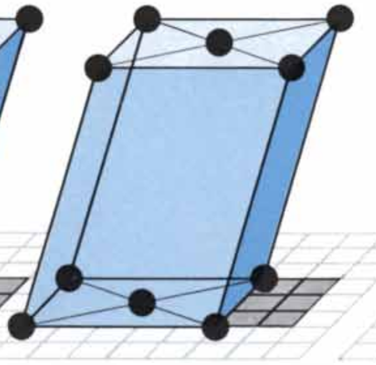
RHOMBOHEDRAL



HEXAGONAL



SIMPLE
MONOCLINIC



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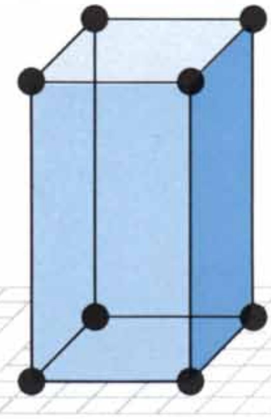
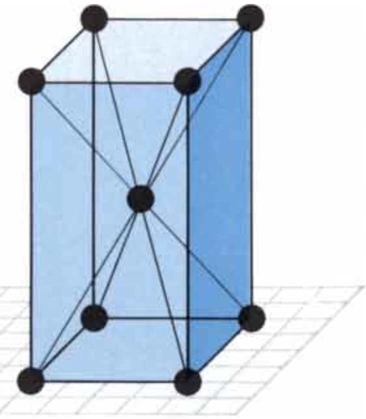


SIMPLE
ETRAGONAL



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TETRAGONAL

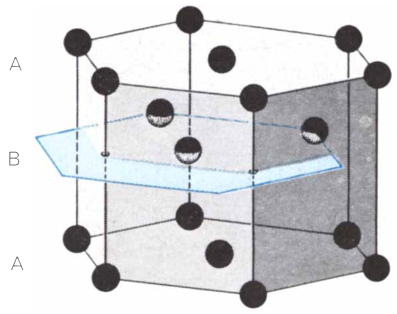
cube and one in the center. The arrangement of atoms in all crystalline solids falls into 14 such categories [*see illustration on opposite page*].

The commonest of the amorphous group of solids is glass. Its atoms are put together in a more disordered way than those of a metal [*see lower illustration on next page*]. The structure of an amorphous material is much more difficult to discover than that of a crystalline solid, and considerable effort is now being made to learn more about the arrangement of atoms in such materials.

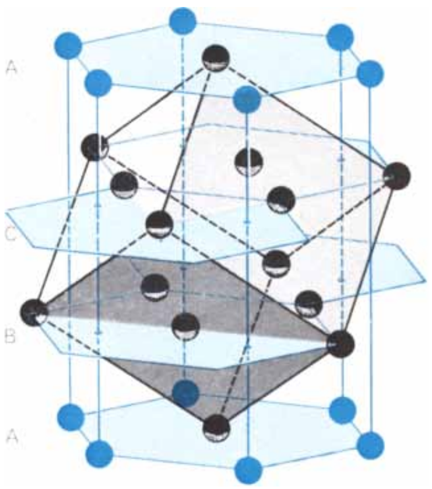
The crystalline structure of a metal such as iron presents to the eye a formidable array of atoms. How does an electric current manage to flow through such a material? One would think that no electron could get farther than from one atom to another without a collision, and that the electrons must percolate through the crystal the way hailstones sift through the leaves and branches of a tree and fall on someone taking shelter below. If this were the case, it would mean that the rate of drift of an electron gas, and therefore the current for a given voltage, would depend little on whether the arrangement of the atoms was regular or haphazard. That is far from being the truth. One of the most marked characteristics of metals is that they conduct much better at low temperatures than at high ones. For example, the amount of energy wasted by resistance in an electric cable is about 10 percent less in a typical Temperate Zone winter than in summer. At the very low temperatures obtainable in cryogenic laboratories an electron can go straight through millions of planes of atoms without being deflected from its path.

Electrical resistance occurs only if the atoms are *not* in a regular array. One such irregularity arises as the temperature increases; the atoms then start to swing around their average positions, each one being displaced up to as much as 10 percent from its normal position. Other evidence is provided by the fact that most metals conduct worse when they melt, and also by the fact that an alloy such as brass (a mixture of copper and zinc) conducts much worse than pure copper. A really good conductor is one in which atoms all of the same kind are arranged in a perfect crystalline array.

**FOURTEEN CRYSTAL SYSTEMS** on the opposite page encompass all crystalline solids. The number of ways in which atomic arrangements can be repeated to form a solid is limited to 14 by the geometries of space division. Any one of these arrangements, when repeated in space, forms the lattice structure characteristic of a crystalline material. For example, cadmium sulfide, the crystal shown in color on page 81, has a lattice formed of hexagonal units. The shadows indicate the tilt away from the vertical.



**HEXAGONAL CLOSE-PACKED** structure, a lattice arrangement common to many metals, is built of tightly nested layers of atoms. Three layers of hexagons provide the 17 atoms that form a crystal unit. Atoms in the layers labeled *A* fall directly over one another. Three atoms in layer *B* nest between.



**ALTERNATIVE CLOSE-PACKED** structure can be built from layers of hexagons stacked in the sequence *ABCA*. In this arrangement 12 atoms can be selected that form a face-centered cube with the same packing density as the hexagonal close-packed structure. Metals commonly crystallize in either the hexagonal or the face-centered configuration. A less common form of metal crystal is the body-centered-cubic one.

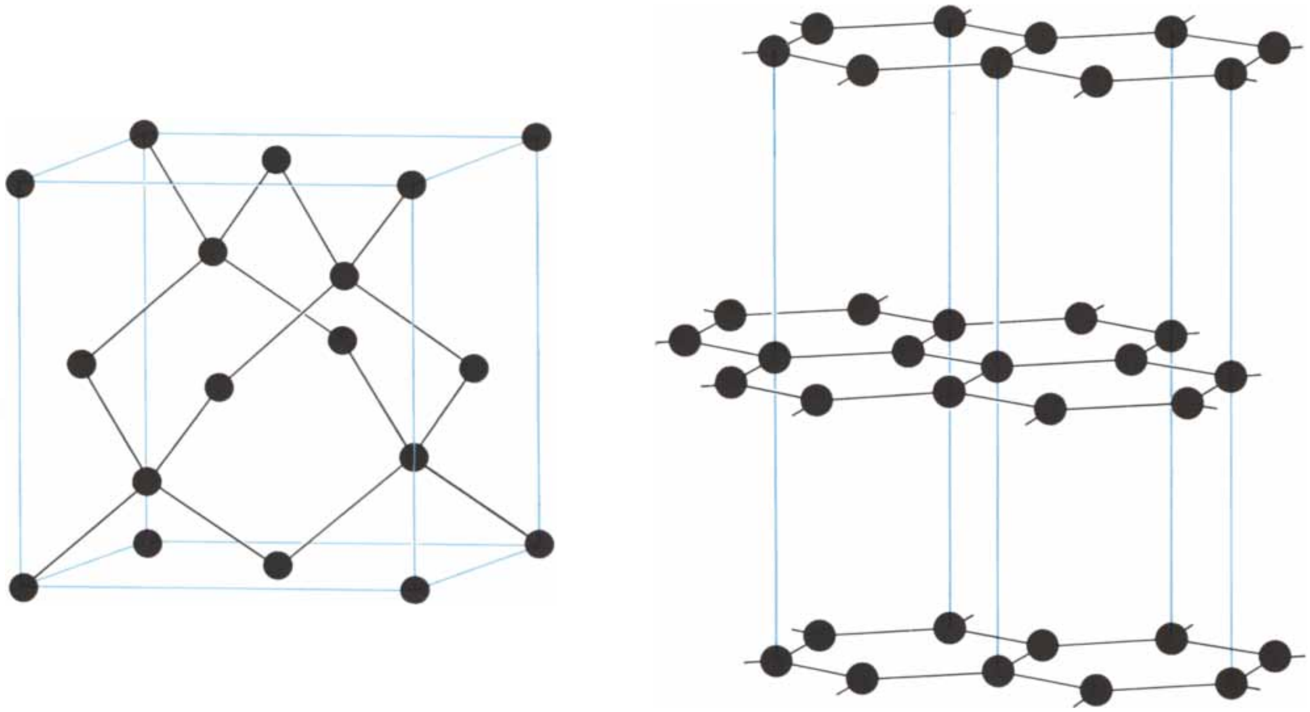
This was completely incomprehensible before the invention of quantum mechanics. Between 1924 and 1926 Erwin Schrödinger, Werner Heisenberg and Max Born showed how to set about explaining a host of phenomena that had formerly been mysterious, and in the five years that followed the foundations were laid for the understanding of solids and of much else besides. One learned to say, when asking anything about electrons in atoms, molecules or solids: If you want to know what an electron does, forget about it and pretend there is a wave there. Calculate where the wave goes, and there you will find electrons.

It is a well-known property of waves that they can go through a regular array of obstacles of any kind. At first this seems surprising. It is easier to grasp that waves do not go through an irregular array of obstacles. That is why the headlights of a car cannot penetrate very far into a fog; the droplets of water scatter the light out of the headlight beams. If the droplets were arranged in some regular way, as the atoms in a crystal are, this would not happen; the light would go straight through.

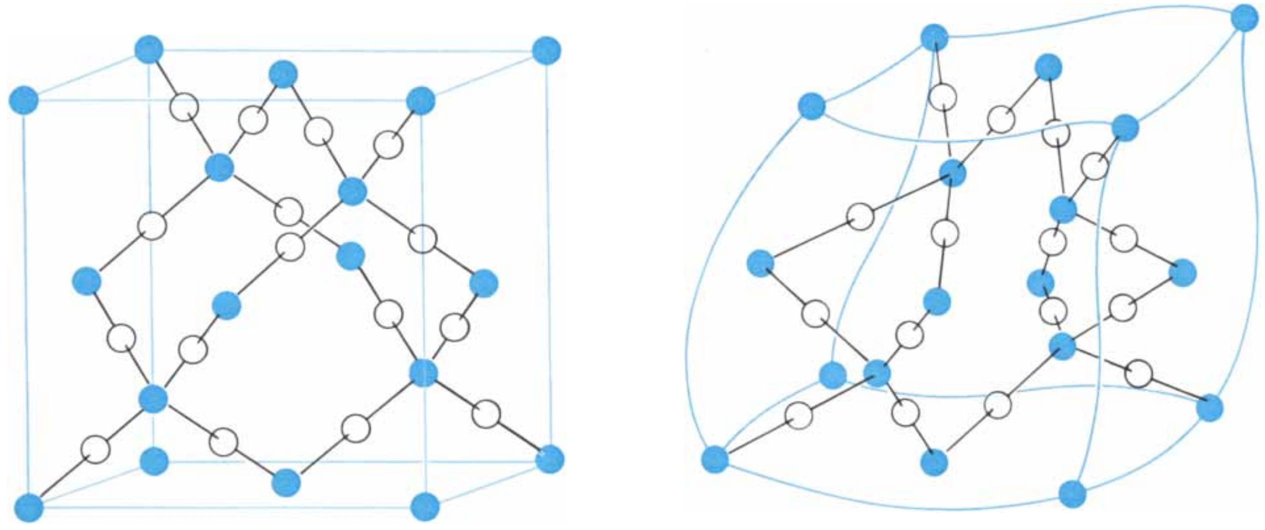
This property of waves, which could be proved by quite simple mathematics and had been known long before quantum mechanics, showed in principle why good conductors of electricity have to be pure, crystalline and cold. Another property of waves enabled us to understand in the early 1930's why some materials were insulators and some conductors. The explanation was first given by A. H. Wilson of the University of Cambridge. The argument did not, as one might expect, seek to tie the electrons to the atoms in nonconducting materials. For both kinds of materials Wilson started by thinking of the electrons as being free to pass through the crystal as waves. The theory went on to show, however, that in some materials there cannot be any current because there will always be just as many electrons moving one way as the other.

The argument is a sophisticated one; it is based primarily on Wolfgang Pauli's exclusion principle, which says that no two electrons can ever move on exactly the same path with exactly the same speed. It is this principle that gives rise to the electron shells of atoms; there it is expressed by saying that no two electrons can have the same quantum number. Applied to metals, the exclusion principle means that electrons in a metal will have velocities lying between zero and some maximum velocity. For an insulator it happens that the limiting velocity has a value that is extremely awkward in view of the mathematical relation that exists between an electron's velocity and its wavelength. This relation is given by Louis de Broglie's formula in which wavelength equals Planck's constant divided by the mass times the velocity of the particle ($\lambda = h/mv$). The wavelength of electrons in an insulator is awkward because it has a dimension that just fits into the distance between the atoms of which the material is composed. Under these conditions the wave will become a standing wave, and such a wave describes a situation in which the movement of electrons in one direction is exactly offset by the movement of other electrons in the reverse direction.

In many crystalline materials one finds this situation in which there can be no electric current. To overcome it a considerable amount of energy is required; an electron must be hit rather hard to put it in a position where its movement is not balanced by the movement of another electron. The needed energy is gained, of course, if the material is heated to a temperature that is high enough. All solids will conduct electricity to a certain extent if they are hot; they can also be made to conduct by energetic radiation such as ultraviolet or X rays.

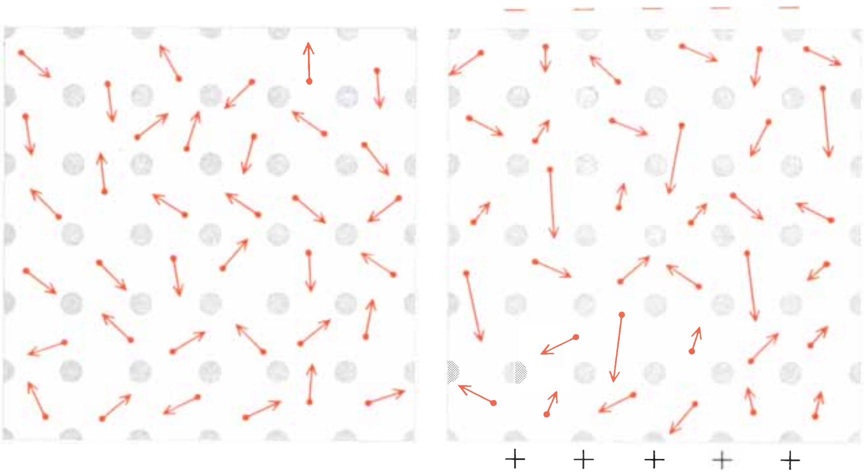


**TWO FORMS OF CARBON** exhibit markedly different properties owing to their different crystal structure. Diamond (*left*) consists of pairs of carbon atoms in a face-centered-cubic array. Each carbon atom is bound to four others. This tightly joined lattice contributes to diamond's hardness. In graphite (*right*), a soft material, carbon atoms are arranged in layers that are bound by weaker forces.

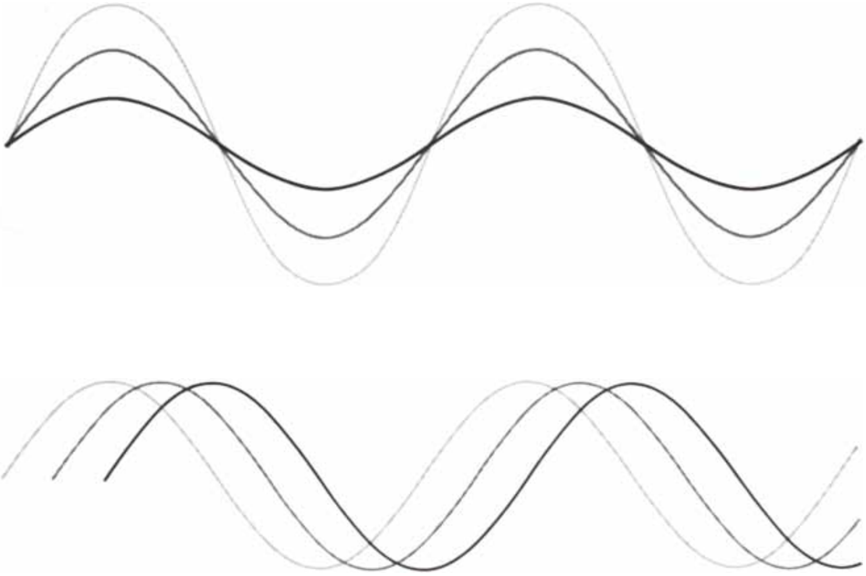


**TWO FORMS OF SILICA** demonstrate how molecules of the same composition can exist either as a crystal or as a glass. Cristobalite (*left*), a high-temperature form of quartz ($SiO_2$), is similar to diamond in that it has a face-centered-cubic structure. Silicon atoms (*color*) occupy the sites filled by carbon atoms in the diamond lattice. In addition an oxygen atom sits between every two silicon atoms. A conceivable glass structure (*right*) resembles a cristobalite structure that has been distorted. Also the three rings, each containing six silicon atoms, found in the cristobalite cell have been reconnected to form two rings with four silicons and one with eight.

No material can be a good insulator while it is exposed to X rays.



ELECTRICAL CONDUCTIVITY in a metal can be thought of as the movement of valence, or free, electrons (*color*) in a preferred direction. In the absence of an external electric field (*left*) the movement of any one electron is offset by the movement of another in the opposite direction. Within an electric field electrons move toward the positive plate (*right*).



QUANTUM VIEW OF CONDUCTIVITY substitutes a wave for the motion of electrons. In an insulator (*top*) electron velocities correspond to a standing wave, one that does not move in any particular direction. In conductors electron velocities correspond to a running wave (*bottom*). The lines in the drawings show the form of the waves at successive moments.

The theory I have just described makes use of difficult concepts of quantum mechanics, but the mathematics of it is not very complicated. It is the kind of theory a physics student learns in his final undergraduate year or first graduate one. The same cannot be said of the theoretical work that is currently being done in an effort to correct a grave omission in the theory. In the electron gas of a solid material the electrons are moving about all the time and bouncing off one another. To describe this bouncing mathematically is a formidable problem; it is very difficult to solve problems involving even three interacting bodies. Many-body theory is a subject of intensive research in many leading laboratories; it may be that when it is further along the metal-insulator problem will look rather different.

Meanwhile the simple model I have described has proved perfectly adequate for understanding the part of solid-state physics that is most important to technology, namely the semiconductors. These are materials that will carry an electric current but only a small one compared with a metal. Basically semiconductors should be classed as nonmetals; when they are pure and at low temperatures, they do not conduct electric current. One makes them conduct by adding electrons to them. The simplest way to do this is to dissolve in the crystal of a semiconductor traces of some chemically different material, each atom of which easily gives up an electron. Germanium, a common raw material of transistors, becomes quite a good conductor when very small quantities of phosphorus (one part in a million) are added to it. The germanium atom has four outer electrons it can easily lose; the phosphorus atom has five. It is the extra electron of phosphorus that does the trick. When it is free of the atom, it can move about quite easily, like an electron in a metal, and its motion is not offset by the motion of any other electron. Germanium that has been "doped" with phosphorus is a semiconductor of the *n* type, the *n* standing for the negative charge contributed by the additional electrons.

The technological importance of semiconductors arises mainly from the fact that the contact between a semiconductor and a metal (or between two semiconductors) acts as a rectifier. This means that the material will pass electric current much more easily in one direction than in the other. A crude form of semiconductor rectifier was used in the earliest radio receivers; it was supplanted by the vacuum tube. The replacement of the vacuum tube by the transistor represents the return of the semiconductor rectifier in refined form.

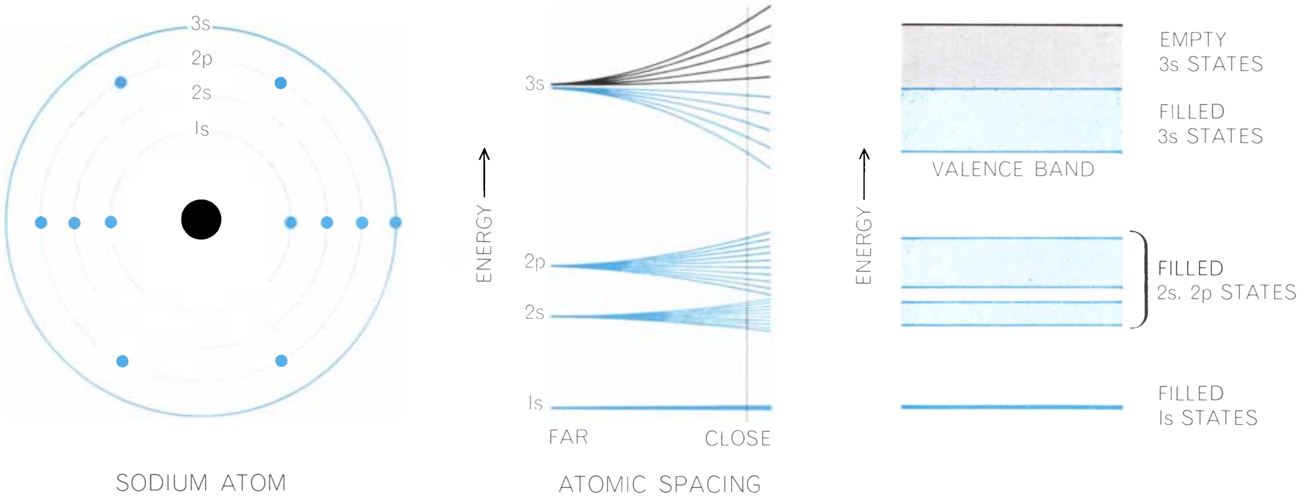
In the *n* type of semiconductor I have described free electrons will flow from the semiconductor to a metal but not in the reverse direction. This is hardly surprising. A cold metal does not emit electrons; it must be heated until it glows to do so in a vacuum tube. In the semiconductor, however, the extra electrons donated by foreign atoms can move into the metal without undue difficulty. The barrier (more exactly the change in potential energy) that keeps electrons from going from the metal to the semiconductor helps them to go the other way.

The important properties of semiconductors, then, depend on the presence in the crystal of minute quantities of some impurity. This brings me to an important point about solids. They are never quite pure and their crystal lattices are rarely quite perfect; they have what we call defects. Such defects determine many significant properties of materials, particularly the mechanical ones.

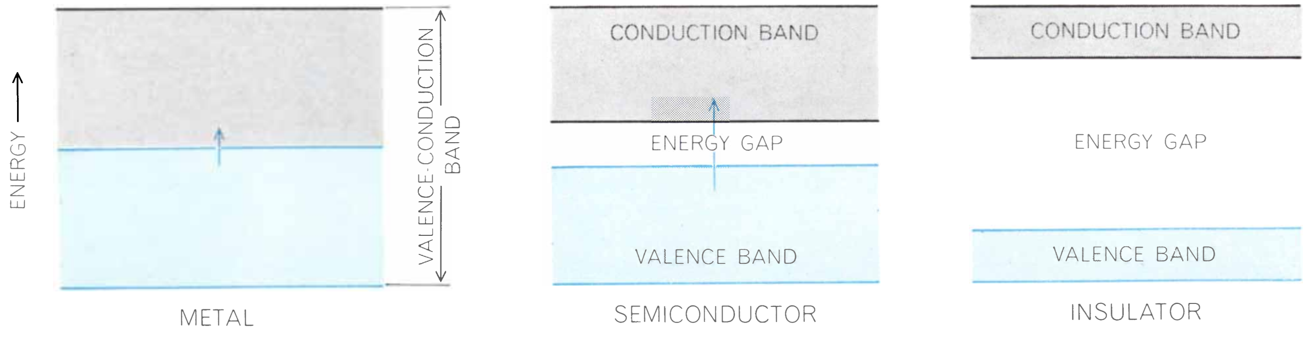
One can obtain materials with impurities present in less than one part in 10 million, but even in such materials the impurity atoms will be only $10^{-5}$ centimeter apart, a distance shorter than a wavelength of light. Thus quite a small speck of even a very pure material will have plenty of impurities in it. Usually the impurity atoms simply replace an atom of the surrounding crystal. This is what happens when germanium is doped with phosphorus; four of the five outer electrons of a phosphorus atom participate in bonds with germanium atoms, so that the phosphorus atom is taken into the structure of the crystal.

Other forms of impurity can impart color to a crystal, and indeed the systematic study of colored rock salt and other salts such as potassium chloride by R. W. Pohl and his colleagues at the University of Göttingen before World War II makes Pohl one of the founders of solid-state physics. It takes only a trace of blue ink to color a glass of water, and in the same way traces of potassium in an initially transparent potassium chloride crystal will make the crystal dark blue [see "The Optical Properties of Materials," by Ali Javan, page 238]. The potassium is added by heating the crystal in alkali vapor. How is the extra potassium accommodated? It turns out that some of the sites that ought to be occupied by chlorine are empty, so that adding potassium makes the crystal expand by a readily calculable amount; this has been verified by experiment. But potassium chloride is a member of the class of ionic crystals, and one cannot have such a crystal in which a large number of chlorine sites are empty. It is not an atom that normally occupies any one of the sites but an ion, in this case a chlorine atom with an extra electron stuck to it. A crystal with all those vacant sites would have an enormous electric charge. What happens is that each of the vacant sites has an electron in it. It is these electrons that give the crystal its color, by absorbing certain wavelengths of light. Vacancies with an electron in them were named by Pohl *F* centers, from the German word *Farbe* (color).

It is not only impurities that make a crystal deviate from perfection. In metals at high temperatures, for instance, a number of sites—perhaps one in a mil-



**THEORY OF ELECTRICAL CONDUCTIVITY** involves the behavior of an atom's outermost shell of electrons, the valence electrons. Sodium, for example, has 11 electrons arranged in four shells (*left*). The three inner shells are filled, but the valence shell could hold another electron. The electrons in each shell occupy specific energy levels (*middle*). As atoms are brought close together and begin to influence one another, the electrons are forced to have slightly different energies, since only two electrons can occupy precisely the same quantum state. The vertical line indicates the spacing of atoms in a crystal of sodium. Within a crystal containing some $10^{20}$ or more atoms the energy levels become densely filled bands (*right*). Since sodium has only one valence electron, only half of the energy states in the valence band are filled. As a result negligible energy is required to raise a valence electron to an empty state, where it is free to move inside the crystal and to conduct electricity. This is not true of nonconductors (*see illustration below*).

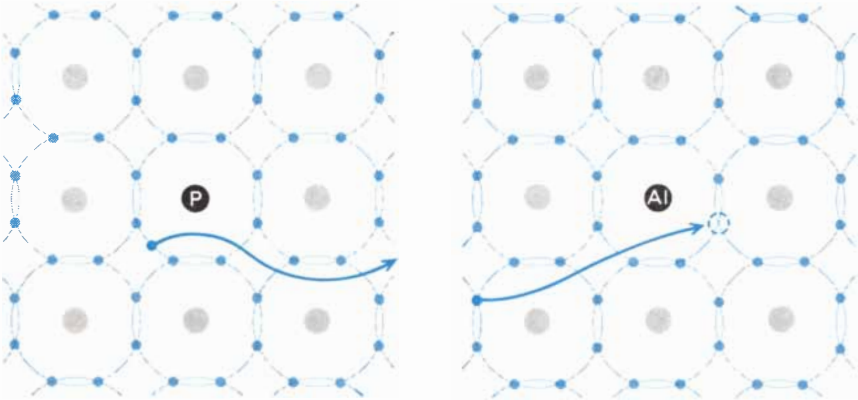


**ELECTRICAL CONDUCTIVITY** of a solid depends on the spacing and state of occupancy of the energy bands within its crystals. Many metals (*left*) resemble sodium in having a valence band that is only half-filled with electrons and therefore can readily act as a conduction band. Other metals have more complicated band structures but the net result is the same. In semiconductors (*middle*) there is a small energy gap between a filled valence band and the first permissible conduction band. It is not too difficult, however, for some of the electrons to acquire the energy needed to jump across the gap. In an insulator (*right*) the gap is not easily bridged.

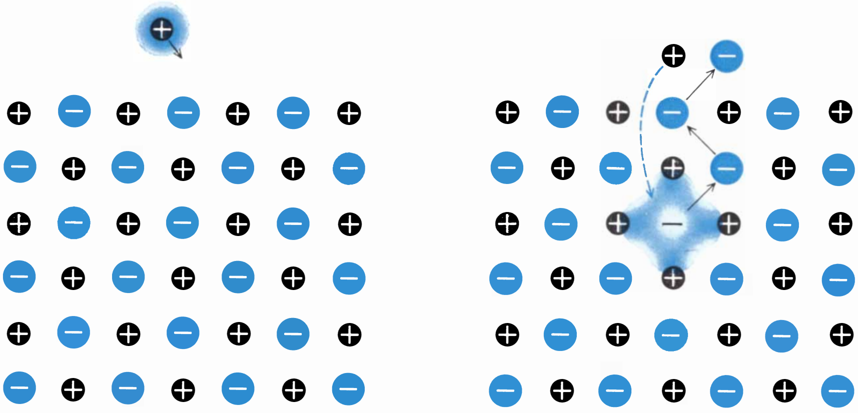
lion—will be empty. Such sites are called vacancies. They arise because at high temperatures the atoms are vibrating, and now and then a vibration is so vigorous that a vacancy is produced at the surface; then it can move inward. Of course, vacancies will also move to the surface and disappear, and eventually a balance is set up, the number formed and the number disappearing being equal.

Vacancies move around in a crystal, much as molecules move in a gas but much more slowly. It is believed that when one metal mixes with another, which is what happens when two materials are welded together, atoms change places by jumping into vacancies, so that vacancies play an extremely important part in all the arts of metallurgy. It would be interesting if we could see vacancies, but that is beyond the power even of present-day electron microscopes. What we can see is little clusters of vacancies. When a metal is quenched (cooled quickly), any two vacancies that accidentally meet will stick together; the vibrations of the atoms are not vigorous enough to make them move apart. Little cavities form that have curious shapes varying from one material to another, some of which are shown in the illustrations on page 89.

The technique by which these pictures are made is transmission electron microscopy, and it turned out to be one of the most important techniques of solid-state physics. The electron microscope has the advantage that one can see objects much smaller than the wavelengths of light, which is of course not possible with the light microscope. Moreover, electrons will penetrate thin specimens of metals.



**IMPURITY ATOM** in the structure of germanium, a semiconductor, increases its conductivity. Each atom in a germanium crystal shares four valence electrons (*color*) with adjacent atoms. A phosphorus atom (*"P" at left*) has five valence electrons. The extra electron cannot fit into the regular structure. It is in a high-energy position like the free electrons of a metal. An impurity of aluminum (*"Al" at right*) also enhances germanium's conductivity. Aluminum, with only three valence electrons to contribute to the germanium structure, creates a vacant site, or electron hole, into which a nearby electron can move.



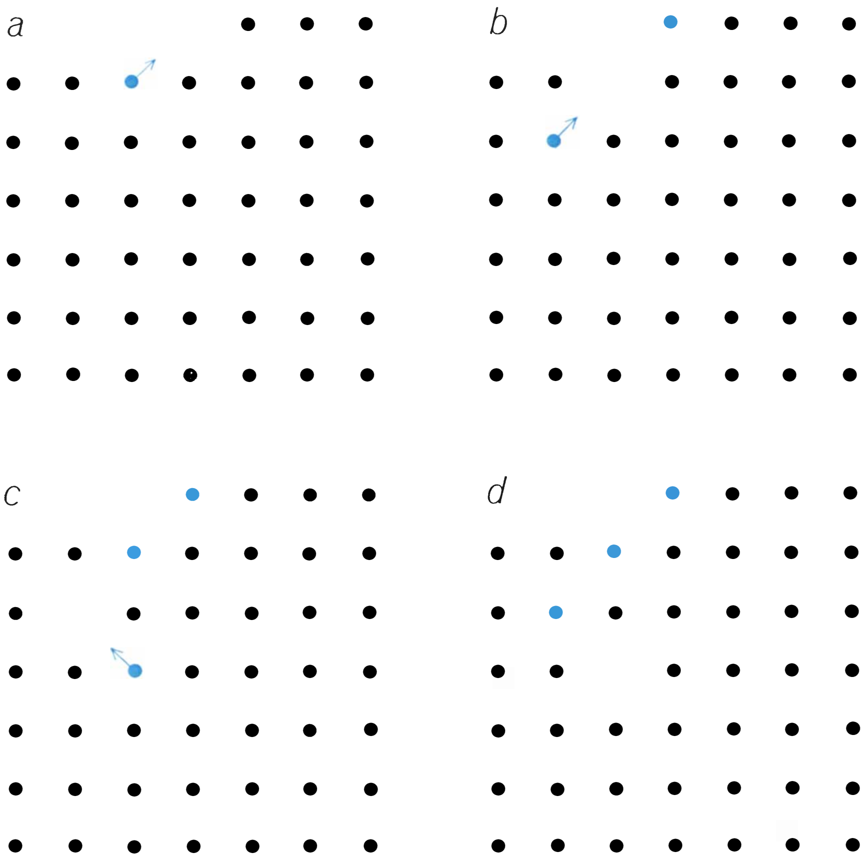
**COLOR CENTER** arises when electrons are trapped in certain crystals. The transparent crystal of potassium chloride (*left*) turns blue when potassium is added to it. A potassium atom (*black arrow*) attaches itself to the surface of the crystal and subsequently loses an electron (*broken arrow at right*). The electron trades places with a negatively charged chloride ion that has migrated outward to pair with the newly arrived potassium. The electron, which is held by adjacent positive ions, absorbs light, producing the color change.

One of the great successes of this thin-film electron microscopy was the observation of another form of defect, namely the dislocation. This brings me back to the question of why a metal paper clip bends and a glass rod breaks. I remember discussing many years ago with Lawrence Bragg, the codiscoverer of X-ray crystallography, the possibility that this had something to do with the presence in metals of free electrons. It doesn't, except that metals usually have rather simple crystal structures; their atoms, having lost their outer electrons, don't form bonds with some specific number of atoms. It turns out that materials with simple crystal structures are often ductile and those with complicated ones are rarely so. Those that are amorphous are never ductile unless they are so hot that their atoms can change places quite easily. The key to the understanding of such behavior is the dislocation.

This concept was introduced in 1934 by Geoffrey I. Taylor of the University of Cambridge. The question Taylor asked himself was: When a crystalline substance is deformed, do the atoms all slip over one another together? Does the crystal pass suddenly from the undeformed state to the deformed one? For various reasons he thought that it would not, that it would instead deform through the motion of a kind of wrinkle in its structure—a dislocation in the regular array of its rows of atoms.

One of the reasons that led Taylor to put forward this hypothesis is that very pure metals are normally much softer than alloys and impure materials. The dislocation model makes it clear why impurities make a metal harder: the impurities collect in the dislocation and keep it from moving. In complicated crystal structures the dislocation itself is a complicated structure and cannot move easily. In glasses one cannot have dislocations at all.

Taylor's hypothesis explained facts known since the Bronze Age, but no one had actually seen dislocations in motion until 10 years ago. At that time some of my colleagues in the Cavendish Laboratory were examining thin metal films by transmission electron microscopy, and somewhat to their surprise they found that dislocation lines were visible. Moreover, the screen of the electron micro-



**VACANT LATTICE SITES** are created by shifting atoms. In a hot metal atoms can vibrate so vigorously that some at the surface leave their positions. From the row of atoms below one will move into the vacant site, called a vacancy. As a result of the sequence of events ("*a*" *through* "*d*") a vacancy moves inward. When two different metals are welded together, their atoms probably change places by jumping into each other's vacant sites.

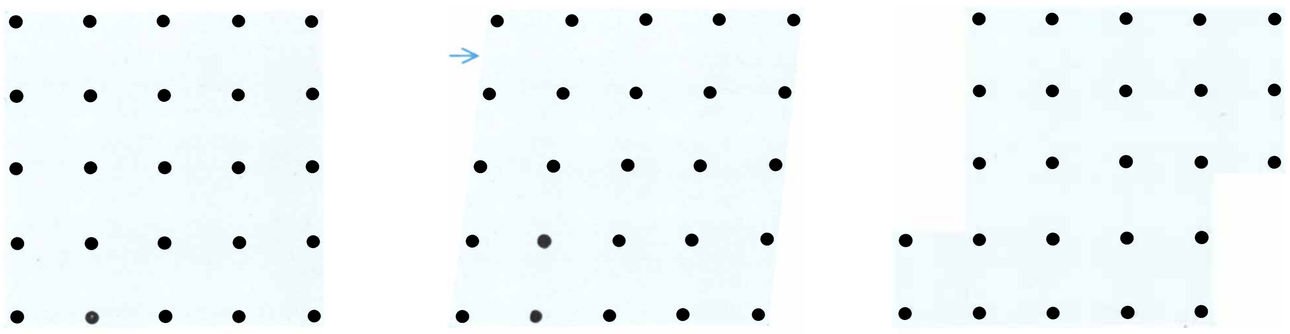
scope showed the little lines darting forward; doubtless the metal film was buckling as the electron beam heated it up. I well remember our excitement the day one of our graduate students came into my office and said: "Prof, come and see some moving dislocations!"

Thus far I have described some of the main properties of solids that are important to the solid-state worker, particularly the electrical and mechanical properties. I have emphasized the great difference between the properties of one solid and another. There is another way of looking at these differences, namely the mechanisms by which the atoms or molecules of various materials stick together.

Perhaps the simplest of all solids are the frozen inert gases: helium, neon, argon and so on. These chemically unreactive gases do not form molecules; at any rate, if two atoms stick together, they stick so weakly that they will quickly be knocked apart by collisions with other atoms in the gas. But if you cool an inert gas, it will first liquefy and then solidify, and this shows that there is some kind of weak attraction between even the most inert atoms. The force between such atoms is called the van der Waals attraction. It is explained by quantum mechanics, but the explanation is not simple. In general it can be said that the negatively charged cloud of electrons surrounding the positively charged atomic nucleus can slightly shift its position, so that the center of negative charge does not quite coincide with the center of positive charge. As a result of this electrical imbalance a weak force is established that can attract other atoms.

The chemically inert atoms are those in which the electrons form what is called a closed shell; such shells are found in atoms with two electrons (helium), 10 (neon), 18 (argon) and so on. Certain ions have this property too. If an electron is removed from a sodium atom, 10 electrons are left and so the remaining negatively charged ion is inert like neon. By the same token, if one adds an electron to chlorine, which has 17 electrons, one gets 18 electrons and a positively charged inert ion. An important class of solids is the ionic salts, of which sodium chloride is the best known; it is made up of inert positive and negative ions and holds together simply because the positive and negative charges attract each other.

There are solids made of atoms that are not chemically inert. Most atoms consist of an inert shell and a number of electrons in addition that can help the atom stick firmly to another atom. Car-



**DEFORMATION OF METAL,** in which dots represent atoms, takes place in successive steps: before deformation (*left*), following an elastic deformation such that the atoms will spring back (*center*) and after permanent bending (*right*). The atoms do not jump to their final positions all at once but move through the wrinkling process called a dislocation. The malleability of materials depends on the presence of dislocations in the crystal structure. A discussion of dislocations appears in the following article.

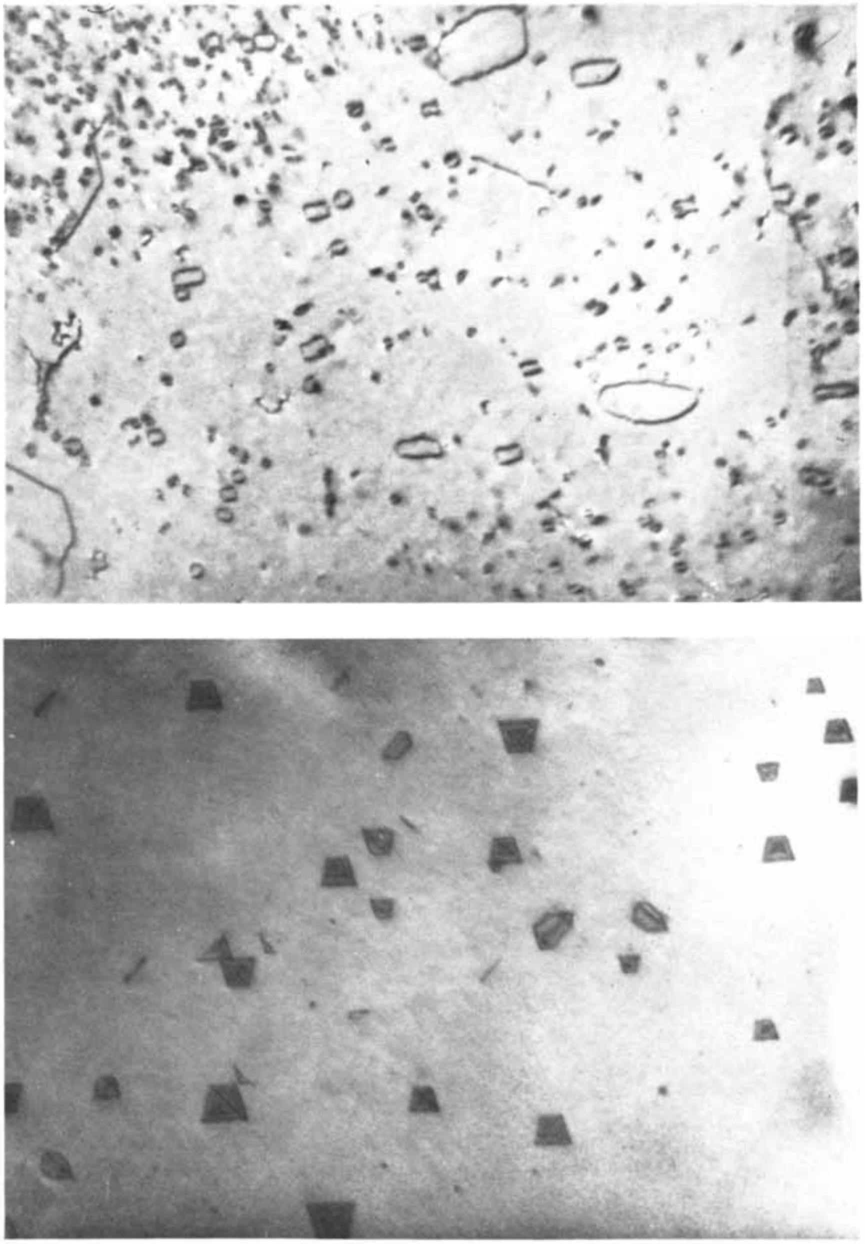
bon, silicon and germanium have four electrons outside an inert shell, and each of them can take part in forming a bond to another atom of the same kind. This kind of bonding is called "homopolar" or "covalent." The covalent bond involves the sharing of electrons between pairs of atoms.

These divisions are not hard and fast. Most of the minerals that make up the rocks of the earth's surface fall in neither one nor another. They are compounds, and the different atoms are to some extent charged; therefore they stick together partly like ionic substances such as salt. But there is a lot of electron-sharing too, and the simple classifications are not always useful.

Then there are molecular crystals. Hydrogen is the simplest example, although solid hydrogen can be obtained only at very low temperatures. The hydrogen atom has only one electron and can form a very strong bond with one other hydrogen atom, resulting in the molecule $H_2$. In solid or liquid hydrogen the molecules stick weakly together because only the van der Waals force holds them. Another example is water or ice, in which the $H_2O$ molecules stick through a mechanism (the hydrogen bond) that seems to be halfway between ionic and covalent. Many organic materials are of this kind—wood and cotton, for instance. These are made up of polymer molecules, which have the form of long chains; covalent bonds link the atoms in each chain, and something like van der Waals bonds attract adjacent chains to each other [*see* "The Nature of Polymeric Materials," by Herman F. Mark, page 148].

Finally there are the metals. Here the outer electrons have left the atoms and can contribute to a current. The matter is discussed in the following article ["The Nature of Metals," by A. H. Cottrell, page 90]. Here we need only say that to obtain an adequate theoretical description of cohesion in metals is complicated; the electrons are free, they repel one another but they are attracted by the ions. Of course attraction must win—otherwise no solid metal could exist. Detailed calculations have been carried out for only a few metals, although research in this area is very active, particularly with respect to accounting for the crystal structures observed in alloys. What one might say is that it is not surprising that one can form so many alloys; metal atoms are not particular about what other metal atoms they stick to. If all the electrons come off in any case, strong cohesion exists whatever the strength of the charge is on the ion and however many electrons there are.

Reflecting on solid-state science in 1967, one perceives the following main lines of advance. In theoretical physics and in fundamental physics generally the many-body problem—the interaction of all the electrons in a metal—continues to be of great interest and abounds in unanswered questions. Allied to this subject is our recent understanding of superconductivity, the complete disappearance of electrical resistance at very low temperatures. Then the study of surfaces and of the interface between metals and semiconductors has moved into the center of the picture, partly because of its extreme importance for electronic devices and partly because new techniques for investigating them have been introduced. Finally, many solid-state physicists are looking over their shoulder at biology. Since solid-state science deals mainly with the movement of charge and energy through relatively simple solids, it ought to have a lot to say about these processes in the vastly more complicated living tissues.



**VACANCY CLUSTERS** can assume different shapes in different metals. In aluminum (*top*) they are like disks; in gold (*bottom*) they are shaped like tetrahedrons. A single vacancy is too small to be visible. These electron micrographs were made by John Silcox of the University of Cambridge. The metals had been rapidly cooled. Magnification is 30,000 diameters.

# THE NATURE OF METALS

The gas of electrons that binds metal atoms together makes metals behave as they do. Their mechanical properties in particular flow from the close-packed crystal structure favored by the metallic bond

by A. H. Cottrell

Metals are opaque, lustrous and comparatively heavy. They are strong, but they can be rolled or hammered into shape and can be alloyed and welded. They are good conductors of heat and electricity. All these properties of metals flow from the metallic bond. The basis of the bond is that in a metal each atom is closely surrounded by many similar atoms, each with only a few electrons in its outer electron shell. In this situation the electron clouds overlap and the loosely held outer electrons are so completely shared as to be no longer associated with individual atoms. Leaving the metal atoms in place as ions, they form an electron gas, a pervasive glue that moves freely among the ions and binds them together.

Because the electrons are free to move in an electric field, metals conduct electricity. Because free electrons absorb and then radiate back most of the light energy that falls on them, metals are opaque and lustrous. Because free electrons can transfer thermal energy, metals conduct heat effectively. The thermal, electrical and optical properties, which are responsible for many of the most advanced uses of metals, will be taken up by subsequent articles in this issue. Here I shall be primarily concerned with the mechanical properties of metals.

The metallic bond is nonspecific, which explains why different metals can be alloyed or joined one to another. It is also nondirectional, pulling equally hard in all directions. It therefore binds the metal atoms tightly, so that their cores (nuclei and inner-shell electrons) fit closely among one another. The close packing favored by the metallic bond is best realized in certain regular crystalline structures. These structures, although resistant to tension, offer less resistance to shearing forces, and thus they explain the ductility of metals. They are by definition dense, and thus they explain the comparative heaviness of metals. The mechanical properties of metals, then, derive from their crystalline structure, which is favored by the free-electron metallic bond.

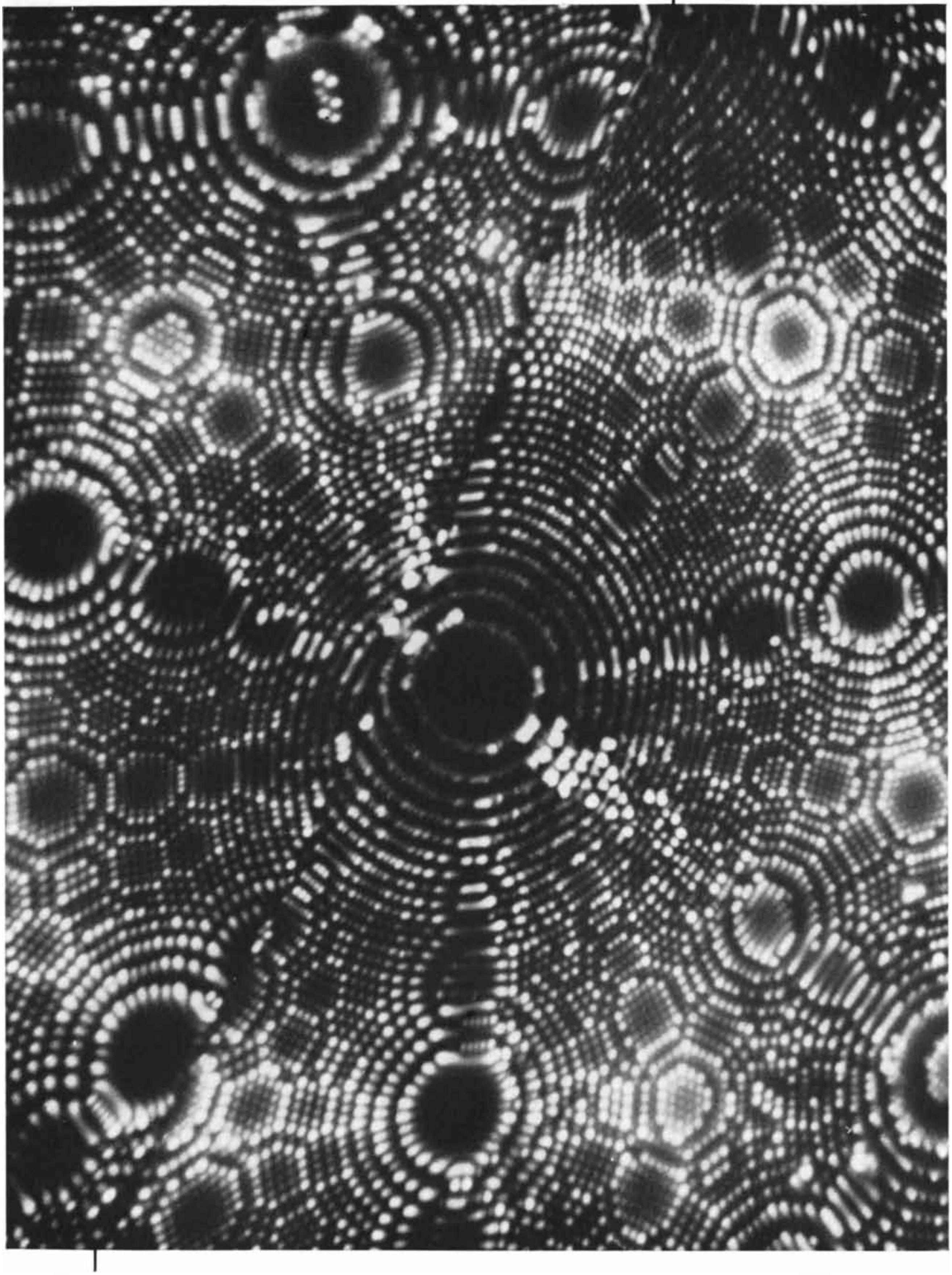
As early as 1665 Robert Hooke simulated the characteristic shapes of crystals by stacking musket balls in piles, but it was 250 years before anyone could know that he had exactly modeled the crystal structure of familiar metals, with each ball representing an atom. Although the crystallinity of some substances with complex structures was recognized centuries ago, the simple crystal structures of the common metals remained doubtful until recent times. There were hints of crystallinity, such as the solidification of molten metals at a precise temperature and the bright facets sometimes seen on a fractured metal surface. Other features, however, suggested an amorphous structure. Molten metals can be cast and set in any shape, solid metals can be plastically deformed by beating them, and a polished metal surface appears to be quite featureless.

The door to the structure of metals was opened in 1864, when Henry Clifton Sorby of England developed a method for viewing metals under the microscope by reflected light instead of by light transmitted through thin specimens (the traditional biological and mineralogical technique). Apart from his new optical method, the key to his success lay in the removal of the polished surface layer by a careful etching treatment with a weak and nonstaining chemical reagent.

This procedure reveals an irregular honeycomb of boundaries that partition the metal into small polyhedral cells called grains, typically about .01 inch across [*see top illustration on page 93*]. Some reagents etch deep grooves along the grain boundaries; others reveal the microstructure by their attack on the grains themselves. At a given angle of illumination some grains appear bright and others dark. The distribution of light and shade among the grains changes rapidly, rather like the image in a kaleidoscope, as the angle is varied, showing that the etched surface of each grain consists of small, flat, reflecting terraces all set at the same inclination to the surface of the metal. Clearly each grain, however irregular in shape, is a single crystal, and a piece of metal consists of a mass of differently oriented crystals joined together along common boundaries.

This metallographic technique of Sorby's has proved to be of lasting value for determining grain shape and size

**MICROSTRUCTURE OF ALUMINUM is seen in the photomicrograph on the opposite page, made by Heraldo Biloni of the National Atomic Energy Commission of Argentina. The sample, aluminum more than 99.99 percent pure, was first polished by immersion in an electrolytic solution. Then the current was reversed to lay down on the metal a film of oxide only some 25 millionths of a centimeter thick. The precise thickness of the film varied according to the orientation of the grains, or individual crystals, in the metal and the concentration at each point of the dissolved impurity atoms. The variations in thickness produced interference effects in the "dark field" microscope, and these show in the photograph as different colors. The large areas of color delineate the grains and their boundaries. The dendritic pattern traces concentrations of impurity atoms. The magnification is 200 diameters.**

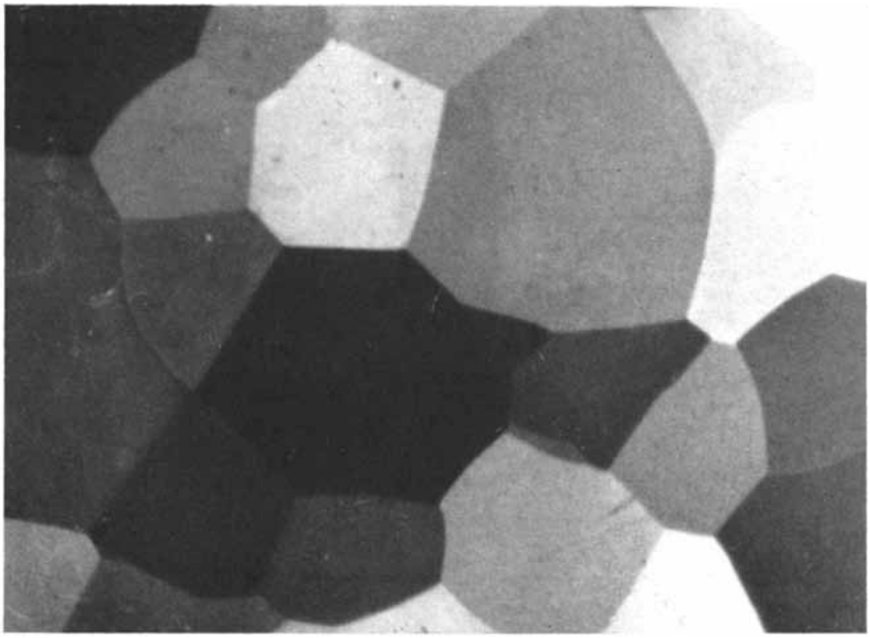


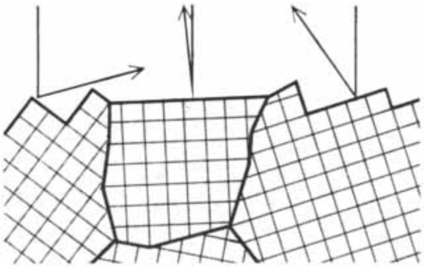
GRAIN BOUNDARY between metal crystals is only a few atoms wide, as seen in a field ion micrograph. Here the tip of a tungsten needle is enlarged some five million diameters. Each bright spot represents a tungsten atom; their pattern, which depends on the way the curved surface of the tip intersects successive crystal planes, changes abruptly at the grain boundary (*bottom left to top right*). The micrograph was made by J. J. Hren and R. A. Newman of the University of Florida, who used a new fiber-optical technique.

(which influence many engineering properties of metals), for identifying foreign particles and unwanted films of impurities along grain boundaries and for unraveling the microstructures that result when different metals are dissolved in one another to make alloys. Optical metallography was not able to determine the structure of the grain boundaries themselves, however. Gradually people came to the view that when a metal was cooled below its melting point, adjoining grains would crystallize as many as possible of the atoms that lay between them and so reduce the boundary to a mere interface, only about one or two atoms thick, across which the crystallographic orientation changed abruptly from that of the one grain to that of the other.

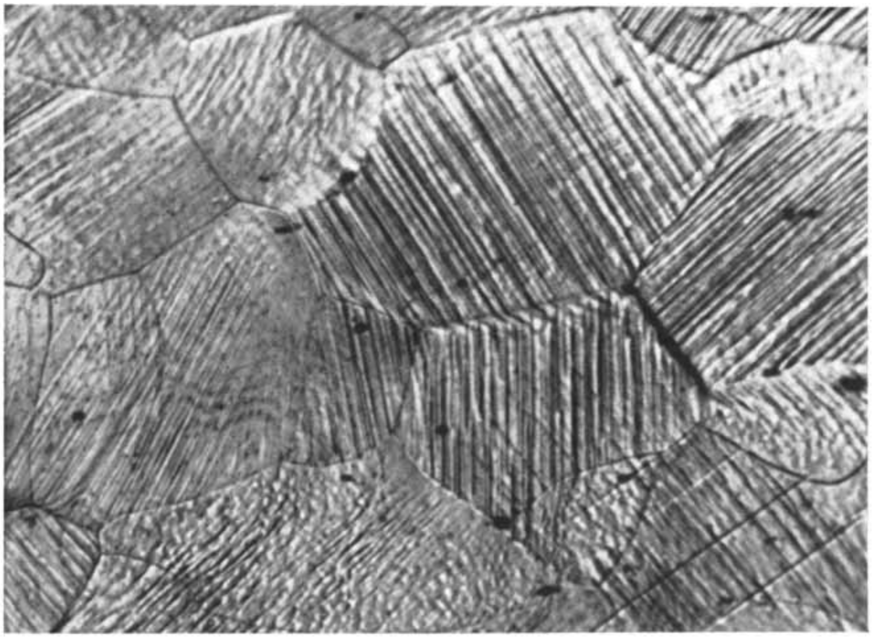
This view has been confirmed recently by the field ion microscope. In this instrument, invented by Erwin W. Müller of Pennsylvania State University, the sharp tip of a needle-shaped metal specimen is viewed end on. The tip is held in vacuum at a high positive voltage, so that lines of electrostatic force radiate from it to a fluorescent viewing screen. A trace of a gas such as helium is let into the chamber. When a helium atom touches an atom of the tip, it becomes a positive ion and then flies down the particular line of force from that metal atom to the screen. A visible image is produced by the impact of the ions on the screen. The geometry is such that an area of one atom on the tip diverges to about one square millimeter on the screen; in this sense we "see" the atomic structure of the tip. When metal crystals with grain boundaries that bisect the tip are examined by this technique, the continuation of crystal structure right up to the boundary itself, only one or two atoms thick, is clearly seen [*see illustration on opposite page*].

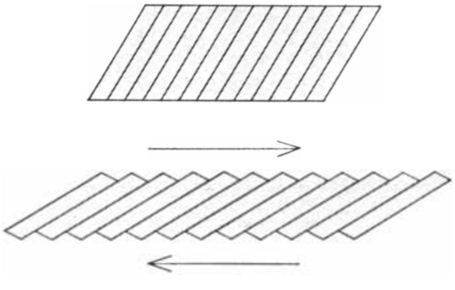
In 1900 James A. Ewing and Walter Rosenhain reported to the Royal Society of London that when a metallographic specimen was slightly deformed—for example by having its sides squeezed in a vise—its surface became crossed with fine lines. The lines generally ran straight and parallel across each grain in well-defined directions that were different in different grains [*see bottom illustration at right*]. Careful study showed that these lines were the traces of steps formed where neighboring thin sections of the crystal had slid past one another like sliding cards in a deck. Later investigations, particularly studies of large single crystals of metals, showed that sliding occurred in certain planes of atoms in the crystals and along



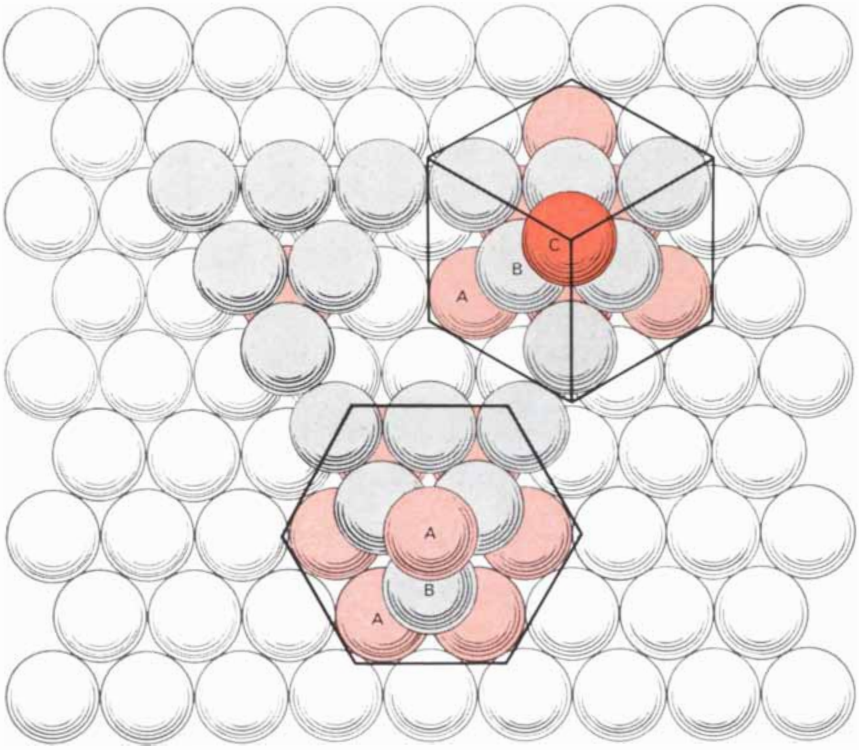


**GRAINS IN ALUMINUM** are revealed in reflected light in a photomicrograph made by G. C. Smith, S. Charter and S. Childerley of the University of Cambridge. The sample was electrolytically etched and oxidized. As shown schematically (*left*), some grains have crystal orientations that reflect most of the incident light and therefore appear to be bright; others reflect less light and appear darker. The magnification is 60 diameters.

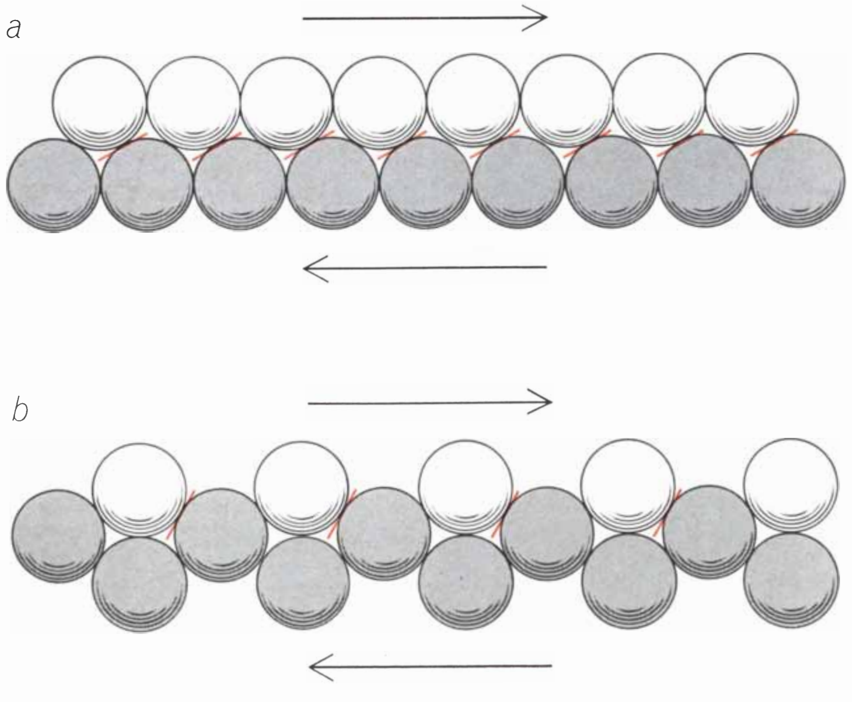




**PLASTIC DEFORMATION** reveals the slip planes in the crystals of a metal. The photomicrograph, taken by the same investigators who made the one at the top of the page, shows a deformed sample of aluminum. The parallel lines within each grain are steps formed, as with a pack of cards (*left*), when the metal was stressed and slip occurred on certain crystal planes in each grain. The sample has been magnified 60 diameters.



CLOSE PACKING of atoms is characteristic of most metals. The two close-packed structures are shown in the illustration on page 83. Here they are modeled by layers of close-packed spheres. On a first layer of spheres at sites *A*, a second layer (*gray triangles*) is placed at sites *B*. There are two sets of sites for a third layer: either at *A* (above the first layer), or at *C*. If the layers are stacked *ABCABC*, face-centered cubes are formed (*top right*). If the layers are stacked *ABABAB* (*bottom*), hexagonal close-packed structures are formed (these would have seven atoms in the third layer, only one of which is illustrated).



PLASTIC FLOW occurs when planes of atoms slip past one another. Close-packed planes do this more easily (*a*) than planes aligned in another direction (*b*). The atoms in a row are closer and the rows are farther apart in *a* than they are in *b*, and so less force is required for a given horizontal displacement, as suggested by the pitch of the colored bars. Moreover, less displacement is required to move atoms into unstable positions, from which they will be pulled forward into stable ones, when these stable positions are closer together (*a*).

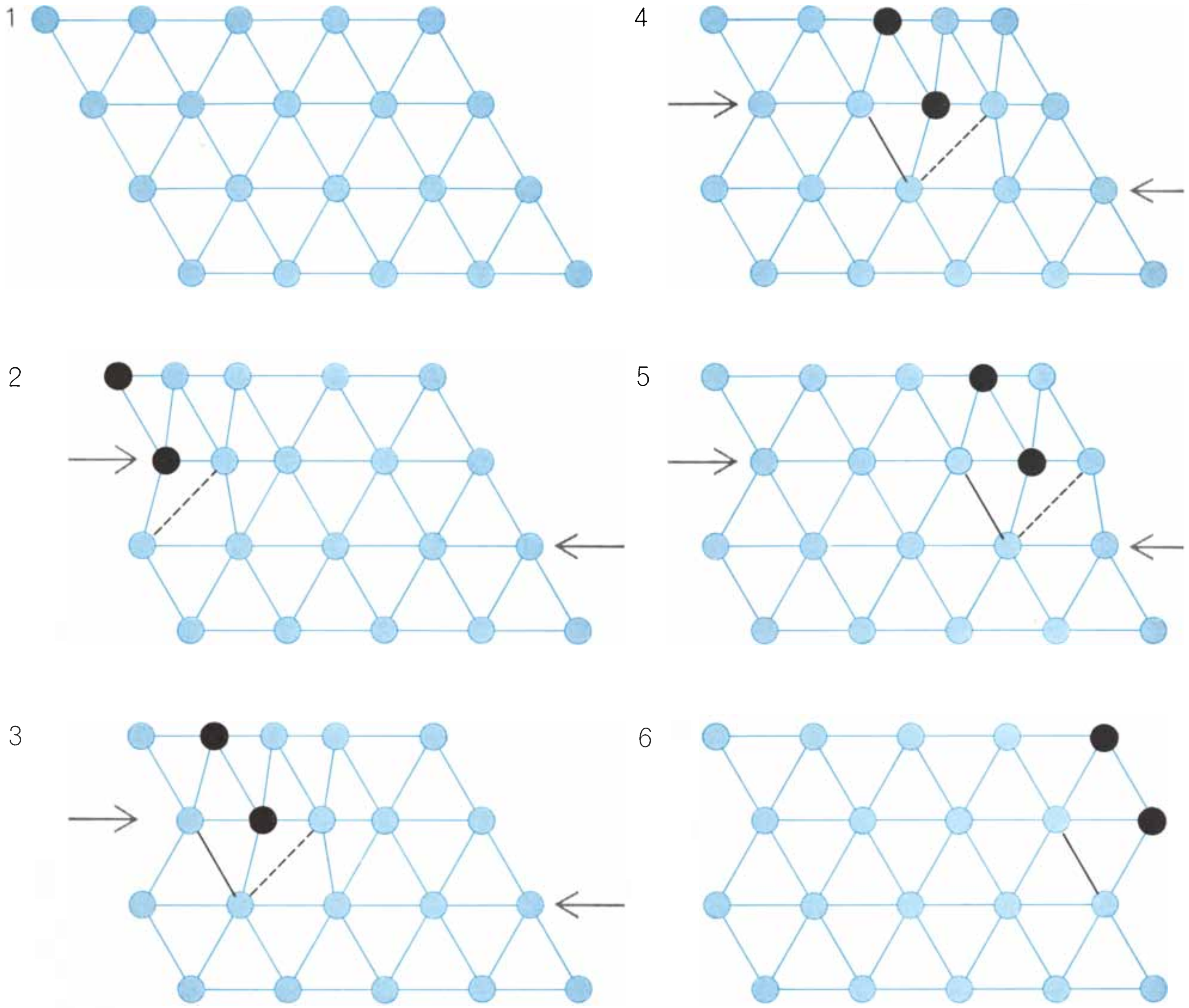
certain crystal axes in these planes. The mechanism by which a metal is plastically deformed was thus shown to be a new type of flow, vastly different from the flow of liquids and gases. It is a flow that depends on the perfectly repetitive structure of the crystal, which allows the atoms in one face of a slip plane to shear away from their original neighbors in the other face, to slide in an organized way along this face, carrying their own half of the crystal along with them, and finally to join up again with a new set of neighbors as perfectly as before, thereby restoring the original properties and internal structure of the crystal.

If plastic slip is a consequence of the regular structure of a crystal, why does it occur in metal crystals rather than in nonmetallic crystals such as diamond and sapphire, which generally prefer to break instead? Why, that is to say, are metals so ductile and most nonmetals so brittle? To understand this we shall have to go more deeply into the nature of metals.

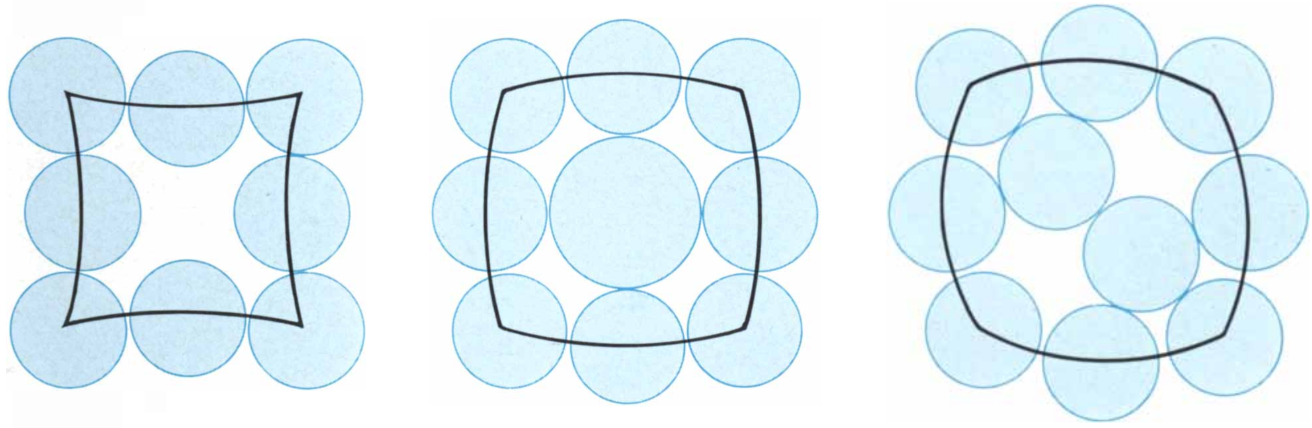
Three kinds of crystal pattern are common in metals. In the body-centered-cubic structure an extra atom is packed into the center of a simple cubic cell. The alkali metals, such as sodium, and also iron at room temperature, chromium, tungsten and molybdenum have this structure. In the face-centered-cubic structure there are atoms at the center of each face of a simple cubic cell. Iron at high temperatures, copper, silver, gold, aluminum, nickel and lead have the face-centered-cubic structure. In the hexagonal close-packed structure three extra atoms are located in alternate interstices of a simple hexagonal cell. Among the hexagonal close-packed metals are zinc, magnesium, cobalt and titanium.

In both the face-centered-cubic and the hexagonal close-packed structures the atoms are packed as close as possible. Both can be built up from close-packed planes laid one on top of the other [*see top illustration at left*]. Each trio of neighboring spheres in a close-packed layer provides one hollow in which a sphere of the next layer above can rest. There are two different sets of such hollows, each providing all the sites for a close-packed layer. If the sites of the first layer are labeled *A* and those of the two sets of hollows are labeled *B* and *C*, the face-centered-cubic structure is formed when the layers are stacked in the sequence *ABCABC* and the hexagonal close-packed structure when the stacking is *ABABAB*.

In metal crystals slip occurs in directions in which the atoms are most closely



**DISLOCATIONS** cause metals to flow more easily than the mechanism outlined in the preceding illustration would predict. Dislocations move through a metal crystal in effect one line of atoms at a time. The diagrams illustrate plastic flow in a close-packed crystal (*1*). Under a shearing stress (*arrows*), a plane of atoms (*black spheres*) moves (*2*) and a bond is broken (*broken black line*). The extra plane (*black*) continues to move; bonds break and then re-form (*solid black lines*) as it passes (*3–5*). When the dislocation (region of broken bond at edge of extra plane) has traversed the crystal, the crystal is deformed by one atomic spacing (*6*).



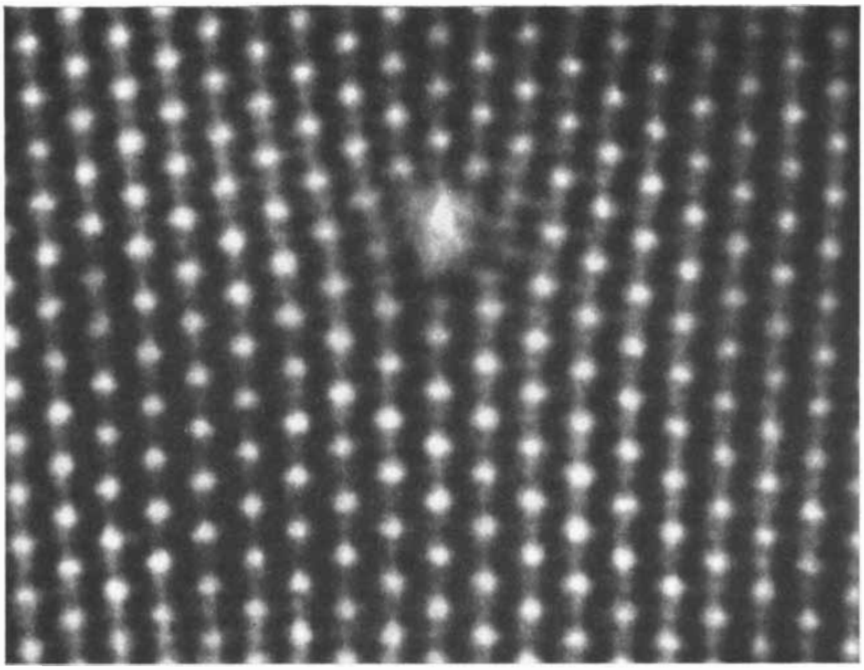
**POINT DEFECTS**, like dislocations (which are line defects), are imperfections in a crystal. There are three categories (*left to right*): vacancy, in which an atom is missing; substitutional, in which a different atom is present; interstitial, in which an extra atom is present. Each type distorts a cubic crystal lattice in a characteristic way (*black*). Point defects often interact with dislocations.

packed. It is easy to see why this should be so: Close-packed rows necessarily lie farther from each other than other rows do, so they can slip past each other with less interference. Moreover, as we shall see, atoms sliding along close-packed rows pass through stable positions most frequently. Because of their high symmetry, cubic crystal structures have close-packed rows running in many directions and can therefore slip in many directions. This has an important effect on ductility. By slipping simultaneously in several directions a crystal can change into any shape that has the same volume. It can adjust its shape exactly to fit its neighboring grains without having to open up holes or cracks at the grain boundaries, and so the entire mass of grains can be reshaped arbitrarily without breaking up. The hexagonal structure, because of its lower symmetry, does not have this property to the same extent, and so the hexagonal close-packed metals tend to be more brittle and less easy to work mechanically.

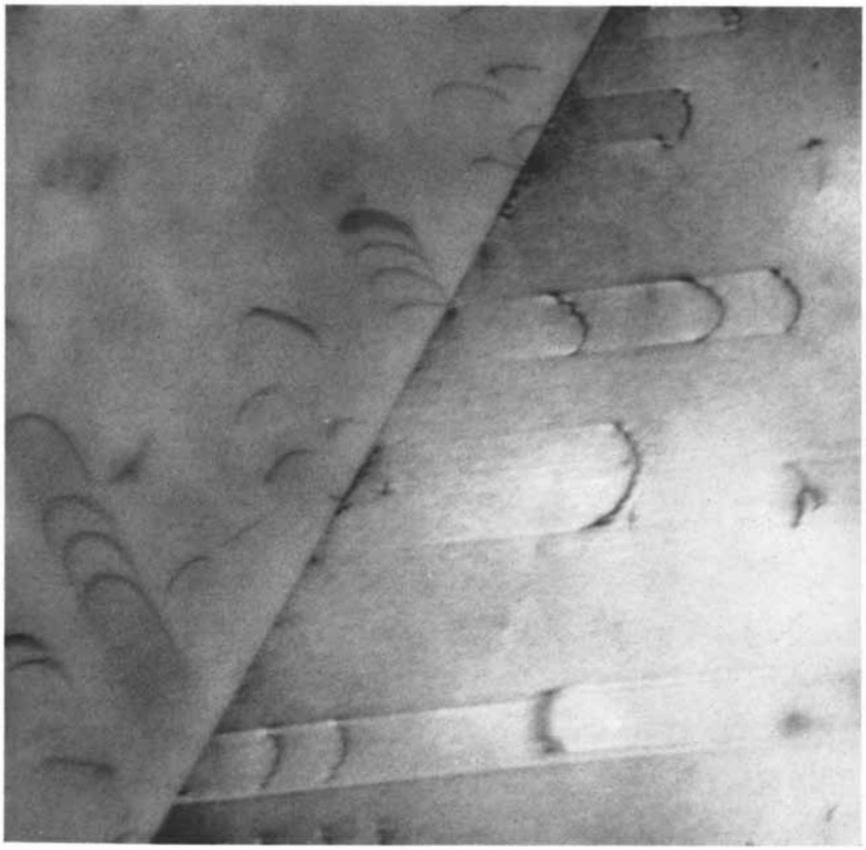
The plastic properties of metal crystals thus depend largely on the simplicity of these crystal structures, which provide close-packed directions and planes suitable for slip. Why are such structures formed? To answer this question we must turn to the electronic structure of metals.

In 1900 the German physicist Paul Karl Drude proposed that a metal contains free electrons—free to move anywhere throughout the entire piece of metal—and that the flow of these electrons under an applied electric field gives rise to the high electrical conductivity of metals. The theory was later greatly improved by the application of quantum mechanics, but the basic picture remained unchanged: A gas of mobile electrons, being negatively charged, acts as a kind of mobile glue that holds the positive metal ions together by its electrostatic attraction to them. The electron gas and the spherical ions pull each other together into a compact mass, the structure and volume of which are governed largely by the geometry of close-packed spheres. When the spheres are of equal size, as they are in a pure metal, the simple crystal structures we have been discussing result. In some alloys the difference in atomic size makes for different structures and even denser packing.

Because the free electrons act as a universal glue for all the atoms, metallic crystals are largely free from the restrictions of chemical valence that are so important in most nonmetallic substances. Different metallic crystals can be bonded



**SINGLE DISLOCATION** in cadmium is visualized in an electron micrograph made by J. W. Menter and D. W. Pashley of Tube Investments Research Laboratory in Cambridge. A thin cadmium crystal was grown on a substrate crystal of molybdenum sulfide. The mismatch between the two crystal orientations produced a moiré effect that reproduced, on a larger scale, the pattern of a dislocation in the cadmium. The extra planes and region of disorder associated with the dislocation are seen at a magnification of 2.4 million diameters.



**DISLOCATION LINES** in a thin film of stainless steel are enlarged 70,000 diameters in an electron micrograph made by P. B. Hirsch and M. J. Whelan of the University of Cambridge. The dislocations, which extend from the upper to the lower surface of the film, are seen as arrays of dark, curved lines that run out from a grain boundary along various slip planes.

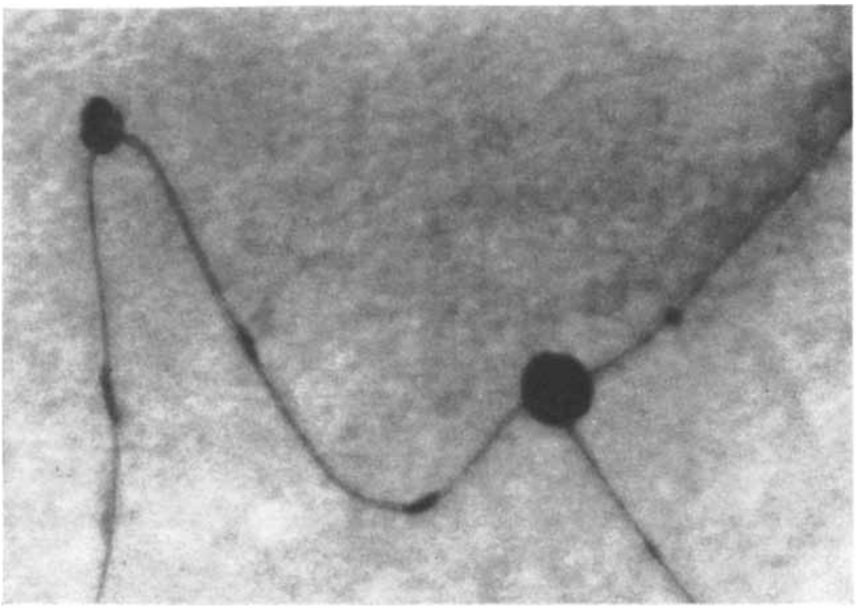
readily by their free electrons, so that the cohesive strength of grain boundaries in metals is very high; in fact, it is extremely difficult to break a cold metal along its grain boundaries unless the boundaries have been contaminated by impurities. This same unselectivity of the metallic bond makes it possible to join one piece of metal to another by simply bringing their clean surfaces together, as in welding and soldering. On an atomic scale it allows metal atoms of different kinds to intermingle in various distributions and proportions on a common set of atomic sites in a crystal, which explains why alloys can form over wide ranges of composition.

How does the free-electron structure determine the strength and ductility of metals? We have already seen one effect: It produces in the common metals (and also in many alloys in which the atoms are of roughly equal size) simple crystal structures with close-packed directions and planes that are geometrically suitable for slip. We might also expect, since the atoms are not bonded directly together but are merely held together by the free-electron gas, that these close-packed rows of atoms could slide past each other particularly easily, without coming apart. This is so, but the argument turns out to be surprisingly subtle.

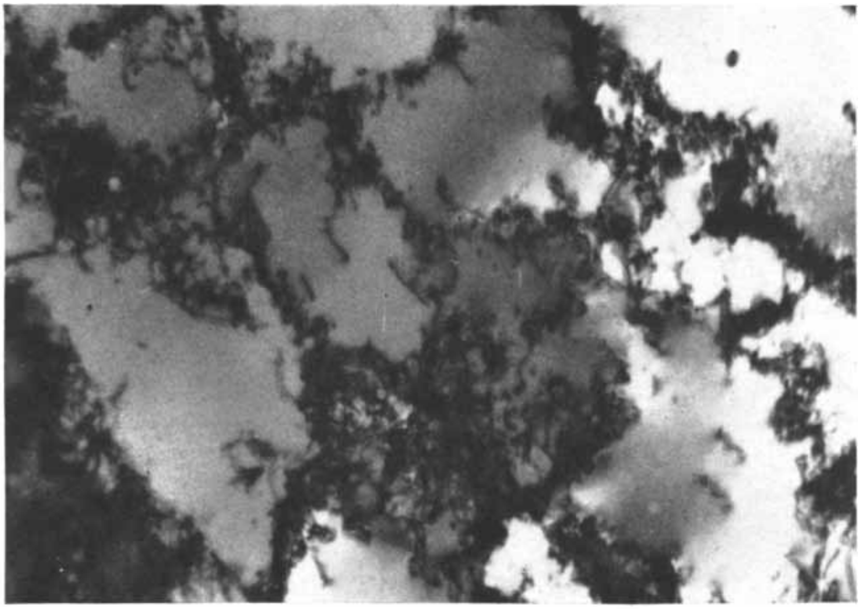
If there were no resistance to the close-packed rows' sliding along one another, the material would have no rigidity at all. A solid is a substance that has some rigidity, however, and its modulus of rigidity is a measure of the amount of shearing force required to attain a given small amount of deformation. Consider two situations involving sliding planes of atoms [*see bottom illustration on page 94*]. In one case (*a*) the atoms in each row are more closely packed horizontally (and the two rows are therefore more widely spaced vertically) than in the other case (*b*). It is clear that a given amount of deformation (lateral displacement of the top row) requires less force (less "climb" in terms of the illustration, less distortion of the atom's electron clouds in reality) in *a* than in *b*. In other words, the modulus of rigidity is lower for shear along close-packed planes.

To know the strength of a material, however, we must know not only its rigidity but also the amount of deformation required to initiate plastic flow—to make the atoms slip. In the case of sliding planes of atoms plastic flow begins when the atoms of the upper layer reach an unstable position where there is the maximum difference between the electronic forces holding the atoms back and those pulling them forward to the next crystal sites. The amount of deformation that brings the atoms to that point is clearly less for *a* than for *b*. Thus for two reasons—the lower modulus of rigidity and the smaller deformation required to reach the point of plastic flow—slip is more likely along close-packed planes of atoms.

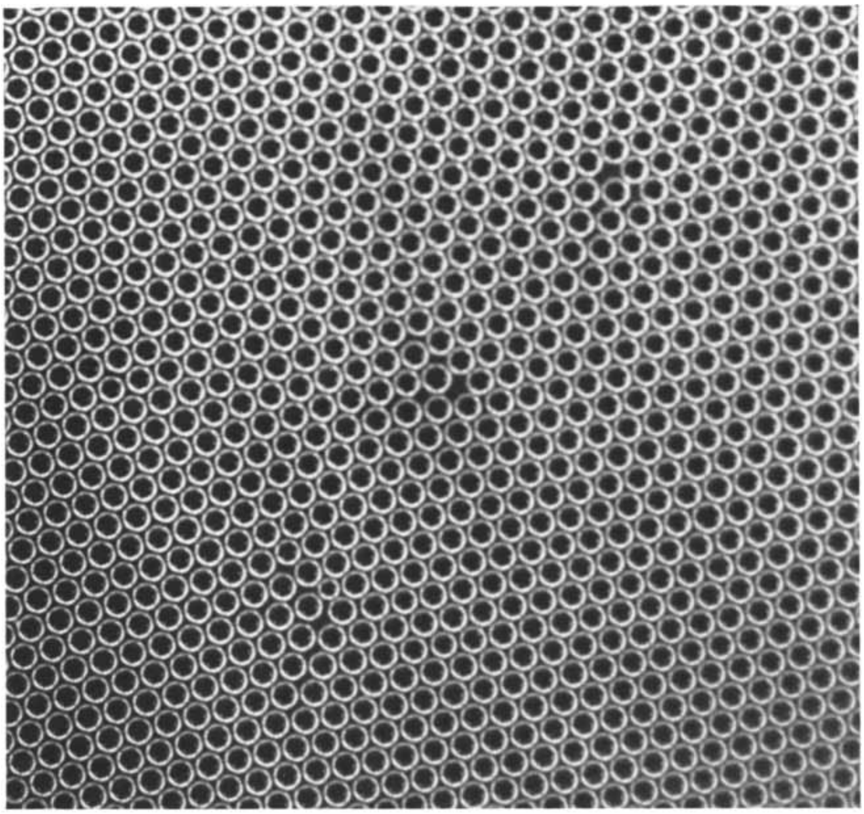
This argument shows why cubic metals such as aluminum and copper are particularly ductile, but it fails by orders of magnitude to account accurately for the shear strength of metals. Calculations of the ideal shear strength, based on this line of reasoning, long ago indicated that a metal should deform elastically some 3 to 10 percent before beginning to flow. In practice, however, a crystal of pure metal usually flows at deformations as low as .01 percent. This thou-



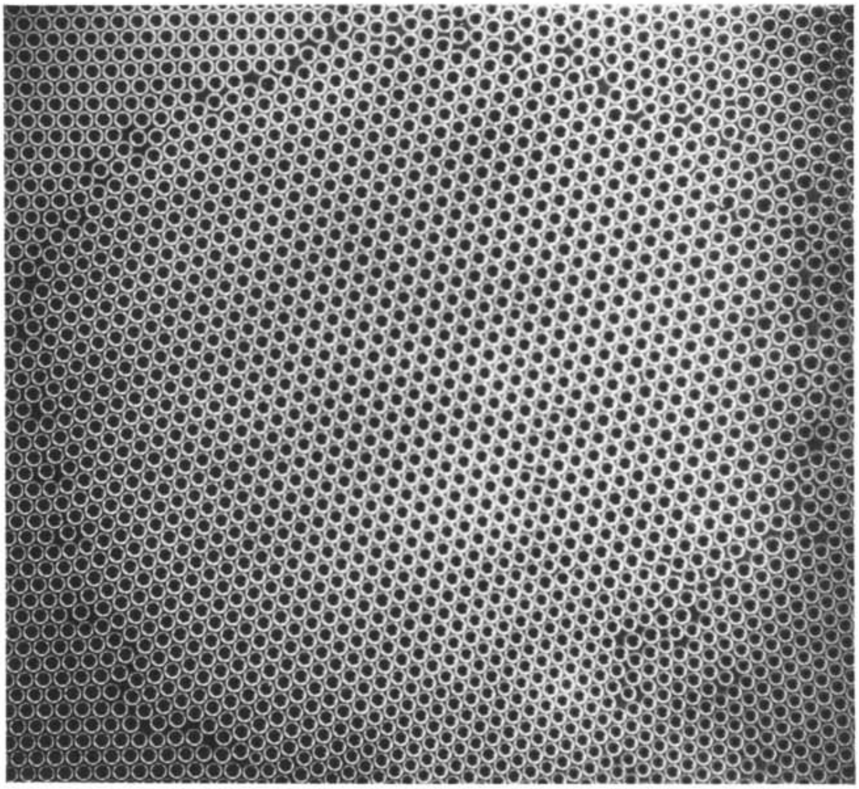
**IMPURITIES** may act to "pin" a dislocation line, sometimes arresting it and sometimes making it bow out or cross into a different plane and thus keep moving. In the electron micrograph, made by Gareth Thomas and Jack Washburn of the University of California at Berkeley, dislocations pinned by impurities in magnesium oxide are enlarged 90,000 diameters.



**TANGLE OF DISLOCATIONS** acts to strengthen a metal by obstructing subsequent dislocations. The electron micrograph, made by Thomas and R. L. Nolder, is of a film of nickel that has been cold-worked by rolling to strengthen it. The dislocations are concentrated in certain areas, creating a system of small dislocation-free "cells," or subgrains, in the metal.



**THREE DISLOCATIONS** are simulated by the "bubble raft" technique, in which a layer of bubbles models a layer of close-packed atoms. The dislocations, each involving an extra row of atoms, are arrayed from bottom left to top right. They form a "low-angle grain boundary"; the angle between grains can be seen by sighting along rows from the lower right.



**CRYSTAL GRAIN** is simulated with the bubble raft. The roughly circular grain boundary is made up of a number of dislocations. This photograph and the one at the top of the page were made by William R. O'Day, Jr., of the Mitron Research and Development Corporation.

sandfold discrepancy between ideal and real strengths is of great practical as well as scientific interest.

When the discrepancy was first discovered, it was thought that the theory of ideal strength might be wrong. It is not wrong; metal crystals grown in the form of thin "whiskers" do in fact have strengths near the ideal value. The softness of large crystals of pure metals is not due to any change in the laws of atomic forces but to the presence of dislocations in the crystals: irregularities of crystal structure that allow atomic planes to slip much more easily than they would in a perfect crystal.

Sir Nevill Mott has likened slip to the sliding of a large, heavy rug across a floor. If you try to slide the entire rug as one piece, the resistance is too great. What you can do instead is make a wrinkle in the rug and then slide the whole thing a bit at a time by pushing the wrinkle along, thereby enlarging the slipped region behind it at the expense of the unslipped region in front of it.

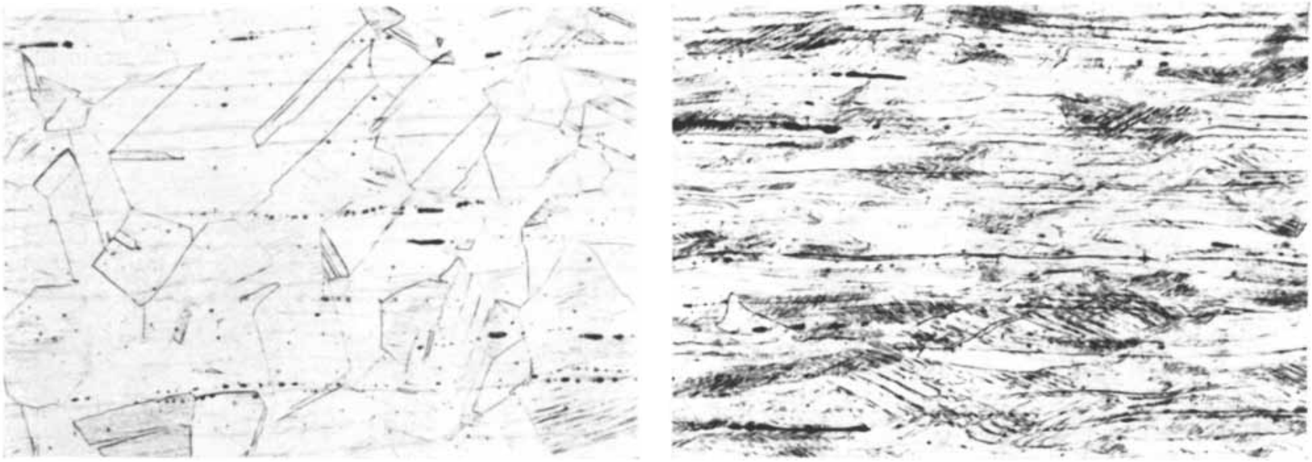
Such a process is directly analogous to plastic flow caused by a dislocation. When the part of a crystal above a slip plane slides over the part below, it does not do so all at once as in the theoretical examples we have been considering but a bit at a time. During slip there is necessarily a boundary line—the dislocation—between the slipped and the still-unslipped regions. In the case of an "edge" dislocation the dislocation is the edge of an extra vertical plane of atoms crowded into the upper, slipping part of the crystal. The dislocation line lies at right angles to the direction of slip [*see top illustration on page 95*]. When the direction of slip is parallel to the dislocation line, the result is called a "screw" dislocation. Most dislocations are actually combinations of the two and tend to take the form of loops.

Dislocations are almost inevitable in a crystal, if only because of irregularities in the process of crystal growth and the fact that every grain boundary is in effect an array of dislocations. When a crystal is subjected to a shearing force, dislocations in it are made to move along slip planes. If a crystal contained a single dislocation line and no other imperfections, under stress the line would move right out of the crystal, deforming the crystal by one atomic spacing at most. In reality crystals usually contain complex networks of interconnected dislocation lines as well as other defects and impurities in the crystal lattice. When the dislocations begin to move, their ends remain tied to other parts of the network or to other defects. Because the ends are anchored, the active slip planes can never get rid of their slip dislocations. In fact, the dislocations in a plane multiply when the plane slips.

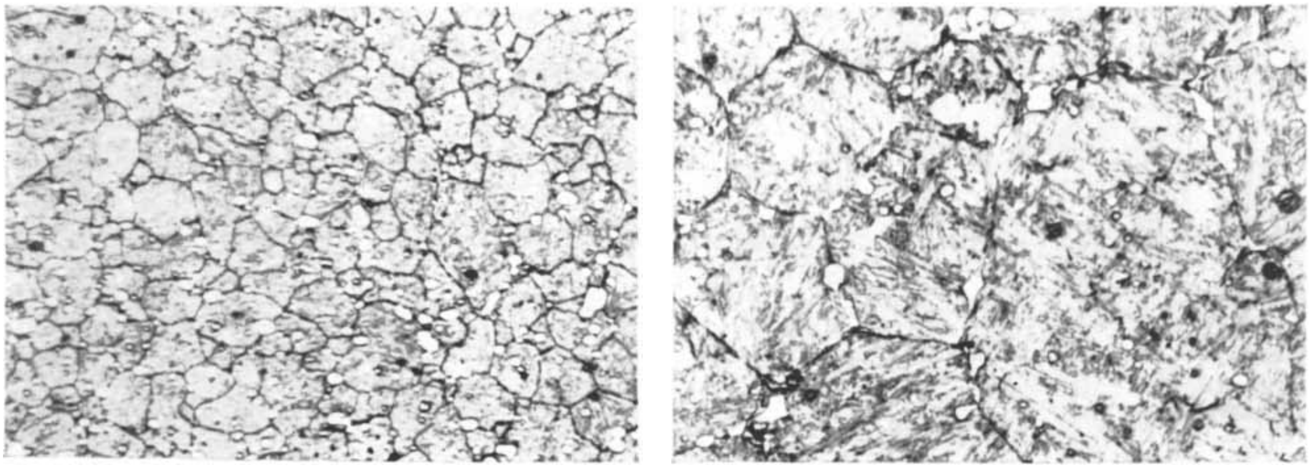
The important question with regard to the strength of a metal therefore becomes: How easy is it to move a dislocation? In the slip process the dislocations are of course pushed along by the shear stress acting on the slip planes, which comes from the applied forces—tension, compression and torsion—on the material. How much shear stress is needed to move a dislocation in a slip plane? This is really two questions, one about the natural resistance of an ideal crystal to the passage of dislocations and one about the effect of blocking the paths of dislocations with foreign particles and other obstacles in real crystals.

Let us consider the natural resistance of the crystal lattice. The atoms immediately ahead of a dislocation resist its approach, since it forces them out of their stable crystal sites. The atoms immediately behind the dislocation push the dislocation forward, since the farther away it gets the more completely they can fall into the new stable sites to which they have been brought by the slip process. Since the dislocation is thus pushed both forward and backward, the natural resistance of the crystal to its movement is approximately zero! This spectacular property of the crystalline state of matter holds when the region of dislocation is wide, that is, when the transition from the slipped to the unslipped areas of the slip plane occurs gradually over a width of many atoms; there are then so many atoms on both sides to exert this reverse tug-of-war on the dislocation that they are always in almost perfect balance. On the other hand, when the region of dislocation is narrow, there are too few displaced atoms to maintain a good balance and an applied shear stress is needed to move the dislocation. In the limiting case of a dislocation only about one atom wide, this stress can be nearly as large as the ideal shear strength of the material.

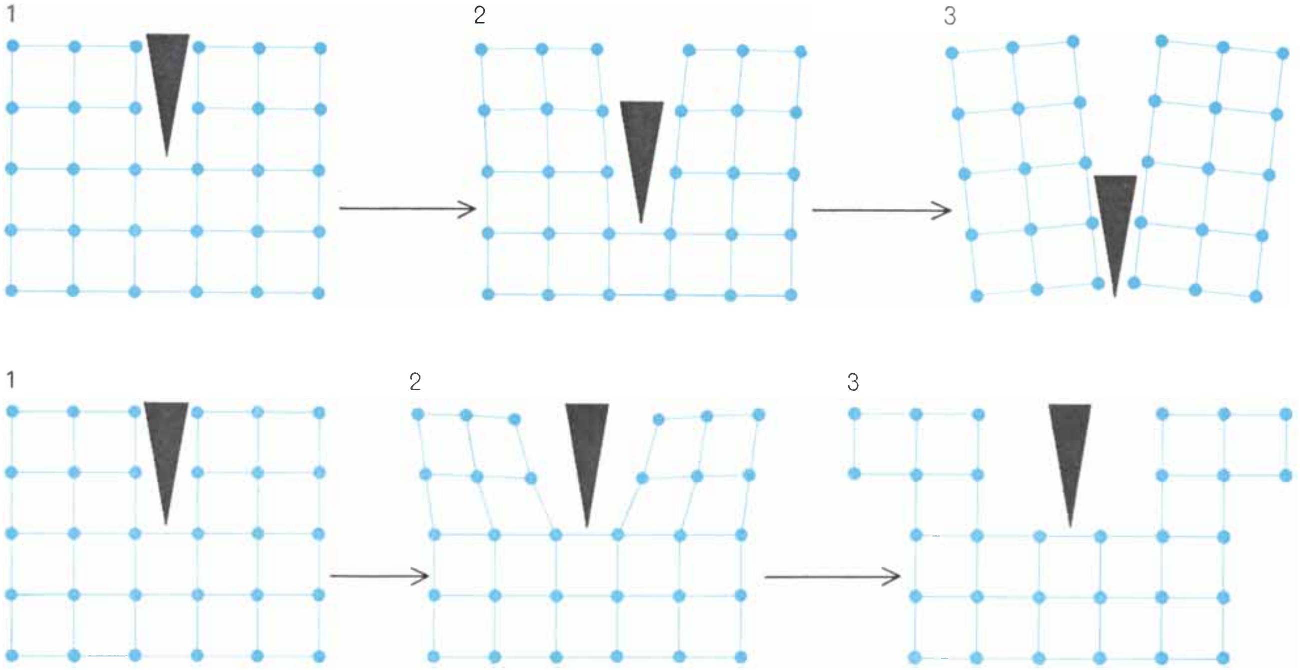
One expects narrow dislocations in crystals such as diamond, where the highly directional covalent bonds hold the atoms at definite angles to one another and there is great resistance to shear. In agreement with this, such materials are very hard, even with dislocations. By the same token, one expects wide dislocations in metals, where the close-packed structure and free-electron bonding allow the atoms to slide over one another with relative ease. This ex-



**COLD-WORKING** is an important method of strengthening and hardening metals. It multiplies the number of dislocations and also reorients the grains. These metallographs were made at the IIT Research Institute. They show (at the same magnification) two samples of the same stainless steel, one before (*left*) and one after (*right*) a 40 percent reduction in cross section by cold-rolling.



**GRAIN SIZE** is related to the strength of a metal because a fine microstructure pins dislocations more completely than a coarse one. Grain size is affected by the heat treatment given a metal, as in annealing. In these photographs from IIT a sample of high-speed tool steel treated at 2,200 degrees Fahrenheit (*left*) is compared with a sample of the same steel treated at 2,267 degrees (*right*).



**HIGH-SPEED CRACK** moving into a metal may cause atoms to break apart or merely to slide past one another. In a brittle material (*top*) the bonds stressed in tension fail first; the crack propagates rapidly and the metal breaks apart. In a ductile material (*bottom*), the bonds stressed in shear fail first; the bonds break and re-form, allowing the atoms to slip, and the crack is blunted and stopped.

plains the extreme softness of pure close-packed cubic metals such as copper, gold and aluminum.

The practical problem with such metals and many others, of course, is not how to make them more ductile but how to make them harder. Metallurgists do this by putting various obstacles in the way of the dislocations. Since dislocations pile up at grain boundaries, metals can to some extent be hardened by reducing the size of their grains. Alloying introduces foreign atoms that distort the crystal locally around themselves, and these local distortions offer resistance to a nearby dislocation. If the alloy atoms are gathered into clumps, their effect is enhanced, and this can be accomplished, as it is in the alloy Duralumin, by heat treatment.

In the hardening that is produced by various processes of plastic-working such as hammering or rolling, the obstacles are paradoxically the dislocations themselves. When the number of dislocations in the worked metal becomes large enough, those moving along intersecting slip planes obstruct one another's movement—an effect readily appreciated by anyone who has been held up at a road junction in dense traffic.

We have seen that in metals dislocations in close-packed planes are intrinsically mobile and that this makes for softness and ductility. What happens, however, when a metal is attacked by a high-velocity crack? This is not an idle question. Commercial metals and alloys usually contain particles of brittle foreign substances; when such a particle suddenly splits, the metal nearby is attacked by a crack that comes out of the particle at high speed. Experience has shown that face-centered-cubic metals such as copper resist such a crack, which is blunted and changed to a wide notch by plastic deformation. The body-centered-cubic "transition" metals, such as iron, usually behave in the same way when they are warm, but they allow the crack to run through them in a brittle manner when they are cold.

Why do the face-centered-cubic metals blunt the crack? If the crack passed through the metal slowly, the dislocations already present could be moved about by the stresses accompanying the crack, and the plastic work done by their movement might drain away the crack's energy and so halt it. But what if the metal is being attacked by a high-speed crack? To understand the consistent ductility of the face-centered-cubic metals, we have to consider whether in a given specimen the atoms at the leading edge of a sharp crack are likely to pull apart, propagating the crack in a brittle manner, or to slide past one another, starting a slip process [*see illustration above*].

Anthony Kelly, Bill Tyson and I have recently looked at this problem. We calculated that the tensile forces on the atoms directly ahead of a sharp crack are about five to six times larger than the shear forces. With the approach of the crack these forces grow, but they stay in the same ratio until the failure point of the atomic bonds, either by tension or by shear, is approached. If the ratio of tensile strength to shear strength in these bonds is less than the ratio of tensile forces to shear forces, the failure should occur by cracking; if it is greater, the failure should be by slip. It is possible to estimate the approximate tensile and shear strengths of the bonds in various types of materials. When this is done, the comparison of the ratios of strengths to stresses shows quite clearly that materials such as diamond must be brittle. The issue is finely balanced for the body-centered-cubic transition metals, which agrees with the fact that these are sometimes brittle and sometimes ductile. For the face-centered-cubic metals the shear strength is so low compared with the tensile strength that these metals must always be ductile.

The low shear strength of face-centered-cubic metals follows directly from the low modulus of rigidity and the small deformation required to initiate plastic flow on their closely packed planes. These qualities, as we have seen, are implicit in the geometry of close-packed spheres that is so characteristic of the structure of metals and that is a direct consequence of the nature of the metallic bond.

# The hope of doing each other some good prompts these advertisements

## The Visualmaker

Teachers who refuse to act like teaching machines have their place, and it is a place of honor for men and women who count it a duty to use eyes, ears, and mind continually to fish for material that makes teaching an act of life-sharing. If an outfit priced slightly over $110 can help, the price is very low indeed.

This man is using a KODAK EKTAGRAPHIC Visualmaker for his students back home. In years to come, any allusion to the Hessians will bring an image to mind of the slide he is making. Beneath the 8 x 8-inch copy stand is a document "relating to the Hanau and Anspach Troops 1776-1778." The slide of the roster of Major Martens' company will show how the name of Henrÿ Lehberg (umlaut over the ÿ? Lekberg?) was written at the time by someone dealing with the affair in North America.

For smaller subjects, a 3 x 3 copy stand that similarly eliminates all problems of lighting, focusing, and parallax is part of the Visualmaker as we furnish it in its attaché case. If the user teaches geology instead of history, the 3 x 3 frame might have been held against a rock. Then, switching in a moment to the 8 x 8 frame, he might have shown the interesting mineral in its lithological context. Then with the KODAK INSTAMATIC® 304 Camera alone, he might have stepped back a few feet from the rock face for the larger pattern, then 100 feet away, then from a neighboring rise of ground, and finally from a bend half a mile up the road. At the first letterbox he would have dropped the film cartridge in the AVP-1 KODAK Prepaid Processing Mailer sold by the Kodak audiovisual dealer. Even if his classroom were at the opposite corner of the U.S.A., we'd have those color slides there mounted for his projector within three days after we got the cartridge.

*Eastman Kodak Company, Education Division, Rochester, N. Y. 14650, can direct you to the dealer. For what detail is worth in 18th century penmanship or grain alignment in minerals, the quality of the camera lens you are buying in the outfit will be appreciated.*

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## Ayari, Bardawil, Gomes, Häyrén, Imbert, Sidek

People in this country or any other country who seek employment and can't find it are tragic figures. Our particular contribution to the solution of the problem is to offer jobs. Jobholders, however, expect payment for their work. This is possible only to the extent that our products are wanted at prices customers are willing to pay. Last year the arrangement worked out well enough to create Kodak jobs for some 10,000 more people around the world. Many of these differ in appearance and other respects from the folks in the house across the way from your house, whoever you are. Nor are they all Americans, or want to be. Among the non-Americans:

Elias Ayari, member of the Luo Tribe, citizen of Kenya, native of Kisumu where he made Standard VIII at Ramba Intermediate School, skilled employee of Kodak (East Africa) Limited. After your next camera safari drop off your 126 cartridges at one of the many photo dealers in Nairobi who offer Kodak's Color Photofinishing Service. You will like the quality of the KODACOLOR Prints from the electronic color printer he operates. It is considerably more complex than the black-and-white darkroom equipment with which he learned photographic technology before becoming a Kodak man in October, 1966.

Miss Odette Bardawil, already promoted from telephone operator at Kodak (Near East) Inc. to secretary for an executive. Evenings find her at a course in English literature at Beirut's American Language Center. At Adventists High School, her alma mater, Arabic and English get equal emphasis.

José Fernandes Gomes, salesman who joined Kodak Brasileira at São Paulo in October last year and is proud to have already sold two automatic x-ray processing machines, aside from other products. Not only does he sell the processing machines, but he also installs them and sees to it that they keep turning out highest-quality radiographs at a speed such that the radiologists need not keep the crowds waiting as long as before at the Clínica Roaldo Amundsen Koehler in Curitiba and the Clínica Dr. José Silva Villela in Araçatuba.

Kaarlo Hayrén, who last year changed his profession from the chemistry of aniline dyes, high polymers, and edible oils to a new career with Kodak Oy, our Finnish name that is bursting far beyond an identification with family snapshots. He is busy feeding all kinds of professional photographic materials into scientific, industrial, and government activities of his country as well as into its studios (portrait, movie, and TV). His present career really had its start when his home town of Viipuri became Soviet territory and he turned his thoughts at 18 to learning how to process his own color film.

Christian Imbert, chemical engineer who finds himself at 27 responsible for quality control of the polyester that Kodak-Pathé started manufacturing for film base last year at Chalon-sur-Saône, a town 200 miles southeast of Paris which had been better known for the magnificent vineyards which surround it. Despite the substantial investment we have already made in the plant, most of its 200-acre expanse looks as though it were still available for rugby, a sport that greatly interests M. Imbert.

Mohammed Sidek bin Mohammed Nor, driver of Kodak (Malaya) Limited trucks in and around Kuala Lumpur, formerly peon (which means general messenger) at Headquarters of the 17th Gurkha Division in Seremban, capital of one of the 11 states of West Malaysia. Where other members of our Malay staff have an average of six children—one with 13—Sidek and his wife have only one to lavish affection on.

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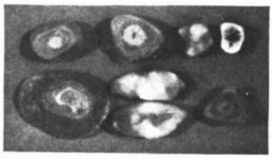
## The infrared look of things

Direct photography in the infrared has been making progress of late in two quite different directions: 1) exploitation of color perception to see infrared as red, red as green, green as blue, and blue as black; 2) luminescence recorded when infrared is filtered out of *all* light striking the subject while over the camera lens another filter passes *only* infrared.



As an example of the luminescence technique, observe these gallstones.

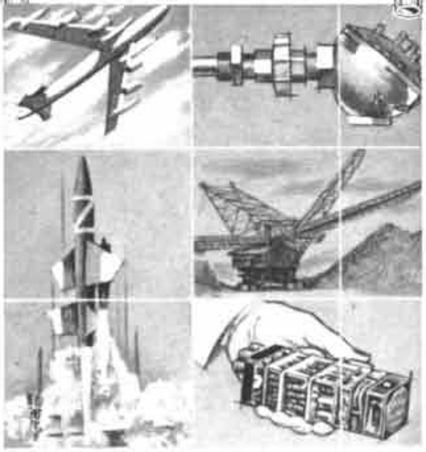
By ordinary panchromatic photography they look like this.

*Medical Infrared Photography*, a $2 book we have just published, tells about the films needed, exposure, processing, and easing the strain of tuning up for the new perceptions. Their significance is yours to determine for your own game, in the event that the medical language in the book is wasted on you.

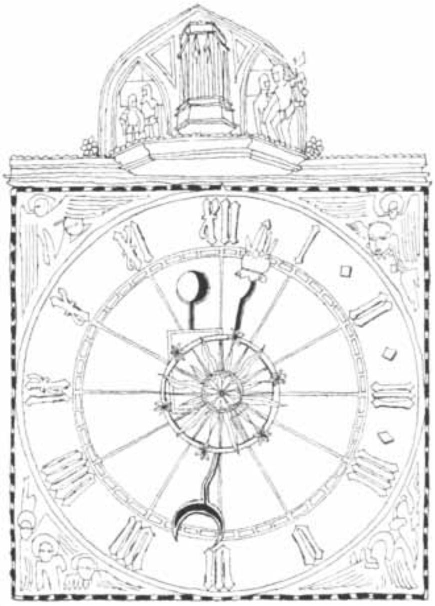
*Send check with order for "Publication N-1" to Department 454, Eastman Kodak Company, Rochester, N.Y. 14650.*

Kodak

*Prices subject to change without notice.*



# SCIENCE AND



### *Technology and the Negro*

The technological revolution that has doubled the U.S. gross national product in the past 20 years, providing 18 million new jobs, increasing real personal income per capita 49 percent and reducing the average work week into the bargain, has had other effects: it is one of the primary causes of unemployment, social dislocation and hopelessness among Negro Americans. It is not just that Negroes have been "left behind" by the soaring U.S. economy; to a large extent they have been its victims.

The primary problem is the changing equation between jobs and training. This was pointed out by Herbert Bienstock, Middle Atlantic Regional Director of the U.S. Bureau of Labor Statistics, in a recent interview with *The New York Times*. In brief, World War II, fair employment practices legislation and years of dramatic technological change in agriculture combined to move Negroes north off the farm. They got a foothold on the bottom rung of industry. Then technological change in industry largely chopped off that rung. Now millions of Negroes are untrained for the jobs that are available and find no demand for the work they can do.

In 1940, 77 percent of American Negroes lived in the South; now about half of them do. In 1940, 41.5 percent of all Negro men worked on farms; now only 8 percent do. Half of the Negroes in large Northern cities are "immigrants," mainly from the South. The jobs immigrant Negroes got were chiefly as unskilled and semiskilled workers. Since 1953 there has been an absolute decline in the total number of such jobs in the U.S. economy, and the new factory jobs are moving away from the central cities where Negroes live. Meanwhile other occupations are expanding: professional and managerial, white-collar and skilled worker. These are precisely the occupations in which the Negro is underrepresented, barred either by discrimination or by lack of training and even lack of the basic education and motivation to make the required training possible (see "The Social Power of the Negro," by James P. Comer; SCIENTIFIC AMERICAN, April).

Young Negroes have been the hardest hit of all. In 1948 the unemployment rates for white and Negro boys and girls from 16 to 19 were all about 9 percent. Now the rates are about 16 percent for whites, 26 percent for Negro boys and 37 percent for Negro girls. Forty-six percent of Negro youngsters drop out of high school before graduation. Untrained, they find it difficult to break what Bienstock calls the "first-job barrier." On the other hand, the motivation for Negroes to stay in school is low: among nonwhites the unemployment rate for graduates is not much better than it is for dropouts—and it is higher than for white dropouts.

Bienstock sees some hope for the future. He points out that the post-World War II baby boom has by now dumped its added population on the labor market. The next major demographic effect has now set in, that of the decrease in births during the depression of the 1930's. By 1970 there will be a decrease of 700,000 in the U.S. work force in the economically important age group from 35 to 44. At the same time there will be increasing demand for white-collar and technical workers. There will be real pressure on employers to seek out Negroes and other marginal workers and give them on-the-job training. The combination of a manpower shortage and increased demand may provide an opportunity, Bienstock says, "to overcome a century of neglect."

### *Subatomic Relativity*

One of the cornerstones of Einstein's theory of relativity is the principle of microscopic causality, which assumes that signals do not travel faster than the speed of light even at subatomic distances. This principle has now been verified for distances less than $10^{-15}$ centimeter in an experiment performed with the giant alternating-gradient synchrotron at the Brookhaven National Laboratory. The distances involved correspond to between a hundredth and a thousandth of the radius of a single proton. The measurements were arrived at by studying the effects of high-energy pion-proton collisions inside the accelerator. On-line computers connected directly to the experiment were used to record and analyze several million such interactions per hour. The eight-member experimental team was headed by S. J. Lindenbaum of Brookhaven.

### *Smallest Copy*

What may be the smallest self-duplicating entity has been created in an "extracellular Darwinian experiment" by D. R. Mills, R. L. Peterson and Sol Spiegelman at the University of Illinois. In the *Proceedings of the National Academy of Sciences* they explain how they subjected a self-duplicating molecule of ribonucleic acid (RNA) to a test-tube environment in which "selection pressure" favored the molecular species that could replicate the most quickly. After 74 transfers from one test tube to another the surviving molecular descendants were only a sixth as big as the original molecule and replicated 15 times faster.

The original RNA molecule was obtained from a bacterial virus called Q$\beta$. Such viruses, which can multiply only inside a host cell, consist of nothing but a molecule of RNA encased in a protein jacket. The RNA contains all the instructions for producing a new virus particle, including the instructions for making an enzyme, termed a replicase, that carries out the replication of the RNA itself. Spiegelman and his colleagues learned how to isolate the Q$\beta$ replicase and found that it would produce infectious RNA molecules when provided with a template of viral RNA, together with the necessary chemical building blocks.

It occurred to the group that the molecular sequences in the RNA that code for the proteins forming the jacket of the virus, as well as for components of the replicase, might be dispensable. This led them to ask: "What will happen to the RNA molecules if the only demand made on them is the Biblical injunction 'Multiply,' with the biological proviso that they do so as rapidly as possible?" To answer this question they devised an experiment that allowed the viral RNA to multiply for 20 minutes, after which a small amount of RNA was transferred to another test tube to prime a new generation of RNA molecules. After 13 such transfers the replication time was reduced to 15 minutes and maintained for the next 15 transfers. Transfers No. 30 through No. 38 were incubated for 10 minutes; transfers No. 39 through No. 52 for seven minutes, and transfers No. 53 through No. 74 for five minutes. The experiment showed that 83 percent of the original RNA molecules was expendable and therefore presumably associated with the coding of coat protein and other functions not essential for self-duplication.

### *Loused-up Lice*

Synthetic juvenile hormone has proved effective in killing the human body louse and therefore holds the promise of curbing epidemic typhus, which is one of the diseases transmitted by the lice. Experiments in which the hormone not only killed lice but also prevented lice eggs from hatching are reported in the *Proceedings of the National Academy of Sciences* by J. W. Vinson of the Harvard School of Public Health and Carroll M. Williams of the Harvard Biological Laboratories. The authors write that the findings "are of special interest because in many parts of the world the human body louse—vector of epidemic typhus, trench fever and epidemic relapsing fever—has become virtually resistant to all presently known insecticides."

Juvenile hormone, secreted by all insects, is vital at certain stages of growth but at other stages must be absent or the insect will develop abnormally. The synthetic juvenile hormone used by Vinson and Williams was made by bubbling hydrogen chloride gas through an ice-cold solution of farnesenic acid. Applied to small pads of wool or nylon on which lice and eggs were maintained, the synthetic hormone was lethal to adult lice at a concentration of 10 milligrams per pad. Nearly all eggs on pads with one milligram or less failed to hatch, and larvae on such pads failed to mature.

The synthetic hormone had already proved effective against the mosquito that transmits yellow fever. Williams has expressed the hope that various analogues of juvenile hormone can be found that will be effective only against particular species of insect pests and will not have the broad toxicity of pesticides now in use (see "Third-Generation Pesticides," by Carroll M. Williams; SCIENTIFIC AMERICAN, July).

### *Crystalline Ribosomes*

Ribosomes, the particles in the living cell where proteins are made, are themselves composed of some 35 protein chains (all of which may be different) and two chains of ribonucleic acid (RNA). It has now been shown that these complex bodies can arrange themselves into lattices that form sheets, cylinders and even three-dimensional crystals. Electron micrographs of these structures made by Breck Byers of Harvard University are published in a recent issue of the *Journal of Molecular Biology*.

The crystalline arrays of ribosomes appear within the cells of chick embryos when chick eggs are cooled to the region between five degrees and 15 degrees centigrade for periods ranging from several hours to two days. Briefer periods and lower temperatures lead to the production of crystalline sheets, which frequently form dense stacks. Prolonged cooling at around 10 degrees C. tends to yield sheets that curl up into cylinders and pack together in parallel arrays. Although these ribosome crystals would not normally appear in chick eggs incubated at the customary temperature (37 degrees C.), eggs that have been chilled to 10 degrees can survive. Thus it is apparent that the crystallization of ribosomes is not harmful to the cell.

The crystallization provides convincing evidence that the internal structure of the ribosome is itself highly regular. Byers is now trying to separate the ribosome crystals from the cellular material in which they are normally embedded in the hope that they can be studied by X-ray crystallography. If they can, they will be by far the most complex crystals ever investigated by this technique.

### *Oldest Reptile*

An incomplete skeleton found embedded between two seams of coal in Nova Scotia is evidently the oldest known representative of the reptiles, the animals that dominated land and sea during the Mesozoic era, 230 to 70 million years ago. Donald Baird of Princeton University and Robert L. Carroll of McGill University presented this conclusion recently in *Science*. The reptile's fossilized remains were discovered

# ALLOY STEELS

*The interaction of solute elements, their thermodynamic relationships with each other and with iron... how these interactions control subsequent solid state transformations to produce a microconstituent which determines the properties of the alloy.*

by James Smith

Alloy steel studies were once measured in terms of "the state of the art." Not so now. Steel research activity is moving forward so rapidly it now includes such sophisticated concepts as atomic scale interactions, solid state reactions and micron scale defect measurements.

This rapid advance in alloy steel development can be attributed to the interaction of physicists, chemists and engineers—often working as a team. Separately as well as together, they make careful studies of the intimate structure of metals and the mechanisms by which the structure controls engineering properties of steel, such as strength, toughness, ductility and joinability.

True, iron is the backbone of steel. But it is only that until researchers work to develop in it properties many times superior to those inherent in iron. Strength is an important example. The yield strength of iron is approximately 4,000 psi. But research has developed commercial steels with strengths two orders of magnitude greater.

Research studies begin with the periodic table. Here is where the researcher makes a finite choice of those elements that may be alloyed with iron.

The treatment the alloy then receives ultimately determines what engineering properties the steel will develop.

Alloy studies delve into the interaction of these (alloying) solute elements. Their thermodynamic relationships with each other, as well as with the iron are investigated. These interactions control subsequent solid state transformations to produce a microconstituent which can enhance the properties of steel. These transformations are also studied. The internal structure or atom array within the microconstituent is examined by electron microscopy, electron and/or X-ray diffraction and by microstraining techniques. This examination can reveal the presence of dislocation networks which determine the deformation characteristics of the alloy steel.

These tools are useful in observing the contribution made by the clustering of solute atoms. Also, the precipitation of intermetallic compounds to the strengthening by coherency binding and strain hardening mechanisms.

Through these observations, new concepts are being introduced. Concepts such as the interaction of precipitates or foreign particles with dislocation structures and vacancy concentrations. These new concepts permit the interpretation of why and how steels can be made tougher, stronger and more ductile. The way these mechanisms operate to form the microconstituents which comprise the composite microstructure determines the engineering properties of the steel.

Just as chemistry determines what is to be alloyed with the steel, the treatments which can be given to the steel are determined by the variables of pressure, temperature and time. These alter the thermodynamics and kinetics of the solid state transformations in alloy steels.

Every time steel is heated or cooled, compressed or stretched, squeezed or expanded, its properties are changed. Science and engineering are combined to exercise a control over these variables under conditions where the research investigator can examine the contribution of each variable. And where he can optimize the combination of variables to produce steels with superior properties.

Recently this type of investigation has resulted in a physical simulation of hot rolling steel through experiments in the laboratory — experiments in which the steel is not even rolled!

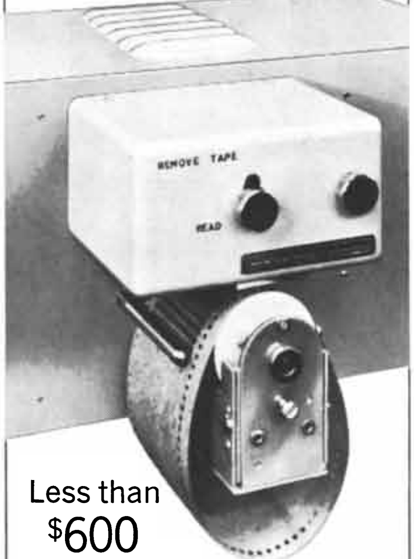
Greatly enhanced thermal transfer systems used in cooling steels provide an excellent example of advances in engineering. This kind of advancement has enabled steel production to make use of the thermal-mechanical treatments. Previously, this treatment could be performed only in the laboratory.

Alloy steels which take advantage of these increased capabilities are now evolving. Concepts are developing from a combination of chemistry, physics and engineering, and will produce the engineering properties required by an advancing technological age.

This article gives you a glimpse of just a few developments in alloying steels. It's only a small part of the continuing, widespread research effort that is going on 24 hours a day at Youngstown's research center. If you think our researchers might be able to help you, just give us a call or write Department 251B6.

**Youngstown Steel**

THE YOUNGSTOWN SHEET AND TUBE COMPANY · YOUNGSTOWN, OHIO 44501



by Baird and F. W. Take of the Nova Scotia Museum in 1959. Subsequent analysis indicated that it belongs to the order of cotylosaurs, the "stem" reptile lineage that evolved from amphibian forebears of reptiles more than 300 million years ago, early in the Carboniferous period.

The fossil reptile from Nova Scotia is about 300 million years old. Only four other representatives of its family—the Limnoscelidae—are known; three of these come from formations of the Permian period, 280 to 230 million years ago. The new find (named *Romeriscus* in honor of the veteran U.S. paleontologist Alfred S. Romer) is therefore the oldest both of its family and of its kind. In spite of its great antiquity *Romeriscus* shows a specialized anatomy that prevents its being ancestral to the several families of reptiles that appeared during the next few million years. The earliest ancestral reptile therefore remains undiscovered.

## *Hard Faces*

A technique of diffusing atoms of one material into the surface of another, thereby obtaining surface properties radically different from those of the bulk material, has been developed by the General Electric Company. The technique has been given the name "metalliding." The company foresees the process as a means of meeting some of the demands of space and nuclear technology by shielding various metals and alloys against corrosion and erosion. Other potential applications include the formation of extremely hard surfaces for bearings and dies; the solving of difficult problems of lubricating certain metals, and the creation of decorative finishes on base metals.

Metalliding, invented by Newell C. Cook of the General Electric Research and Development Center, is a high-temperature electrolytic technique. The bulk material, serving as a cathode, and the diffusing material, serving as an anode, are suspended in a bath of molten fluoride salts. When a direct current is passed from the anode to the cathode, the anode material diffuses into the surface of the cathode, producing a coating that is an alloy. By thus coating molybdenum, which is a fairly soft metal, with boron Cook has produced a surface with a hardness second only to that of diamond. He has given copper improved strength, flexibility, hardness and resistance to oxidation—without significantly impairing its electrical conductivity—by diffusing beryllium into it. Silicon can be diffused into tungsten, rhenium, niobium and molybdenum to produce a surface with greatly enhanced resistance to oxidation. The company believes metalliding will prove superior to such present techniques as gaseous diffusion and dipping a bulk material into a molten bath of coating material.

## *Twentieth-Century Adobe*

Man has been mixing earth with asphalt for one reason or another since the days of Babylon. Now a means of combining a petroleum-based binder with any of a variety of soils to produce a light, inexpensive building block has been developed beyond the experimental stage by the Esso Research and Engineering Company. The product, called BMX block, has physical properties somewhat superior to lightweight concrete block. It is manufactured by mixing screened soil in a 10-to-1 proportion with the asphaltic binder, shaping the blocks at a pressure of some 2,000 pounds per square inch and "curing" them for 10 hours or so at a temperature of 400 degrees Fahrenheit (clay brick must be fired at a temperature of 1,400 degrees F. for 40 hours).

The process for making BMX, patented by its developers, has been licensed to two U.S. manufacturers and the prospect of additional licenses, both foreign and domestic, is being examined. The developers estimate that, starting from the ground up, a plant with an annual capacity of 15 million BMX blocks, eight by eight by 16 inches in size, could produce them at a unit cost of less than 10 cents, or 15 to 30 percent below the cost of similar concrete blocks.

## *(Laughter)*

What is the social function of humor? Around the turn of the century Henri Bergson and Sigmund Freud considered the question, but they were handicapped by the fact that little was known about the subject in cultures other than their own. Now Frank C. Miller of the University of Minnesota has examined the role of "ribbing" and "wisecracks" in an American Indian tribal council.

Writing in *Ethnology*, Miller notes that the council at a Chippewa reservation in Minnesota where he worked for four summers is modern in its political structure. Of its 11 members, the three executive officers (chairman, secretary and treasurer) are elected at large, and four reservation districts each elect two representatives. Hereditary chiefs,

# Materials Systems Bulletin

Stress environments, where unusual and extreme corrosive, erosive and abrasive forces are at work, demand new solutions to the materials problem. Union Carbide is delivering solutions in the form of new materials and *systems of materials*. The systems capability includes: physical working of selected materials into fabricated products; transforming materials to provide wholly different and more useful properties and physical forms; physically or chemically combining materials to produce systems with enhanced characteristics. Here are some examples:

**Huge distillation tower made of corrosion-resistant alloy keeps product pure.** In one of the largest applications of HASTELLOY Alloy C to date, a distillation tower section 6 feet in diameter and 40 feet long, weighing some 11 tons, was fabricated of this high-performance nickel-base alloy. Not only does the corrosion resistance of the alloy protect the tower against the deteriorating attack of the chemicals being processed, but this same internal integrity provides assurance of the highest possible product purity. The tower section was fabricated at Union Carbide's Materials Systems Division facilities in Kokomo, Indiana.

**Titanium upgraded for wear resistance.** Titanium parts can now be given the high-temperature fretting wear resistance and other high-performance qualities of tungsten carbide. Detonation-plating a precise 0.010-inch shield of UCAR tungsten carbide onto critical wear areas is accomplished without distorting the parts or adding noticeably to their weight. Useful service life of titanium compressor blades and compressor hubs has been increased dramatically by the use of UCAR coatings. Also, the successful soft landing of the 620-pound Surveyor spacecraft on the moon was accomplished with the assistance of titanium shock absorbers that had been coated by the detonation process. Over 60 different coatings—refractory metals, ceramics, and cermets—are in use today solving the toughest wear problems in the aerospace, electronics, textile, chemical and other industries.

**Chemical process equipment combines both HASTELLOY alloy and KARBATE impervious graphite.** Heat exchangers that handle corrosive fluids on both the shell and tube sides were fabricated by physically combining two high-performance materials to achieve a system with the highest possible performance rating. The tube bundles contain 139 KARBATE impervious graphite tubes. Each tube is 16 feet long, with an outer heat transfer area of 726 square feet. The shells were made of HASTELLOY Alloy B. The inter-changers are designed to operate at a pressure of 75 psi on both the shell and tube sides, and at a temperature limit of 338°F. HASTELLOY Alloy B and KARBATE impervious graphite were used because of their excellent corrosion resistance. Combining the materials took maximum advantage of the fabricating economies inherent in the production of the HASTELLOY Alloy B shell and a KARBATE tube bundle.

For additional information about any of the above materials systems write to: Union Carbide Corporation, Materials Systems Division, 270 Park Avenue, New York, N.Y. 10017.

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UNION CARBIDE MATERIALS SYSTEMS

once all-powerful in tribal affairs, may still speak at council meetings but have no vote. Meetings are conducted almost exclusively in English; the pace of business is slow and, on occasions when unanimity of agreement is not achieved, the discussion usually continues until dissenters at least acquiesce.

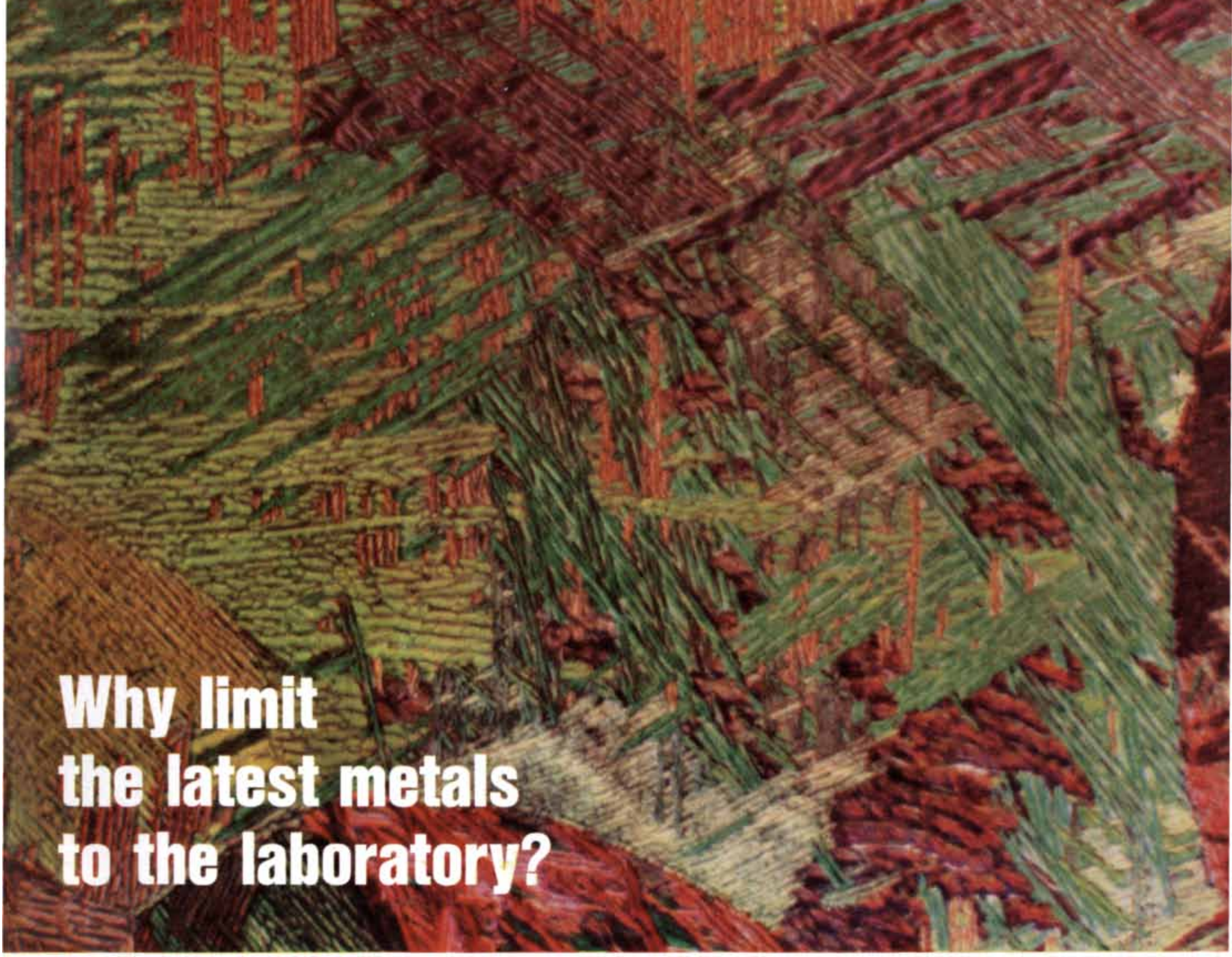
Among Miller's observations are the following:

Some nonmembers of the tribe who occupied reservation land had been in constant trouble with their neighbors, the law or both. One of the troublemakers, a woman named Alice, was notorious for promiscuity. A resolution to evict the group came before the council; some of the squatters attended the council meeting, and the situation was tense. The council passed the resolution and recessed for lunch in an atmosphere of gloom. Leaving the room, one council member said: "See you guys later—I've got a date with Alice." The remark restored everyone's good spirits.

A Protestant fundamentalist, the only authorized missionary in the most traditional community on the reservation, circulated an open letter complaining about the "illegal" activities of a visiting Episcopalian. His final complaint was that the intruder "does not see anything wrong with the use of alcoholic beverages ... uses them himself [and] smokes like a diesel engine. How can you expect a man like that to lead you to heaven?" The council chairman, who was reading the letter aloud, added *sotto voce:* "Follow his smoke, I guess." The council subsequently revoked the fundamentalist's lease.

One summer a television program featured opportunities for fishing and other recreation on the reservation. Discussing the tourist trade, the council chairman reported that one visitor, drawn by the program, had been able to recognize the council secretary on arrival because "he was still wearing the same shirt." In a similar vein of joking self-deprecation another council member reported that when some tourists asked him where they could get souvenirs, he suggested that they buy hamburgers.

Miller notes that, in terms of formal analysis, the council's humor can be said to "promote group solidarity," to make "indirect comment on sensitive matters" and to "relieve tension." He considers it much more to the point that, whatever their formal category, the jokes allow council members to communicate to one another what would be difficult to say in any other way. "Through humor," Miller concludes, "human contacts, always problematical, become less fragile."



**The Most Advanced Metals Are Now Available Commercially From Cameron, World's Largest Integrated Producer of Vacuum Melted Alloys.**

In the middle and late 50's vacuum melting of high temperature, high strength alloys was generally limited to the laboratory or pilot plants. The development of high performance gas turbine engines precipitated a substantial requirement for metals beyond even the highest state of the art of electric furnace steel making. To meet this demand for high strength, highly consistent metals for critical components, Cameron designed and erected facilities for volume production with the consumable electrode vacuum remelt process. Using material produced in vacuum induction furnaces, this process produces the purest, most segregation-free ingots commercially available.

In responding to these primary demands and recognizing the potential of the wider market, Cameron has become, in four years, the world's largest fully integrated manufacturer of vacuum melted specialty alloys.

As Cameron has built beyond the needs of these applications, the general demand for these advanced metals in primary form has also expanded. Cameron has answered this challenge as well, and now produces specialty metals in billets, bars, sheet, plate, and closed-die forgings for aircraft, aerospace, nuclear installations, petrochemical and chemical plants, refineries and general industry.

The latest addition to Cameron facilities is a company designed rolling mill capable of producing specialty plate and sheet to 60 inches in width and a minimum thickness of .010 inches. Located on a new 1600 acre site, this mill with its hot and cold lines incorporates the latest innovations in heat treating and finishing.

Today Cameron is producing high strength, high temperature, corrosion resistant metals — including nickel and cobalt based alloys — which meet the most rigid industry specifications. Cameron customers are now being provided with known quality and reliable deliveries for a wide variety of the most advanced metals.

Your own plant or operation may now be purchasing or producing products that can be improved through the utilization of the integrated melting and conversion facilities available at Cameron.

**Cameron**

Cameron Iron Works, Inc.

World Headquarters, Houston, Texas

Illustrated is a billet micro structure in etched condition and sixteen of Cameron's twenty consumable electrod

# This geologist wants to improve the wildcatter's chances of tapping a gusher.

## What's he doing at IBM?

"Thousands of people have dreamed of striking oil," says IBM's Bob Hodgson, "but just a few know what's actually involved."

Bob Hodgson knows. Before joining IBM, he was an oil company geologist.

"Some wells cost a million dollars to drill," he says, "and never hit anything but hard rock. In fact, your chances of tapping a gusher are roughly one in eight."

Oil exists in underground layers of porous rock—trapped there, perhaps, by some ancient convulsion of the earth. The best way to find those traps is to analyze data obtained from wells that have already been dug, and from the results of seismic exploration. Literally, millions of pieces of information. The oil industry spends $500,000,000 a year just collecting this information. To analyze it can take months. That's where computers come in.

This mass of information—words, numbers, even graphs and charts—can be stored in the computer's memory, retrieved instantly and projected on IBM's TV-like graphic display units.

Bob Hodgson and his IBM associates are working on computer techniques for displaying any information the oil hunter needs, the moment he needs it—from geologic information on a ten-thousand-foot well to a contour map of an oil field. Analysis time can be cut drastically—and the chances of being on the money vastly improved.

You may not have the occasion to look for oil. But IBM computers are helping solve problems in almost every business—stacking the odds in your favor.

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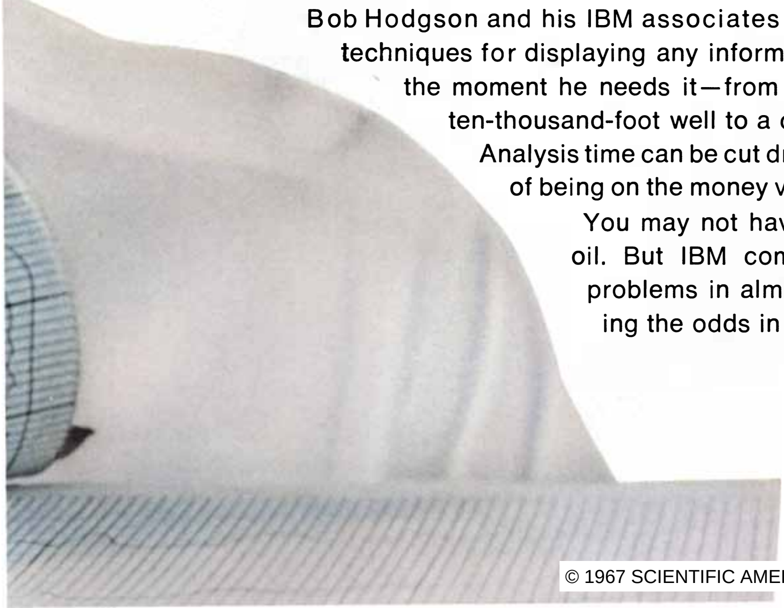

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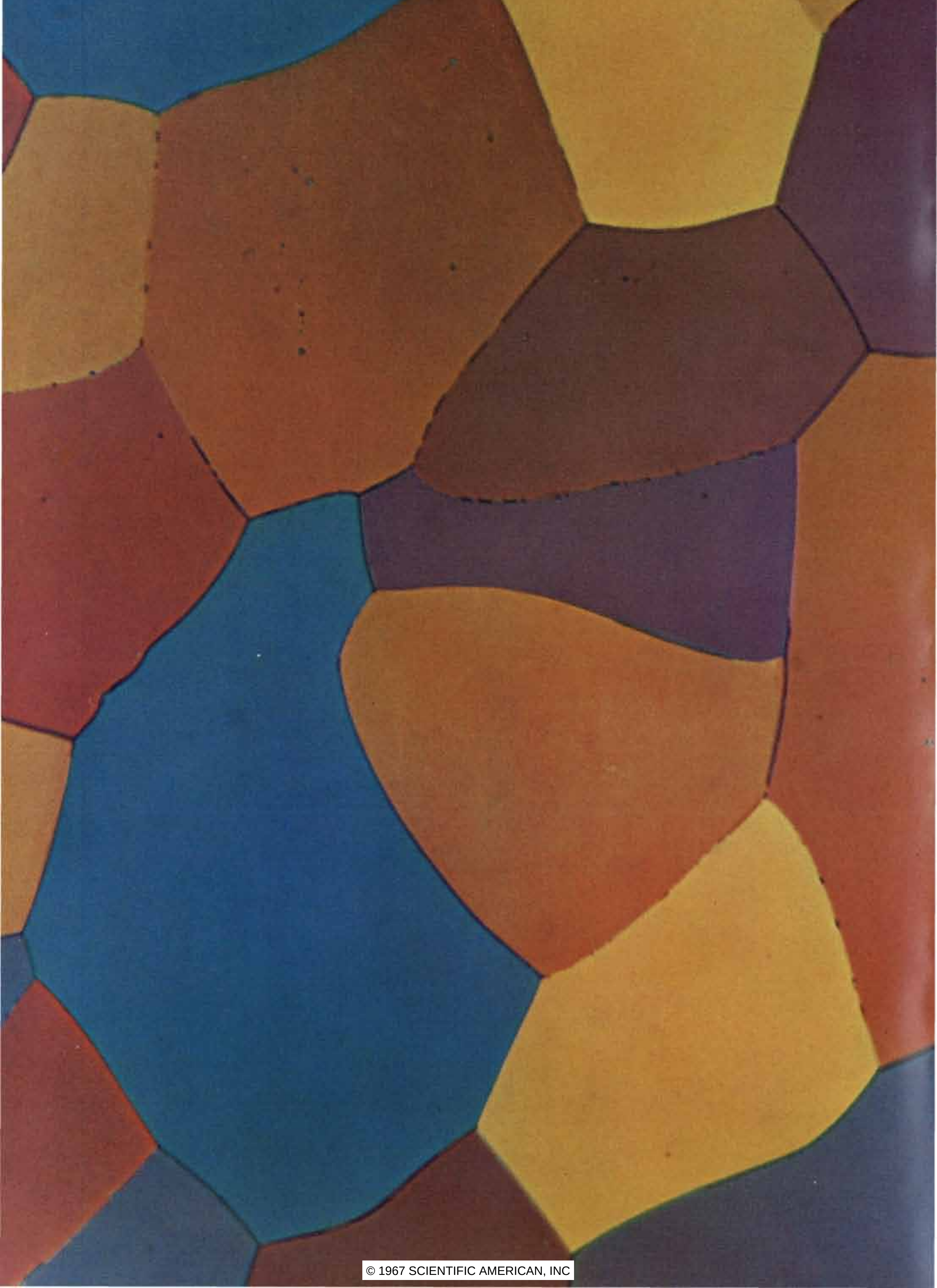


# THE NATURE OF CERAMICS

## They usually consist of metallic and nonmetallic atoms joined by bonds that are partly ionic and partly covalent. This gives them properties such as hardness, brittleness and resistance to heat

by John J. Gilman

One of the first solid materials, if not the very first, that man learned to use was a ceramic, natural stone. It was suited for a variety of applications because of the characteristic properties of a ceramic: hardness, strength, imperviousness to heat, resistance to chemical attack and brittleness, which makes it comparatively easy to shape the material by chipping it. This natural ceramic provided man with tools, durable containers and even a roof over his head (in caves).

It is not surprising that man turned to creating ceramics of his own: pottery, bricks, concrete, glass. These products continue to be major industries to this day. Few people realize, however, how richly the field of ceramics has developed in this century. Ceramic materials have now been extended to a wide spectrum. They range in appearance from dull clay to lustrous ruby, and in technical service from the refractory linings of steelmaking furnaces to delicate electronic control devices. New understanding of the chemical and physical attributes that determine the nature of ceramics has expanded our view of the possibilities inherent in this class of material. Just as the understanding of structural principles and of the elements that go into the construction of a building (stone, mortar, steel, wood, glass and so on) gives an architect wide scope for the design of structures to suit particular purposes, so the ceramist's understanding of how atoms and crystals can be put together to form the architecture of a ceramic now provides a wide range of opportunities for obtaining specific properties. The architectural analogy is a pertinent one, because the properties of ceramics depend crucially on their microscopic structure.

What is a ceramic? Essentially it is defined as a combination of one or more metals with a nonmetallic element, usually oxygen. The comparatively large oxygen atoms serve as a matrix, with the small metal atoms (or semimetal atoms such as silicon) tucked into the spaces between the oxygens [*see illustrations on next page*]. A cardinal characteristic of the construction of ceramic crystals is that the atoms are linked by bonds that are primarily ionic but also to a significant extent covalent. These firm bonds are primarily responsible for the stability and strength of ceramic materials. In the combination of oxygen atoms with metal atoms the ionic bonds are particularly strong, because each oxygen, with two electronic vacancies in its outer shell, borrows two electrons from its metal neighbors; thus both kinds of atom become strongly ionized—one negatively, the other positively—and are held together by a correspondingly strong electrostatic attraction. In this sense ceramic compounds resemble salts, which are characterized, however, by more purely ionic bonds. The bonds are stronger in ceramics, which therefore dissolve in water only under high pressure.

As highly oxidized compounds the ceramics are strongly resistant to attack by nearly all chemicals. This accounts for many of their uses—in plumbing, household utensils and so forth. They are indispensable where a structural material must withstand very high temperatures, at which the ravages of oxygen will destroy the strength of a metal. Indeed, the making of steel depends on the use of ceramic bricks to line the inside of the container.

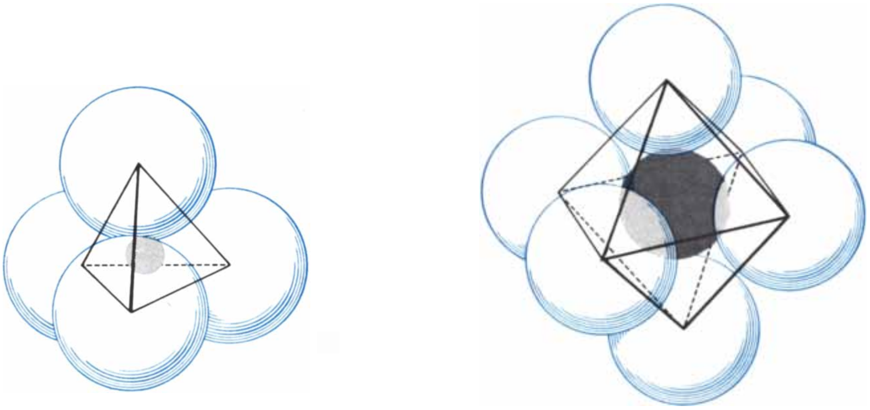
Since the art of ceramics-making has a long history, it is of interest to review its evolution briefly before we examine the present state of the art and its future prospects. The first man-made ceramics probably were simple mud pots, sometimes reinforced with straw, that were dried and baked in the sun. Gradually the ancients learned to improve the product by selecting suitable clays and baking their pottery at higher temperatures, at first in open fires, later in crude kilns. These early earthenware pots must have been disappointingly porous, and it was a large step forward when some clever artisan in Egypt learned to seal the surface by firing a glassy material onto it. With this step, and the addition of natural stains to color the glaze, ceramics became an aesthetic art as well as a useful one. The art grew in beauty and utility as people gained increasing control of it by grinding rocks into powder to produce more uniform clays and built kilns that provided higher firing temperatures, making possible the production of a wider variety of ceramic materials.

Scientific knowledge of ceramics began with chemical analysis of the components that make up these materials. Chemists found that the principal elements in natural clays were oxygen, silicon and aluminum, forming the compounds known as aluminosilicates. The precursor of common clay is feldspar, a

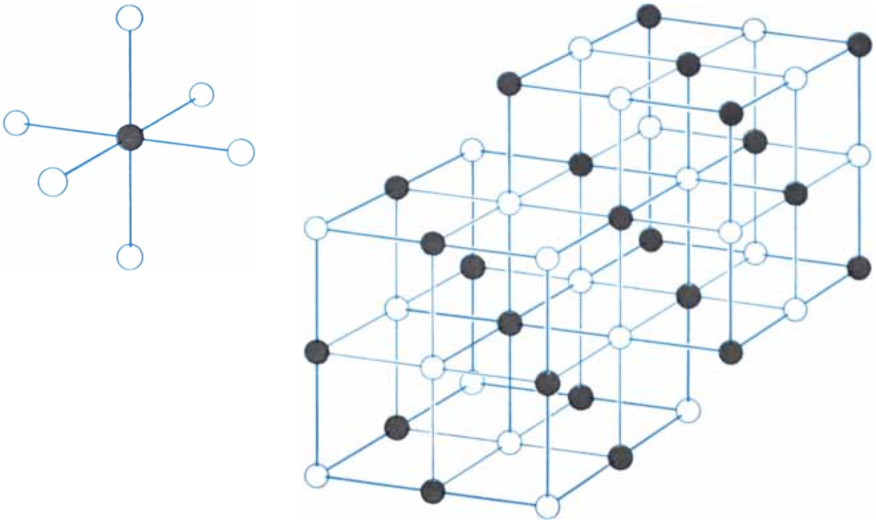
**URANIUM CARBIDE, a nuclear reactor fuel, is a ceramic: a combination of a metal (uranium) and a nonmetal (carbon). The photomicrograph on the opposite page, made by William E. Bruce of the Battelle Memorial Institute, shows uranium carbide stained by an acid etchant. The etchant stains different crystal faces differently and therefore delineates the variously oriented crystals of the compound. The sample is magnified 300 diameters.**

mineral found in rocks such as granite. It usually contains potassium and has the chemical formula $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. Rain and carbon dioxide in the atmosphere convert the feldspar crystals into potassium carbonate (which dissolves and is washed away) and silica and aluminum oxide. These combine with water and usually form kaolinite, whose basic formula is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. This material is often mixed in the soil with small amounts of iron oxide, which gives it the reddish color of common clay (pure kaolinite is white and is the basis of fine china).

The crystals of kaolinite are very small—thin platelets only about 5,000 angstrom units (.00005 centimeter) wide and about 300 angstroms thick—and have an irregularly hexagonal shape. When wet, they cling together like wet sheets of paper, and with water acting as a lubricant the crystals readily slide over one another; this accounts for clay's plasticity. As the clay begins to dry, the crystal platelets tend to become interlocked, and the clay object becomes rigid enough to be removed in one piece from the potter's wheel or mold. The firing of the clay in a kiln evaporates most of the remaining water, and during the process some of the silica ($SiO_2$) combines with impurities to form a liquid glass that glues the crystal platelets together. Thus a clay ceramic becomes a kind of microscopic concrete, consisting of a "gravel" of aluminum silicate particles held together by a glassy cement.



**OXYGEN AND METAL ATOMS** (or semimetals such as silicon) are the basis of most ceramics. In the simplest ceramics equal numbers of oxygen (*color*) and metal (*gray*) atoms are packed together in arrangements that depend largely on the relative sizes of the ionized atoms. In beryllium oxide (*left*) the "coordination number" is four; each beryllium atom is surrounded by four oxygens (and each oxygen atom by four beryllium atoms, although only one is shown). In magnesium oxide (*right*) each atom has six nearest neighbors. The ceramic bond is primarily ionic: each metal atom gives up two electrons to each oxygen.



**MAGNESIUM OXIDE,** or periclase, is a good refractory material because it withstands high temperatures. The ball-and-stick model (*left*) shows the relative locations of the atoms in the magnesium oxide crystal lattice, which is face-centered cubic: it consists of interpenetrating face-centered-cubic structures, one of magnesium and one of oxygen (*right*).

Not all ceramics are crystalline. Glass, of course, has a noncrystalline structure, and that distinctive form of ceramic is discussed in a separate article in this issue [*see page 126*]. Nor are all ceramics compounds of oxygen; certain other substances, among them graphite, diamond, silicon carbide (Carborundum), tungsten carbide and uranium carbide, also have ceramic properties, such as high mechanical strength and resistance to heat and chemicals. For illustration of the basic nature of ceramics, however, we shall confine ourselves here to the crystalline, oxygen-containing compounds, which are the typical and by far the most common ceramic chemicals.

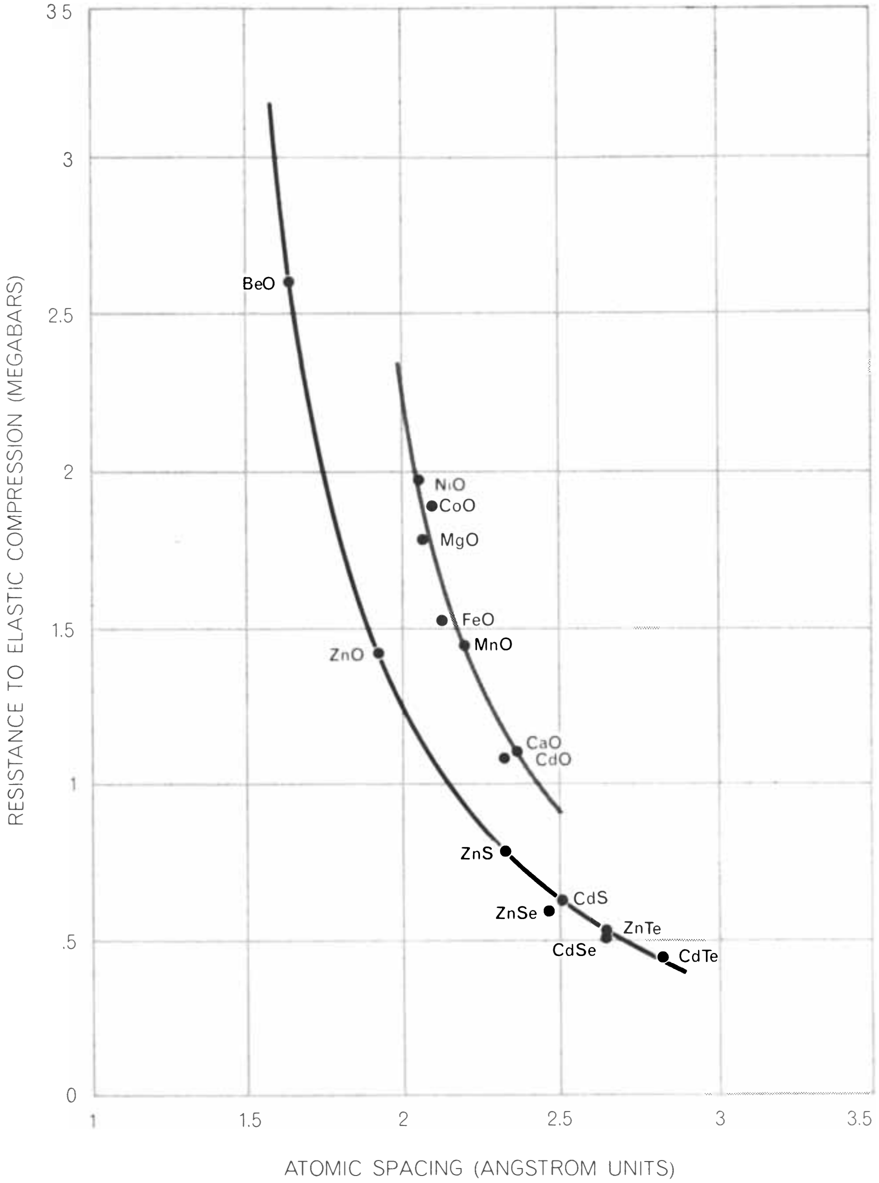
The secret of these ceramics' properties lies as much in the internal structure of their crystals as in their chemical composition. A ruby and a rough brick may both be made of the same substance—aluminum oxide—yet how different they look and how differently they behave! The difference is in the fact that a ruby consists of one large crystal with its atoms arranged in a periodic pattern, whereas the brick consists of a collection of many crystals cemented together.

A giant step forward in ceramic science came when crystal structures were analyzed by means of X-ray diffraction. The findings led to detailed calculations by the physicist Max Born of electrostatic forces in crystals. He showed that the atoms in crystals, in particular those in oxides, are bound together in accordance with Coulomb's law: the electrostatic attraction, or binding force, between two ions of opposite charge increases in inverse proportion to the square of the distance between them. Consequently the more closely the atoms are packed, the greater will be the crystal's elastic strength and resistance to alteration by heat or chemical assault [*see illustration on opposite page*].

It follows, then, that in the construction of a ceramic material much depends on how the atoms are stacked. If the growth of a crystal is closely controlled, layers of tightly packed oxygen atoms form with small metal ions in the crevices between the oxygen atoms; then another closely packed oxygen layer forms above the first, and the process continues. In this way a highly stable structure can be built. The simplest structural forms are produced during the growth of crystals consisting of equal numbers of oxygen and metal atoms, such as beryllium oxide, magnesium oxide or zinc oxide. When the metal atoms are outnumbered by oxygen atoms, as in aluminum oxide ($Al_2O_3$), the holes between the oxygens are not all filled; in this particular case the aluminum atoms occupy only two-thirds of the available spaces.

The most interesting and important structures are generated by silica ($SiO_2$). The silicon atom, like carbon, has four valence electrons, and it forms a tetrahedral grouping with oxygen: four oxygen atoms surrounding each silicon atom. These groups can link together in various ways [*see top illustration on next page*]. Attached only end to end (by way of one of the oxygen atoms), they form a fiberlike chain, such as appears in asbestos. Built up in sheets, they produce layered minerals such as talc or mica. They can also be linked to produce a three-dimensional network—the quartz crystal. The versatility of the silica tetrahedrons in forming bonds with one another and with other groups explains how silica serves as the glue that cements the clay particles in bricks and earthenware and bonds the glaze to porcelain.

When the silica tetrahedrons link up in a three-dimensional structure, the structure may have holes large enough to accommodate atoms of various kinds. By filling the holes with sodium and sulfur atoms one can produce the beautiful blue stone known as lapis lazuli (which in powdered form is the pigment ultramarine). The holes in a silica layer can also serve to bind it to an entire layer of a quite different but complementary structure. This is how kaolinite clay is organized. In kaolinite the water is dissociated into hydrogen and hydroxyl ions. The hydroxyls, bound together by aluminum ions, form a rather loosely packed layer, and a set of its nearly spherical ions mesh into the pattern of holes in a silica layer, thus putting the two layers in intimate contact. The aluminum ions nestle into cavities between these layers; as a result each aluminum ion is surrounded by six closely adjacent oxygen or hydroxyl ions [*see lower two illustrations on next page*]. It would be difficult to design a more sophisticated atomic architecture.

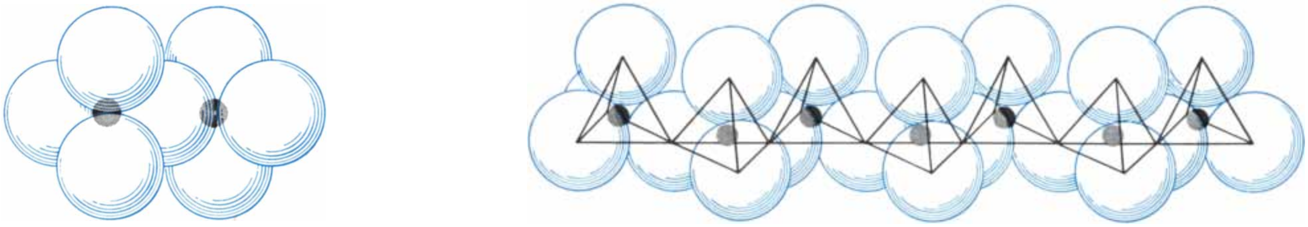


**PACKING** of atoms in a ceramic affects its elastic strength. Here the spacing between atoms is correlated with the resistance to compression of a number of compounds of metals and oxygen (*O*), sulfur (*S*), selenium (*Se*) and tellurium (*Te*). Experimental findings are plotted, along with the theoretical curves based on computation of electrostatic forces between atoms. In the compounds on the black curve each atom has four neighbors and in those on the gray curve each atom has six; the number of neighbors affects the strength.

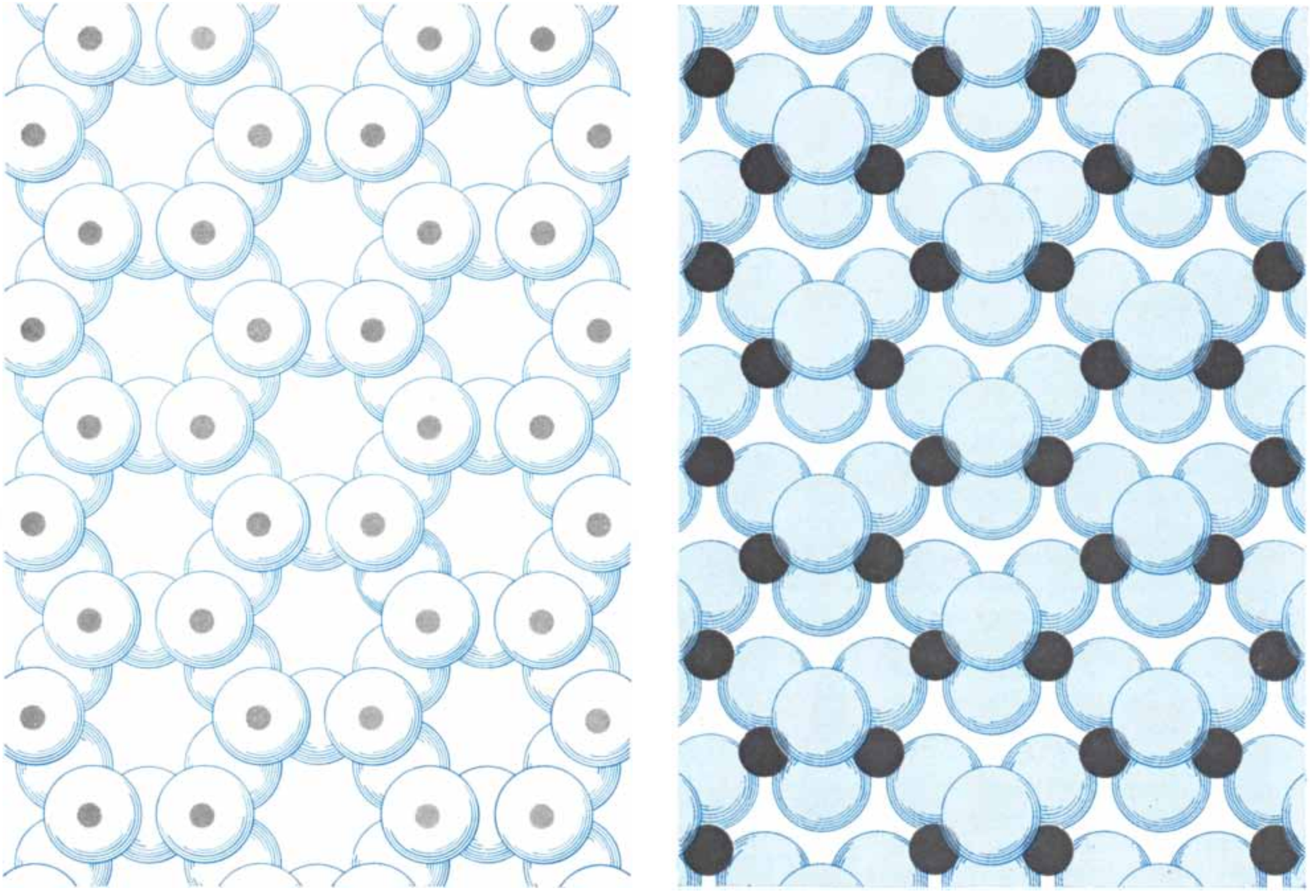
If the ceramic structures were perfectly organized and uniform, ceramic materials would be a great deal stronger than they are. They are greatly weakened by the irregularities that occur at crystal boundaries—much more so than metals. These irregularities are of three kinds. Local separations, or voids, may occur between the crystals, with the result that atoms can wander through the spaces, gases can permeate the material and the crystals can slide past one another. Because of this ceramics tend to flow at very high temperatures like wet sand. A second cause of weakness at a boundary is that if one crystal is out of line or twisted with respect to its neighbor, the bonds between them may be stretched or otherwise disrupted. The third source of trouble is that ions with the same charge (positive or negative) may be brought close together; the consequent electrostatic repulsion produces strain in that region of the material and may generate cracks.

Because boundaries between the crystal particles are a highly characteristic feature of ceramic materials, ceramists have given careful study to their properties, and much current research is directed toward eliminating the internal boundaries or minimizing their effects.

To complete our summary of the basic structural features of a ceramic we need to consider another type of imperfection. As other articles in this issue point out, all solid materials are marked by structural imperfections that affect their dy-



**SILICATE UNIT** is a primary building block of many ceramics. It consists of a silicon atom surrounded by four oxygen atoms. This is the same tetrahedral arrangement as in beryllium oxide (*see upper illustration on page 114*). Since each of the silicon atoms has four valence electrons to give up, each of the surrounding oxygens gets one, leaving its outer shell one electron short. It can get that electron from another silicon atom by linking two groups (*left*). In this way a chain of silicate groups can be built up (*right*).



**SILICATE SHEET** formed by linked chains is the basis of many minerals (*left*). Each silicon atom (*gray*) is surrounded by four oxygens; each tetrahedron shares three of its oxygens with three other tetrahedrons. Notice the hexagonal pattern of "holes" in the sheet. An aluminate sheet (*right*) consists of aluminum ions (*gray*) and hydroxyl (*OH*) ions (*color*). The top layer of hydroxyls has a hexagonal pattern. If the two sheets are superposed (as if they were facing pages of a book), they mesh, forming kaolinite.

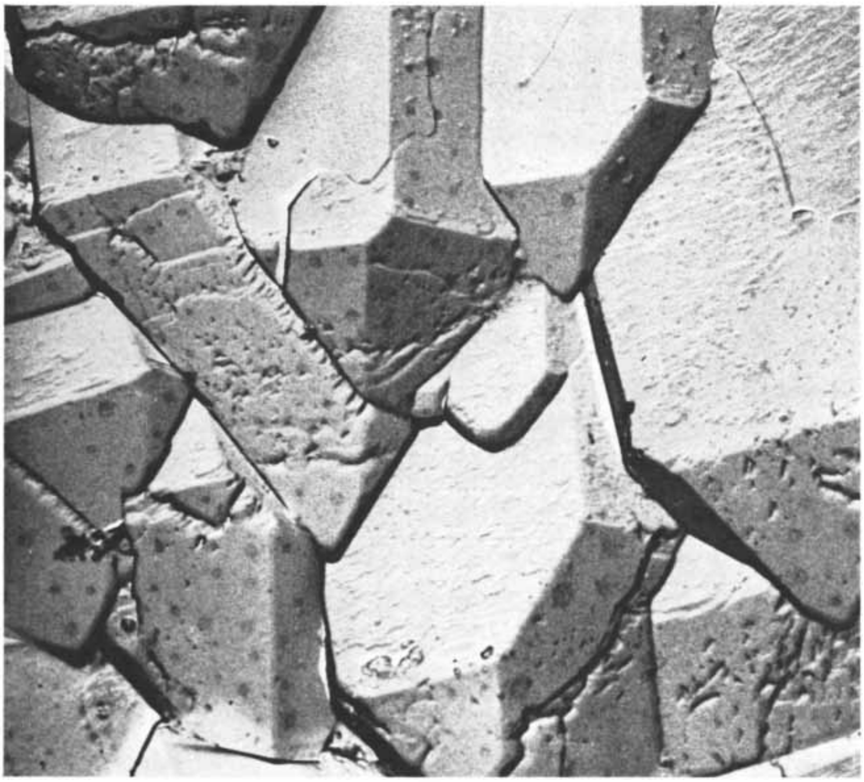
**KAOLINITE SHEET,** here seen from the side, is a "laminate" of the silicate and aluminate sheets shown in the middle illustration on this page. In kaolinite each of the aluminum ions becomes surrounded by six close neighbors: oxygen ions and hydroxyl ions.

namical properties, that is, the flow of heat, electricity, mass, magnetism and so forth within the solid. An important class of these imperfections is atomic vacancies, or holes, in the crystal structure. In the case of a ceramic such holes are essential for the consolidation of the material in the hardened form, as the particles must change their shape (which involves a movement of atoms) in order to become tightly packed in the firing process.

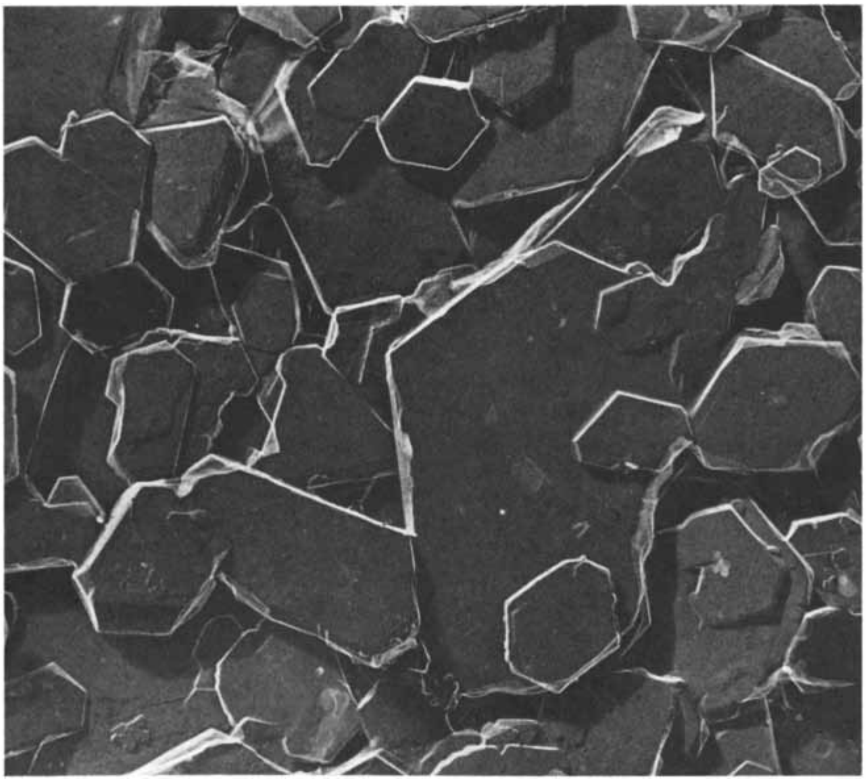
The presence of vacancies in ceramic crystals can be demonstrated experimentally by placing crystals in an electric field. Because they have no free electrons most ceramics are insulators—highly resistant to the flow of electricity. They can, however, conduct electricity to some extent by movement of their ions, and this occurs when a hot ceramic is placed between two electrodes connected to a battery [*see illustration on page 120*]. Metal ions in the crystal (which are usually more mobile than the larger oxygen ions) may jump to the surface near the negative electrode; the jumps are made possible by the normal thermal agitation of atoms in a hot crystal. Other metal ions can then jump into the vacant sites left behind. Thus the holes move toward the positive electrode and the crystal gradually becomes polarized, with a preponderance of metal (positive) ions near the negative electrode and a surplus of oxygen (negative) ions left near the positive electrode.

If the battery is then disconnected, the ions will gradually diffuse back to a balanced distribution in the crystal. On the other hand, if the battery is left on and its voltage is high enough, some of the metal will become completely separated from the oxygen and will be concentrated near the negative electrode. Note that the behavior of the metal ions in the ceramic is like that of the positive ions of a salt dissolved in water, which also travel to a charged negative electrode. There is an important difference, however. In the salt solution the negative ions migrate just as readily as the positive ions, whereas in most ceramic crystals the metal ions are much more mobile than the oxygens. This means that a ceramic is differentially permeable to one species and can therefore be used to separate charged particles. This property of ceramics promises to make them useful in fuel-cell devices.

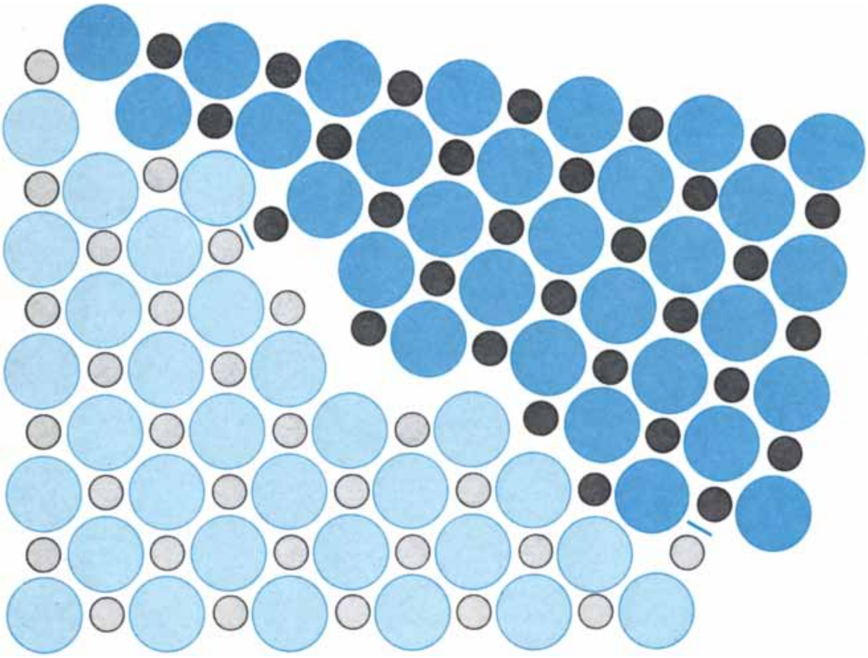
The basic knowledge that has been gained about the microstructure and the physical and chemical behavior of ceramic materials not only has provided



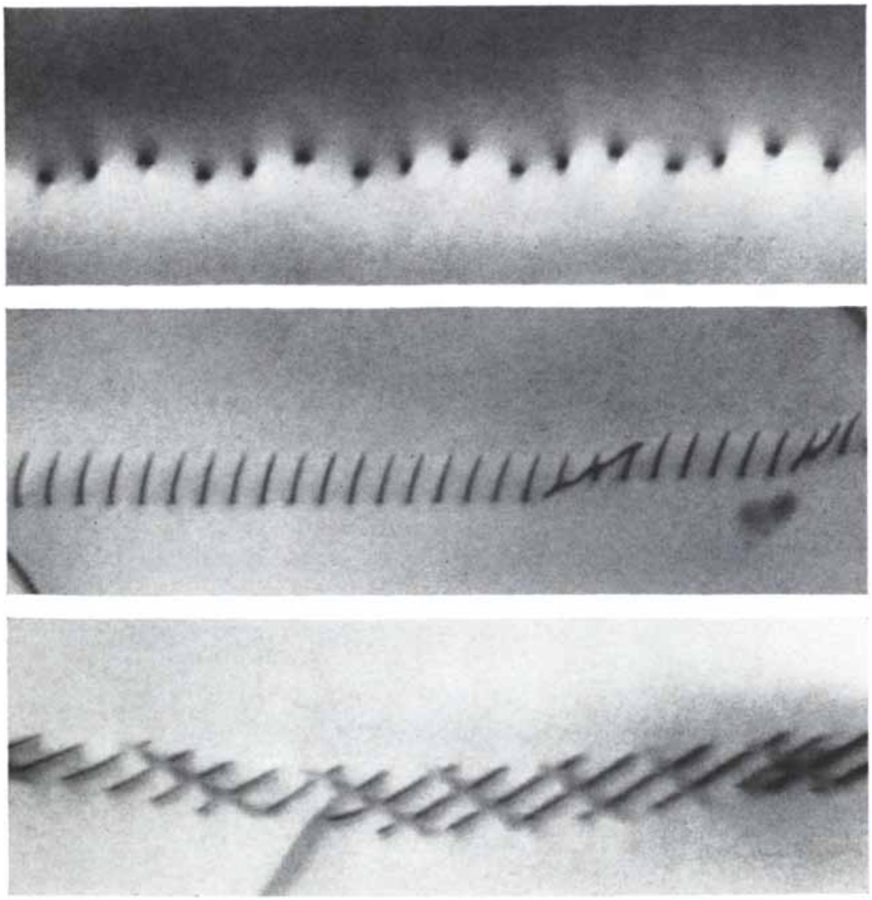
**QUARTZ** is a three-dimensional structure of silicate units. In this electron micrograph quartz crystals are enlarged 11,000 diameters. Since such crystals are opaque to the electron beam, a "replica" technique is used: the specimen is first shadowed by evaporating platinum vapor onto it at a shallow angle. Then a layer of carbon is deposited, forming a replica of the surface. Finally the clay is dissolved away in acid and the replica is micrographed.



**KAOLINITE CRYSTALS** are enlarged 19,000 diameters in this electron micrograph made, as was the one at the top of the page, by Joseph J. Comer of the Sperry Rand Research Center. The technique was the same, but in this case the image was printed as a negative.



**BOUNDARY** between two crystal grains disrupts the ordered structure of a ceramic. These two crystals (which have the structure of magnesium oxide) are rotated 10 degrees with respect to each other; the boundary leaves vacancies in the lattice, distorts bonds between ions and brings together ions of like charge, which tend to repel each other (*colored bars*).



**DISTORTIONS** at boundaries in aluminum oxide are seen in micrographs made by D. J. Barber and N. J. Tighe of the National Bureau of Standards. A boundary between tilted crystals is seen edge on, magnified 220,000 diameters (*top*), and from the side, at 130,000 diameters (*middle*). A boundary between twisted crystals is magnified 100,000 diameters (*bottom*).

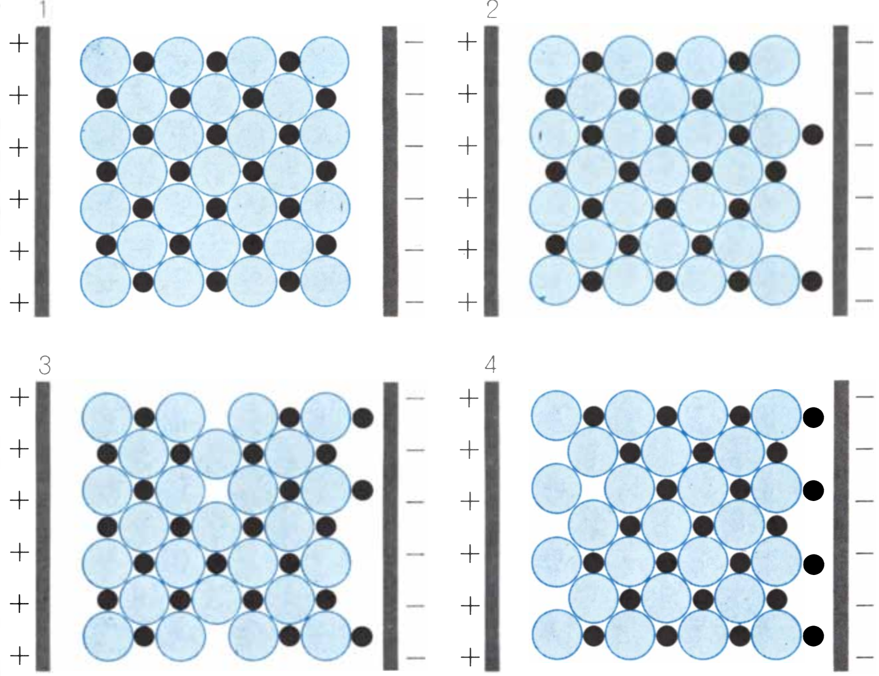
a set of principles for their construction but also has led to the development of new techniques for making them. By careful attention to the control of chemical composition, particle sizes, uniformity, purity and the arrangement and packing of atoms it has become possible to synthesize high-performance ceramics in almost limitless variety. Electric kilns have been developed to provide precision in the firing process. Several new methods have been devised to synthesize ceramics in special forms. Among these are the use of very high pressure to squeeze and consolidate fine particles prior to firing; the decomposition of ceramic chemicals at high temperature to deposit a coating or shell on a background material; the use of a plasma gun that liquefies fine particles at high temperature and sprays a paintlike ceramic coating on objects; the precipitation of ceramics from aqueous solutions at high pressure and temperature (called hydrosynthesis); the slow solidification of liquids to form individual ceramic crystals with ideal properties.

To illustrate the potential versatility of ceramic materials one need only enlarge a little on the case of aluminum oxide, to which I have already referred. I have mentioned gem rubies, which are high-quality crystals of aluminum oxide containing a small amount of chromium oxide, which colors them red. The same basic substance ($Al_2O_3$), with titanium atoms added, yields blue sapphires. Individual crystals of aluminum oxide have great utility as watch bearings, phonograph needles, pressure-resistant windows and other products. In transparent form multicrystalline alumina ceramics are employed in place of glass as envelopes for lamps and electronic devices. A thin film of aluminum oxide is often formed electrochemically on aluminum metal to protect it. As a loose powder (corundum) it is a hard, heat-resistant abrasive. In the form of fine particles bonded together by silica glass, aluminum oxide is the basis of spark-plug insulators, refractory bricks and crucibles for molten metals. Consolidations of aluminum oxide powder are also employed as electric insulators and windows or radomes transparent to microwaves.

Without attempting to survey the entire voluminous catalogue of ceramic materials now available, I shall indicate their range by mentioning examples of various groups that can be classed according to their salient properties.

One large group exemplifies properties in the field of optics. In that area, as we have already seen, ceramic techniques


COMICS
SASON



**IONS MOVE** through a schematic oxide, conducting electricity. The crystal is in an electric field. Positive ions (*black*) jump toward the negative electrode; other ions fill successive vacancies until there is an excess of metal ions on one side and of oxygen ions on the other.

are notably useful for the coloring of materials, including paints and plastics. A ceramic pigment is exceptionally durable because it is completely oxidized and hence not subject to chemical attack or deterioration. Various metallic oxides can serve as the pigments, each yielding a specific color because of the metal's selective absorption of light. (The cobalt ion, for example, absorbs red light, thereby giving a bluish tint to glass.) Coloration can be introduced into a ceramic in various ways. A salt containing the chosen metal can be dissolved in molten glass and applied to ceramic objects as a colored glaze. Alternatively, the color can be incorporated in the form of very small colored crystals embedded in a glasslike matrix. These crystals are often spinels (normally compounds of magnesium, aluminum and oxygen) in which metal atoms producing the desired color are substituted for the magnesium or the aluminum. The color sometimes depends on the concentration: a small amount of chromium, in place of aluminum, colors spinel red, but a larger concentration of chromium will color it green. Still another way to color is to precipitate colloidal particles of a metal in a glass. The particles selectively scatter light to yield rich colors. For example, gold particles about 400 angstroms in size provide the color in the ruby glass of stained-glass windows.

There are many other optical applications of ceramics; three examples will illustrate their diversity. Calcium tungstate (found in the mineral scheelite) is fluorescent and has long been used to make blue screens for oscilloscopes; in the form of individual crystals it has now been found to be, like ruby, an excellent material for lasers. In the field of decoration, thin films of metal oxides are coated on glazes to produce an iridescent effect, and objects so coated are called lusterwares. And not the least interesting of the optical ceramics is a new material (called Yttralox) that is as transparent as window glass and can resist far higher temperatures. It is the product of a new technique based on the microscopic study of ceramic structure. Ceramics are generally opaque because of the presence of tiny pores within them that scatter light, and the new technique serves to eliminate these pores during the firing stage.

Methods have also been developed to improve the refractory quality of ceramics, one for which they have traditionally been famous. One of these advances is the fabrication of beryllium oxide (a highly toxic material), which has an exceedingly high melting point and serves as a useful material in some nuclear reactors. It has also become possible to reduce the brittleness of ceramics—a traditional shortcoming. By prestressing them, particularly at the surface, ceramic

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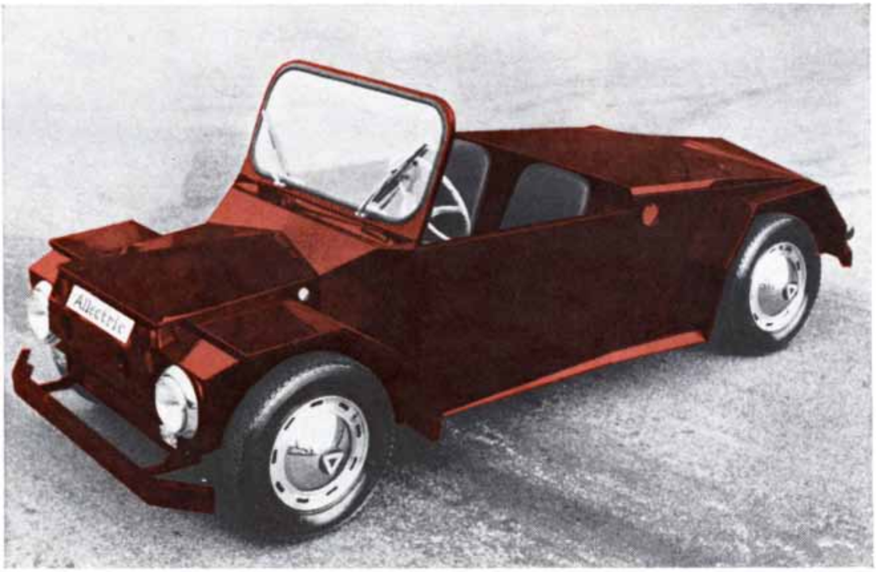

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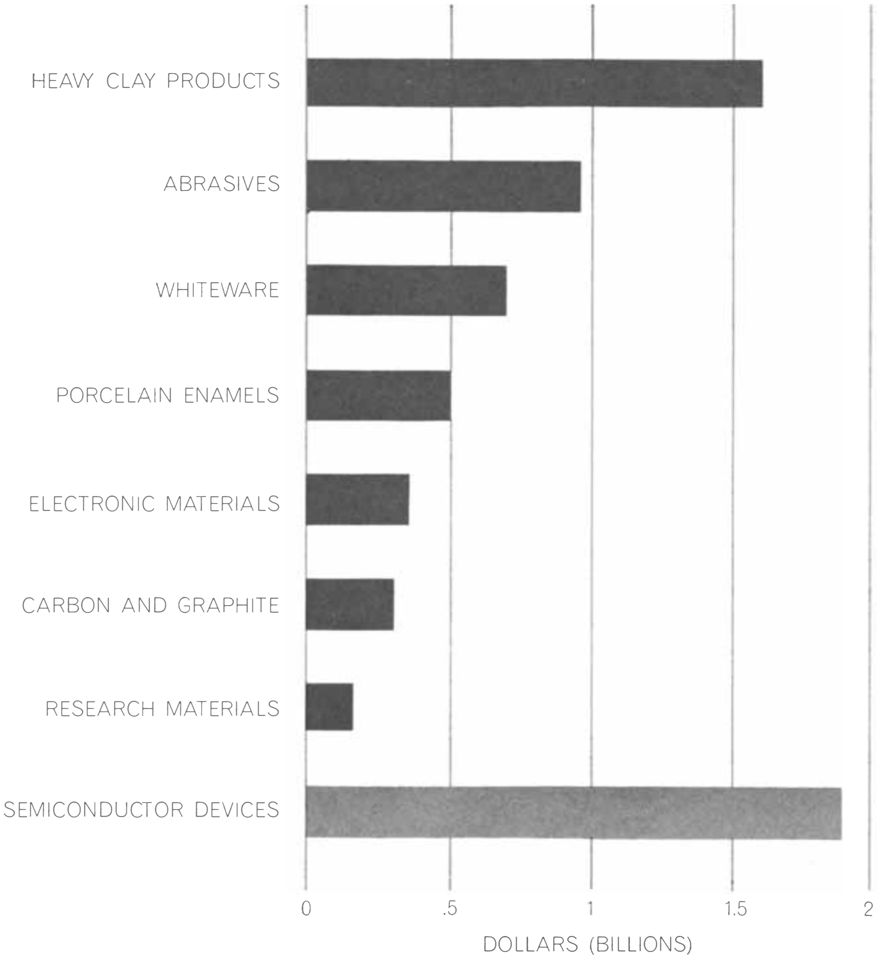
materials can be made resistant to breakage. Among the products of this improvement are "unbreakable" dishes and stronger structural materials.

In the field of electronics and magnetism ceramics are launched on a new career. They have long served, of course, as electrical insulators. Now they play more active roles based on certain unusual electrical and magnetic properties. One of these is the piezoelectricity of quartz crystals: the electric fields produced when the crystals are compressed. This property makes it possible to excite and detect the mechanical oscillations of the crystals electrically. The crystals are therefore used for precise control of the frequencies of oscillators and for the generation of high-frequency sound waves. The precise electrical measurement of the frequencies of mechanical oscillations in quartz crystals is the basis of sensitive thermometers and weighing balances. Crystals related to magnetite (iron oxide) are useful as components in high-frequency electronic elements and memory devices in computers.

Ceramics may become a much more significant factor in the electronics field than they are at present. They have many properties in common with well-known semiconductors such as germanium and silicon. Further technical development may reduce the distinction between them. Some engineers already regard semiconductors and ceramics as provinces of the same industry.

The proliferation of ceramic products is dramatically reflected in the current production figures for the industry [*see illustration below*]. If we exclude glass and cements, which are major industries in themselves, the total production of the new ceramic products in money value already outweighs the manufactures of the more traditional materials—essentially building materials and pottery wares.

This trend is certain to continue. The advances in theoretical understanding of



**CERAMIC PRODUCTS have found increasing applications in recent years, with new products overtaking the conventional ones. Semiconductors are considered by some to be a part of the industry. (Glass and cements, which are actually industries in themselves, are excluded from the chart, which is derived from 1967 production estimates made by *Ceramic Age*.)**

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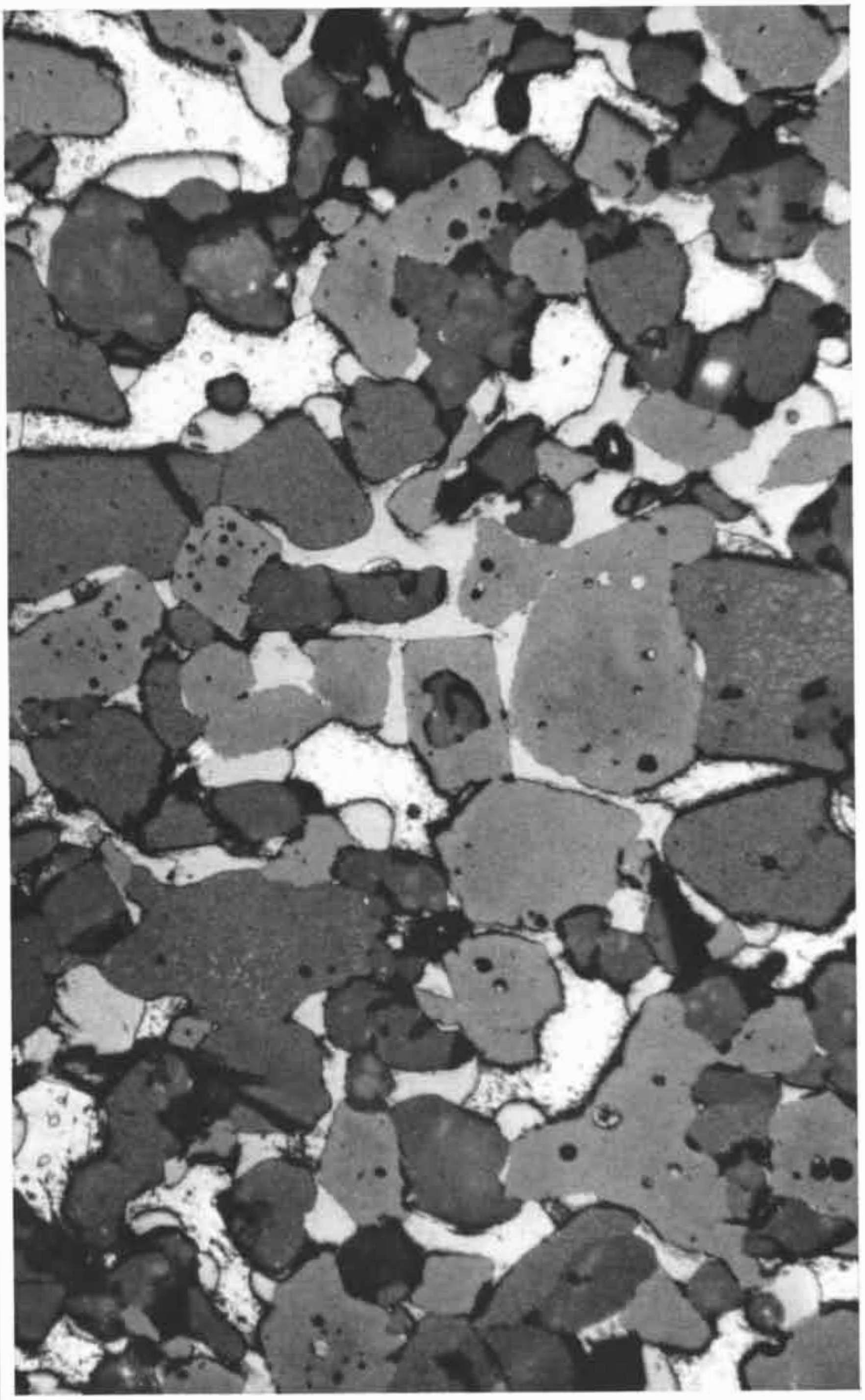
the solid state and in engineering manipulation of materials are giving rise to an ever increasing diversity of new ceramics. The movement in this field is toward increasing simplicity and more rigorous control of the materials: toward purification of the component elements, simplification of the internal structure and refinement of the production techniques. At the same time research is going forward on combining the refined building blocks into composites with desirable properties. What began as the synthesis of rocks and gems by men has developed far beyond the achievements of nature. The elements can now be fabricated into superior materials that have the heat resistance to transport us to the planets, the strength to explore ocean depths and a response to electric fields that can condense the world through the medium of optical communications.



STRUCTURE of brick used in copper production is magnified 240 diameters in a photomicrograph made by H. A. Freeman of Harbison-Walker Refractories Company. Constituents (*in order of increasingly light gray*) are magnesium oxide, spinel, copper oxide and copper.

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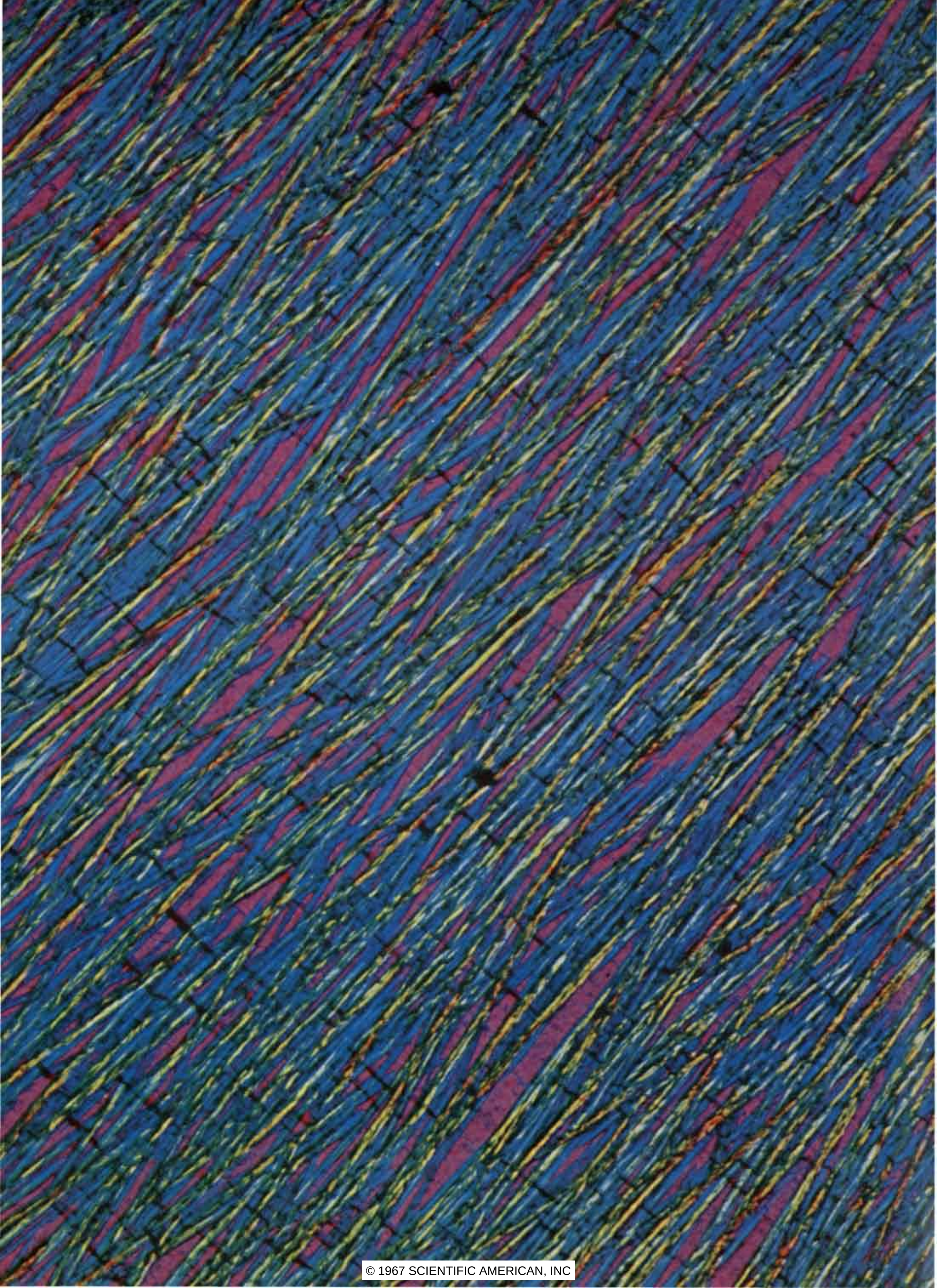


# THE NATURE OF GLASSES

The geometry of glass structure is the geometry of disorder on the way to order. The art of the glassmaker can be explained in terms of thermodynamics, chemical bonding and molecular architecture

by R. J. Charles

The study of solids is largely a matter of geometry. This is so because the geometric arrangement of the building blocks of solids is simply an expression of the binding forces between the assembled units. It is these forces that determine physical and chemical properties. The building blocks of a solid can be considered as arrays of atoms, clusters of molecules or simply single atoms or molecules. The properties of the solid depend on the placement or arrangement of these units over distances that vary from atomic dimensions to perhaps several centimeters. Many precise techniques are available for studying the atomic arrangement of matter in crystalline solids. These techniques generally depend on the scattering, diffraction or refraction of energetic radiation. In order for the resulting pattern of radiation to convey information about atomic positions the structure must be periodic, or regular, over distances that are large compared with the wavelength of the radiation. We are concerned here with glasses, a class of solids that do not crystallize when they are cooled from a melt and thus do not exhibit long-range periodicity of atomic structure. These materials yield their atomic configurations only slowly to the usual methods of structure analysis.

The structure of a glass is often inferred from the analysis of some crystalline modification of the material that forms it. Information on the disordered structure of glass itself, however, can be obtained by thermodynamic measurements. Such information cannot be specific since it is expressed in terms of a few simple variables that are themselves averages. The approach is nonetheless a useful one because in a system as complex as a glass average characteristics should have unusual significance.

Since a glass is distinguished from other solids by its lack of crystallinity, it is pertinent to examine how crystallization normally takes place when a liquid is cooled. Initially let us consider a pure liquid, that is, a liquid whose composition will not be changed by the freezing process. As a further restriction we shall require that the cooling be sufficiently slow for no changes in the liquid to occur if the cooling is halted for some period of time.

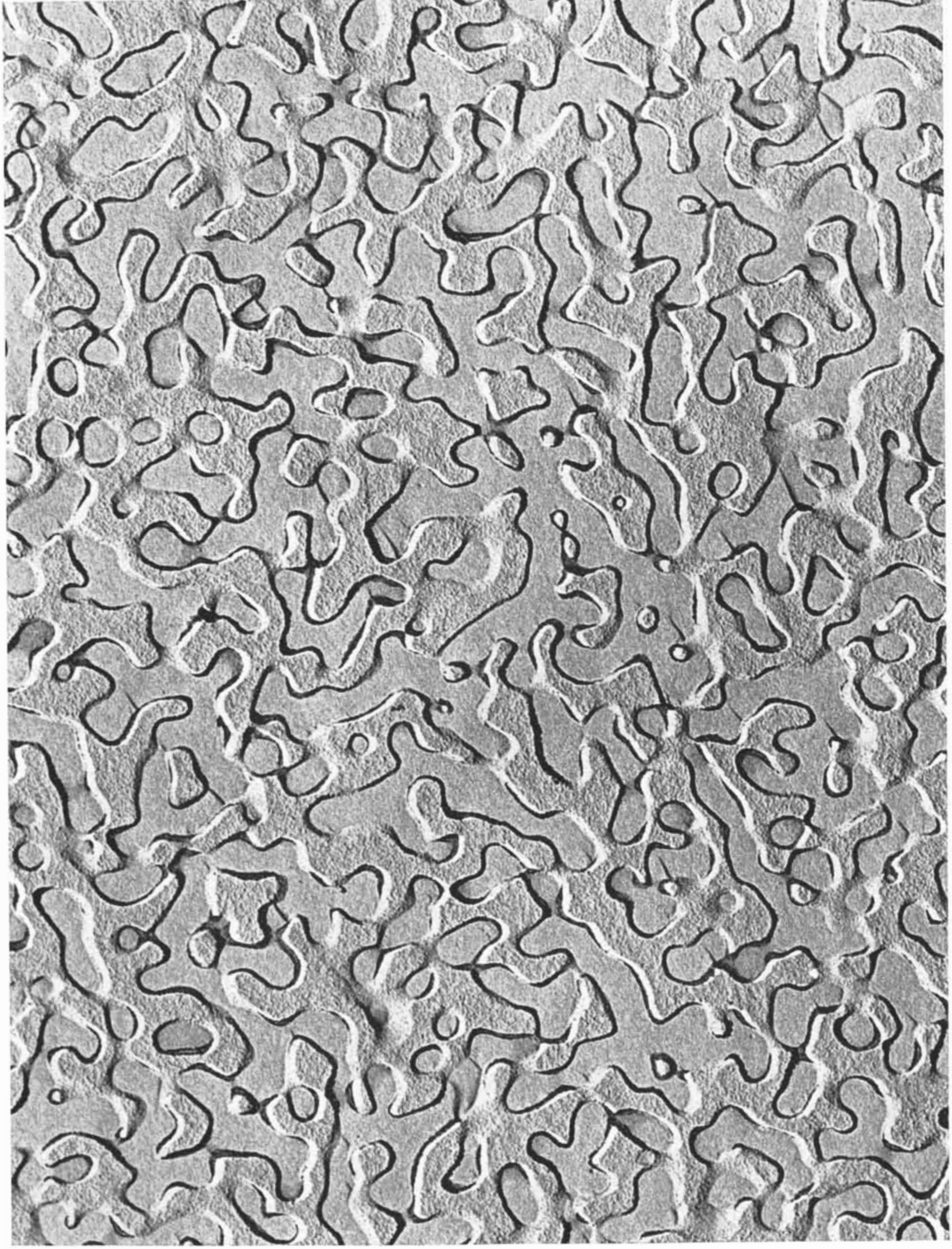
The main effect observed in cooling is that the change from a liquid to a crystalline solid is usually abrupt and occurs at a particular temperature. One might reasonably ask: Why that temperature and no other? Close observation will reveal not only that heat is passed continuously from the liquid to its surroundings during cooling but also that at the freezing temperature the surroundings receive a sudden burst of heat from the liquid.

This burst of heat is a consequence of the process by which atoms or molecules, initially in some state of chaos in the liquid, form the geometric arrays found in the crystal. One can appreciate that if there are attractive forces between particles in an assemblage, then energy, as heat or work, may be released if the particles relax into a closer and less random association with one another. Even though one can see no particularly marked change in the liquid during the initial stages of cooling, it must be assumed that the steady contraction of the liquid and the release of heat indicate that the molecules forming the liquid are engaged in a continuous ordering process. This ordering consists of many factors, such as the formation of new molecular aggregates and the development of a more geometric organization of atoms or aggregates of them, together with a reduction in the amount of random oscillation of atoms around mean positions.

At this point one might ask: Is there a simple means of measuring the amount or degree of ordering of atoms or molecules in a process such as freezing? Certainly the amount of heat given off is related to the amount of ordering that occurs on crystal formation, and one might expect a simple proportionality between the two. There is, however, an important difference between the heat transferred at a high temperature and the heat transferred at a low temperature: the first is a much rarer and more useful commodity. Assuming that the geometric arrays produced by freezing are fairly independent of temperature, a suitable measure of the amount of geometric ordering that occurs on crystallization can be provided by the ratio of the quantity of heat transferred to the temperature at which transfer takes place. This ratio, which can be put on a firm thermodynamic basis, is the measure we seek. Physicists will recognize it as entropy.

In applying this measure one can immediately see that the heat received by the surroundings on the freezing of a liquid must produce a degree of structural change in the surroundings equal and opposite to the change that occurred

**GLASS-CRYSTAL MIXTURE** (*opposite page*) **was produced by melting ordinary soda lime window glass in a crucible and then holding it at several hundred degrees centigrade for a period of days while crystal needles grew inward from the slightly cooler edges of the crucible. In this color micrograph, which was taken through crossed polarizing filters, the crystal needles are predominantly yellow and blue. The glass matrix shows up as magenta. The micrograph was made by the author at the General Electric Research Laboratory.**



TWO-PHASE GLASS can be contrasted with the mixed system of glass and crystals illustrated on page 126. This electron micrograph shows a sodium borate glass that has separated on cooling into two continuous and interpenetrating phases, each of them a glass. The two phases differ markedly in chemical composition and properties. The character of the resulting product depends not only on these differences but also on the manner in which one phase is distributed in the other. The photograph was made by the author.

in the liquid. Thus the net ordering (or disordering) that occurred in the total system composed of the liquid and its surroundings suffered no change during freezing. It is a consequence of the second law of thermodynamics that this is so for a system that changes yet has no capability for doing useful work during the change. If a net change in order had taken place in the freezing process, then we could say with confidence that the change could only have been in the direction of decreased order, because processes that might give rise to a net increase in the state of order of the universe are, as far as we know, impossible. These are the thermodynamic requirements that establish the temperature at which a particular liquid can freeze; at no other higher temperature can the geometric ordering required for crystal formation occur and leave the order of the universe undisturbed.

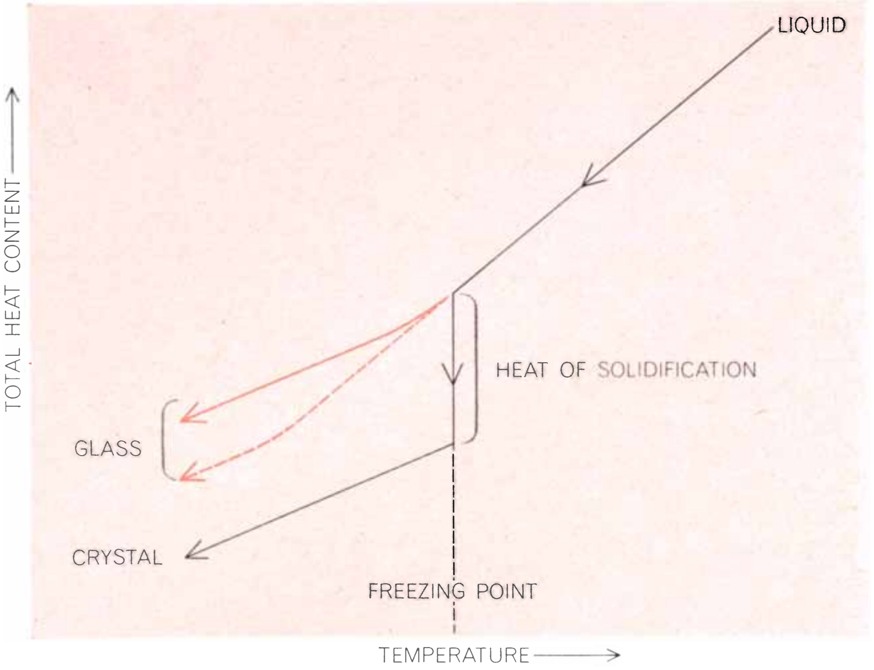
Let us now consider how the freezing process is affected when foreign atoms or molecules are added to a liquid. Let us suppose these foreign atoms are relatively inert in that they interact with the atoms of the original liquid in much the same way that they do with one another. When the solution is cooled to produce the same crystals as before, the atoms that form the crystal not only must become organized in the same geometric fashion but also must undergo an additional degree of ordering by first being unmixed from the foreign atoms. Although the total ordering in the solution that is forming crystals is thus greater than it is in the pure liquid, the amount of heat passed to the surroundings at the freezing temperature (per unit weight of crystal formed) remains the same.

The only way for the ordering in the surroundings to be equal and opposite would be for crystals to form at a lower temperature than the one needed to freeze the pure liquid and for the liberated heat to pass to the surroundings at the lower temperature. This follows because a lower transfer temperature means a smaller number in the denominator of the fraction, or ratio, mentioned earlier that indicates how much ordering can occur on crystallization. Since the amount of heat transferred (the numerator) is unchanged, reducing the size of the denominator yields a larger value for the amount of ordering (or equivalent disordering) that can be produced. This argument illustrates the important phenomenon of freezing-point depression, which governs the freezing of seawater and the melting of road ice by salting and aids greatly, as we shall see, in the formation of complex glasses.

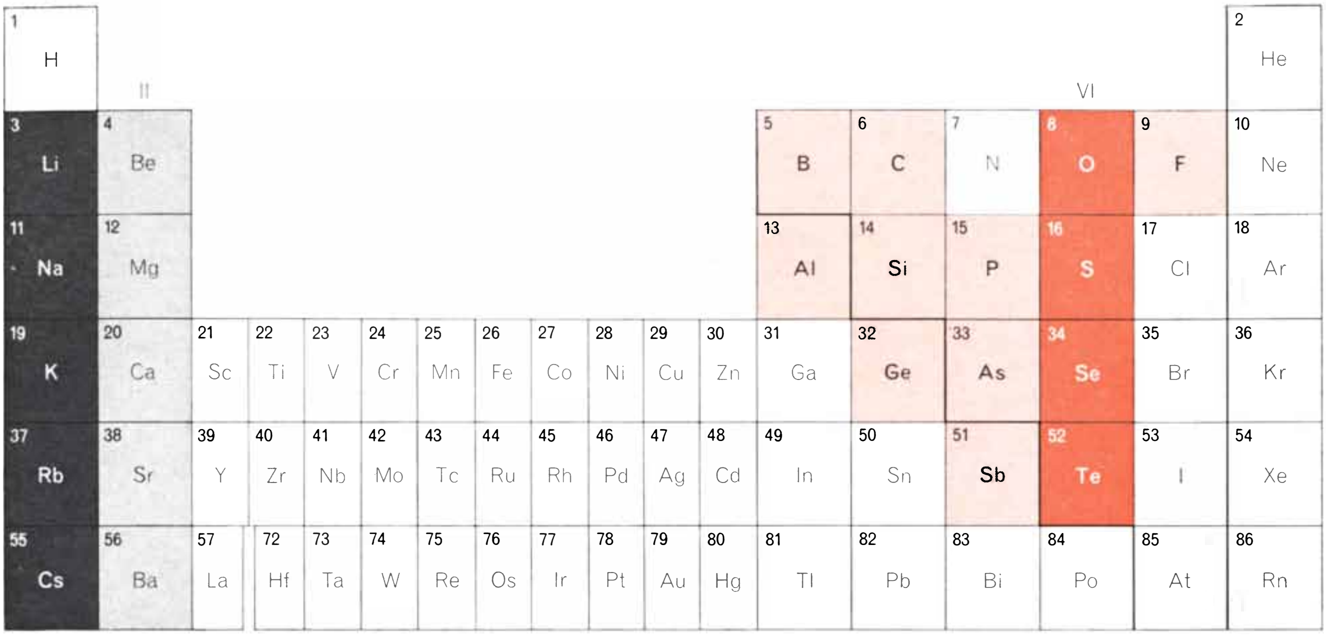
What I have just described are the conditions necessary for a liquid to be converted into a crystalline solid. Cooling to or below the freezing point is not, however, a *sufficient* condition for crystallization. I have simply dealt with the characteristics of assemblages of atoms before and after solidification. The mechanism for bringing about such a transformation is another matter.

Before a liquid can crystallize it must have in it a seed—a tiny crystal. A seed often consists of atoms or groups of atoms that have become attached to foreign particles or to irregularities on the surface of the container holding the liquid. Under certain circumstances, however, small numbers of atoms will spontaneously aggregate to form a tiny crystal nucleus on which other atoms can then deposit. In much the same fashion that energy is stored in the surface of a bubble, energy is stored by those atoms on crystal surfaces that find themselves in an environment that is partly liquid and partly solid. If the growing nucleus is small, the energy (per unit weight of nuclei) may be appreciable, because the exposed surface of the nucleus is so large with respect to its mass. This energy, which is stored on nuclei surfaces and is in excess of the heat energy that must be evolved for solidification, can be obtained only if the temperature of the liquid is lowered somewhat below the thermodynamic freezing temperature. In other words, a certain amount of supercooling is needed to form the nuclei that trigger the process of crystal growth.

Now let us turn our attention to time factors, which often play a crucial role in determining whether or not such nuclei, even under supercooled conditions, can form and grow. The reader will recall that so far the discussion has been limited to a situation in which the freezing process takes place so slowly that the molecular configurations attained are determined only by temperature and not by the time elapsed in reaching any given temperature. Because molecules must slide past one another to change their configuration, it is evident that the time required for molecules to assume new relations depends on the ease or difficulty of the sliding. For most common liquids, which are composed of individual atoms or molecules that are more or less spherical, sliding proceeds easily and the attractive forces developed among atoms or molecules during cooling are more than adequate to move them into place at normal rates of cooling. In such liquids crystal nuclei form and grow easily with supercooling of only a few degrees centigrade.



**SOLIDIFICATION OF LIQUID** can lead to either a crystal or a glass. When a liquid solidifies into a crystal, it gives up a burst of heat at some particular temperature, which identifies its freezing point. This burst, or heat of solidification, coincides with the final ordering of atoms or molecules into a crystalline array. Liquids that cool to the rigid state without crystallizing are called glasses. Glasses that are cooled slowly (*broken colored curve*) more closely approach crystalline state than glasses that are cooled rapidly (*solid colored curve*).



**CONSTITUENTS OF GLASSES are found in two widely separated regions of the periodic table. The chief glass-forming elements appear in Group VI: oxygen, silicon, selenium and tellurium. Many neighboring elements (*light-colored boxes*) enter into chain-forming structures that provide great variation in the kinds of glasses obtainable. Elements found in Groups I and II (*gray boxes*) are used primarily as fluxing materials, which help to control the viscosity of glass as well as the temperatures of melting, firing and forming.**

Certain liquids, however, become particularly viscous near the freezing point, and the formation and growth of crystal nuclei may be prevented even when the cooling rate is slow. These liquids, unable to form or grow nuclei, follow the supercooled route to the glass state. In addition, because their viscosity increases as the temperature falls, their molecular configuration lags further and further behind the temperature. As a result the molecular arrangement at any instant will correspond to equilibrium for a temperature much higher than the actual temperature.

If cooling is continued until the glass becomes rigid, random structures characteristic of liquids at much higher temperatures will be frozen into the structure of the glass. Moreover, the faster the rate of cooling, the higher the temperature to which these frozen-in liquid states will correspond. Since the amount of relaxation, or ordering, achieved by the molecules on cooling is strongly dependent on cooling rate, the amount of heat given off will likewise depend on cooling rate. Thus we see that glasses are rigid solids whose atomic structures, and hence properties, depend not only on composition but also on thermal history. For this reason close attention is paid in glassmaking practice to schedules of quenching (rapid cooling) and annealing (slow cooling).

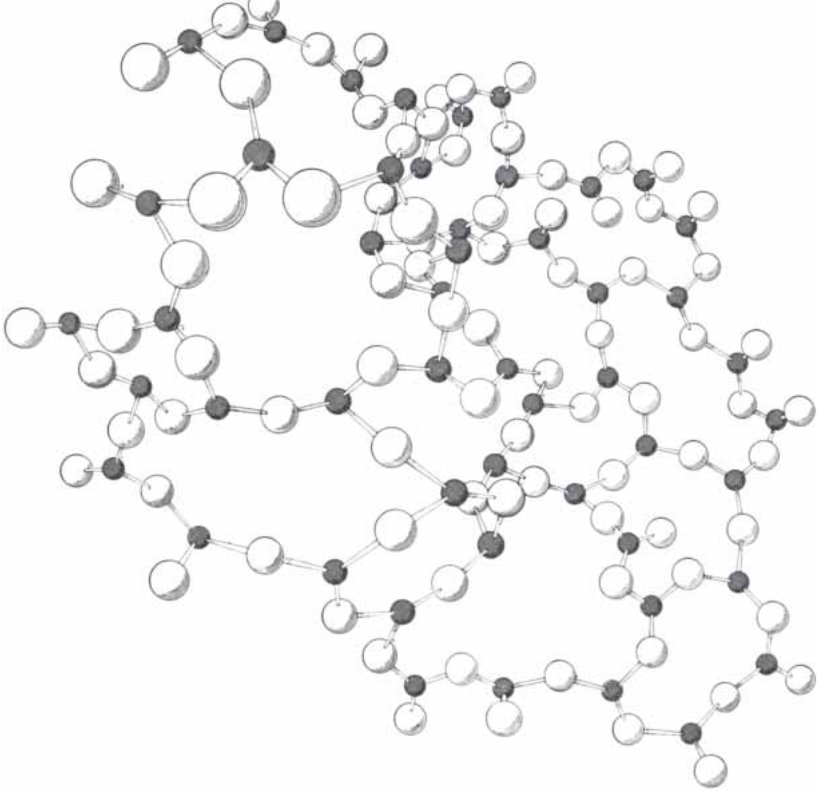
From the foregoing, one can adduce two important conditions that favor glass formation. These conditions are not exclusive and may in practice require proper balancing. On the one hand the glassmaker understands that he should select complex or impure solutions in order to depress as far as possible the freezing point of any crystal that might tend to form. This procedure has been used empirically for millenniums; many ancient glass compositions correspond to regions on composition-temperature diagrams where the freezing point is at a minimum. On the other hand the frictional forces inhibiting the formation of new molecular configurations in the liquid should be as high as possible. The glassmaker can achieve this either by fast cooling or by choosing materials that exhibit inherently high viscosity.

Simple mechanical considerations suggest that a particular molecular configuration should be more conducive to high liquid viscosities than any other. This configuration is a flexible chain or, when the chains are cross-linked, a net. In order for a chain to form, individual atoms must link up with at least two other atoms. The number of linkages specifies the "coordination." For a simple chain the coordination is two: each atom is joined to one on each side. If the chain is to have side groups or if it is to be cross-linked to other chains, at least some atoms in the chain must have a coordination of three or four.

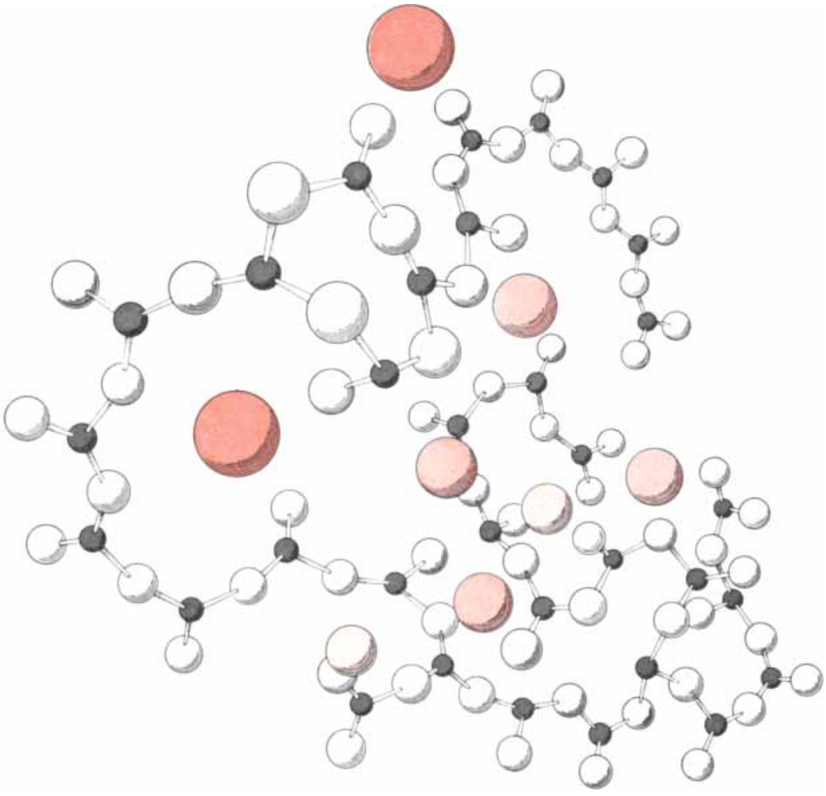
Such low coordination is favored by covalent bonds, that is, by bonds created when atoms share electrons. Atoms bonded in this way exhibit a high degree of directionality. An examination of the periodic table [*see illustration above*] shows that the elements most likely to form chains by covalent bonding are in the higher-numbered columns. These are the elements whose outer electron shells are shy only a few electrons. These elements, therefore, would rather share electrons than part with them. The Group VI elements (oxygen, sulfur, selenium and tellurium) are particularly good candidates for chain formation because the addition of only two electrons makes their outer shell complete. Thus they might easily exhibit a covalent coordination of two.

X-ray-diffraction analysis has shown that when selenium and tellurium are packed in hexagonal crystals, they consist of continuous spiral chains aligned along one axis of the crystal [*see top illustration on page 134*]. Crystalline sulfur and another form of selenium form chainlike rings, usually of eight atoms, that pack together in various geometric patterns [*see bottom illustration on page 134*]. Some of these rings open into extended chains when sulfur and selenium are melted; if the melt is cooled fairly fast, these elements, as well as tellurium, become supercooled and form glasses.

In spite of considerable study it is still debatable whether or not elemental glasses can be prepared from various



**PURE OXIDE GLASS** consists of a random three-dimensional network in which each oxygen atom (*white*) is bonded to two atoms of a metal such as boron. Here each metal atom is bonded to three oxygen atoms. However, there are other kinds of glass, such as silica glass, in which each metal atom is bonded to four oxygen atoms, producing a more complex network.



**FLUX-CONTAINING GLASS** also consists of a random three-dimensional network, except that flux atoms such as sodium (*color*) have reduced the amount of cross-linking. Thus some oxygen atoms are now strongly bonded to only a single atom and have weaker ties (*not shown*) with one or more flux atoms. As a result the melting point of the glass is reduced.

near neighbors of the Group VI elements, for example boron, silicon, phosphorus, germanium and particularly carbon. Amorphous forms of most of these elements are known, but this description may simply reflect the inability of present methods to detect crystalline regions less than 20 angstrom units in size. It is well known that when carbon is combined with other elements, particularly hydrogen and oxygen, an almost unlimited variety of chain or polymeric structures can be created. Most synthetic polymers have a glass state, and many natural organic compounds, such as alcohols, glycerol and glucose, can be supercooled to form glasses.

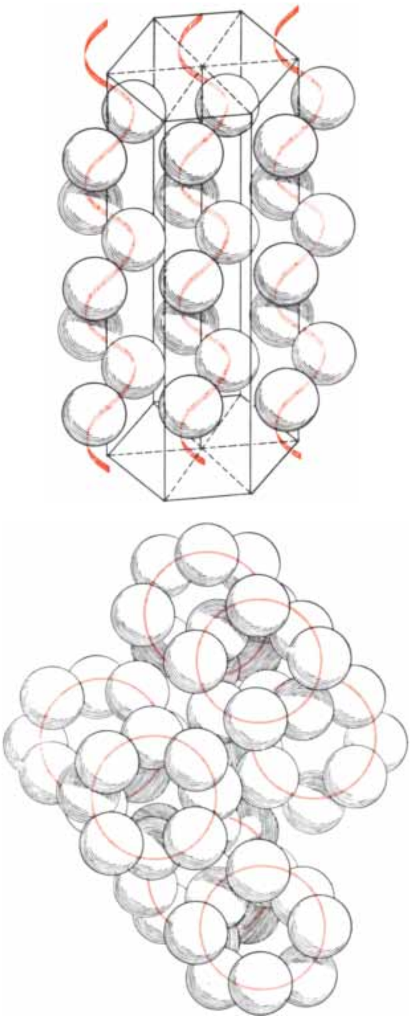
The physical and chemical characteristics of nitrogen, oxygen and fluorine suggest that they too may exist in the glass state, but I am not aware that this has yet been demonstrated. The well-known role of oxygen in glassmaking is to act as a glass-former by establishing stable bonds (mainly covalent) with small, multivalent ions such as those of silicon, boron, germanium, phosphorus or arsenic. The combination of oxygen with these ions yields low-coordination polyhedrons—primarily tetrahedrons or triangles—that have oxygen atoms at the corners and a multivalent ion at the center. The polyhedrons link flexibly with each other through the corner oxygen atoms. Pure oxides produce a completely cross-linked network because every oxygen atom is linked by electron-sharing to two positive ions. Such oxide glasses, or their crystalline counterparts, are very stable and have relatively high softening temperatures. The cross-linking can be reduced and the softening temperature lowered by introducing into the melt metals such as sodium or potassium, which shed electrons easily and thus form fairly weak ionic bonds with oxygen that lack directionality. These additives, called fluxing ions, are used extensively in glass production to lower melting temperature, inhibit crystallization and control fluidity.

Because I have been discussing glasses in terms of atomic structure, I may have given the impression that macroscopic structure in glasses—on a scale, say, of 100 to 100,000 atomic diameters—is simply a continuation of a much finer structure and so contributes little to the properties of glass. Such is not the case.

The addition of fluxing ions to oxide or elemental glasses frequently causes the components of a melt, on cooling, to separate into two or more distinct but intermixed liquids of markedly different

chemical composition. When these different liquids are frozen into a rigid glass, the way they are distributed can have a profound effect on properties such as mechanical strength, electrical conductivity, chemical resistance and optical clarity.

This oil-and-water behavior is quite remarkable because there are many cases in which a melt successfully passes a temperature at which crystals might ordinarily precipitate but does not pass a lower temperature without forming two liquids. Yet the process by which one liquid nucleates and grows out of another is very similar to the process by which a crystal nucleates and grows out of a solution. This separation phenomenon seems to be a general characteristic of chain structures and is now of recognized importance in glass technology.



**GLASS-FORMING SUBSTANCES,** when crystallized, often take the form of spiral chains in a hexagonal array (*top*) or nests of eight-member rings (*bottom*). Selenium and tellurium exhibit the spiral structure. Selenium also crystallizes in the ring structure, as does sulfur. When such ring structures are heated in a melt, the rings tend to open and link up into extended chains. If the melt is quickly cooled, the rings do not have time to re-form and a glass results. Glasses are also readily produced from spiral-chain arrays.

Although separation mechanisms have only recently received close attention, and much remains to be learned, it is possible to describe some features of the process in general thermodynamic terms. Consider a system that consists of one beaker, *A*, containing chains of molecules and a second beaker, *B*, containing the same type of chains to which a considerable number of fluxing atoms have been added [*see illustration on page 136*]. In beaker *A* the entangled chains are essentially continuous and are held together only by weak forces between chains. In beaker *B* the chains are broken up into short segments by the fluxing ions; moreover, the electrons given up by the fluxing atoms have migrated to the ends of the segments. Thus the liquid in *B* is held together not only by weak forces between chains but also by the stronger ionic forces between the positive flux ions and the negatively charged chain ends.

Now imagine that a single molecule is transferred from a chain in beaker *A* to a chain in beaker *B*. This molecule, removed from a condition in which its highly directional covalent bonds were distorted to conform with entangled chains, now finds itself in a short segment of chain in which its bonds are much relaxed. As a result energy in the form of heat is given off to the surroundings, and the disorder of the surroundings increases. The total system, consisting of both beakers, is also disordered because in the transfer the impure liquid *B* has gained in volume at the expense of the pure liquid *A*.

Let us assume that this kind of transfer is repeated many times. In due course the chain molecules in beaker *B* become so long that they start to undergo bending strains as they try to occupy the space between fluxing ions more efficiently. This means that as each additional molecule is transferred from *A* to *B* the heat evolved becomes less and less. Finally a point is reached where the relaxation energy given up in the transfer of a molecule of *A* will just balance the ionic bond energy taken up by the incremental separation of fluxing ions and chain ends. At this point no heat at all is evolved, and the disorder that results consists solely of the disorder due to mixing pure molecules with impure solution. Since the system and the surroundings taken together experience a net increase in disorder, the transfer process is still thermodynamically possible.

The next molecule transferred, however, will require external energy if it is to be incorporated into a chain segment in *B*. This energy must come from the surroundings as heat, and it is utilized partly in distorting the covalent bonds of the lengthening *B* chains and partly in separating chain ends and flux ions. Finally a state may be reached in which the ordering taking place in the surroundings, because of the loss of heat to beaker *B*, may become equal to the disordering resulting from the further mixing of *A* and *B*. Such a condition may arise easily if the attractive forces between chain ends and flux ions are fairly strong and if the temperature is fairly low. Once this condition is reached something of a dilemma is presented: on the addition of further *A* molecules to *B*, a net increase in the ordering of the "universe" would tend to occur, and this, as far as we know, cannot happen. The difficulty is resolved, however, because the last molecules transferred simply gather together in local regions, partially exclude fluxing ions so that the attractive forces in these local regions are reduced, and pack themselves as long chains in an open structure resembling their original configuration in *A*. In this fashion separation of one liquid into two liquids with different properties overcomes the impending dilemma and provides an avenue for continued mixing.

Numerous two-phase structures are possible in glasses [*see illustration on page 128*] and are present in many commercial forms of glass. Recently it has been found that a prior two-liquid formation may play a significant role in determining the path of crystallization and the final properties of "crystallizable" glasses. These are glasses that are first melted and formed in a desired shape and then, by prolonged heat treatment, converted into a strong and durable ceramic that is part glass and part crystal. Ceramics of this type, with such trade names as Pyroceram, Re-X and CER-VIT, are finding increasing use in industry and in the home.

One of my colleagues maintains that glasses are the next best thing to universal solvents. His point is well taken; practically all elements can be dissolved in glasses to a considerable degree. In addition, many kinds of chemical reaction—decomposition, precipitation, dissolution, ion-exchange, oxidation and reduction—can be carried out directly inside a glass. There is the added ad-

# VACUUM COATED STEELS

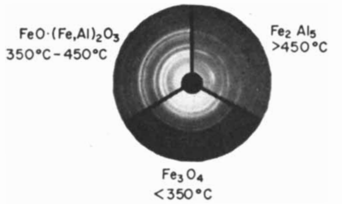
*An idea borrowed from the electronics field, "vacuum evaporation", has multiplied the number of potential steel coatings to create a new generation of valuable products.*

by R. P. Morgan, Research Manager

As if to emphasize the technological changes which are taking place in many of its processing operations, the steel industry recently borrowed an idea from the electronics field, scaled it up a hundred times and introduced a new steel coating process. The technique, used in the production of transistors and other space age electronic components, consists of evaporating metallic or non-metallic materials in high vacuum and condensing them onto a prepared substrate to form a coating. Youngstown Steel has been working with this process for the past four years, exploring its general utility. In many cases, special surface properties have been obtained on steel strip which could not have been economically achieved by other means, and from this work a new generation of coated steel products has emerged.

Research has reached a stage where a high speed pilot line is being used to prepare coils of steel with different coatings for customer evaluation. A key feature of the system is a series of remarkably effective roll seals. These seals enable a clean strip to pass continuously from the atmosphere into the high vacuum evaporation chamber operating at a pressure below $10^{-4}$ Torr, and out again. Inside the evaporating chamber, a specially designed crucible containing the coating material is heated by a beam of high energy electrons to some characteristic temperature at which large quantities of vapor are rapidly evolved. For example, with aluminum this temperature is about 1700°C. The vapor is immediately condensed onto the moving steel strip to form the desired coating. A number of individual evaporators is used in order to increase the operating speed and to produce a coating on both sides of the strip ranging in thickness from 0.001 to 1.0 mil. The use of the electron beam as a heating device permits the evaporation of a wide range of coating materials including those with very high evaporation temperatures.

One of the important technical problems in this field is that of obtaining good adhesion between the condensate and the steel substrate. Procedures vary for each material; however, again taking aluminum as an example, the steel must be pickled and subsequently preheated to a temperature of 400°C in vacuum before deposition of the coating. Electron diffraction studies of the interface between the steel and the aluminum have shown that a magnetite film is present at substrate temperatures below about 350°C, (see illustration) and is accompanied by poor adhesion.



VARIATIONS IN INTERMEDIATE LAYER BETWEEN VACUUM DEPOSITED ALUMINUM AND STEEL

As the substrate temperature is increased towards 450°C, an alumina spinel of varying composition is formed and the adhesion and corrosion resistance of the coating increase markedly. At temperatures above 450°C, an $Fe_2Al_5$ phase can be detected. Adhesion at this point is excellent but rapid total conversion of thin films to the brittle intermetallic can occur. This operating range is therefore generally avoided. Other coating metals of low melting point and high vapor pressure, such as zinc, require more critical control of substrate temperature. In addition, they require the use of an intermediate layer of a second metal to secure acceptable adhesion.

Other aspects of the process are under investigation including those connected with the control of coating properties and those related to the development of new equipment designs for more efficient operation. Data are steadily being accumulated through operation of the pilot facility and this information will eventually be used to further the construction of full scale production equipment.

Much of the work which has already been carried out points to the unusual flexibility of the new technique and the commercial significance of the products. For example, the "tin" can which is, of course, basically a "steel" can could be manufactured by substituting another metal for tin. Aluminum or chromium are contenders in this respect. They provide an attractive finish, are readily available, and have chemical properties which encourage their use in certain food containers.

There are many additional examples of ways in which vapor deposited coatings can be used to broaden the performance of a steel product. Zinc, for special automotive applications, and stainless steel for architectural usage are both promising materials. Experiments have already shown that stainless steel compositions can be evaporated and condensed to form finishes with great corrosion resistance. The application of metals such as copper for brazability, or titanium for chemical inertness is also under consideration.

A great deal of additional research and development will be necessary to create the systems which will economically process a hundred thousand tons of these new strip products a year. Nevertheless, it is apparent at this time that the steel industry in its search for effective new techniques has discovered in vacuum evaporation a method with significant potential.

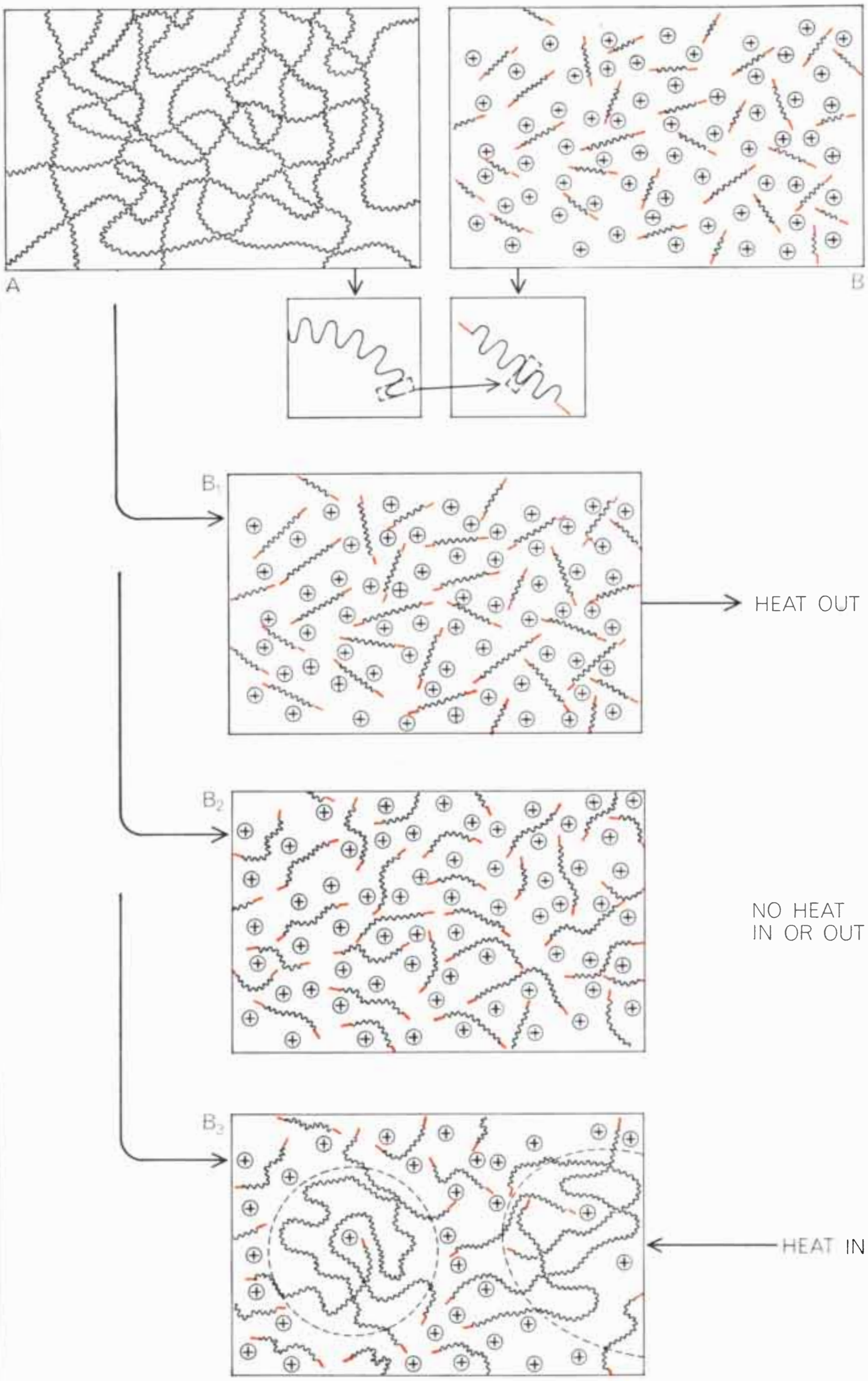
Steel and steel application problems are continually under investigation at Youngstown's research center in support of Youngstown's position as a major supplier of a wide variety of low carbon and low alloy products. The work on coated products represents only a small part of the 24 hour a day research effort. If you think Youngstown can help you, call at your convenience, or write Department 251 E6.

**Youngstown Steel**

THE YOUNGSTOWN SHEET AND TUBE COMPANY · YOUNGSTOWN, OHIO 44501

halted, or frozen in, at any stage desired.

Control over such processes has made it possible to produce glasses that show laser action, lighten or darken in response to light, exhibit semiconduction and photoconduction, fluoresce and a hope that a glass may eventually demonstrate superconductivity. As glass science continues to provide a rational basis for the glassmaker's art many new and unexpected phenomena will certainly be encountered.



**TWO-LIQUID GLASS STRUCTURE,** like that shown in the photograph on page 128, is believed to arise through a process similar to that schematized here. *A* is a melt of pure glass made up of long, tangled chains. *B* is a fluxed glass in which the positive charges of flux ions are matched by the number of electrons (*color*) at the ends of short, straight chains. The sequence $B_1$, $B_2$, $B_3$ shows what happens if *A* chains are slowly transferred to a beaker of *B* chains. As the detail shows, the short *B* chains lengthen by repeated transfer of molecules from the longer *A* chains. At first there is an outflow of heat. Later the flow is reversed, but thermodynamic considerations indicate that the melt will then separate into two phases ($B_3$).

## Getting Boron Atoms Together...Alone, in Amorphous Form, and in Useful Quantities

The "corncob" shown is a section of 4-mil diameter boron filament, magnified 500 times. It shares with the potential of carbon filaments the distinction of being about the highest-performance material known to man. It approaches the strength of glass filaments and is six times as stiff.

These boron filaments are being used as reinforcements in plastics and metals to produce some remarkable improvements in strength and stiffness. For example, the strength and stiffness of aluminum have been increased by a factor of five above the pure metal by inclusion of these filaments. Imagine how much lighter a boron composite might make a future reentry vehicle or aircraft.

### From Ounces to Pounds

Wonderful! But how far can one go with a material whose total annual production a few years ago was only a few ounces at a price of thousands of dollars? The problem of producing useful quantities of high-strength boron filaments comes in two parts: understanding the techniques by which these filaments can be made, and then transforming these techniques from laboratory operations into an economical mass-production process.

The most successful technique that will create high-strength boron filaments consists of bringing boron-containing gas in contact with an electrically-heated wire where the boron is vapor deposited onto the wire substrate with the characteristic "corncob" surface. Avco, under Air Force sponsorship, has taken this laboratory process and developed it into a continuous, well-automated process which has been set up in a pilot plant. This type of processing equipment is capable of producing hundreds of pounds per year of this exotic material and is being used to provide information for scale-up to a larger facility.

### How it works

In this pilot plant, a series of ½-mil tungsten wire substrates are unwound from reels and fed through long glass reactor tubes in which flow boron trichloride ($BCl_3$) and hydrogen. The filament emerges at the other end of the reactor tube and is rewound as 4-mil boron filament. The 1¾-mil thick sheath of boron "corncob" is gradually built up on the substrate by vapor deposition as it moves through the glass tubing.

The tungsten substrate throughout the reactor tube is heated to a cherry-red 1000-1100°C temperature by an electric current introduced into the substrate by mercury-filled standpipes spaced at intervals along the reactor. The current levels in the substrate are not unlike those in the filament of the common incandescent lamp; the voltage levels are much higher.

The boron trichloride and hydrogen gas is automatically passed through the tubes and the unreacted boron trichloride is recovered for recycle while the unreacted hydrogen is vented through a flare.

### The "Composites Age"?

With the filament being automatically reeled along at tens of feet per minute, and the numerous deposition units in the pilot plant working around the clock, Avco has become one of the nation's major producers of high-strength, high-modulus boron filament. Avco's future success in turning what is being learned in this pilot plant into a large-scale production facility could play a vital part in determining whether the "steel age" will ever be followed by the "composites age."

Avco has openings in many project and research areas, such as boron, high average-power lasers, artificial circulatory aids for medicine, advanced ballistic missile decoy systems, scientific satellites, higher-performance gas turbines. If you'd like to be out in this advance guard, write: The Avco Corporation, 750 Third Ave., N. Y. 10017.
An equal opportunity employer.

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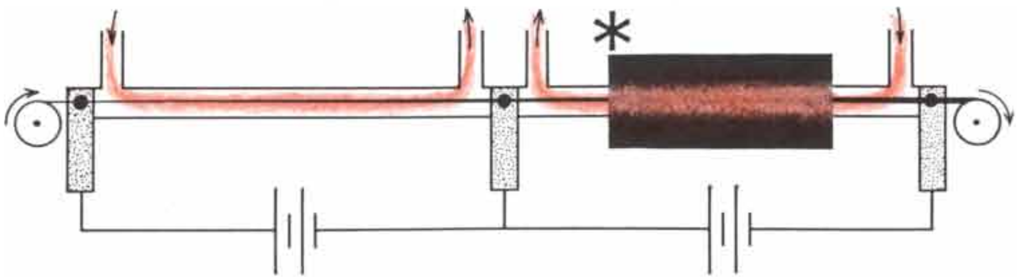


# CERAMIC MAGNETS

**A-B ceramic magnets**
used in the 500 *Selektronic* shaver
shown actual size.

**Remington takes advantage of the high energy of Allen-Bradley ceramic permanent magnets to achieve the small size required for the ideal performance of their 500 *Selektronic* shaver**

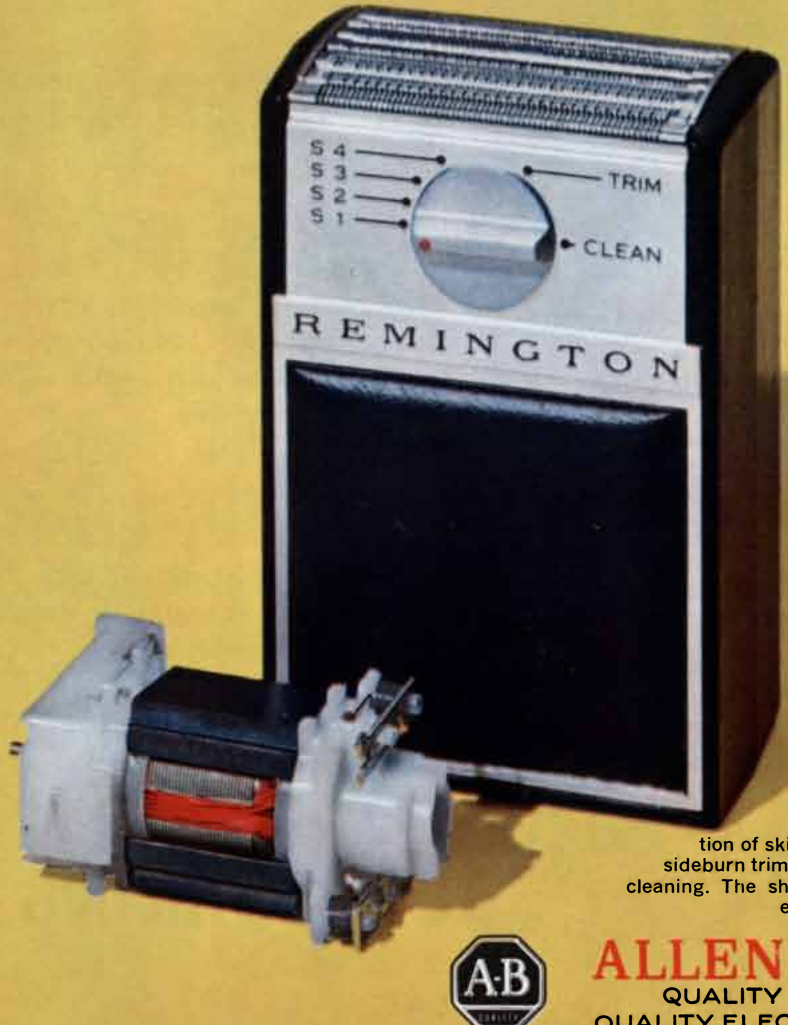
This custom designed ceramic magnet is the result of cooperative efforts by Remington and Allen-Bradley engineers. Despite the complex geometry of the magnets, Allen-Bradley was able to achieve high volume production at reasonable cost.

Allen-Bradley MO5-C ceramic permanent magnets are radially oriented and can be furnished in segments for d.c. motors measuring no more than ¾″ diameter up to a maximum rating of 10 hp. Coordinated and adequate manufacturing facilities at Allen-Bradley and tight quality control assure delivery in quantity—on time!

Allen-Bradley application engineers will be pleased to cooperate in the design of your motor magnets to obtain optimum performance. Allen-Bradley Company, 222 W. Greenfield Ave., Milwaukee, Wis. 53204. In Canada: Allen-Bradley Canada Limited. Export Office: 630 Third Ave., New York, N. Y., U.S.A. 10017.

**TYPE MO5-C CERAMIC PERMANENT MAGNETS** Typical Characteristics—stated values have been determined at 25° C.

| Property | Unit | Nominal Value |
|---|---|---|
| Residual Induction ($B_r$) | Gauss | 3300 |
| Coercive Force ($H_c$) | Oersteds | 2300 |
| Intrinsic Coercive Force ($H_{ci}$) | Oersteds | 2400 |
| Peak Energy Product ($B_dH_d$ max) | Gauss-Oersteds | $2.6 \times 10^6$ |
| Reversible Permeability | — | 1.09 |
| Curie Temperature | +°C | 450 |
| Temperature Coefficient of Flux Density at $B_r$ | %/°C | −0.20 |
| Specific Gravity | — | 4.85 |
| Weight per Cu. In. | Lb. | 0.175 |



The 500 *Selektronic* shaver features a unique dial which adjusts the shaving heads to four shaving positions for any combination of skin and beard, plus TRIM position for sideburn trimming and CLEAN position for instant cleaning. The shaver operates on its rechargeable energy cells or from an electric cord.

ALLEN-BRADLEY
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74-07-7CE

**Basic Research at Honeywell**
*Research Center*
*Hopkins, Minnesota*

# The Effects of Pulsed Laser Bombardment of Surfaces

## Studies of the interaction of pulsed laser beams and opaque surfaces in vacuum have revealed some unexpected non-thermal effects. New experiments now suggest a theory to explain this phenomenon.

Much work has been done to develop the laser since it was first operated in 1960, yet little is known about what occurs when the beam strikes a surface.

Earlier work in the U.S. and abroad confirmed that when a laser beam strikes a surface, heat is pumped in so fast that the surface temperature rises to the vaporization point of the material. Ions, electrons, neutral atoms and molecules are emitted. Unexpectedly, however, high-energy particles are observed. These ionized atoms are emitted with too high an energy (several hundred electron volts) to have resulted from ordinary thermal effects. Normally such energies would require surface temperatures above 1,000,000°C, yet the vaporization points of the materials examined do not exceed 6000°C.

Honeywell scientists, supported by the Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland, are conducting experiments hopefully to explain this phenomenon.

Their approach is to observe the particle energy emitted in relation to the power in the laser beam as it strikes a surface. They are working with a Q-switched or giant pulsed, laser which generates short, very high-power pulses in contrast to a normal pulsed laser where the energy is higher but the power lower.

In Honeywell's experiments a quadrupole mass spectrometer is used as a mass filter to detect particles emitted as the laser beam strikes the target. Using it scientists can identify and count the number of particles of a given mass regardless of energy. Thus all species desorbed can be identified.

Also, a time-of-flight spectrometer developed by Honeywell is used to detect all charged particles and to separate them by time of arrival. With proper calibration masses and energies can be identified.

Using tungsten as a target, Honeywell scientists have observed desorption of gases and the emission of high-energy neutral molecules and high-energy ions. For example the quadrupole spectrometer has recorded CO, $CO_2$ and $H_2$ pulses plus hydrocarbons, water vapor and oxygen emitted through normal desorption processes.

However, some high-energy neutral CO, $CO_2$ and $H_2$ molecules were detected with energies of the order of 100 electron volts per molecule, an energy far too high to have been produced by normal vaporization processes. Figure 1 shows a series of these high-energy pulses. The narrow initial pulse is caused by ultraviolet light. The second, higher pulse is due to hydrogen molecules; the third to CO molecules.

On the time-of-flight spectrometer, ions were identified as mainly sodium and potassium but were also lithium, carbon, hydrocarbons and, of course, tungsten. Very few CO and $CO_2$ ions were observed. Sodium and potassium ions registered energies of 200 electron volts per ion, again far too high to be produced by vaporization.

These measurements produce results that appear to be different. Sodium is observed on the time-of-flight but not on the quadrupole; mostly CO and $CO_2$ are observed on the quadrupole but only traces appear on the time-of-flight. These apparent contradictions can be explained by considering that the quadrupole spectrometer is better suited to detect neutral molecules, while the time-of-flight is primarily an ion detection instrument.

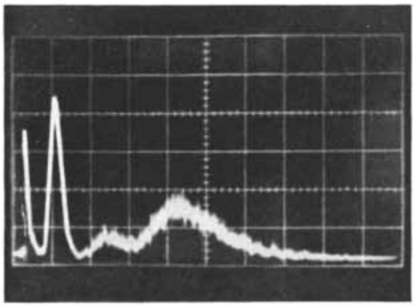


FIGURE 1. Oscilloscope trace of quadrupole spectrometer output. Pulses are of high-energy molecules emitted from a tungsten surface struck by a laser beam with a power of about 50 million watts per sq. cm. Horizontal time scale: 10 microseconds per major division. Vertical: 10 millivolts per major division.

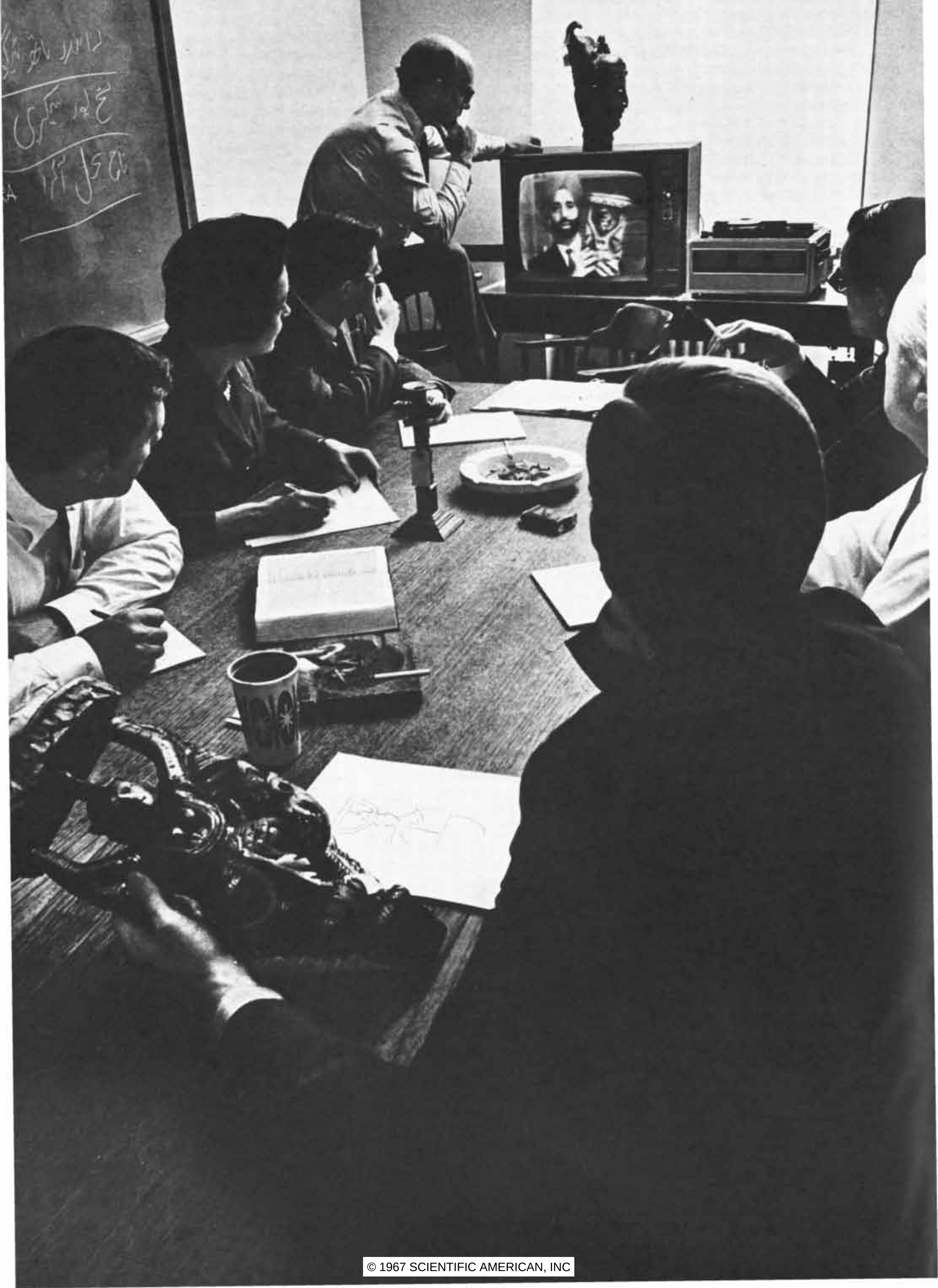
From their observations Honeywell scientists have developed this hypothesis: when the laser pulse strikes the surface a small amount of material vaporizes early in the interaction, forming a thin sheath of electrons and ions. The laser light is absorbed by the charged particles in this thin sheath. The ions become hot because of the absorption of energy. Since the rate of energy exchanged by collision is slow, the neutral molecules remain cool. The sheath goes to several hundred thousand degrees centigrade while the surface itself is at the boiling point of tungsten (5900°C). The relatively small component of neutral high-energy molecules results from energy exchanges in collisions with the hot ions. The sheath and the surface are then out of equilibrium and are thermally decoupled. Thus the heat of the sheath cannot flow to the material.

When the laser pulse ends and the heating stops, the high-temperature gas expands. This adiabatic expansion gives the high velocity to the ions and explains the emission of high-energy ions. Similar effects have been observed using targets of titanium, nickel, platinum and carbon.

Hopefully further work will lead to new laser applications and further understanding of the nature of materials.

If you are engaged in research in laser surface interactions and wish further information on Honeywell's plans for work in this area, write Mr. John F. Ready, Honeywell Research Center, Hopkins, Minn. 55343. If you are interested in a career at Honeywell's Research Center and hold an advanced degree, write Dr. John Dempsey, Vice President Science and Engineering at this same address. Several important new staff positions are unfilled at the present time.

**Honeywell**



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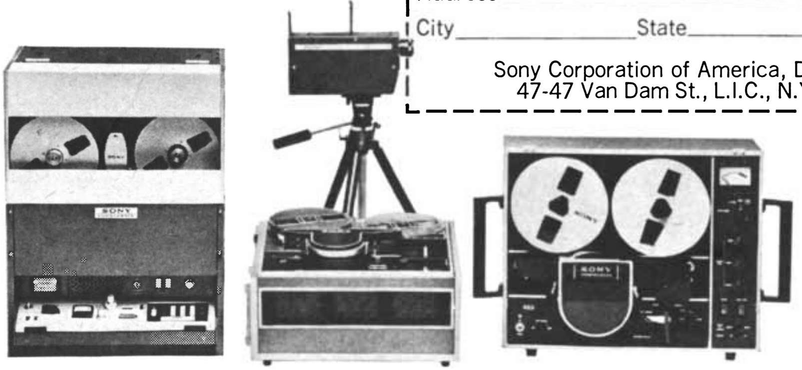

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# When they said, "Aluminum can't take submarine pressures"... the men at Reynolds took the Aluminaut down over a mile.

The deepest a World War II submarine could safely dive was 400 ft. Like all submarines, it had a steel hull. Few people believed aluminum could take the pressure at that depth.

Then the men at Reynolds developed the Aluminaut, an all-aluminum submarine, designed to go as deep as 3 miles. It has already made test dives to 6,250 ft.

The Aluminaut has an aluminum hull that can withstand pressures up to 9,000 lbs. per square inch. Yet the 50-ft. craft weighs only 75 tons. A steel hull thick enough to take the pressure would be too heavy to provide a payload at the design depth; the Aluminaut carries a 6-man crew and 3 tons of equipment.

The research voyages of the Aluminaut have already opened new frontiers in oceanography and marine geology—and helped solve an international problem. The submarine was used by the U.S. Navy in searching for a lost hydrogen bomb off the coast of Spain at 2,800 ft.

Technically, as well as scientifically, the Aluminaut was a voyage into uncharted waters. But Reynolds—working closely with marine designers, independent fabricators and a shipyard—combined their aluminum know-how, facilities and experience to make the voyage a success.

The men at Reynolds are helping launch new ideas every day—on sea, land, and air. So whether you're interested in aluminum for transportation, packaging, building or architecture, or industrial products, see the men at Reynolds first.

Call your local Reynolds office or write *Reynolds Metals Company, P.O. Box 2346-LS, Richmond, Virginia 23218.*

**REYNOLDS**
*where new ideas take shape in*
**ALUMINUM**

aluminum

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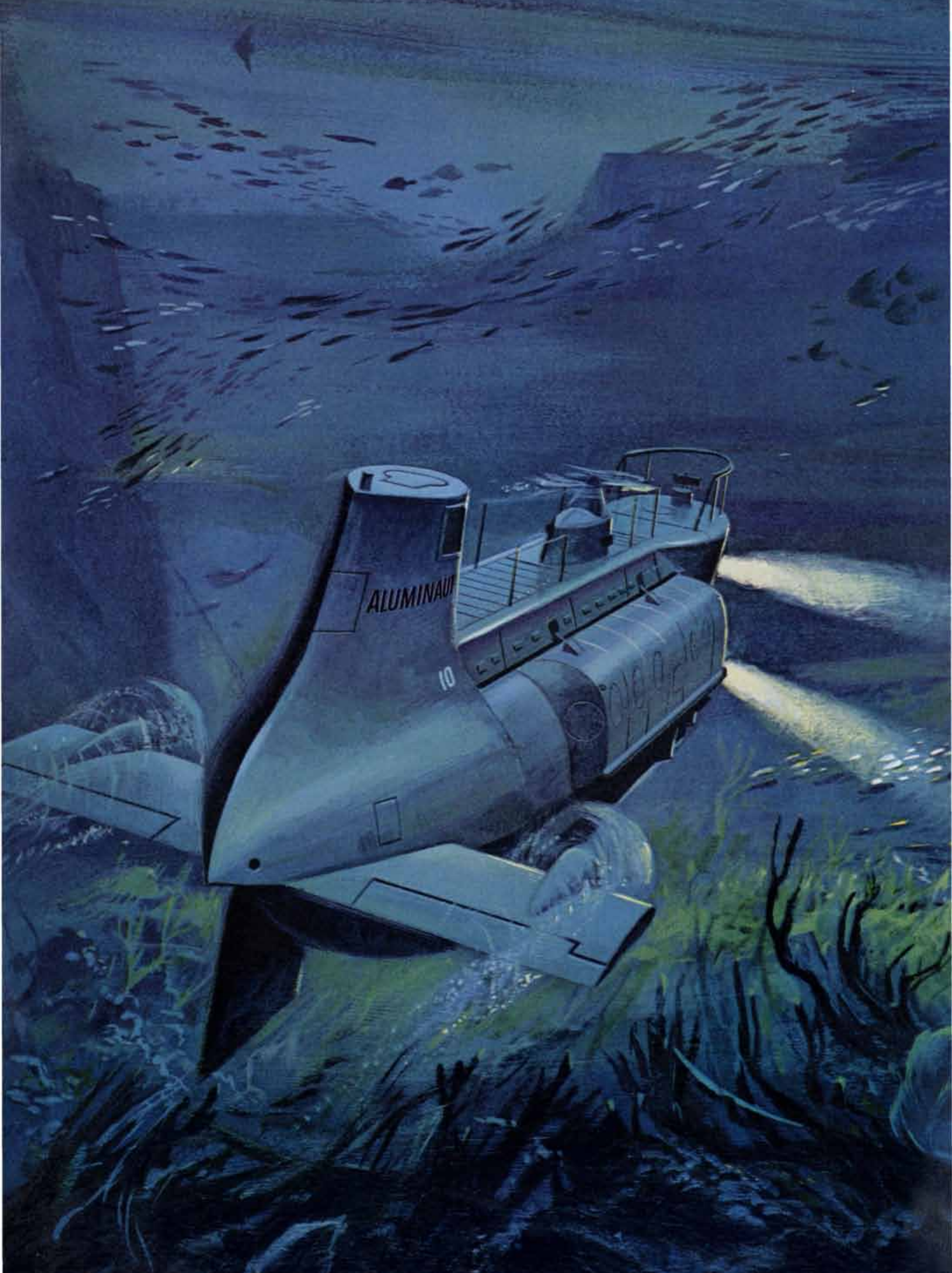
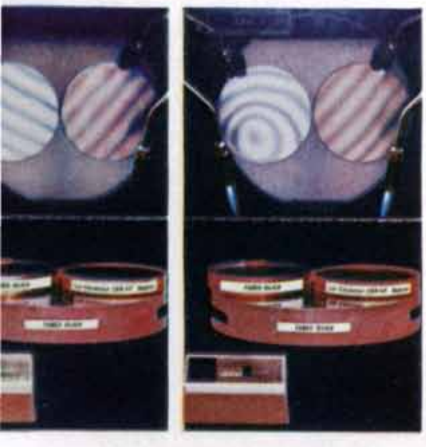

ALUMINAUT
10

# Now...to assure a stellar performance...

New installations of CER-VIT mirror blanks are at Yerkes Observatory, University of Chicago / Solar Observatory, University of Michigan / Ritter Observatory, University of Toledo

*Right: At Owens-Illinois Development Center, a newly cast mirror blank.*

*Below: Zero-expansion characteristic of CER-VIT material cuts down long waits during figuring, grinding, polishing.*



*Above: Left-hand photo shows normal fringe patterns of fused silica and CER-VIT material before flames are applied. Right-hand photo 9 seconds later shows only the CER-VIT material pattern unchanged.*

# with utter stillness

## *Owens-Illinois innovates zero-expansion in mirror blanks of CER-VIT® material with ideal formability, one-piece construction*

The astronomer, pursuing the oldest and purest of sciences, has the universe for his laboratory. Nature herself sets up his experiments. He must wait for her staging, ready to observe and record as the sequence unfolds . . . often frustrated by conditions beyond his control.

When the image reflected by his telescope mirror blurs, observation is interrupted, and viewing time and continuity are irrevocably lost. The reason? It is often a change in temperature which has expanded or contracted the mirror.

### *Zero-expansion lets mirrors sit "still"*

Mirror blanks now being made by Owens-Illinois from its CER-VIT material ("Cer" for ceramic, "Vit" for vitreous) attain a virtual zero coefficient of expansion within the temperature ranges encountered in telescope installations. This material is one of a completely new family which begins as a glass but emerges after a cycle of controlled crystallization as a totally new material.

The new mirror blanks equal or surpass previous materials for ease of grinding and polishing. They are stronger than amorphous glass structures. And because CER-VIT mirror blanks are cast as a single monolithic piece, they permit a broad variety of design and lightweight structuring.

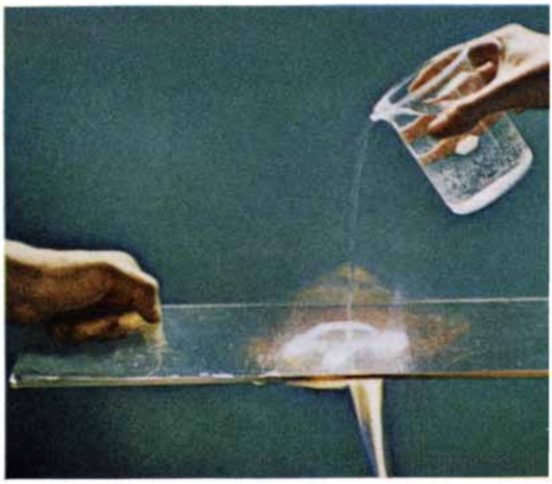
### *Versatility is greatest newness*

The newness of the CER-VIT family of materials lies in its ability to be tailored by changing its physical and chemical properties and using a number of forming processes. The versatility of combining properties in significant new ways offers a unique means of adapting this material to a wide range of specific applications. For example, for different applications the property of thermal coefficient of expansion may be varied from $-20$ to $+120 \times 10^{-7}/°C$.

New applications are on the horizon, from the imaginative interplay of ideas of our technical and marketing people with those of other industries.

*CER-VIT is a registered trademark of Owens-Illinois, Inc.*

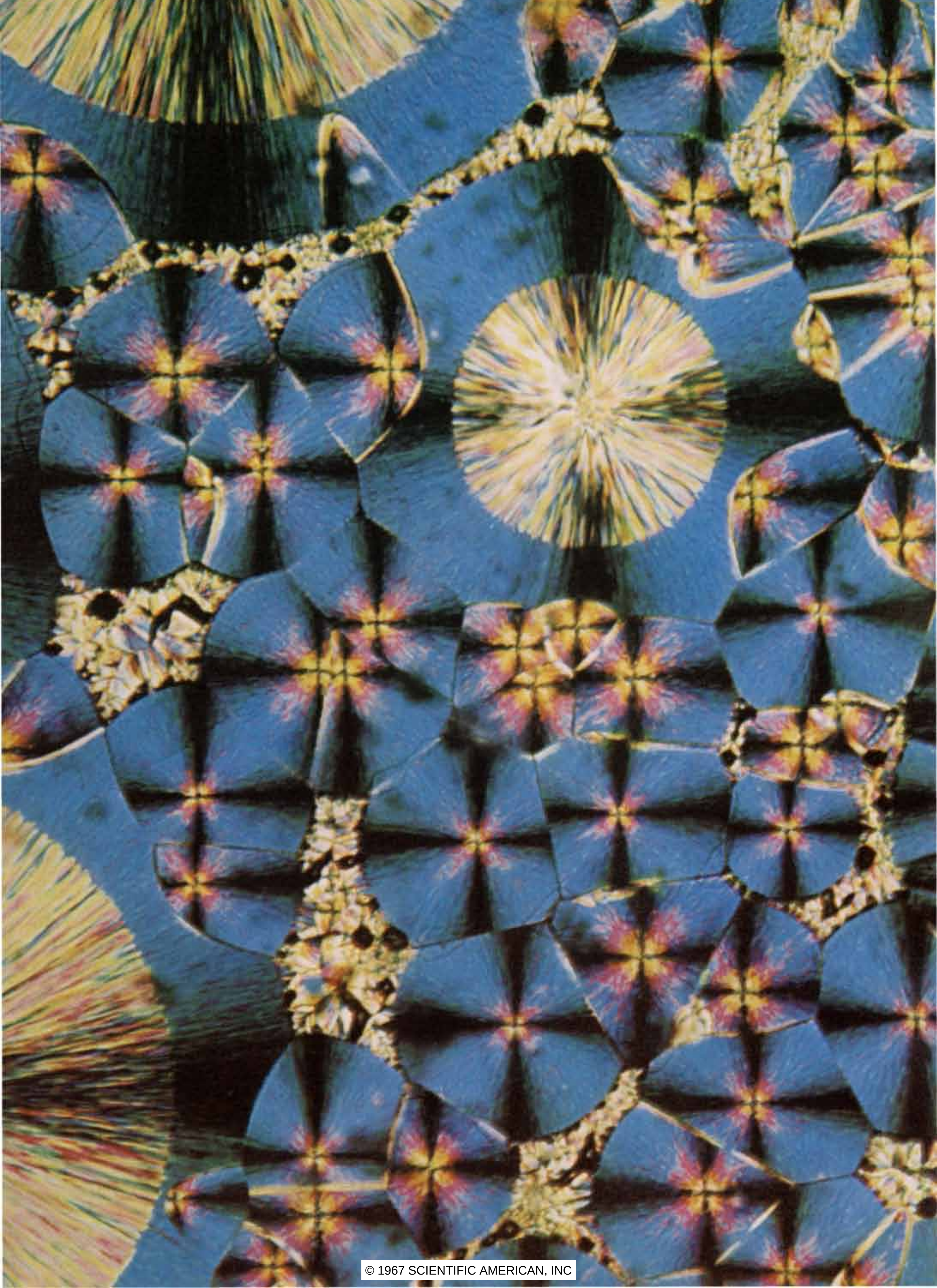
*VERSATILITY of CER-VIT materials is represented by forms which are cast, pressed, blown, drawn, in flat forms, machined, transparent, translucent, opaque – and from clear to brilliant colors.*



*INFRARED TRANSMISSION in a localized pattern is indicated by the bare hand which comfortably holds this panel although water turns to steam only a few inches away.*

**OWENS-ILLINOIS**

Toledo, Ohio 43601



# THE NATURE OF POLYMERIC MATERIALS

In synthesizing long-chain molecules man imitates natural polymers such as cellulose. Today nature is being outdone, and polymers are evolving that may be rigid enough to serve for heavy construction

by Herman F. Mark

Life depends fundamentally on organic polymers. They provide not only food but also clothing, shelter and transportation. Indeed, nearly all the material needs of man can be supplied, and in many times and places they have been, by natural organic products. The list of these materials and things made of them is very long: wood, fur, leather, wool, flax, cotton, silk, rubber, oils, rope, sails, paper, parchment, canvas, paint, stringed musical instruments, bows, arrows, tents, houses, ships and shoes and sealing wax.

The natural organic polymers from which such things are made include proteins, cellulose, starch, resins, lignin and a few other classes of compounds. Because of the complexity and chemical fragility of their molecules, the natural organic polymers, although known and used for ages, defied attempts to analyze their molecular structure until very recently. Since 1920 modern methods of physical and chemical analysis have uncovered the principles that govern the properties of the natural polymers, and organic chemists, going to school to nature, have created a new industry of man-made organic polymers. It has become a major enterprise in all industrialized countries; in the U.S. more than 13½ billion pounds of synthetic plastics and resins, totaling more than $6 billion in value, was produced last year.

The principal products are fibers, packaging materials, synthetic rubbers, coatings, adhesives and a galaxy of the materials called "plastics." The markets for these products are now approaching saturation, and the industry is therefore looking for new worlds to conquer. The most inviting prospect for large-scale expansion of the use of synthetic polymers lies in the field of construction materials—not only for houses and other buildings but also for automobiles, airplanes and boats. Plastics and synthetic coatings are already in common use in the finishing sector of building construction, as floor tiles, insulation, trim and so on. The new field now envisioned by chemists is the creation of organic polymers that will serve in primary structural capacities: as load-bearing members, structural shells, walls and conveyors of various utilities.

Synthetic polymers now available already possess several of the properties required in a structural material. They are light in weight, easily transported, easily installed, easily repaired, highly resistant to corrosion and solvents and satisfactorily resistant to moisture. They fall short of the requirements in structural strength, long-life durability and resistance to high temperatures. The outlook is good, however, for the development of polymers that will meet these demands. The chief question has to do with their cost: it remains to be seen if synthetic polymers can be made inexpensive enough to compete with the traditional structural materials—metals and ceramics.

It may seem odd that man came so late to the investigation of organic polymers. As the principal means of supporting life, the natural polymers—proteins, cellulose and so on—dominated his existence, and even in ancient times people developed great ingenuity, craftsmanship and sophistication in the handling and use of these materials. Yet as late as the end of the 19th century, when the science of organic chemistry excited high enthusiasm and fired many of the keenest minds, polymer chemistry got little attention. Chemists attacked sugar, glycerol, fatty acids, alcohol, gasoline and other ordinary organic compounds—dissolving, precipitating, crystallizing and distilling to learn what these substances were composed of and how they were put together. Only feeble and ineffectual efforts were made, however, to investigate such common materials as wood, starch, wool and silk. The substances composing these materials could not be crystallized from solution, nor could they be isolated by distillation without being decomposed.

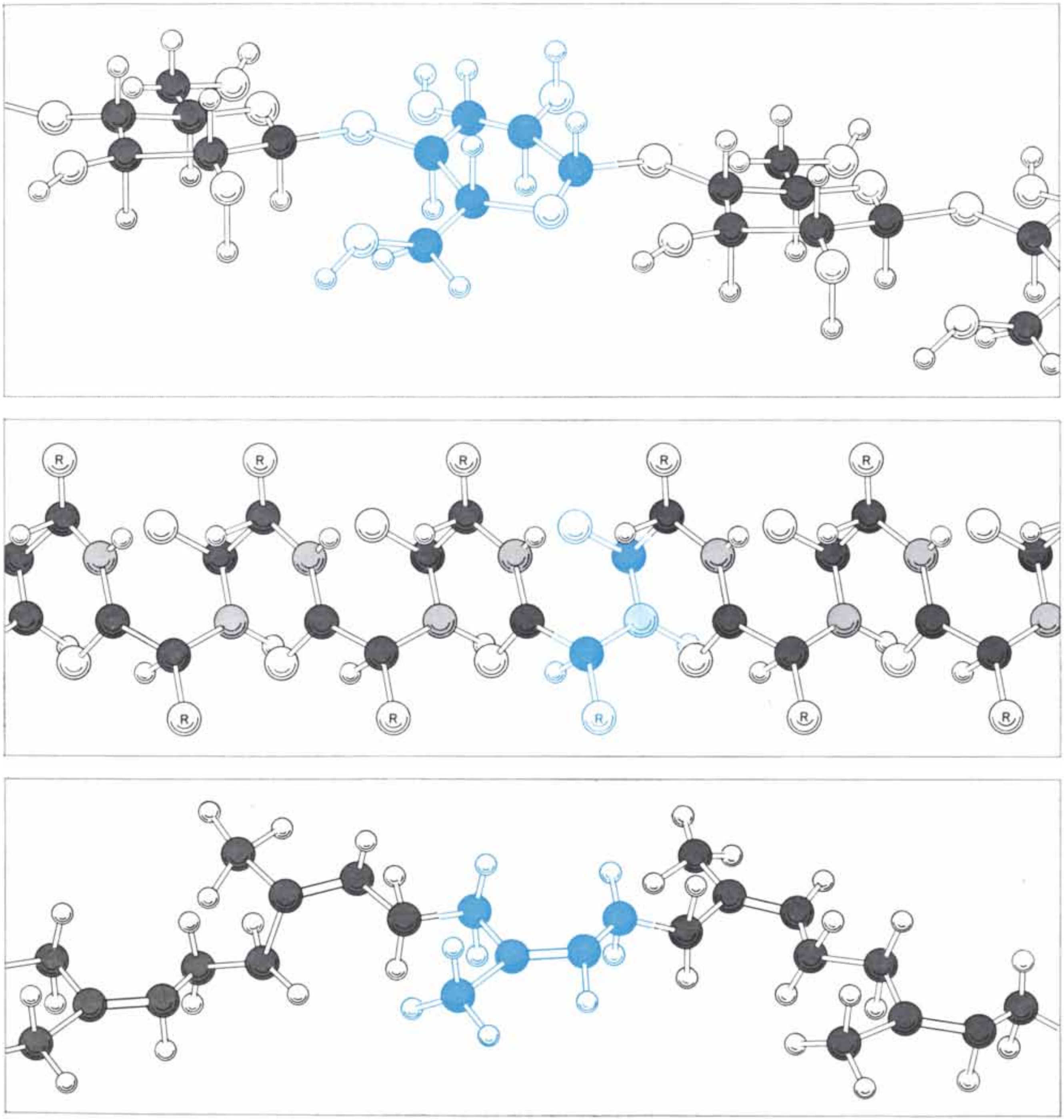
It remained for some powerful physical instruments of the 20th century—the ultracentrifuge, electron microscope, viscometer, osmometer, diffusion cell and X-ray-diffraction apparatus—to reveal the polymers in all their intricacy. Their molecules were discovered to be almost incredibly large: the molecular weights ran as high as millions of units, whereas simple organic substances such as sugar and gasoline have molecular weights in the range of only about 50 to 500. The giant molecules turned out to be composed of a large number of repeating units; they were consequently given the name "polymer," from the Greek words *poly* ("many") and *meros* ("parts"), and the building blocks were called monomers. Most polymers were found to have the form of long, flexible chains. Packed side by side in a bundle, the molecules formed a regular array with a crystalline structure. Examina-

**GROSS STRUCTURE OF A POLYMER** can be partly crystalline and partly amorphous, as shown in the photomicrograph on the opposite page. The material is a silicon polymer that has been melted, resolidified and photographed under polarized light. The radially symmetrical arrays emanating from bright centers are spherulites, or crystalline structures; other parts of the polymer show amorphous domains. The material was photographed at the General Electric Research and Development Center under the direction of F. P. Price.

tion of natural polymeric materials showed that their structure was complex—partly crystalline and partly amorphous. If the crystalline structure predominated, the material was relatively strong, rigid and resistant to heat and dissolution; if the structure was amorphous, the substance was soft, elastic, absorptive and permeable to fluids.

Having learned these ground rules, chemists undertook to synthesize artificial polymers. They soon succeeded in forming new monomers from simple and inexpensive raw materials, in stringing the monomers together efficiently into long chains, in obtaining quantitative data on the molecular weight and structure of polymers and in ascertaining how structural details influence a polymer's properties. These efforts, beginning in 1920, had led by 1940 to the establishment of industries producing synthetic fibers and numerous other polymeric materials, many of which were less expensive and superior in various ways to the natural materials after which they were modeled.

Looking ahead now, what might be done to improve the strength of organic polymers and enlarge their realms of usefulness? The properties that must be built into them to qualify them as structural materials (for buildings and vehicles) can be specified in detail: (1) rigidity sufficient to bear a load of at least



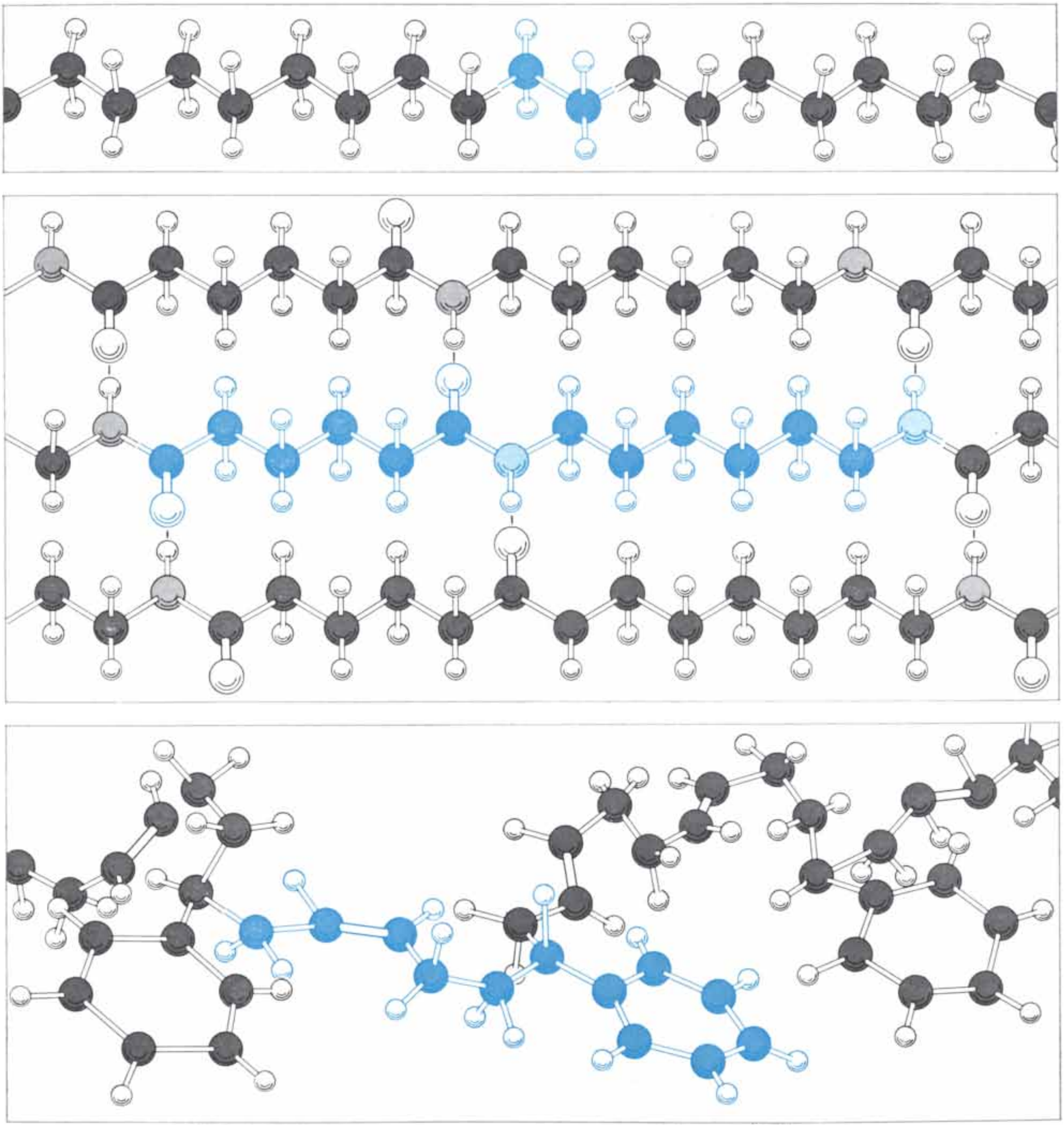
**NATURAL POLYMERS** include cellulose (*top*), animal protein (*center*) and rubber (*bottom*). Monomers are in color. Atoms are carbon (*dark*), nitrogen (*light*), oxygen (*large open circles*) and hydrogen (*small open circles*). Each *R* represents a side chain.

tensile strength of at least 100,000 pounds per square inch; (3) an elasticity of at least 10 percent (to resist breaking or tearing); (4) a melting or softening point above 500 degrees centigrade; (5) high resistance to damage by heat, radiation and corrosive chemicals, and (6) high resistance to the action of solvents and swelling agents, even at elevated temperatures.

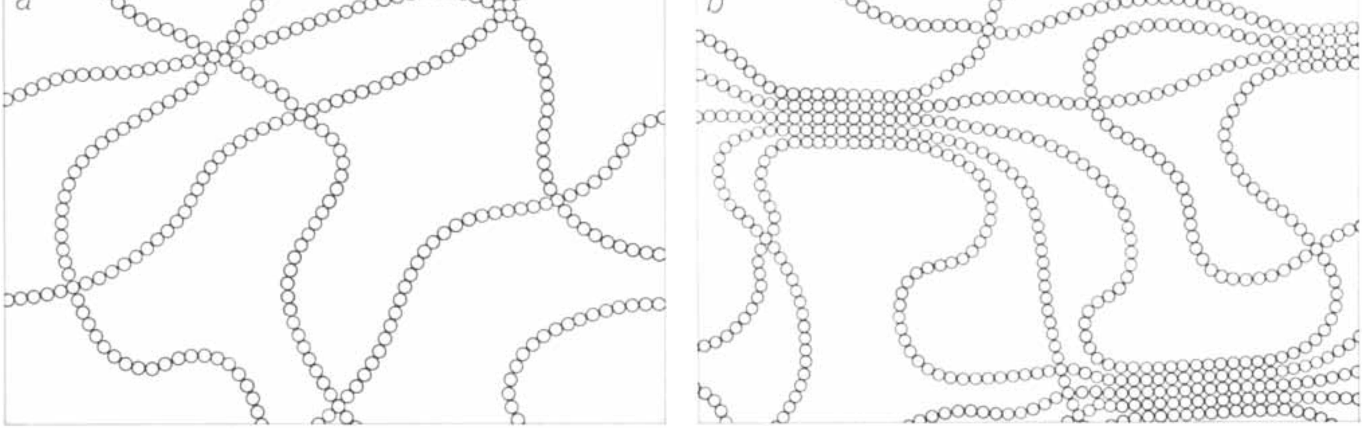
Let us examine the characteristics of

they can be exploited to strengthen the properties of such a compound. One characteristic is the capacity of the chains to organize themselves in a crystalline structure. When a polymer with a regular architecture (that is, a highly ordered arrangement of the atoms or atomic groups in the chain) is subjected to a mechanical treatment that orients the chains, they have a strong tendency to line up in parallel and form crystal-

the chains are not strong, but their large number and regular spacing give considerable rigidity to the structure, hence the material becomes hard, insoluble and resistant to softening by heat. Thus even crystallized polyethylene, whose chains are held together only by weak van der Waals forces, is a strong, tough, abrasion-resisting material with a fairly high melting point (130 degrees C.). Similarly, polypropylene, another poly-



**SYNTHETIC POLYMERS** include polyethylene (*top*), which is probably the most widely used in commercial applications, nylon (*center*), a fibrous polymer, and synthetic rubber (*bottom*). Monomers (*color*) are the basic repeating units of polymer chains.



**SYSTEMS OF POLYMER CHAINS** include amorphous arrays (*a*) and various forms of crystallization. There can be crystallization between chains (*b*) and also chain-folding, which is crystallization of a chain on itself. Chain-folding can take a laminar form

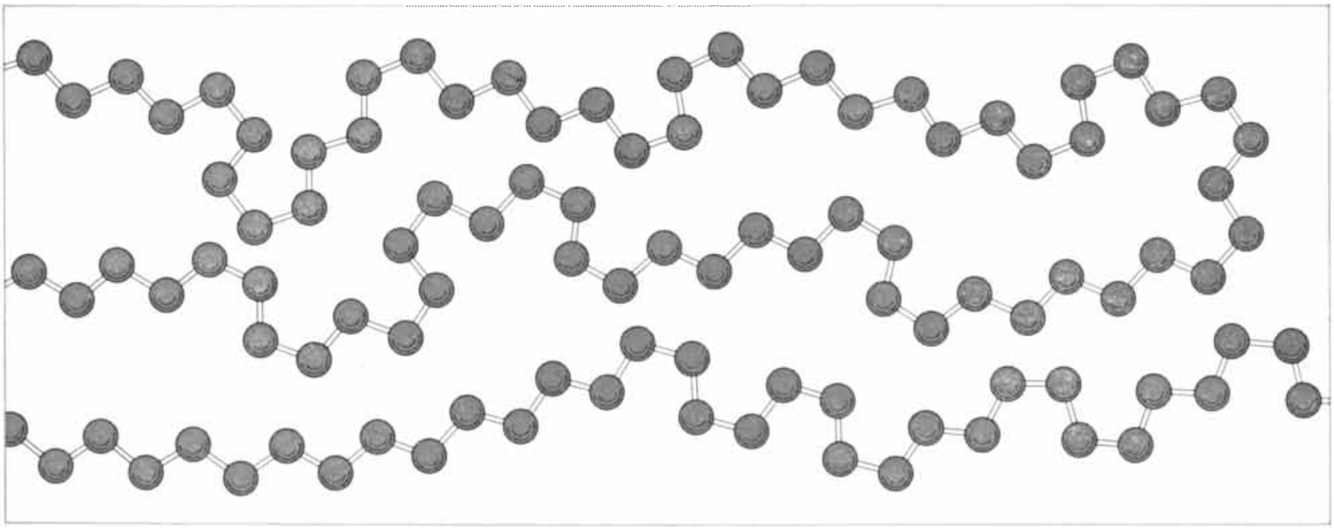
mer with a regular chain architecture, is rigid and has a melting point of 175 degrees in the crystallized form, and polystyrene is still more resistant to softening, with a melting point around 230 degrees. Even stronger and more heat-resistant materials can be obtained by crystallizing polymers that contain polar groups (groups in which there is a separation of positive and negative electric charges), as these provide stronger interchain bonding. Examples of such materials are nylon, Saran, Dacron and Mylar.

Crystallization is one of two principles that have long been applied to give strength and resistance to polymers; the other principle is chemical cross-linking of the chains. A substance such as sulfur is added to the polymer for the purpose of forming strong chemical bonds between the chains. The process is quite different from crystallization. Whereas crystallization is a physical phenomenon that depends on orientation of the chains, is not influenced by temperature and can be reversed without decomposing the polymer, cross-linking is an effect that depends on a chemical reaction rather than on physical orientation of the chains, is strongly accelerated by elevating the temperature and is not reversible; because of the strong and randomly located bonds connecting the chains the material is not merely softened but breaks down altogether at temperatures high enough to melt it.

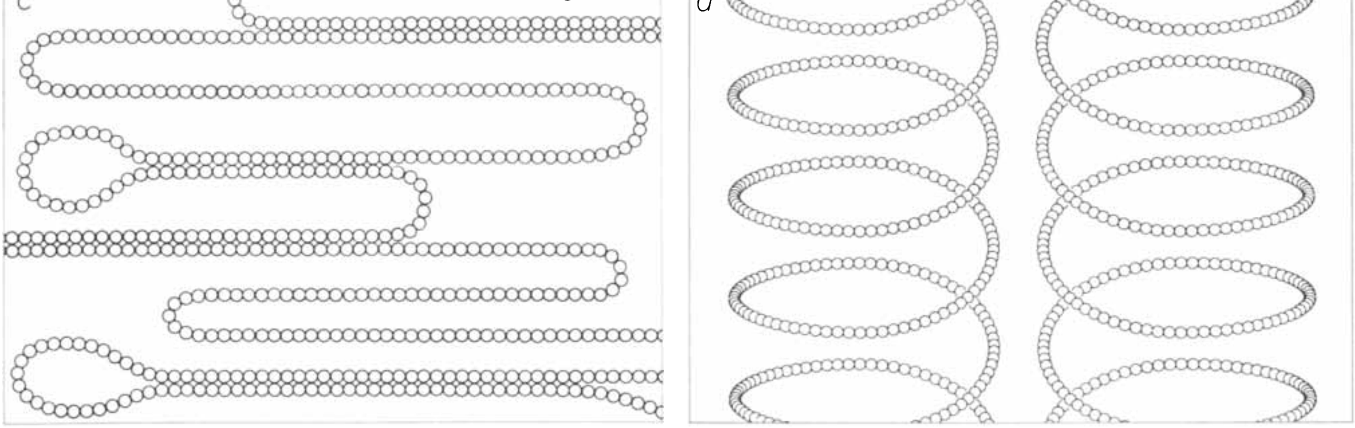
A good example of a cross-linked polymer is rubber. In its most common form (the vulcanized rubber of tires) the chains are linked by a certain quota of sulfur atoms that leaves the rubber elastic. By adding more cross-links one can progressively stiffen the piece until it becomes the hard substance called ebonite—a material that is very rigid, has an extremely high softening temperature and is completely insoluble and unswellable.

Ebonite, one of the oldest of the "plastics" (actually it is not a plastic but a thermosetting material), is a prototype of many other cross-linked polymers. These include various hard rubbers, formaldehyde-based products, polyesters and thermoset resins that are hardened by grafting styrene onto a polyester backbone containing aliphatic double bonds.

If crystallization and cross-linking were the only available means of strengthening and toughening organic polymers, there would be little hope of synthesizing a polymer that would fill the bill as a structural material. Apparently the most that could be achieved by crystallization and cross-linking, even in combination, is a rigidity modulus of around 450,000 pounds per square inch and a melting temperature of about 350 degrees C.—far short of the specifica-



**FLEXIBLE CHAIN** of a polymer is represented by polyethylene above melting temperature. For clarity only carbon atoms are shown. Such a chain is flexible because its segments are linked by rotatable bonds. A polymer of such chains can be strengthened by orientation and crystallization, which are shown in the top illustration on these two pages, or by cross-linking (*top of page 154*).



(*c*) or a helical form (*d*); the helical form can be either left-handed or right-handed. A predominantly amorphous polymer is soft, elastic and permeable to fluids; a polymer with a predominantly crystalline structure is appreciably stronger and more rigid.

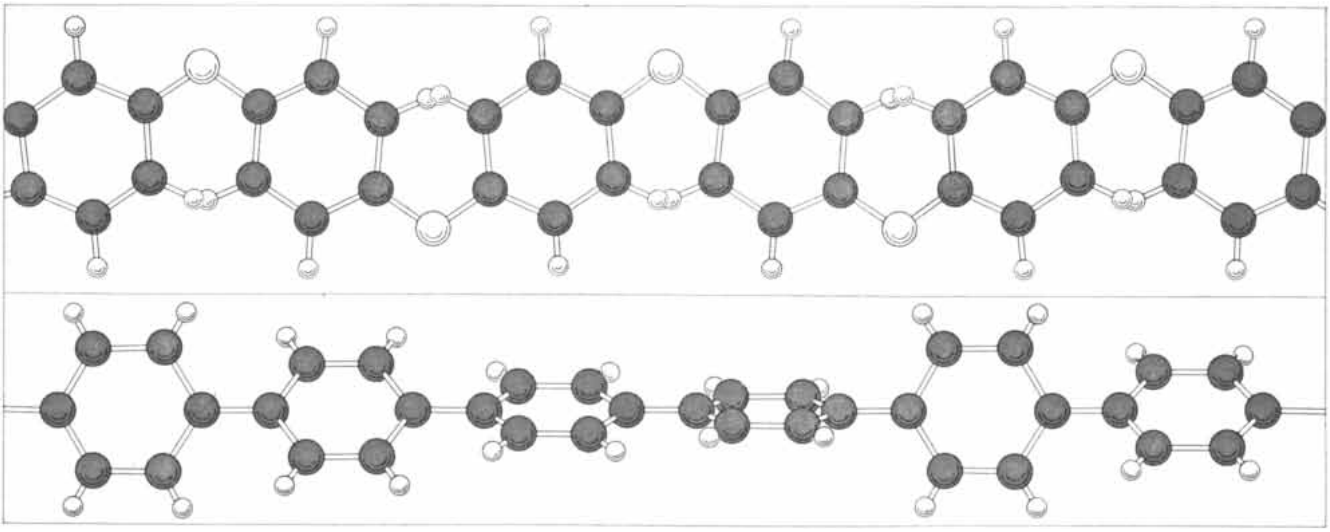
tions required for a building material. There is, however, a third principle, now under active investigation, that holds high promise.

The materials I have been discussing are all composed of inherently flexible chains. The segments of these chains are linked by rotatable bonds and can easily bend, kink or fold on one another (like the jackknifing of a tractor-trailer). Hence the only way to achieve stiffness and strength is to pack the chains together in rigid assemblies, either through crystallization or cross-linking. Obviously the rigidity could be enhanced by assembling chains that were themselves intrinsically stiff.

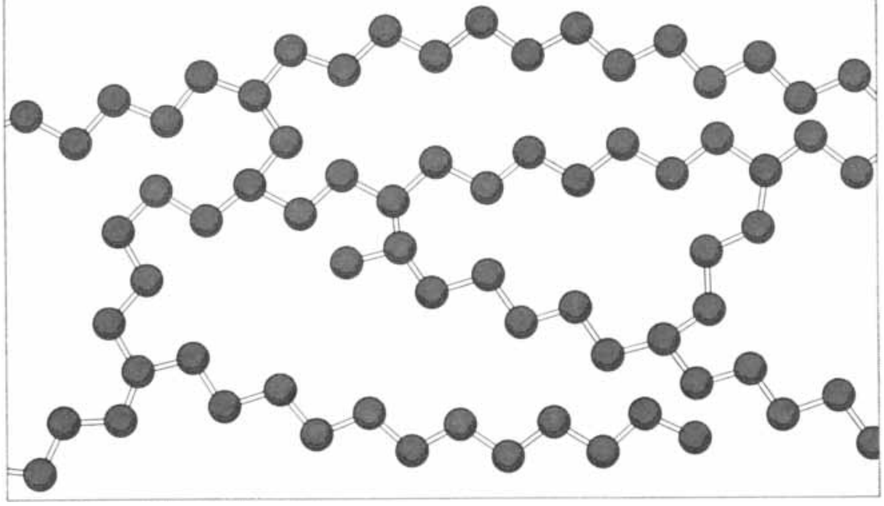
There are several possible ways to stiffen a polymeric chain. One is to hang bulky groups of atoms on the chain to restrict bending. This principle is exemplified by polystyrene. In the polystyrene molecule benzene rings are attached to the carbon backbone of the chain [*see illustration below*]. The consequent stiffening is sufficient to make polystyrene a hard plastic with a fairly high softening point (90 degrees C.), even though its chains are not cross-linked or packed in a crystalline array. The absence of crystallinity makes the material completely transparent, and the absence of cross-linking makes it readily moldable. Another example is polymethylmethacrylate (Lucite), which, by virtue of the methyl ($CH_3$) and methacrylate ($COOCH_3$) groups attached to carbon atoms along the chain, is a hard, brilliantly transparent material with a softening point of 95 degrees.

Materials stiffened by attaching bulky groups to the chain have a weakness, however: they are fairly easy to dissolve and are subject to swelling. It seems that the bulky groups allow ready penetration of the system by solvents and swelling agents. Because of this behavior, research attention is focused on ways to stiffen the backbone of the chain itself.

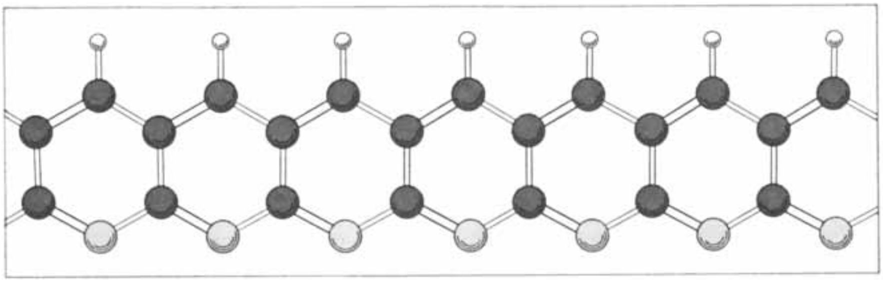
Cellulose, the structural framework of wood, is a classic example of a polymer with an intrinsically stiff backbone. Its chain molecule is a string of condensed glucose (sugar) molecules, which are ring-shaped. Building on this chain, chemists long ago produced cellulose acetate and cellulose nitrate, which are hard, transparent, high-melting and amorphous thermoplastic resins. In these compounds the acetate ($OCOCH_3$) and nitrate ($ONO_2$) groups are attached irregularly along the chain and account for the absence of crystallinity. The attached groups tend, of course, to give the compounds the weaknesses I have mentioned: cellulose acetate is rather sensitive to the action of solvents and swelling agents, and cellulose nitrate, al-



**INFLEXIBLE CHAINS** provide rigidity in a polymeric material. At top is a chain of polystyrene that has been made relatively inflexible by the addition of benzene rings to the carbon backbone of the chain; because of them the molecules cannot bend sharply and so remain relatively straight. At bottom is an intrinsically stiff chain of polyphenylene; it can twist on its bonds but cannot bend.



**CROSS-LINKING** of polymer chains is achieved by adding a substance to a polymer in order to induce the formation of strong bonds between chains. The cross-links usually form at random places between chains. Hydrogen atoms of the chain have been omitted for clarity.



**"LADDER" POLYMER** achieves rigidity by a technique of bonding ring structures at two adjacent carbon atoms. The effect resembles that of hanging a door by two hinges. As a result of the arrangement adjacent rings of the polymer chain have a restricted mobility.

though less sensitive, is still dissolvable by some solvents.

Chemists are now experimenting with other monomers that, like glucose, contain ring-shaped groups of atoms and therefore have intrinsic rigidity [*see bottom illustration on preceding page*]. With these monomers they have synthesized a number of hard polymers endowed with strong properties: some of the materials can be exposed to temperatures up to 500 degrees C. for long periods without softening or deterioration and are completely insoluble in all organic solvents at temperatures up to 300 degrees.

One promising approach is based on manipulation of the polyphenylene chains. The monomer, phenylene, comes from benzene and has the ring structure. In the chain the phenylene rings are linked by carbon-carbon single bonds that do not allow sufficient rotation to kink or bend the chain, and as a result the chain cannot fold even at rather high temperatures. The polyphenylenes are rigid and high-melting, have a pronounced tendency to crystallize and are highly insoluble. So far, however, the inherent stiffness of the phenylene chain has not been fully capitalized on, because no way has yet been found to build up its polymers into sufficiently long chains.

Another interesting group of polymers based on aromatic chains (chains made up of benzene-type rings) are the "ladder polymers." Produced by a series of stages involving the progressive heating of an unsaturated precursor (typically polyacrylonitrile or 1,2-polybutadiene), these polymers correspond to a "chain" of graphite, with one carbon atom in each ring replaced by nitrogen [*see lower illustration above*]. The materials are hard and completely insoluble and unmeltable.

We see, then, that there are many possibilities for synthesizing long, stiff chains, and that the resulting polymers possess the valuable properties predicted for this type of construction. The next question is: Can we obtain even better results by combining two or more of the three principles (crystallization, cross-linking and stiff chains)?

been accomplished by each of the single approaches and by combinations of two principles. The crystallization method has produced a large number of thermoplastic materials, particularly fibers and films; they include polyethylene, polypropylene, polyoxymethylene, polyvinyl alcohol, polyvinyl chloride, polyvinylidene chloride and polyamides such as 6 nylon and 66 nylon. The cross-linking approach has yielded the hard rubbers, thermosetting resins, polyesters, network polyepoxides, polyurethanes and the resins and plastics formed by compounding formaldehyde with urea, melamine or phenol. In the group of polymers based on stiff chains are polystyrene, polystyrene derivatives, chain polyepoxides, polymethylmethacrylate, polycarbonates, polyesters, polyethers and other products.

How much can be gained by combining the stiffening techniques? Consider first the combination of crystallization and cross-linking. The principal materials produced by this combination are the crystallizable rubbers: natural rubber, 1,4-cis-polybutadiene, polyisoprene and neoprene. If a great many cross-links are introduced, the polymer loses its crystallinity and becomes amorphous; ebonite is a case in point. To add stiffness to rubbers and other elastomers that do not crystallize readily, a solid filler is usually introduced. The particles of the filler (a hard, finely divided material such as carbon black, silica or alumina) attach themselves strongly to the polymer chains by adsorption and serve to stiffen the chains by immobilizing the segments; in effect they produce a kind of crystallization of the system.

Crystallinity and cross-linking in combination can raise the rigidity of organic polymers to a modulus of 450,000 pounds per square inch and the melting temperature to 350 degrees C., as I have already mentioned, but that seems to be about the limit.

What if we combine crystallization with the use of intrinsically stiff chains? Again the combination results in substantial gains. Cellulose provides a good illustration. Its rigid chains give a material high tensile strength and a high melting point even at a relatively low degree of crystallinity. With enhancement of the chain stiffness and the crystallinity, compounds based on the cellulose backbone can be built up to polymers that are extremely rigid, do not melt at all and are soluble only in a very small number of particularly potent solvents. Cellulose's excellent potentialities for

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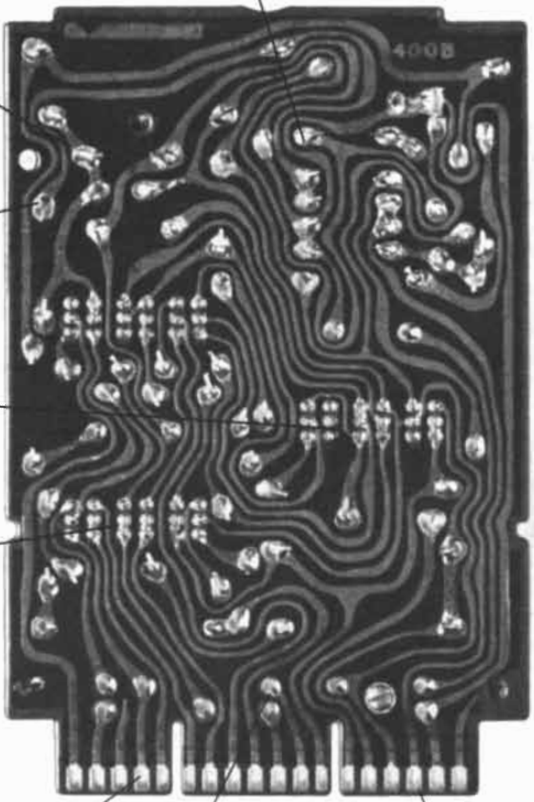

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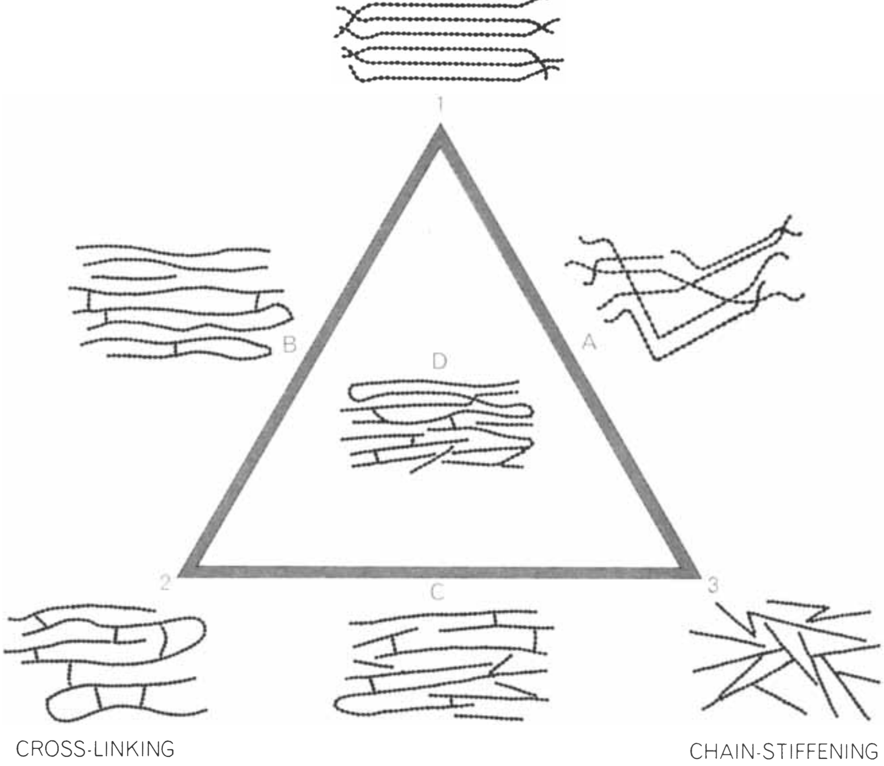

| LOCATION | POLYMER CHARACTERISTICS | EXAMPLES | USES |
|---|---|---|---|
| 1 | Flexible and crystallizable chains | POLYETHYLENE | Pails, pipes, thin films |
| | | POLYPROPYLENE | Steering wheels |
| | | POLYVINYL CHLORIDE | Plastic pipes and sidings |
| | | NYLON | Stockings, shirts, dresses, coats |
| 2 | Cross-linked, amorphous networks of flexible chains | PHENOL-FORMALDEHYDE | Television casings, Telephone receivers |
| | | CURED RUBBER | Tires, transport belts, hoses |
| | | STYRENATED POLYESTER | Finish on automobiles and appliances |
| 3 | Rigid chains | POLYIMIDES | High-temperature insulation |
| | | LADDER MOLECULES | Heat shields |
| A | Crystalline domains in a viscous network | TERYLENE (DACRON) | Fibers and films |
| | | CELLULOSE ACETATE | Fibers and films |
| B | Moderate cross-linking with some crystallinity | NEOPRENE | Oil-resistant rubber goods |
| | | POLYISOPRENE | Particularly resilient rubber goods |
| C | Rigid chains, partly cross-linked | HEAT-RESISTANT MATERIALS | Jet and rocket engines and plasma technology |
| D | Crystalline domains with rigid chains between them and cross-linking between chains | MATERIALS OF HIGH STRENGTH AND TEMPERATURE RESISTANCE | Buildings and vehicles |

**COMBINED FEATURES** make it possible to achieve various properties with polymers. Each corner of the triangle represents one of the three basic principles for making a polymer rigid and temperature resistant; the sides and the center of the triangle indicate various combinations of the principles. The chart at bottom gives examples of the possibilities.

en rise to many spectacularly successful products. One example of an effective merger of chain stiffness and crystallinity is cellulose triacetate: the polymer's capacity to crystallize endows it with several advantages over ordinary cellulose acetate, notably greater resistance to organic solvents and improved thermosetting characteristics.

Terylene is another illustration of the efficacy of combining the two principles. In this crystalline polymer (chemically described as polyethylene glycol terephthalate) the chains are only moderately stiff and are held together by extremely weak lateral forces because no hydrogen bonds are available. Even so, the combination of crystallization and chain stiffness suffices to give the fiber high strength and the high melting point of 260 degrees C.

The third possible pairing of principles—the combination of chain stiffness and cross-linking—has also been explored, and this too has yielded encouraging results. For example, stiff-chain epoxy polymers have been "cured" to greater rigidity and resistance to softening by building up the number of cross-links between the chains.

Since combinations of two of the three strengthening principles have proved effective in enhancing polymer properties, chemists are naturally hopeful of achieving even better results by combining all three principles [*see illustration at left*]. Much exploratory work is now being done along that line, and already certain interesting successes have been obtained. One of these is the application of the three principles to improve the properties of cotton and rayon. The fiber is given two treatments: a mechanical treatment to crystallize the stiff cellulose chains and treatment with a chemical agent that introduces cross-links. It has been found that the cross-linking substantially improves the recovery power and wrinkle-resistance of fabrics made from such fibers, without diminishing their other desirable properties. Similarly, promising results have been obtained in strengthening polymers of the epoxy and urethane types. In these systems, starting with stiff chains that have been cross-linked, the experimenters add fillers to produce the equivalent of crystallization.

There is good reason to expect that thorough and systematic exploration of the new threefold attack will lead to many new and interesting organic polymers, perhaps even to superior materials for building our houses and vehicles.

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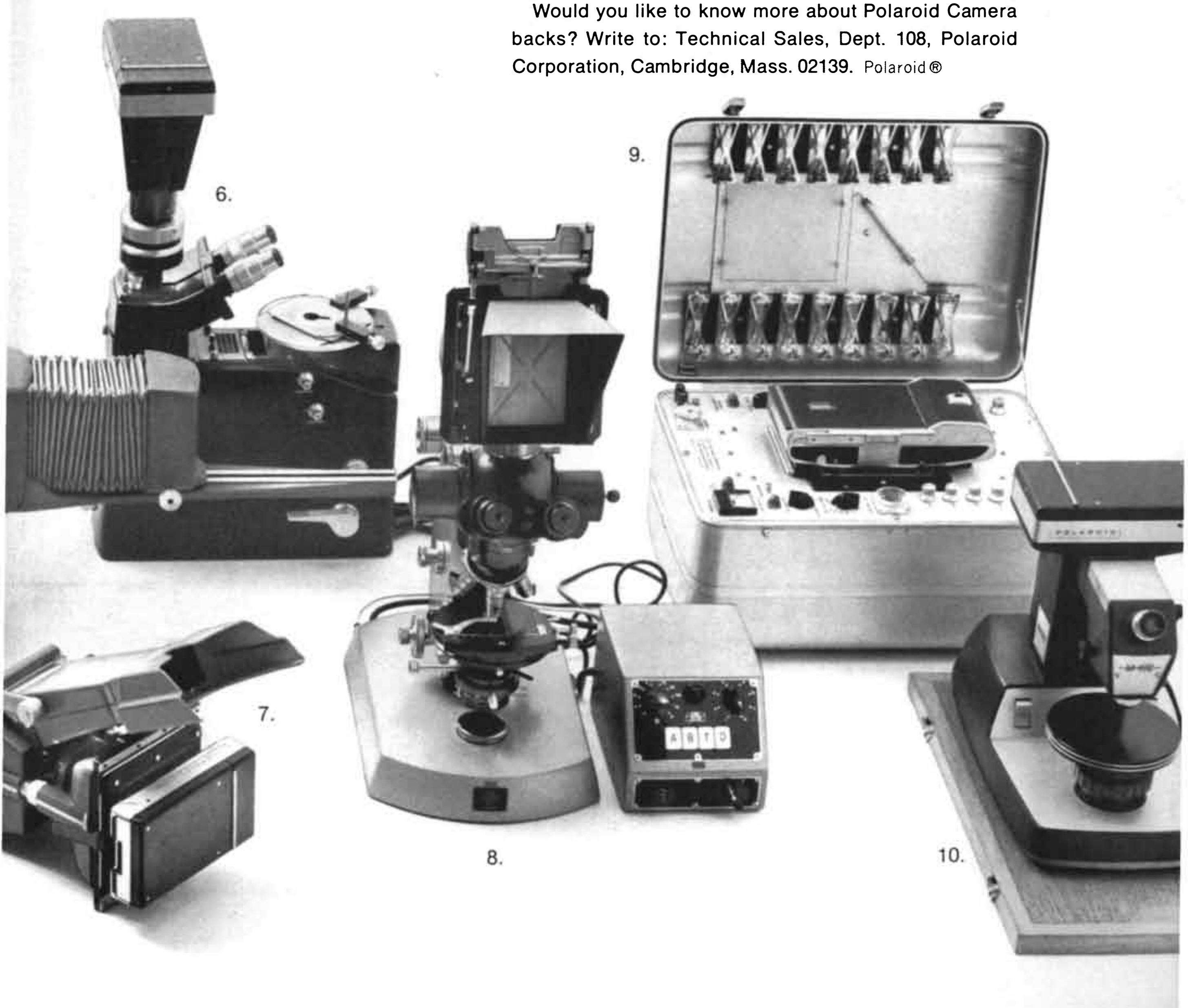
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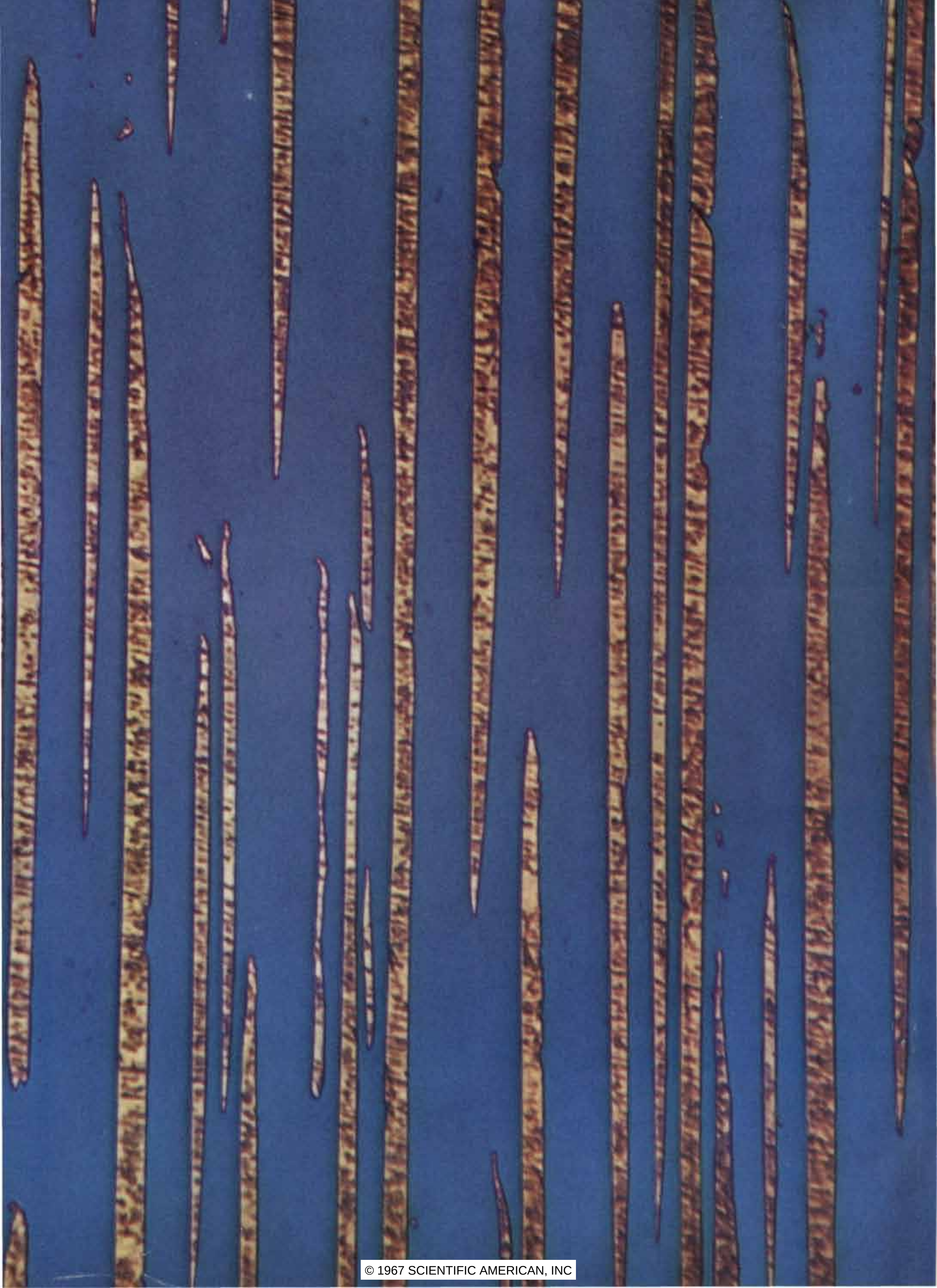


# THE NATURE OF COMPOSITE MATERIALS

## Metals, ceramics, glasses and polymers can be combined in materials that have unique properties of their own. Nature uses this principle in wood and bone; man applies it in a new family of supermaterials

by Anthony Kelly

Until quite recently a composite material was regarded simply as a combination of two materials. It is still that, but in modern technology it has acquired a broader significance: the combination has its own distinctive properties. In terms of strength or resistance to heat or some other desirable quality it is better than either of the components alone or radically different from either of them.

This concept of composite materials is leading to the design and manufacture of a new range of structural materials that may bring about far-reaching changes in engineering and construction. The principal attraction of composite materials is that they are lighter, stiffer and stronger than anything previously made. At present they are used mainly to meet the severe demands of supersonic flight, the exploration of space and ventures into the deep waters of the oceans. Someday they will be put to less exotic uses, such as the construction of buildings. When that happens, one can expect to see square corners and heavy masonry give way to airy domes and delicate tracery.

Like synthetic polymers, modern composite materials imitate nature. Wood, for example, is a composite consisting of cellulose and lignin. Cellulose fibers are strong in tension but flexible; lignin acts to cement them together and endow the material with stiffness. Bone is a composite of the strong but soft protein collagen and the hard but brittle mineral apatite. Modern composites achieve similar results even more effectively by combining the strong fibers of a material such as carbon in a soft matrix such as epoxy resin. A more familiar example is fiber glass, which consists of glass fibers in resin.

Such materials go well beyond the older concept of composites, in which two or more materials were combined to rectify some shortcoming of a particularly useful component. For example, early cannons, which had barrels made of wood, were bound with brass because a hollow cylinder of wood easily bursts under internal pressure. By the same token, ordinary steel is normally covered with paint because of steel's strong affinity for oxygen. In this older sense nearly all engineering materials are composites of some kind.

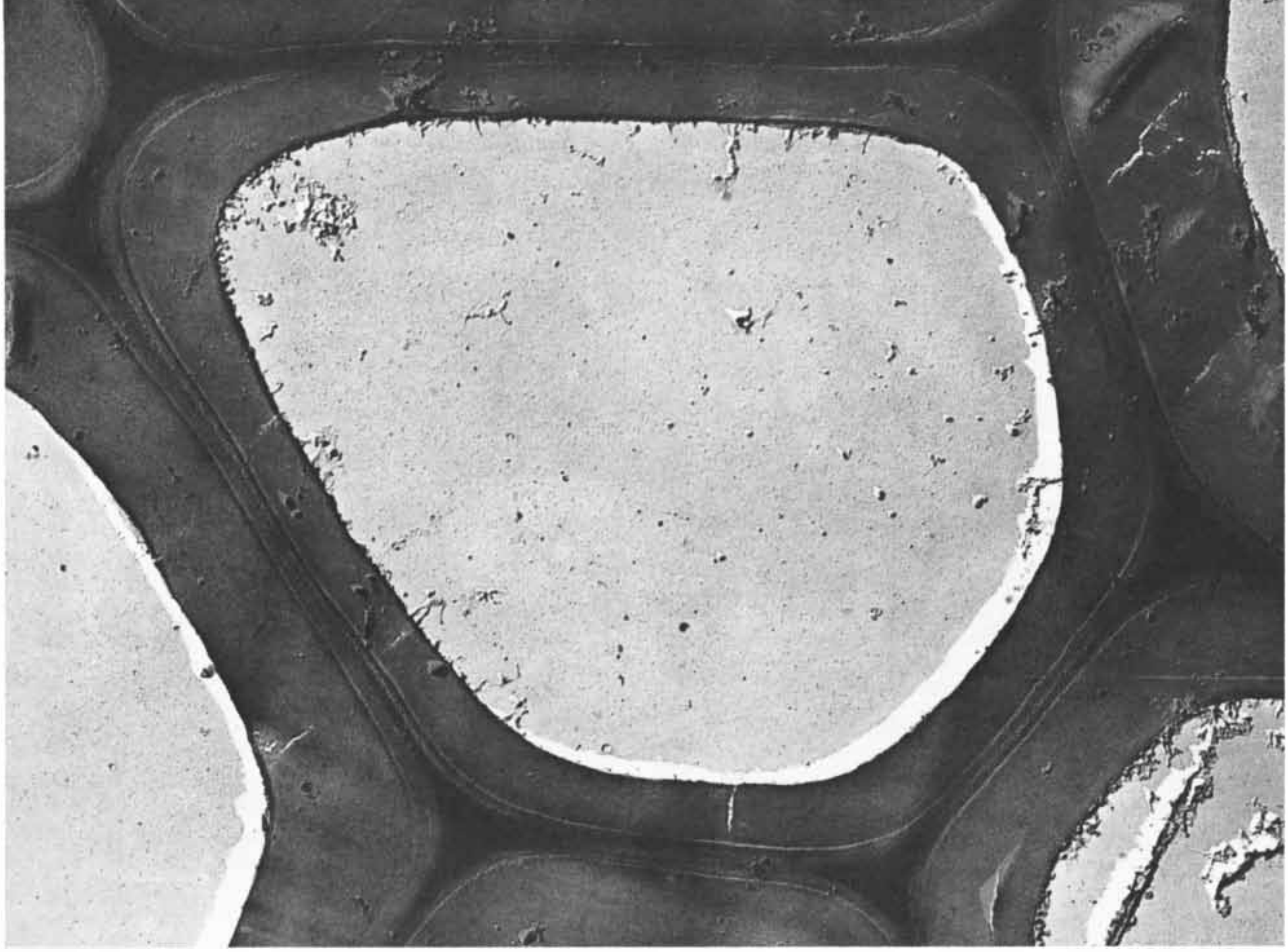
An elementary example of the newer concept of composites is the bimetallic strip used in such devices as the thermostat. The strip might be made of a flat piece of brass and a similar piece of iron. If the two pieces were separate and were heated simultaneously, the brass would expand more than the iron. If the two pieces are welded together and the composite is heated, the greater expansion of the brass forces the iron to bend, and the bending of the iron forces the brass to bend [*see top illustration on page 165*]. The bending can be used to indicate temperature or to activate an on-off switch.

This example illustrates two points about modern composites. The first is that either material alone would be useless in the application; the combination has an entirely new property. The second is that the two components act together to equalize their different strains. This behavior, called combined action, is most important in the design of composite materials, as we shall see.

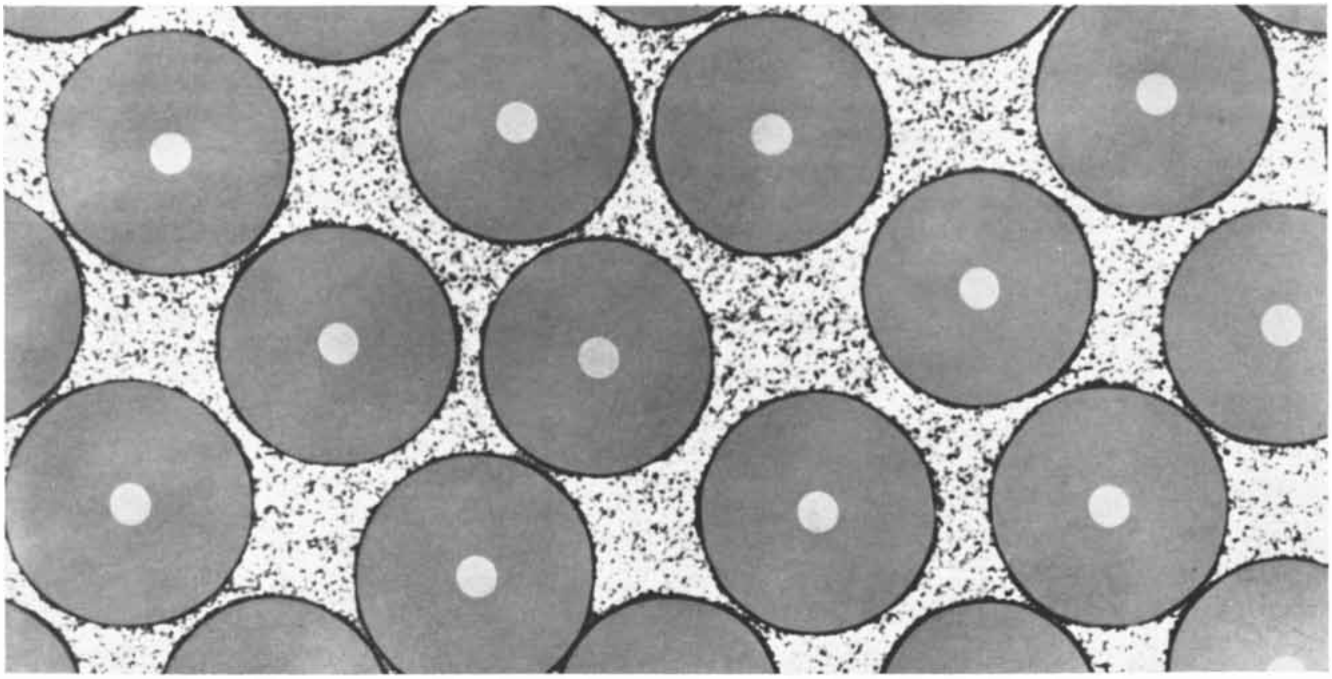
For an engineer designing a structure such as a supersonic aircraft an ideal load-bearing member is made of something that is very stiff, very light, very strong in tension and not easily corroded; that expands very little with changes in temperature, and that has a high resistance to abrasion and a high melting point. Because stiffness and lightness and strength and lightness are required together in contemporary applications, it is the stiffness per unit weight and the strength per unit weight that must always be considered. The manner in which several materials meet these considerations under laboratory testing is set forth in the bottom illustration on page 165. One sees there that the strong materials that are also light and stiff are ceramics: materials such as glass, graphite, sapphire, Carborundum and boron. Metals, which one usually associates with high strength, do quite poorly by comparison. Even the strongest steel—itself more than seven times stronger than normal steel—is an unimpressive material on a unit-weight basis. The resins and polymers do well in terms of strength to weight but badly (much worse than metals) in terms of stiffness to weight.

Glass, Carborundum and graphite not only are superior to the common metals in strength and stiffness per unit weight but also have high melting points and do not expand significantly when they are heated. Moreover, they can be

**FIBER-REINFORCED METAL** in the photomicrograph on the opposite page consists of niobium carbide "whiskers" in a matrix of niobium; enlargement is 2,000 diameters. A whisker is a single, high-strength crystal. These whiskers were grown by careful solidification of a melted alloy of niobium and carbon; part of the alloy became the whiskers and part the matrix. This "eutectic," a name derived from the Greek word for "easily melted," was made at United Aircraft Research Laboratories by Frank Lemkey and Michael J. Salkind.



NATURAL COMPOSITE is wood, consisting of cellulose fibers in a matrix of lignin. In this electron micrograph, which was made at the New York State College of Forestry at Syracuse University, a cross section of aspen is enlarged 11,900 diameters. The darkest material is lignin, the slightly less dark material the wall of a cellulosic cell, and the pale central object the lumen, or cell cavity.



MAN-MADE COMPOSITE, produced at United Aircraft Research Laboratories, consists of boron fibers in aluminum. Fibers (*dark circles*) are each .004 inch in diameter. The lighter circle in each of the fibers was made by the wire on which the boron was formed.

such as sand, coke and coal. Why, then, have they been so little used as structural materials?

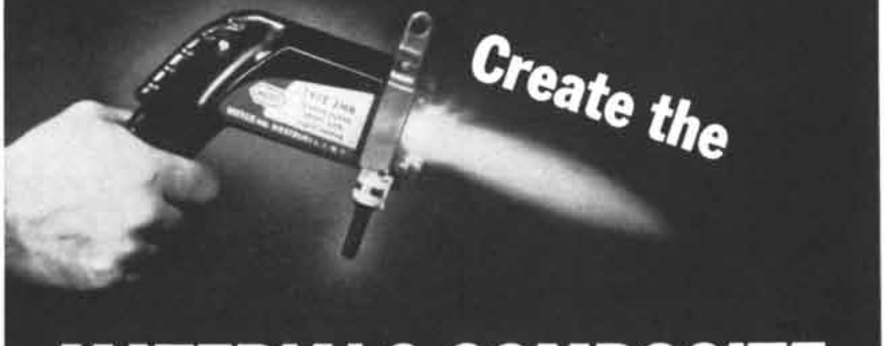
The reason, which held until the discovery of the composite principle, is that their high strength is realized only under rather special conditions. The most important condition is that the specimen have no internal cracks and have a very smooth surface that is also free from cracks, small notches and steps. The significance of cracks and surface dimples can be demonstrated by a comparison of three common materials—strong steel, aluminum and glass—for their resistance to the propagation of cracks.

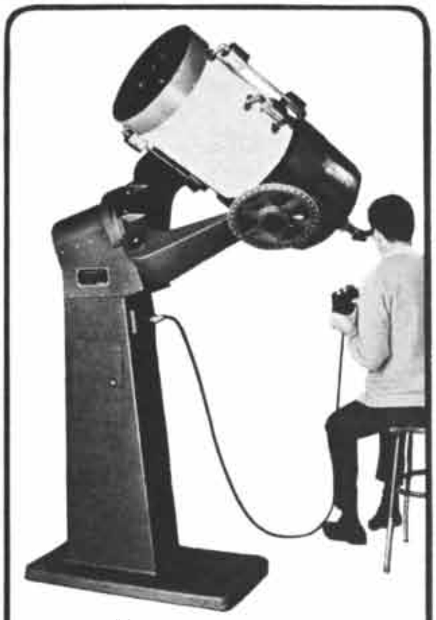
Using as a test the size of crack that would cause immediate breakage of a sheet of the material if it were stressed to 100,000 pounds per square inch, one finds enormous differences. Strong steel can tolerate cracks or machined notches or other sharp surface irregularities up to an inch in depth. In aluminum the crack can be no deeper than 1/64 inch. Glass breaks if the crack is deeper than 1/10,000 inch.

The measure of a material's ability to retain its strength in the presence of cracks is determined by what is called the work of fracture of the material, which is to say the energy required to break it. Glass has a very small work of fracture and well-designed strong steel a very high one. The inherently strong materials such as silicon carbide, boron and graphite all behave somewhat like glass: their work of fracture is small and so they are quite vulnerable to the presence of cracks.

Metals are normally used to bear large stresses because they can accommodate themselves to cracks. With a metal the engineer obtains high strength without having to take extreme care to eliminate all but the tiniest cracks. Polymeric materials such as polyethylene are rather like metals in resistance to cracks, although they will not take as much stress as metals.

The basic chemical reason metals and polymers are so much more resistant to cracks than ceramics are is that the interatomic forces in metals and the intermolecular forces in polymers do not depend on a particular directional alignment to achieve strength. Moreover, the chemical bonds of metals and polymers are unsaturated, that is, the atoms or molecules of such materials are readily capable of forming new bonds. Ceramics, on the other hand, have highly oriented forces and saturated bonds. In metals and polymers atoms or molecules

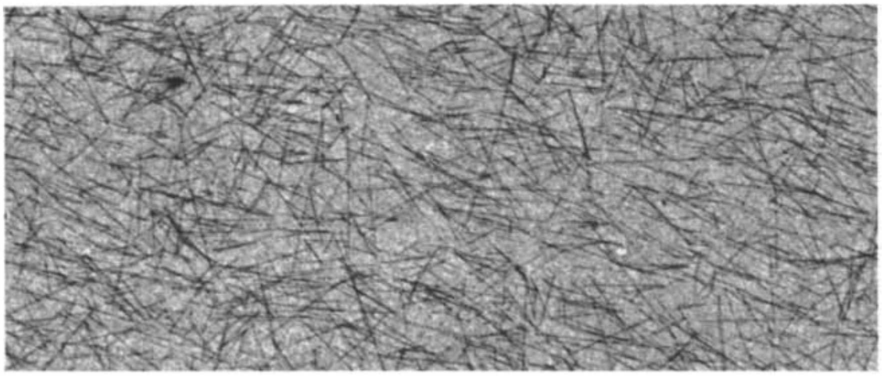




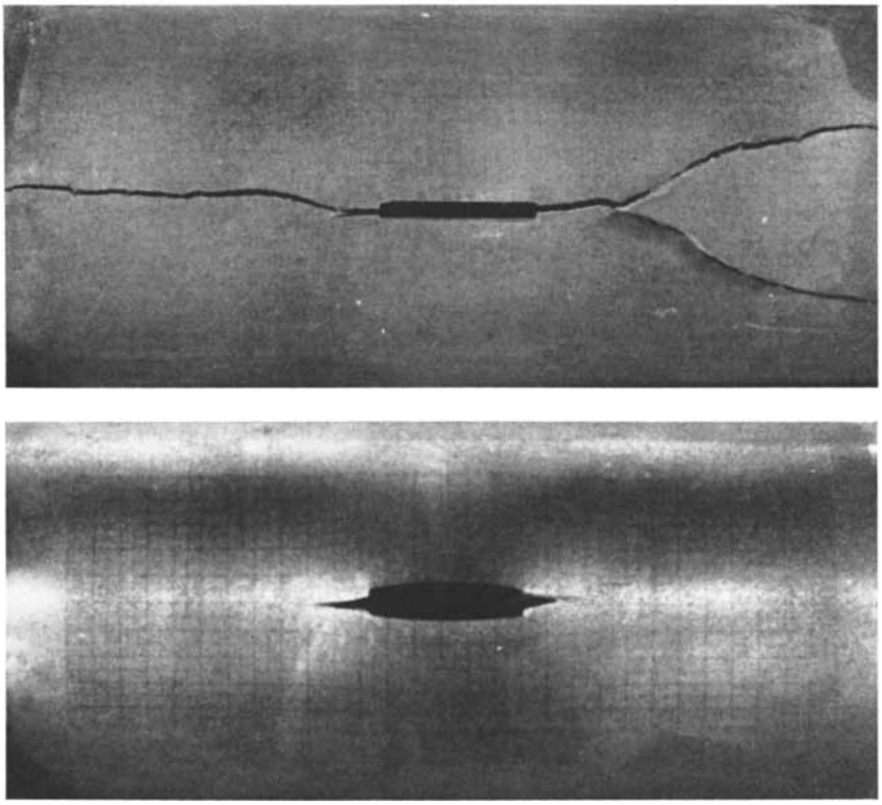
ing edge of a crack. The crack therefore cannot penetrate the internal structure of a metal or polymer as easily as it can the structure of a ceramic; a much larger stress is needed to make a crack run through a metal or a polymer and divide it into two pieces.

The familiar forms of ceramics are represented by glass, chalk and sand; by abrasive powders such as corundum and Carborundum, and by gems such as diamond and ruby. It is because ceramic crystals are so vulnerable to cracks that ceramic materials are often used in the easily reduced. Even as a powder they scratch steel because in fact they are stronger than steel.

In sum, if a ceramic material is unscratched, it can be very strong. If it is flawed in any way, however, it breaks easily. The lack of resistance to cracks is called brittleness. Ceramics are usually fragile because ceramic crystals are almost always marred by cracks or surface irregularities. Even if they are not, such imperfections can be introduced all too readily [*see top illustration on page 166*].



**FIBER GLASS** consists of a mat of glass fibers, which are revealed by X rays in this radiograph, in a matrix of resin. Fiber glass is the most widely produced of man-made composites.



**LAMINATED STEEL** can retard cracks. When pressure vessels were made to burst, one of standard steel (*top*) developed longer and larger cracks than one made of laminated steel (*bottom*), which consisted of steel sheets bonded together. Slots were made before testing as built-in defects and were then sealed on the inside so that the vessels could be burst.

ern composite material it is necessary to divide it into small pieces, so that any cracks present cannot find a continuous path through the material, and to bind the pieces together in a matrix. The ceramic is often put into the composite in the form of fibers. The properties of the matrix are of vital importance. First, it must not damage the fibers by scratching them, which would introduce cracks. Second, it must act as the medium by which stress is transmitted to the fibers; it should be plastic and adhesive so that it holds the fibers much as deep, soft mud holds one's leg when one steps into it. Third, the matrix must deflect and control cracks in the composite itself.

All the required mechanical properties of a matrix are met by a polymer or a metal such as aluminum or copper. Such a matrix is soft, which is to say weak in shear, and so it does not scratch the fibers. To carry out its other two functions the matrix needs qualities that are somewhat at odds with one another and so call for compromise.

To perceive how the matrix performs those functions the reader must bear in mind the difference between stress and strain. Stress is the externally applied force; it is usually measured in pounds per square inch. Strain is the distortion of the material when it is under stress; it is expressed in terms of the change in the original shape of the material.

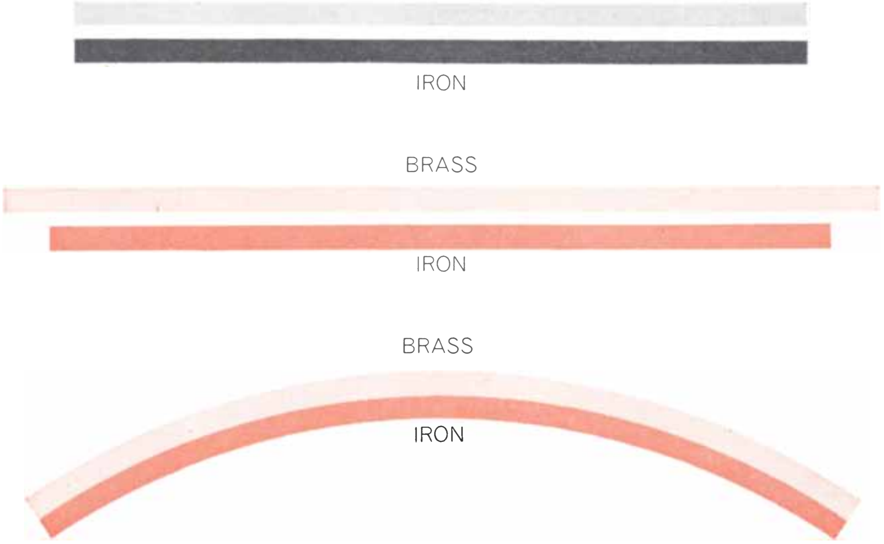
Let us now consider more closely the function of the matrix in transmitting stress. The composites of the highest strength contain aligned fibers. If such a composite is stretched parallel with the fibers, the principle of combined action comes into play, so that the strains in the fiber and in the matrix are virtually equal. One chooses a matrix that yields or flows in a plastic manner, so that when the fibers and the matrix are under equal strain the stress within the fibers is enormously greater than it is in the matrix. The difference is so pronounced that in working out the breaking strength of the composite the contribution of the matrix can be regarded as negligible.

When the fibers are highly stressed, some that have cracks will break. The beauty of a composite material is that such a crack will usually be unimportant. A close look at the leading edge of a crack in such a composite shows that the propagation of the crack through the brittle reinforcing material is hindered by the softness of the matrix [*see bottom illustration on page 166*].

Two other effects prevent cracks from running through a composite material.

fibers may fail, they do not all do so in one plane. To make a crack extend all the way through the material it would therefore be necessary to pull the fibers out of the matrix one by one as they broke. Work must be done by the applied stress in pulling out the fibers against the holding force of the matrix, and so the resistance to crack propagation is increased. The "pull out" work, which makes a large contribution to the work of fracture in composites consisting of brittle fibers in resin, is a true composite property: it cannot be attributed to either component alone.

The second crack-controlling effect is achieved by regulating the degree of adhesion between the fibers and the matrix. If the adhesion is low, the material is weak in a direction at right angles to the fibers. This is an advantage, however, if a crack starts to run at right angles to the fibers; the crack is deflected along the weak interface and rendered harmless as far as the desirable properties parallel to the fibers are concerned.

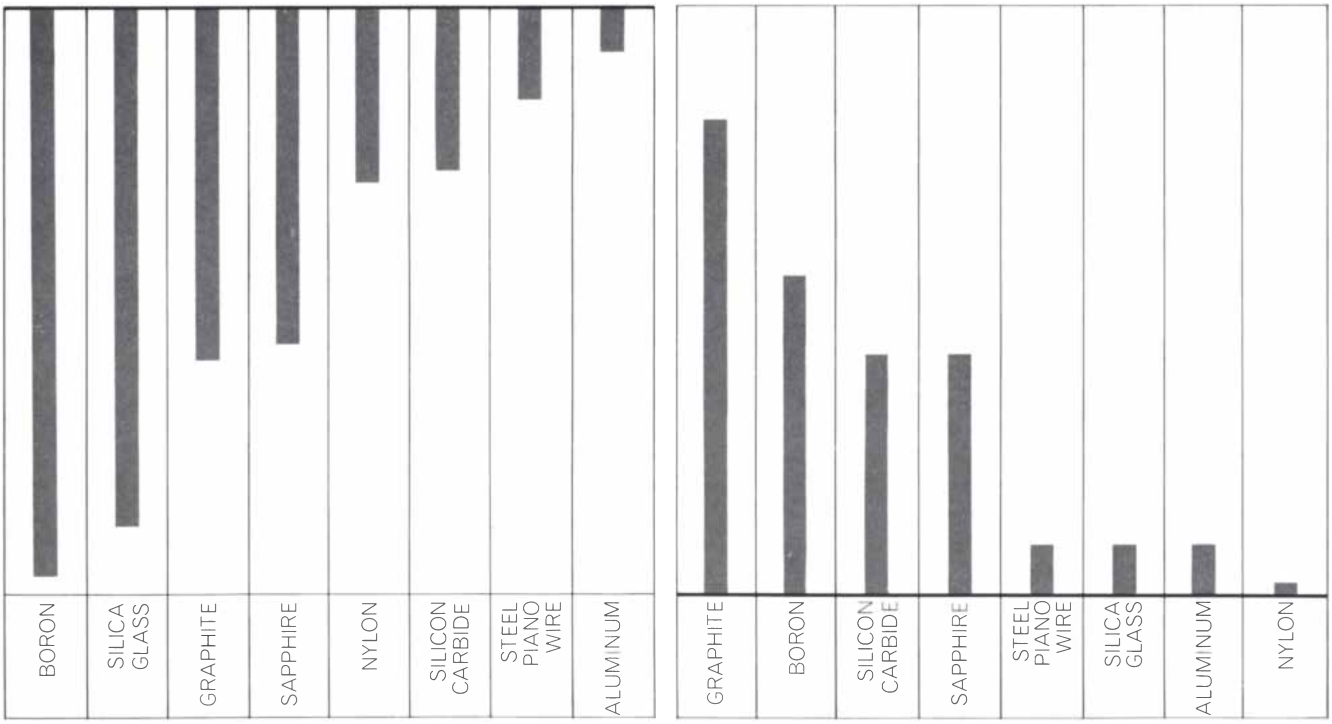


**COMPOSITE PRINCIPLE** is exemplified by a bimetallic strip of the kind used in thermostats. If pieces of brass and iron of the same size (*top*) are heated separately (*middle*), the brass will expand more than the iron. If the pieces are joined and heated (*bottom*), the greater expansion of the brass forces the iron to bend, and the bending of the iron forces curvature on the brass. The effect could not be achieved with either component alone.

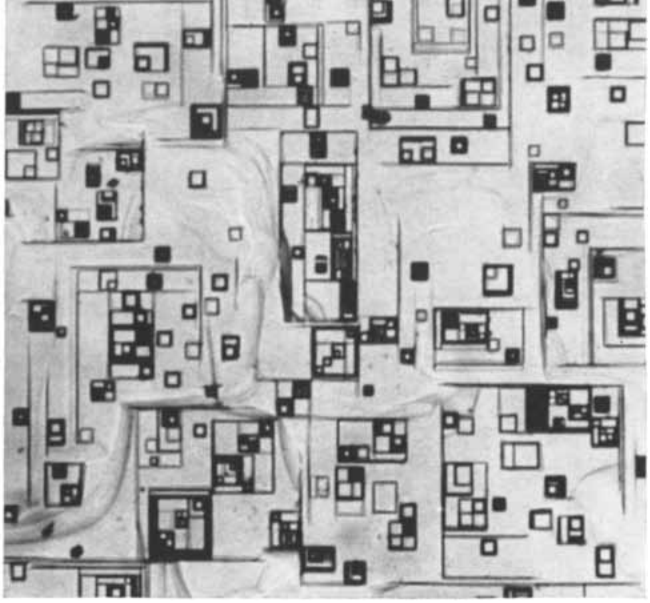
So far we have been dealing with the strength and crack-controlling properties of a composite material being pulled in a direction parallel to the fibers, that is, when the material is under tension. When the material is under compression parallel to the fibers, the specimen breaks down by buckling and shear. Here a need arises for one of the compromises to which I have referred.

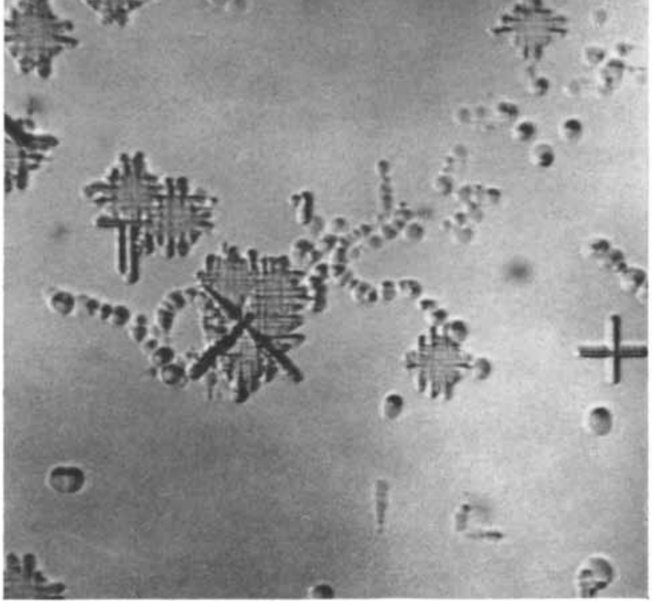
Under compressive loading the stiffness of the fibers should be at a maximum to resist buckling, and the interface between the fiber and the matrix should have a high tensile strength in order to resist splitting. For the material to resist cracking under tension, however, a weak interface is required, so for resistance to both tension and compression a compromise must be made.

Compromise is also required when a composite is pulled in tension at an angle to the fibers, that is, when it is subjected to shear. Under shear, as under compression, the composite is less strong than when it is under tension. In other



**STRENGTH AND STIFFNESS** of various materials are compared. Strength (*left*) is represented as greatest free-hanging length; in the case of boron it is 189.4 miles. Stiffness (*right*) is represented on an arbitrary scale indicating relative stiffness per unit weight.





**SURFACE DEFECTS** on crystals of magnesium oxide indicate the brittleness of most ceramic crystals. The defects in the crystal at left were made by heating the crystal in air; the defects in the crystal at right were caused by dropping small particles of dust onto the surface. The ease with which most ceramic crystals crack is the reason ceramics are so little used for heavy structural work in spite of their great strength. In a composite of ceramic fibers in a matrix the soft matrix prevents the propagation of any cracks.

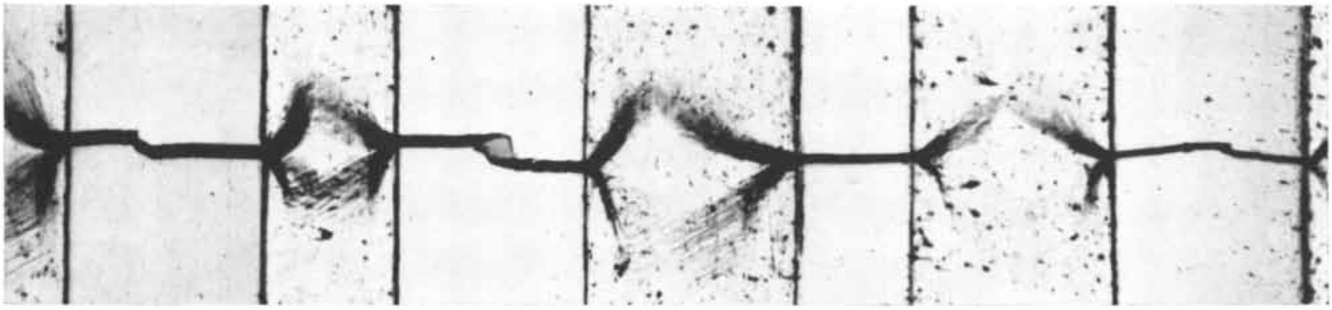
words, the strength of a composite tends to be highly directional, just as wood is strong parallel to the grain and weak at right angles to it. The compromise that is applied to composites to counteract their weakness under compression and shear is one that has long been used with wood, namely lamination, as in plywood. In some modern composites variously aligned layers are stuck together to provide strength in a number of directions. A price has to be paid: the laminated material is weaker in any particular direction than it would be in one direction if all the fibers were aligned.

Crack-controlling properties and lamination have recently been applied in conventional metallurgy. Steel can be made more resistant to cracks by cementing together thin sheets of it with soft solder. This laminated steel is, of course, a composite material.

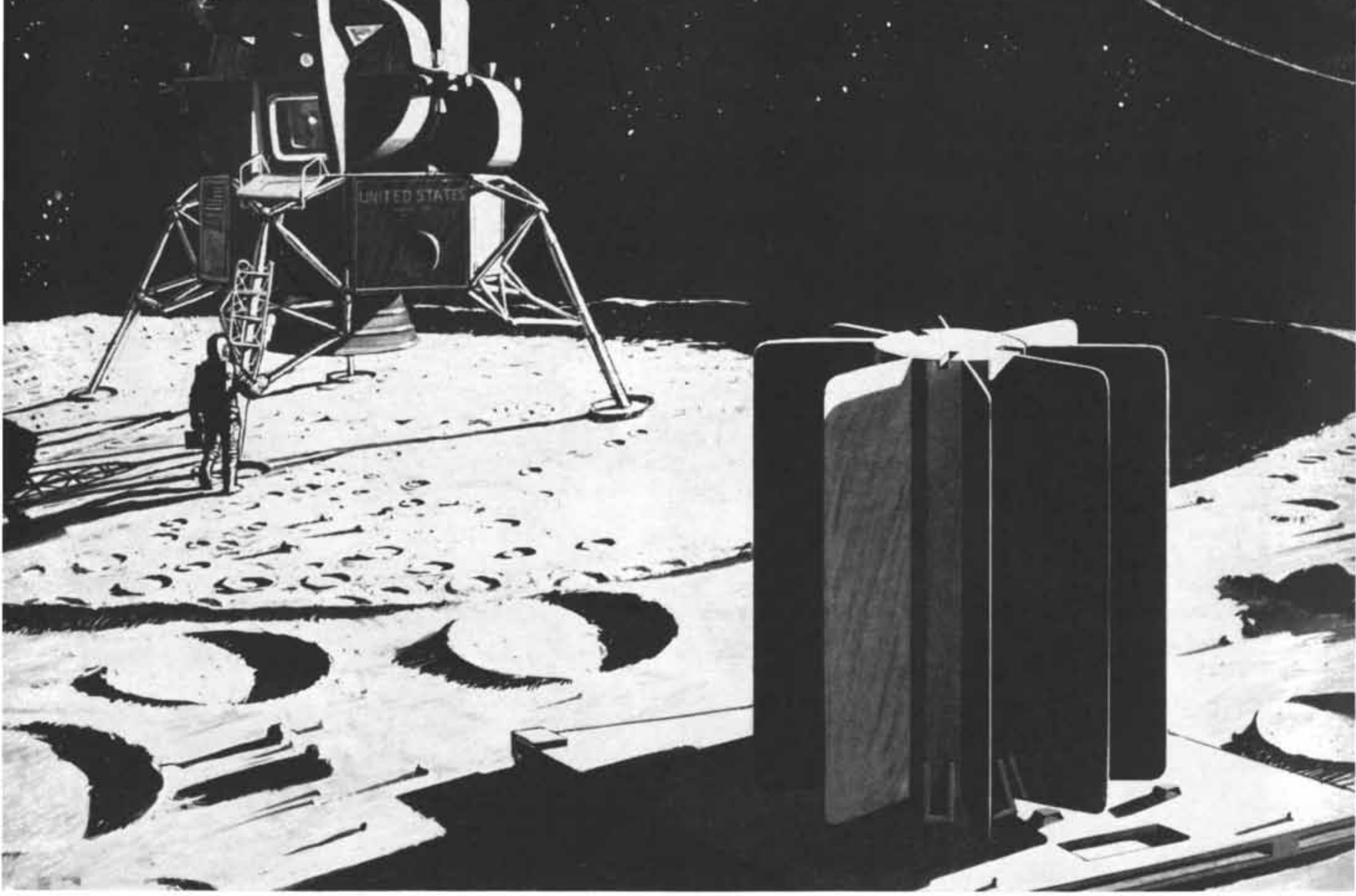
When fibers of an extremely brittle material such as glass are used in a composite, they will always be marred by some flaws. When such a composite material is stressed, some of the fibers break before others. Obviously the part of a broken fiber close to the break will not support any load. A short distance from the break, however, the unbroken part of that same fiber will be carrying as much load as the surrounding unbroken fibers. The reason is that when the fiber breaks, the two ends attempt to pull away from each other but are prevented from doing so by the matrix, which adheres to the fiber. As the fiber attempts to relax, the flow of the matrix parallel to the stress counteracts the tendency. Shear forces come into play and gradually build stress back into the broken fiber [*see illustration on page 168*].

The fact that the matrix in a composite builds stress into broken fibers means that the principle of combined action would still be realized even if all the fibers were broken. Such an effect is achieved with large numbers of small fibers. Composites can accordingly be made with short lengths of fiber, none of which needs to run through the entire piece of material.

This fact has two substantial advantages for the application of the principle of fiber reinforcement. Since small lengths of fiber can be used, pieces of material can be built up (and given multidirectional strength) with layers consisting of matrix and short fibers. The second advantage is a pure bonus. The strongest materials known are the short, single-crystal filaments known as whiskers. Because a fiber-reinforced composite does not demand continuous fibers, whiskers can be used. Although no



**EFFECT OF MATRIX** in blunting cracks is shown in a composite of tungsten fibers in a copper matrix. The tungsten fibers, which are the clearer bars, broke when the material was pulled in a direction parallel to the fibers; the copper did not. The dark flow lines in the copper show that the matrix has retarded the cracking by the process of shear. The movement of the crack was from left to right.



# Solar scientists fabricate advanced beryllium structure for lunar power plant.

Solar scientists and engineers are combining Solar's broad experience and technologies in working with hard-to-work metals and materials to create advanced beryllium structures and components for the SNAP-27 (Systems for Nuclear Auxiliary Power) system.

This radioisotope fueled thermoelectric power system will be left behind on the moon's surface by Apollo astronauts to enable experimental instruments to transmit data back to earth for at least one year.

The Solar structure is a compact, lightweight space radiator which will hold a Pu 238 fuel capsule to generate 56 watts of thermoelectric power. The radiator consists of an all-beryllium cylinder, 18½ inches long and 5¾ inches in diameter. A series of 5-inch-high beryllium fins, coated for maximum emissivity, surround the basic cylinder. All joints are furnace-brazed with a silver alloy and hermetically sealed.

Only recent technological breakthroughs in Solar laboratories permitted the high degree of craftsmanship essential to the SNAP-27 program. These included mastering beryllium's unusual property, the metal's ability to stretch in two dimensions but not in a third, and toxic dust and fumes. Solved were complex problems in fabrication, storage, and general handling.

In addition to its participation in the SNAP-27 program where General Electric's Missile and Space Division is prime contractor for the Atomic Energy Commission, Solar is also fabricating beryllium tubes designed as structural members supporting the thrust-vector-control system for the Saturn 1B launch vehicle that will power the astronauts to the moon.

**For continuing information on Solar's materials research capabilities, send for the SOLAR RESEARCH NEWSLETTER, a quarterly review of Solar's scientific and engineering progress. Simply write on your company letterhead to: Solar, Dept. P-313, San Diego, California 92112.**

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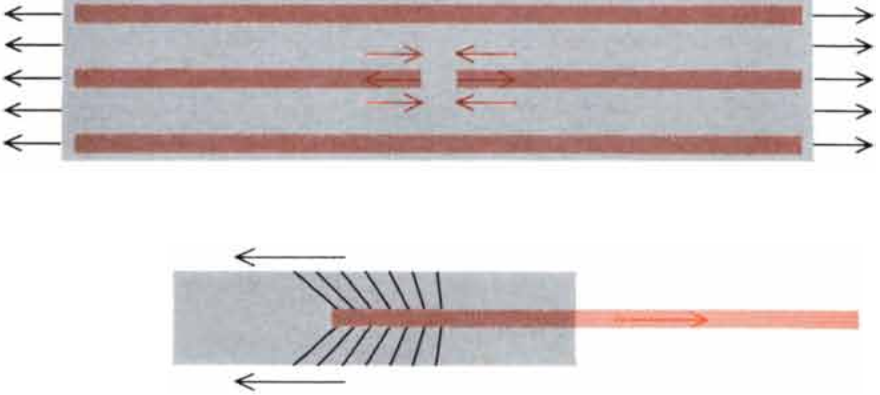

BROKEN FIBER in a fiber-reinforced composite causes little damage. The reason is depicted schematically at top in a representation of a broken fiber and two unbroken ones in a matrix. When the central fiber breaks, with the material stressed as shown by the solid arrows, the two pieces of fiber attempt to pull away from each other but are prevented from doing so by the shear forces (*colored arrows*) in the adhering matrix. Forces at work on a broken end of a fiber are represented in more detail in the illustration at bottom.

whisker-reinforced material has yet been employed in a practical structure, there is much interest in the manufacture of whiskers of such materials as silicon carbide, boron carbide and aluminum oxide, which, being ceramics, are very stiff. Composites reinforced with whiskers have been made in various laboratories and have demonstrated remarkable properties.

The largest tonnage of composite materials now being manufactured is in the form of fiber glass. Glass, because of the manner in which silica melts, is easily drawn from the molten state into thin, high-strength fibers. Drawn glass is vulnerable to attack by water, which drastically reduces its strength, and the fibers have to be given a protective coating.

Fibers so prepared can readily be put into a matrix of unsaturated polyester resin. The resin is originally in liquid form, and the reaction to make it set around the fibers can be promoted at low temperature and low pressure. This means that the glass fiber is not grossly damaged in the process of forming a composite. The fact that the fibers remain largely intact is one of the chief advantages of glass-reinforced plastics. Large pieces of such material can be built up easily by the application of successive layers of resin and glass. Since any required shape can be built up piece by piece, there is in principle no limit to the size of object that can be constructed.

In another technique large vessels to contain gases at high pressure are made with continuous filaments of glass fiber. The filaments are wound onto a mandrel after passing through a bath of liquid resin. The pattern of winding can be controlled so as to put more fibers along the directions to be highly stressed, and the fibers can even be stretched. These methods of fabrication are completely different from conventional metallurgical techniques for making strong alloys and have the enormous advantage of not calling for high temperatures or high pressures.

Glass-reinforced plastics do have some significant disadvantages. One is that glass fiber, although it is very strong, is not very stiff. Bridges and airplane wings cannot be made out of fiber glass because the fibers can stretch, and the material will bend too much under load. Secondly, resins burn, char or flow at temperatures of around 200 degrees centigrade. This disadvantage can be somewhat offset in the most modern materials by the use of high-temperature polyimide resins reinforced with fibers of pure silica glass. Such composites have withstood temperatures of more than 300 degrees C. for several days. There is a limit to the temperature resistance of glass-reinforced plastics, however, because the glass itself does not remain strong at temperatures much in excess of 400 degrees.

Fortunately the stiff materials held together by covalent bonds—boron, carbon and others—have high melting points. In fact, stiffness and a high melting point go together with covalent bonds because of the large amount of energy needed to break such a bond. Therefore the materials that replace glass fiber because of their greater stiffness should also overcome the temperature limitations of glass.

Very stiff fibers of graphite, boron and

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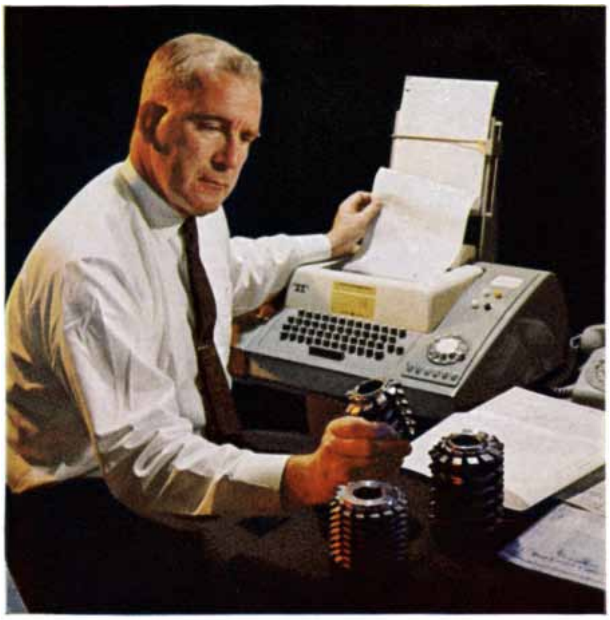

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At left: A simulated thermal stress pattern in a photoelastic model of a steam generator component.

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Utilize a million-volt linear accelerator to make sure weld and base metal of nuclear pressure vessels are properly joined, and thus able to withstand the stress of operating conditions (Utility Division). Put two to three thousand pounds per square inch of pressure into refinery and chemical plant reactors to crack and form new molecular structures (Lummus). Use monolithic refractory furnace bases capable of carrying loads up to 2000 pounds per square inch (R & I).

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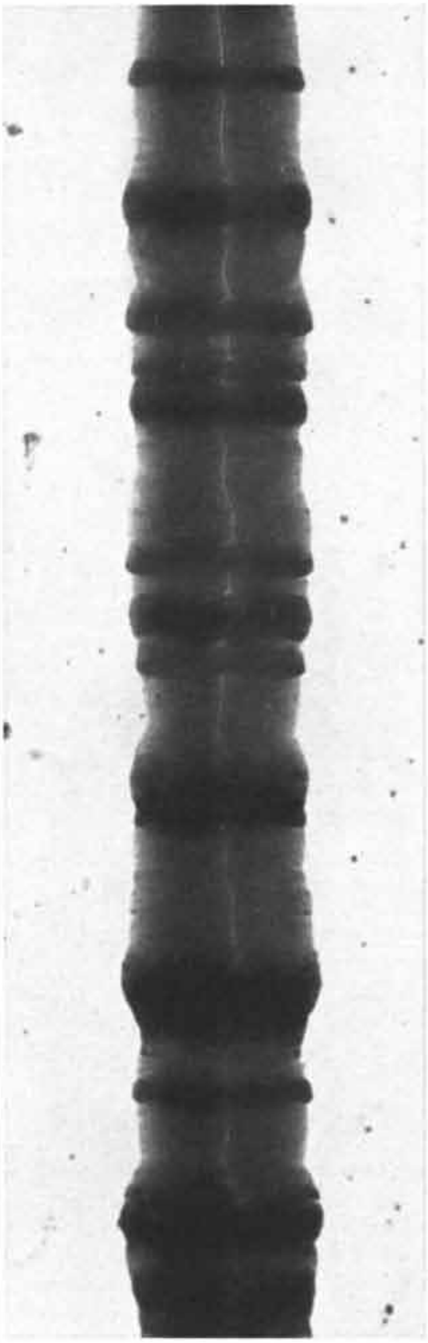
fully. At high temperatures these materials often evaporate instead of melting. Special methods have therefore been used to produce the fibers. Graphite fibers, for example, are made by controlled heating of synthetic fibers of the decomposes the material but the carbon is retained and turned into graphite. The production of boron fibers proceeds essentially by the decomposition of boron chloride or bromide on a hot filament to form a tube of strong boron over the filament. Both tungsten wire and silica coated with graphite (to make it conducting) can be used as the initial filament.



SILICON CARBIDE WHISKER, about .5 micron in diameter, is shown by transmission electron microscopy in a micrograph made by Peter T. Shaffer of the Carborundum Company. Variations within the structure of the crystal are shown by the contrast produced by diffraction of electrons in definite regions of the crystal. Whiskers have been used as fibrous reinforcements in a number of strong composite materials.

The fibers of graphite and boron now in production are more than twice as stiff as steel. Since they are less than a third as dense as steel, when they are put into a resin matrix they make a composite with a stiffness per unit weight much higher than steel's. The fibers are also very strong, and so the strength of steel is also exceeded on a unit-weight basis.

The real advantage of these materials, however, is in their stiffness per unit weight. It is this characteristic that points toward their immediate applications, which are in the developmental stage. Among them are composites consisting of carbon fibers in epoxy resin for strong and stiff compressor blades in lightweight jet engines, and boron in epoxy resin for helicopter rotor blades that turn at high speed.

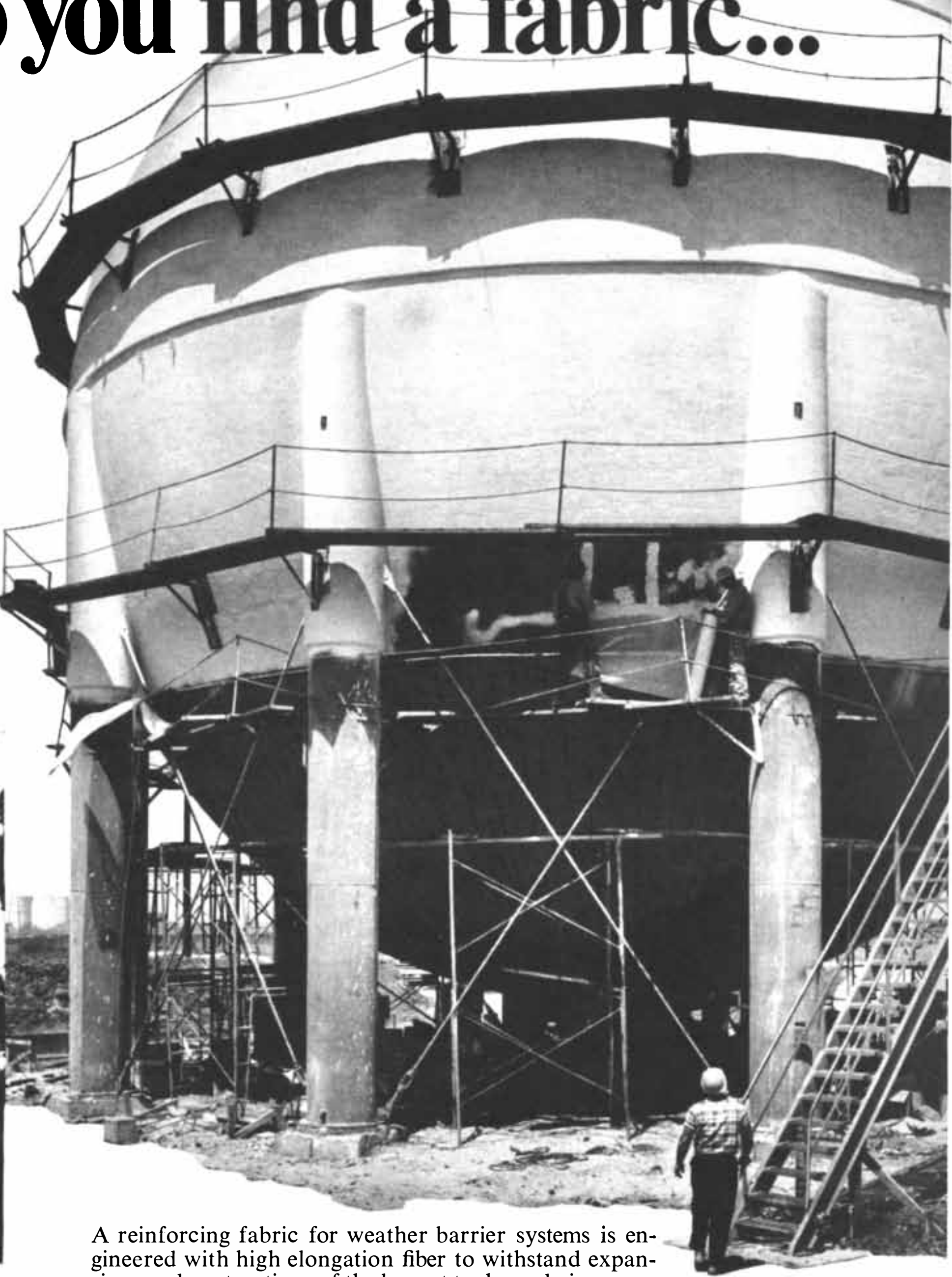
When it is not important to hold down weight, tungsten fibers, which retain high strength up to more than 1,500 degrees C., can be used in a composite. Tungsten wires have been introduced into metal matrices for use at temperatures of 1,000 degrees and higher. The metals cobalt and nickel make ideal matrices because they do not oxidize readily at high temperatures.

Fibers of tungsten, silica coated with carbon, graphite and boron are put into matrices by electroplating. Alternatively the matrix is chemically deposited on the fibers, a technique that avoids damaging them.

Another technique does away altogether with the problems inherent in making fibers and matrix separately and somehow joining them to form a useful composite. The technique makes the matrix and the reinforcing fiber in one operation by the controlled melting of certain metal alloys. In these "eutectics," which take their name from the Greek word for "easily melted," part of the alloy develops into parallel whiskers and part becomes a matrix for the whiskers [*see illustration on page 160*]. The result is a whisker-reinforced composite of great strength and good heat-resisting properties. For example, a eu-

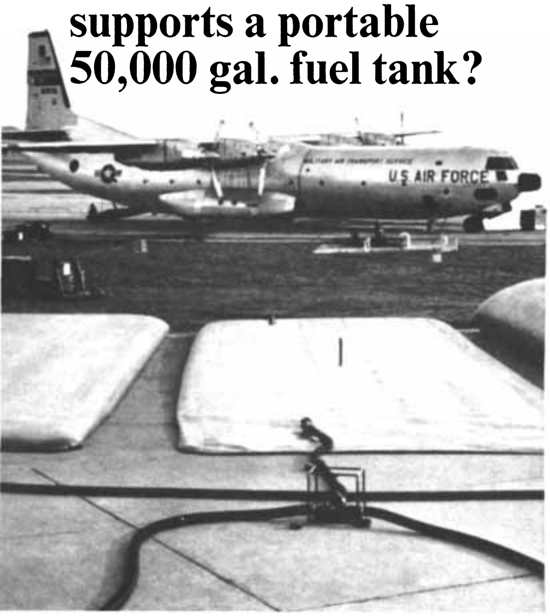
# Where do you find a fabric...

## that puts a weather-proof skin on an insulated tank?



## combines the best of glass and organic fibers?

## supports a portable 50,000 gal. fuel tank?



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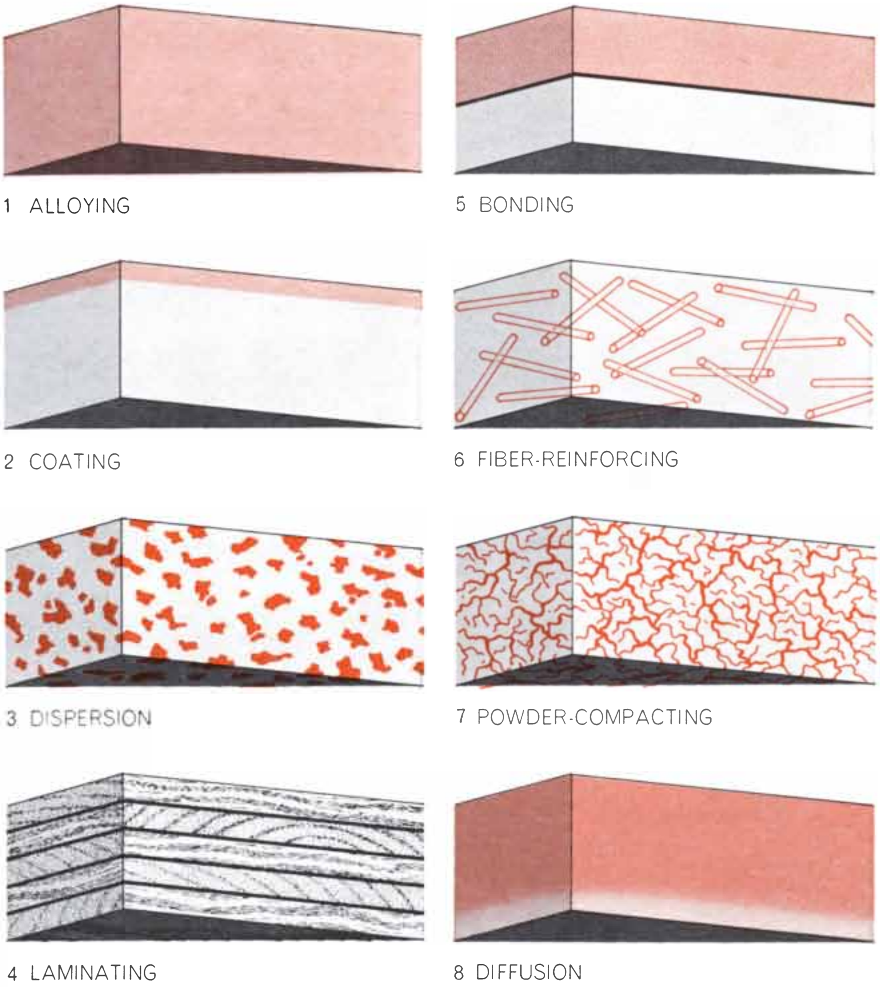
(FORMERLY WELLINGTON SEARS)

Michael J. Salkind at the United Aircraft Research Laboratories consists of niobium carbide whiskers in a niobium matrix; the composite has demonstrated high strength at temperatures up to 1,650 degrees C.

The practical application of new composite materials is inextricably linked with problems of engineering design. The new materials are ideally suited for carrying large tensile loads in one direction but may not be as effective as other materials under compression or under shear occurring at an angle to the fibers. Careful design can overcome such deficiencies. A case in point is a hollow glass sphere needed as a buoyancy tank in a deep-diving submarine. The structure would have been very difficult to make from a single piece of glass, and thus constructed it would have been extremely dangerous when not under pressure. A U.S. Navy research group of glass-reinforced plastic. In it the fibers run radially, so that they support one another against buckling when the vessel is under pressure.

The superior tensile strength of fiber composites makes them ideally suited for use in certain advanced engineering concepts. One such concept is stressed-skin construction, in which the skin of a structure is always in tension, even under compressive forces. (It may be helpful here to think of a football with someone sitting on it; the covering of the football is under tension from the pressure of the air inside it even when the football itself is under compression from the weight of the sitter.) Prestressed structures of the kind that have been made from concrete will also be able to make use of the new composites. As these materials come into general use, they will provide the basis for buildings with the contours of tents and aircraft with the delicate and graceful lines of birds.



**MATERIALS SYSTEM** is a means of providing a variety of composites to meet an engineering problem instead of trying to meet it by adapting a single material. Various ways of putting two or more materials together to make composites are depicted. Techniques of long standing appear at left; the processes represented at right are relatively recent in use.

This storage bed at Molycorp's Mountain Pass, California, plant contains 3 million pounds of lanthanum and 1.25 million pounds of neodymium.

# Rare earths are no longer rare.

They are the largest naturally occurring group of elements. For example, cerium is more abundant than tin and europium is more abundant than cadmium.

Historically rare earths have been rare for two reasons. Their lack of availability due to the difficulty in separating them from each other. And, their lack of application.

Today, Molycorp's liquid-liquid ion exchange process has solved the rare-earth separation problem. This process and the world's largest source of rare earths—namely Molycorp's bastnasite deposit at Mountain Pass, California—have made these elements readily available.

As a result, there are now over 200 known rare-earth applications. Europium and yttrium oxides, for instance, activate red phosphors in color TV picture tubes and fluorescent lighting. And lanthanum is the active ingredient in the latest petroleum-cracking catalyst.

For further proof that rare earths aren't rare and ideas on using them, write Molybdenum Corporation of America, 280 Park Avenue,
Dept. S, New York, N.Y. 10017.

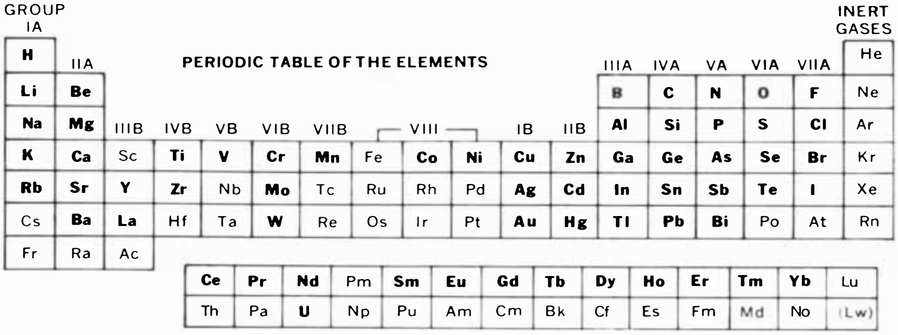
**Molycorp**

# LUMINESCENCE... Ultraviolet through Infrared

Here, generating color under ultraviolet excitation, are three of the hundreds of thousands of phosphor samples which RCA has processed during more than three decades of experience. Other RCA phosphors, under proper excitation, can span the spectrum between 3,100 and 18,000 angstroms.

Many compounds luminesce under excitation by such energy sources as electrons, photons or ions. Materials which exhibit this phenomena (of emission in excess of their thermal radiation) are known as phosphors and find application in a wide range of medical, military, industrial and consumer devices. Among these devices are X-ray equipment, radar and oscillograph instruments, and color and black-and-white TV picture tubes.

(Luminescence is often arbitrarily divided into fluorescence and phosphorescence. The accepted time of fluorescence is $10^{-8}$ to $10^{-9}$ seconds—the approximate


PERIODIC TABLE OF THE ELEMENTS

| GROUP IA | IIA | IIIB | IVB | VB | VIB | VIIB | VIII | VIII | VIII | IB | IIB | IIIA | IVA | VA | VIA | VIIA | INERT GASES |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **H** | | | | | | | | | | | | | | | | | He |
| **Li** | **Be** | | | | | | | | | | | **B** | **C** | **N** | **O** | **F** | Ne |
| **Na** | **Mg** | | | | | | | | | | | **Al** | **Si** | **P** | **S** | **Cl** | Ar |
| **K** | **Ca** | Sc | **Ti** | **V** | **Cr** | **Mn** | Fe | **Co** | **Ni** | **Cu** | **Zn** | **Ga** | **Ge** | **As** | **Se** | **Br** | Kr |
| **Rb** | **Sr** | **Y** | **Zr** | Nb | **Mo** | Tc | Ru | Rh | Pd | **Ag** | **Cd** | **In** | **Sn** | **Sb** | **Te** | **I** | Xe |
| Cs | **Ba** | **La** | Hf | Ta | **W** | Re | Os | Ir | Pt | **Au** | **Hg** | **Tl** | **Pb** | **Bi** | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Ce** | **Pr** | **Nd** | Pm | **Sm** | **Eu** | **Gd** | **Tb** | **Dy** | **Ho** | **Er** | **Tm** | **Yb** | Lu |
| Th | Pa | **U** | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | (Lw) |

Fig. 1

time of a simple electron transition. Phosphorescence is the prolonged emission of photons after irradiation ceases, and is due to a variety of electron trapping states within the compound. The time duration of phosphorescence is called persistence and ranges from microseconds to years.)

*Fig. 1* shows, in bold type, the wide range of elements with which RCA chemists have worked in their continuing program of research, development, testing, manufacture and innovation of luminescent materials. In their development program for phosphors, these chemicals have been used either as the elements themselves or in compounds.

Although some natural minerals exhibit luminescence, their efficiency is unsatisfactory for commercial use. On the other hand, excellent emission characteristics are obtained from synthesized phosphors using controlled amounts of impurities as "activators" in the natural "host" crystal. Synthetic crystals are composed of the host crystal, one or more activators and, sometimes, a trace of one or more fluxes. The fluxes contribute a pseudocatalytic action in crystallizing the material while the activator generally tends to provide control over the energy transfer, spectral emission and persistence. The activators are either deliberately added to the material—often as only a few parts in a million—or are formed as defect centers during crystallization. The end result is the phosphor—a crystalline semiconductor that acts as an energy transducer which can convert a variety of energy inputs into internally-generated, visible or near-visible radiation.

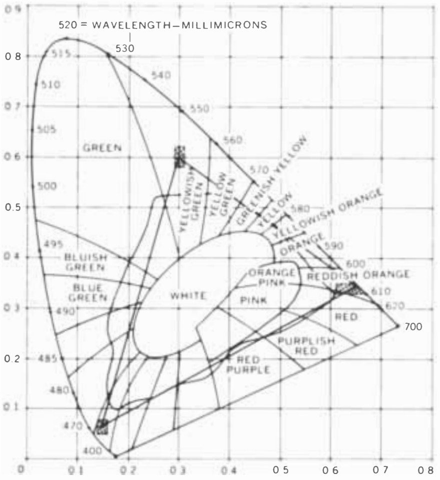


Fig. 2

Since phosphors are self-luminescent primary emitters, the emitted radiation from different phosphors can be combined additively. In color-television picture tubes, for example, the basic colors of red, green and blue—produced by phosphors under electron excitation—are *added* to produce a visual impression of white, including any color or tint, simply by varying the intensities of the three primaries. The area bounded by the triangle in *Fig. 2* shows the range of colors which can be produced *additively* by present-day color-TV picture tubes as expressed in C.I.E. (Commission Internationale de l'Eclairage) coordinates. In contrast, the inks used in color printing function *subtractively*—i.e., the colors subtract from white to produce their visual image.

At RCA, putting phosphors to work reflects a combination of chemical and other skills. Since RCA researches, develops, produces and uses its own phosphors, it requires that its chemists apply many abilities far beyond the chemistry of formulating each phosphor to match an application's requirements. The company calls for highly-developed capabilities in manufacture, stringent quality-control programs and painstaking application techniques.

RCA's outstanding achievements with phosphors can be attributed in great measure to its interdisciplinary activities of physics, chemistry and electronic groups which are involved in correlating the relationships between particle size, brightness, environmental stability, persistence and excitation methods. This organizational approach has brought about marked improvement in the quality of color-TV picture tubes, for example.

Year-by-year improvement in the brightness of color-TV picture tube screens has been achieved through phosphor advancements. The latest announcement from RCA has been of a new, higher-output rare-earth red phosphor which markedly increases picture contrast and brightness for full, living color at high ambient light levels. This phosphor provides a 40% increase in red-field brightness and a 20% increase in the brightness of picture whites, compared with typical phosphors used by earlier RCA tubes.

In working with these and other phosphors, RCA chemists have developed product technology, amassed data, manufactured a tremendous number of samples, and produced many luminescent materials in tonnage quantities. *Fig. 3* shows a rectangular color-TV picture tube, an image-converter tube and a display storage tube—a representative cross-section of the many conversion tube types currently consuming much of RCA's output of carefully-controlled, high-quality phosphors.

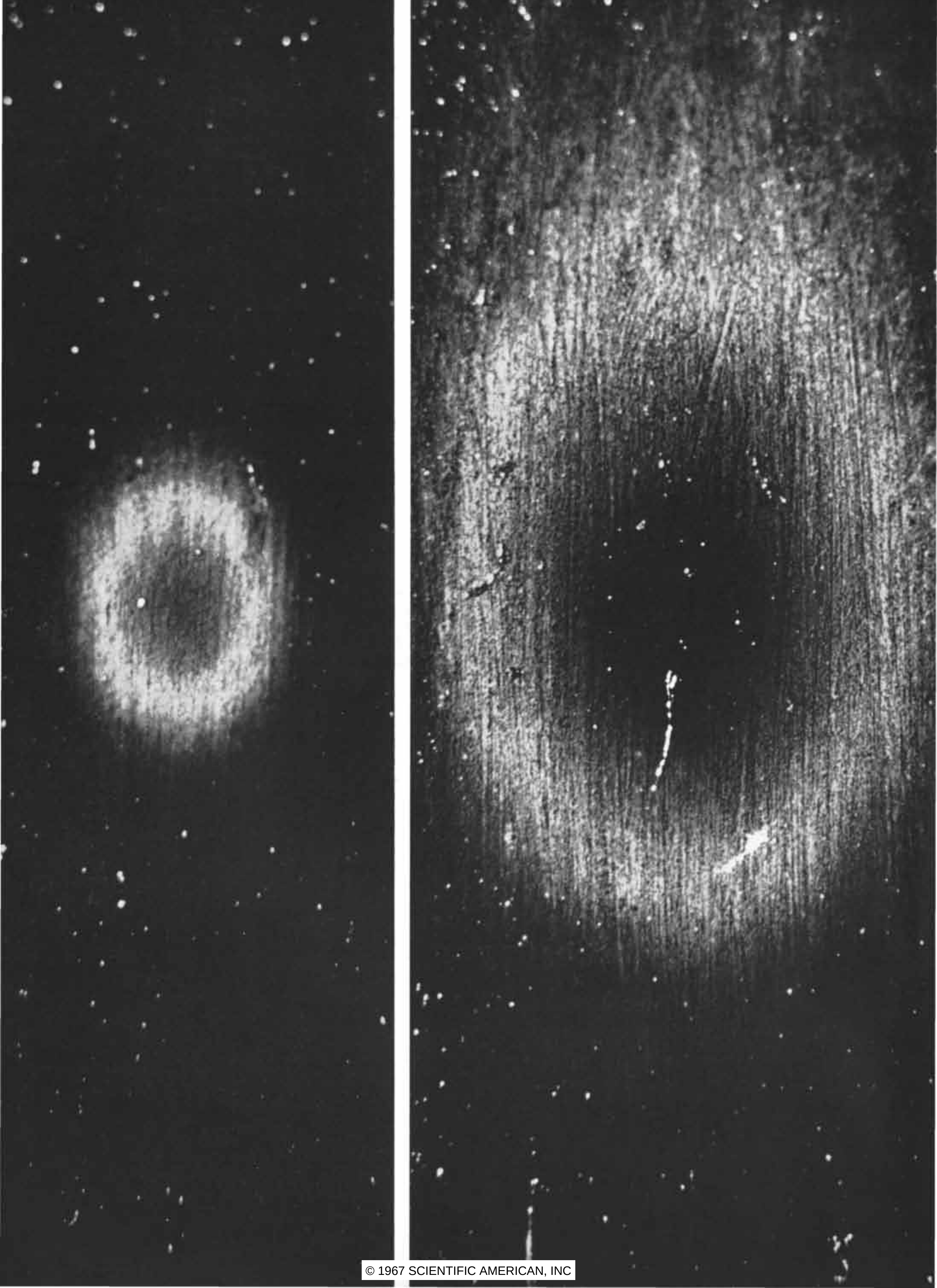
RCA skills, developed in laboratory and production runs, mean that you, too, may well be able to find the phosphor or phosphors best suited for your own use among the range of luminescent materials RCA knows intimately. Take image-intensification screens for X-ray photography, for example, or higher-contrast, shorter-persistence viewing screens for direct roentgenology. Or do you plan to produce thermographic instrumentation for medical use... or electroluminescent panels, industrial tubes and lamps, radar plan-position-indicators and tracking tubes? No matter how you use phosphors—in state-of-the-art devices or well beyond present levels—RCA probably can help you.

For further information about RCA capabilities and specific products in the luminescent materials area, write RCA Commercial Engineering, Section I95EC, Harrison, N.J. 07029.

Fig. 3

RCA ELECTRONIC COMPONENTS AND DEVICES

**The Most Trusted Name in Electronics**



# The Thermal Properties of Materials

*How is heat conducted through a material? The key is the phonon, a particle-like packet of waves that can travel through a solid although the atoms in the crystal lattice are anchored in place*

by John Ziman

The management of heat flow is a major concern of the practical engineer. He wants heat to travel freely from flue gas into the boiler and from steam into the condenser. He tries hard to keep it out of the refrigerator. Thermally conducting and insulating materials are essential to the functioning of a modern industrial society. Merely to calculate the transfer of heat in a complex structure, given the basic thermal properties of the constituent materials, is a formidable task. For such purposes the engineer is usually content to work with tabulated data on materials of every kind, from asbestos, concrete and high-alloy steels to polyurethane foams and window glass.

Can a more analytical approach be achieved? What will be the effect on the thermal conductivity of the metal walls of the heat-exchanger in a nuclear power station if the alloy mix is subtly changed? What proportion of tellurium to selenium in their compounds with bismuth will make the best thermoelectric generator? What types of material are best suited, in principle, for devices to store heat produced from off-peak electric power? A vigorous science of the thermal properties of materials is obviously highly desirable.

For an exact organized science we must build on a firm basis. We need, first, an understanding of the thermal properties of relatively perfect crystals of pure elements or of relatively simple chemical compounds. We must start, indeed, from an understanding of the nature of "heat" itself.

Isaac Newton and his contemporaries knew very well that heat is a mode of motion. But the quantitative experiments of Joseph Black in the middle of the 18th century, establishing that a given mass of matter has a specific capacity for taking up heat, were so persuasively in favor of heat as a fluid (caloric) that it took another century for the dynamical explanation to be reinstated. This explanation, embodied in the classical physics of James Joule, Hermann von Helmholtz, Lord Kelvin, James Clerk Maxwell and Ludwig Boltzmann, was very sound with respect to gases. With the realization that all the properties of gases were primarily kinetic—that they exerted pressure, could take up heat and so on because the gas molecules were all in motion—one had gone most of the way toward a quantitative theory.

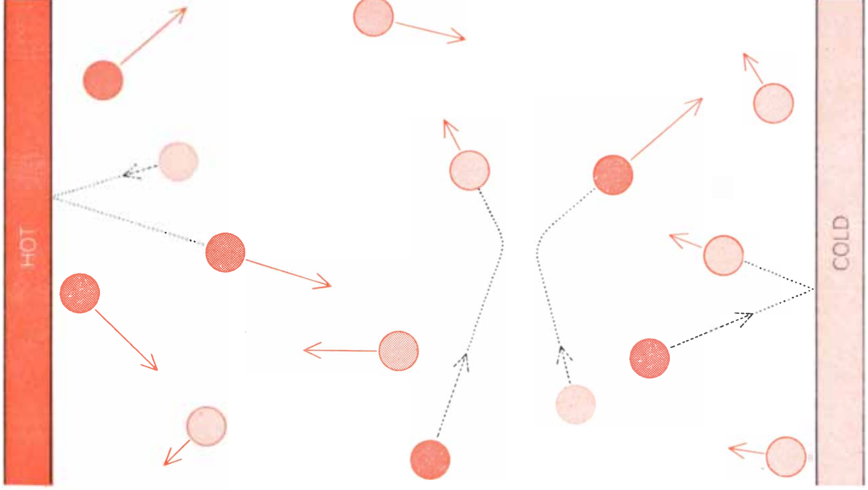
Suppose, for example, that each molecule is an idealized structureless particle. One can then show by a general statistical argument that the average energy of each molecule is proportional to the absolute temperature ($T$) in the relation $3/2\ kT$, where $k$ is the universal Boltzmann constant ($1.381 \times 10^{-16}$ erg per degree centigrade). This means that the heat required to raise the temperature of a volume of gas containing $N$ such particles by one degree would be $3/2\ Nk$. Thus the specific heat, or heat capacity, of an ideal gas is the same for a given number of molecules, and is independent of temperature.

The conduction of heat by gases is also easy to calculate. Because the molecules are in rapid motion, they diffuse throughout any space they occupy. Heating one side of a box of gas increases the average energy (that is, velocity) of any molecules hitting that wall. These "hotter" molecules diffuse into other regions, where they share their excess energy with "cooler" molecules [*see top illustration on next page*]. Even though there may be no net flow of particles from one region to another, energy is transported from the hot wall to the cold wall of the box; we say that heat has flowed through the gas.

From this description one can see that the thermal conductivity of a gas must be proportional to its specific heat ($C$) and to the average speed of the molecules ($\bar{v}$). In addition, and most significantly, the rate of heat transfer will be proportional to the distance each molecule travels between collisions. The larger the value of this "mean free path" ($L$), the farther apart are the regions exchanging energy and therefore the larger is the energy difference to be shared in the final collision. Combining $C$, $v$ and $L$ with a geometrical factor of 1/3, one arrives at the standard kinetic formula for the thermal conductivity ($\kappa$) of a gas: $\kappa = 1/3\ C\bar{v}L$.

The really difficult calculation is finding the mean free path, which depends not only on the number of molecules per unit volume and their collision "cross section" but also on the relative motion of the colliding particles and on their range of speeds. Nevertheless, the above formula contains essentially all the physics of the situation.

**HEAT CONDUCTION IN QUARTZ is faster along one axis of the crystal than along the other two. This is demonstrated in the two photographs on the opposite page. A thin crystal of quartz was coated with a substance that changes color with temperature. Then the beam from a carbon dioxide laser was aimed at the rear of the quartz to produce an intense pinpoint source of heat. The photographs show the pattern of heat distribution within the crystal at two different levels of heat input. The patterns are elliptical because of the asymmetry in thermal conductivity. The demonstration was devised by Morley Lipsett and Anthony Ledger of the Perkin-Elmer Corporation. The temperature-sensitive coating, known as a liquid crystal, was supplied by Frederick Davis of the Westinghouse Research Laboratories.**



**HEAT CONDUCTION IN GAS** is effected by the random motion of gas molecules. A molecule that strikes the hot wall of a container (*left*) absorbs energy and leaves traveling faster than when it arrived. Within the container molecules share energy as a result of random collisions. Thus heat diffuses through the gas, carrying heat from the hot wall to the cold one. The rate of transport depends chiefly on a molecule's mean free path between collisions.

Very well; now apply the same reasoning to heat transfer in a crystalline solid. The problem foxed classical physics. The specific heat was easy enough to calculate. Think of each atom as vibrating inside the cage of its neighbors, to which it is also connected by chemical bonds. For simplicity consider each atom as moving independently of its neighbors. Energy is stored both as kinetic energy in each vibrating atom and as potential energy in the bonds that are continuously being stretched or compressed as the atom vibrates. On this argument the specific heat of a solid is simply 3 $Nk$, or just twice the value for an ideal gas containing the same number of atoms. Nothing could be simpler, and this very result had been discovered experimentally by Pierre Dulong and Alexis Petit in 1819, more than 50 years before statistical mechanics was invented.

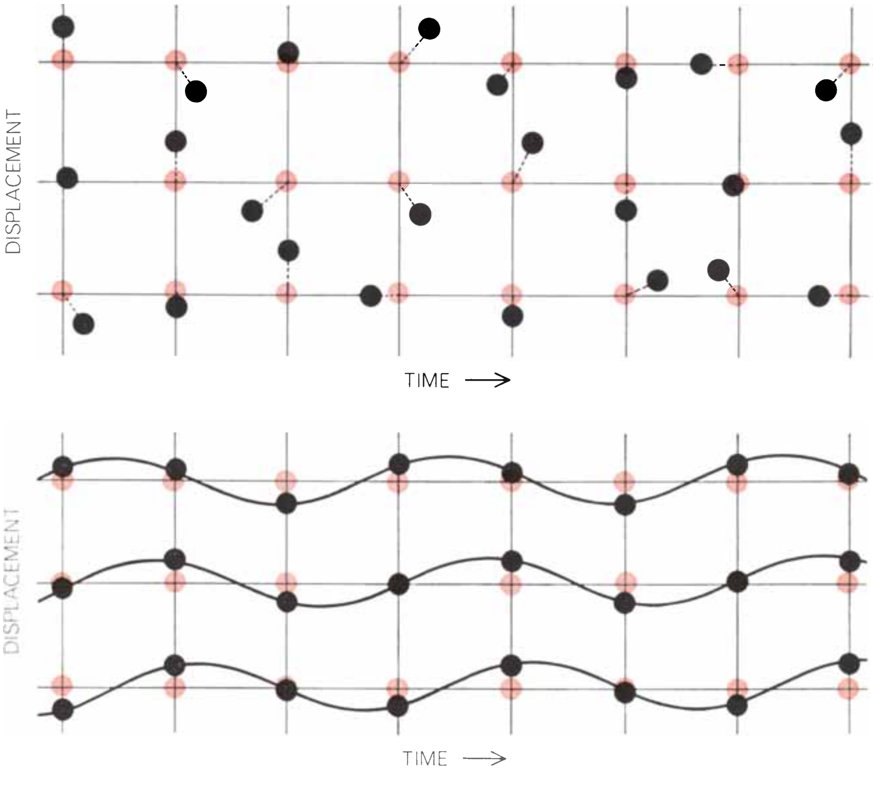
Unfortunately a quantitative theory of heat conduction in solids cannot be built on this basis. The model is much too simplified. By throwing away all the effects of the movement of an atom on its neighbors, one has destroyed the mechanism by which, in fact, heat energy passes from one oscillating atom to the next throughout the crystal.

With the development of statistical mechanics it became possible to link the thermal conductivity of metals with their electrical conductivity. In order for metals to conduct electricity readily it seemed clear that they must contain a dense gas of highly mobile charged particles, subsequently identified as electrons. Since each charged particle can carry heat energy in addition to its electric charge, it follows that the thermal conductivity of a metal should be proportional to its electrical conductivity multiplied by the absolute temperature. This relation, again, had been discovered experimentally by Gustav Wiedemann and Rudolph Franz in 1853.

Paradoxically this free-electron theory of metals, as it became established around 1900, presented a grave difficulty for the theory of specific heat. We have seen that the specific heat of metals, as shown by Dulong and Petit, is 3 $k$ per atom. If the free electrons in a metal behaved as classical particles, each would make an extra contribution of 3/2 $k$, with the result that the specific heat of metals would far exceed the experimentally observed value.

This puzzle was solved only by the development of quantum mechanics after 1925, and by the recognition that a very dense electron gas satisfies laws of statistical mechanics quite different from those of an ordinary classical gas and as a result has a very small specific heat. In such a system the whole basis of calculating electrical conductivity has to be changed. It turns out, however, that the new basis of calculation yields the Wiedemann-Franz relation at room temperature and above. The theory of heat conduction in metals has thus become an offshoot of the theory of the electrical properties of matter [see "The Electrical Properties of Materials," by Henry Ehrenreich, page 194].

Any mechanism that can scatter electrons and give rise to electrical resistance contributes proportionately to



**HEAT CONDUCTION IN SOLIDS** differs from that in a gas because the atoms are tied to lattice positions. In 1907 Albert Einstein devised a formula for heat conduction based on the assumption that atoms vibrate independently (*top*). In 1912 Peter J. W. Debye argued that neighboring atoms, being bonded together, tend to vibrate in unison (*bottom*).

thermal resistance. Indeed, in semiconductors, which are intermediate between metals and insulators, a significant fraction of heat is often carried by electrons or other mobile carriers. The amount of heat conducted in this way significantly limits the performance of thermoelectric generators (devices that convert heat directly into electricity) and thermoelectric refrigerators (devices that use electricity to drive heat directly from one region to another).

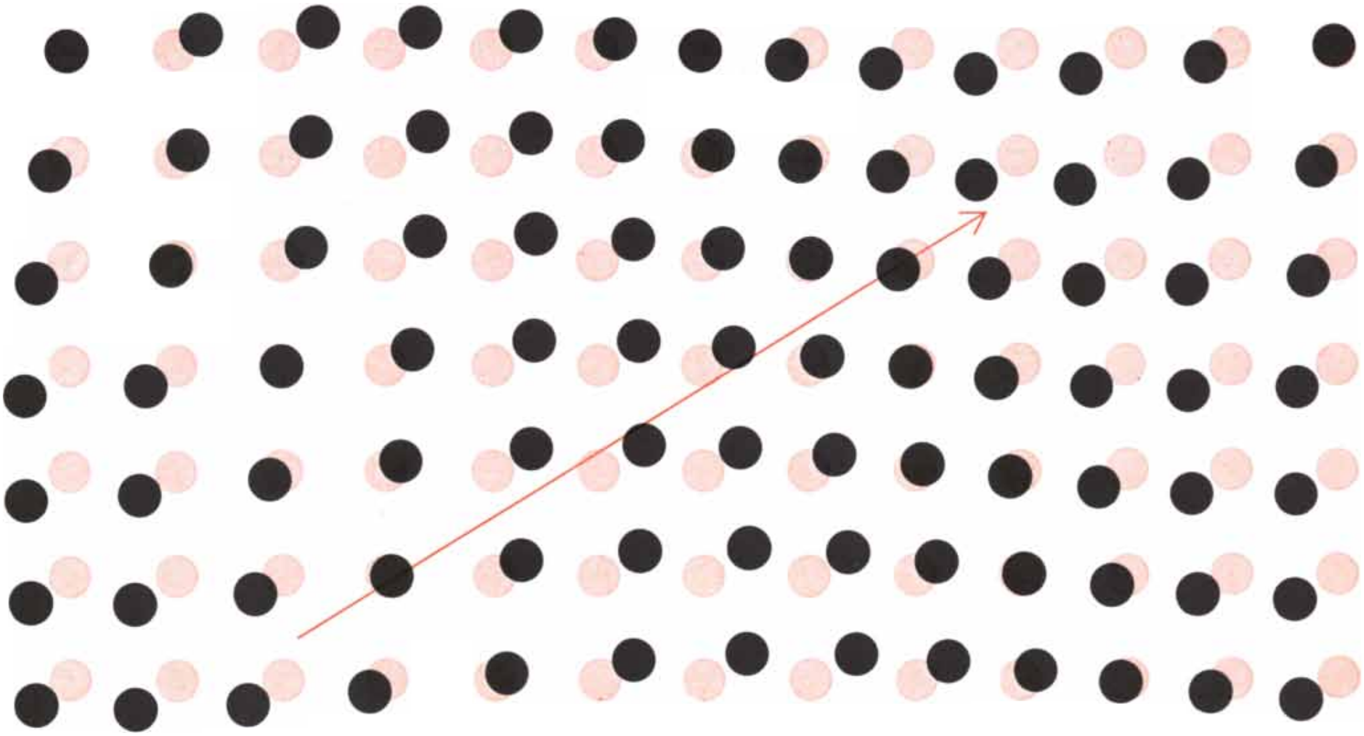
At ordinary temperatures all materials—metals as well as insulators—store heat as a vibratory motion of their atoms. What happens when the temperature is very low? As Albert Einstein pointed out in 1907, Max Planck's hypothesis that this vibrational energy, like all energy, must exist in distinct quanta should have dramatic consequences. As the temperature of a solid was lowered, its heat capacity would fall much more steeply than one would expect from the classical relation 3 *NkT*. In fact, Einstein predicted that the heat capacity would become vanishingly small well before the temperature itself reached zero.

Although Einstein's analysis was substantially correct, careful measurements showed that the actual decline in specific heat was not as rapid as he had predicted. The explanation of this discrepancy between theory and experiment by Peter J. W. Debye, and almost simultaneously by Max Born and Theodor von Kármán, in 1912 was the key to the entire problem of the thermal properties of solids.

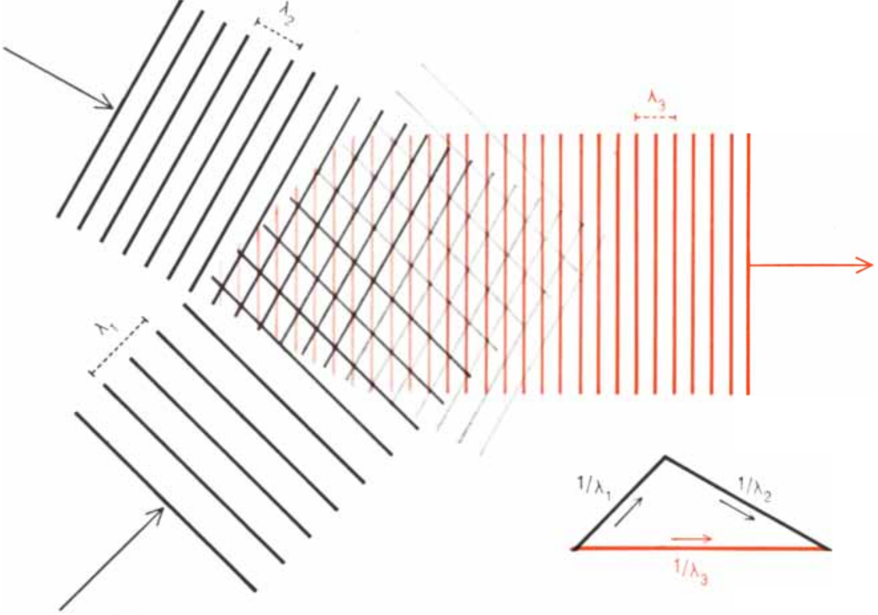
Einstein had assumed, for the sake of simplicity, that each atom in a crystal oscillated independently. Debye saw that one must allow for the coupling forces that tend to make neighboring atoms move together. This seems to present a fantastically difficult mathematical problem. But think of the crystalline solid as a continuous medium, without any fine-grained atomic structure. One knows that sound waves of various wavelengths can be excited in any such solid, and that their velocity will depend on bulk properties such as density and elasticity. Why not, then, describe the heat motion of atoms in terms of a medley of elastic waves batting around inside the solid?

This is what Debye proceeded to do. He treated each different mode of vibration—corresponding to waves traveling in a different direction and with a different polarization or a different wavelength—as an independent dynamical system, to which the basic rules of Planck's quantum theory could still be applied. Now, however, we have many different frequencies right down to acoustic vibrations of the crystal. As a result the low-temperature cutoff in specific heat is somewhat abated by the existence of low-frequency modes of vibration (whose energy quanta are very small) in which heat can still be stored. This led Debye to a formula for specific heat in which the value falls as the cube of the absolute temperature. The formula is known as the $T^3$ law of specific heats, and it was one of the early triumphs of quantum theory.

The Born-von Kármán theory was a more rigorous version of the ideas used by Debye. In many ways their analysis is a complete formal solution of the problem of the specific heat of solids. Given the forces between atoms, one can calculate the spectrum of vibrational frequencies and then compute the specific heat as a function of temperature. (The fact that a crystal system is translationally invariant, meaning that each repeating unit cell of atoms is a replica of its neighbors, allows one to use a theorem of Felix Bloch's that reduces the mathematics to a problem involving only one cell at a time.) By counting modes of vibration one automatically obtains the Dulong-Petit



**LATTICE WAVES IN CRYSTAL,** represented by alternate bunching and separation of atoms, can be inferred from Debye's hypothesis that adjacent atoms in a crystal influence each other's motion. According to this model, thermal energy should travel through a crystal in waves similar to those that carry acoustic, or mechanical, energy. Thermal waves have a higher frequency, however, than any that can be produced mechanically. In accordance with quantum theory such lattice waves can be treated as particles, or phonons.



**INTERACTION OF TWO PHONONS** gives rise to a new one (*color*) whose frequency is the sum of the frequencies of the two interacting phonons. This is the normal, or "*N*," process, in which momentum is conserved. The reaction is represented by the vector diagram at the lower right; the sides of the triangle correspond to frequency. It is also possible for a phonon to split up into two new ones, with energy and momentum again being conserved.

law at high temperatures. At the same time the Born-von Kármán equations contain the elastic-wave solutions required for Debye's $T^3$ law at low temperatures.

For some years the Born-von Kármán equations provided the basis for a vigorous cottage industry: one tried to validate assumptions about the interatomic forces in solids by proving that they gave rise to the observed variation of specific heat with temperature. This laborious and elastic chain of argument has largely been superseded by direct methods of observing individual vibrational modes, such as the inelastic diffraction of neutrons.

As Debye himself showed in 1914, these early quantum theories resolve the major difficulty in the calculation of the thermal conductivity of solids. Each vibration of a crystal lattice can be described as a traveling wave carrying energy. By analogy with the quantum theory of light, according to which light waves exhibit the attributes of particles when they are treated as photons, these traveling sound waves can be treated as particles called phonons. This single quantum principle applied to an otherwise purely classical argument allows us to think of the crystal as if it were an empty box through which phonons travel virtually without hindrance, carrying heat as the molecules of a gas do.

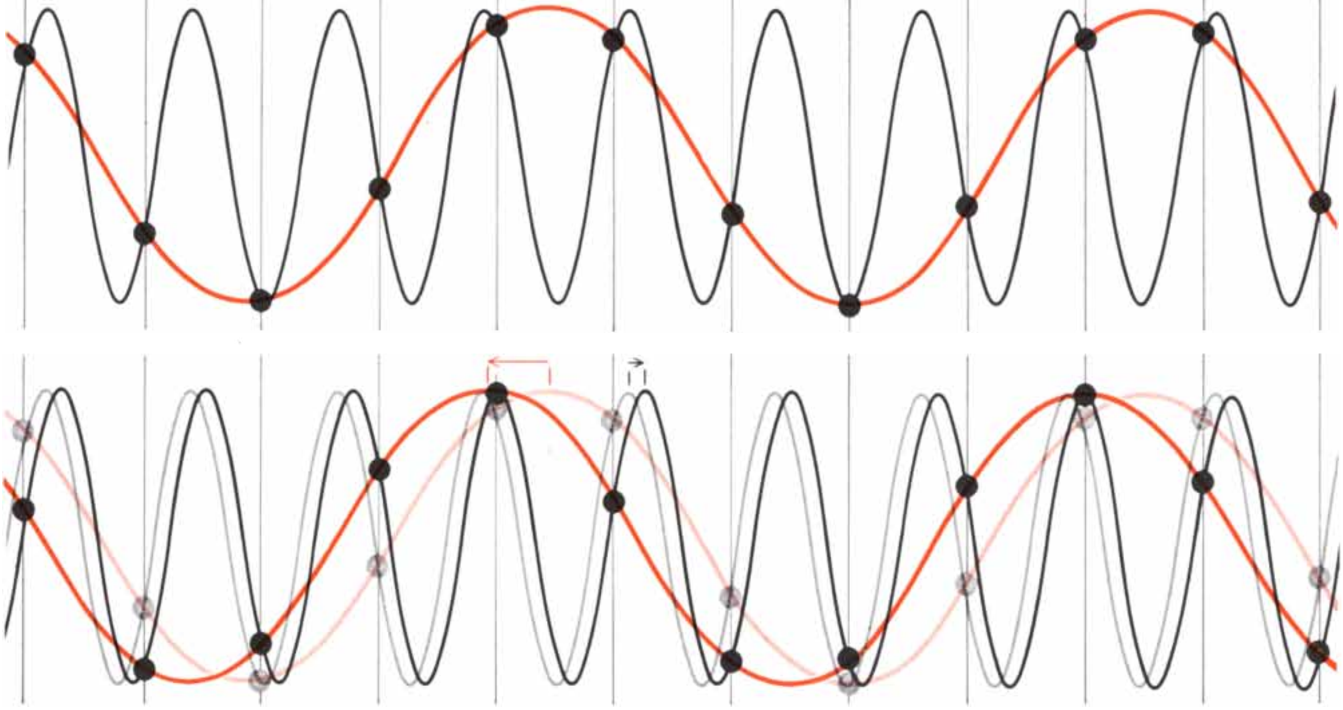
Indeed, the conduction of heat would now seem to be altogether too easy. What would prevent the phonons from traveling from one side of the crystal to the other without let or hindrance? In a perfect crystal the mean free path of a phonon ought to be as large as the crystal itself, in which case heat ought to travel through a crystal as direct radiation, so to speak, from a heated surface to a cooler one.

But as Debye then argued, even ordinary sound waves do not travel through the most perfect crystal without being scattered, except at very low temperatures. The solid is in ceaseless thermal fluctuation, so that at any given moment there will be regions of higher and lower density distributed throughout its volume. The velocity of sound, however, in an elastic medium depends on density. The heat-carrying phonon finds itself being propagated through a medium whose properties vary irregularly from point to point; therefore it is deflected and scattered. The phonon's mean free path is thus limited, and can be calculated roughly.

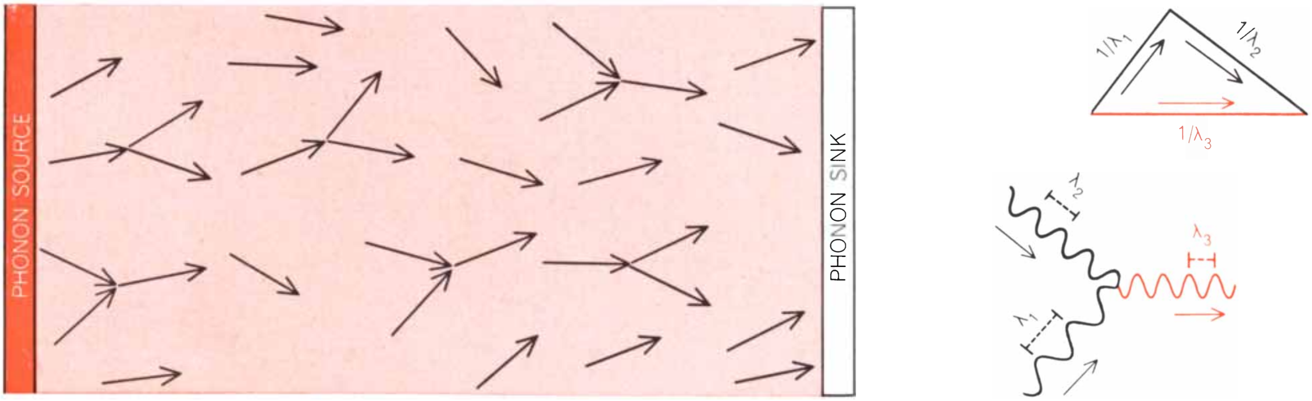
It is easy to show that the rate of scattering of a phonon ought to be proportional to the mean square of the various fluctuations in density, and that this value depends directly on the absolute temperature. To calculate the constant of proportionality, we need to know how much the velocity of sound varies with volume when a solid is compressed or when it expands. In a theory of thermal expansion published in 1912 E. Grüneisen had shown that if there were such an effect, say of magnitude gamma, then the coefficient of thermal expansion ought to be just gamma times the compressibility multiplied by the specific heat. The general idea is that, when heat is fed into a crystal, it pays for the crystal to expand a little so as to reduce the size of the quanta in which the vibrations of the crystal lattice store energy. To calculate gamma itself one would have to know exactly how the interatomic forces vary with distance, which is quite a subtle problem. For most ordinary solids, however, the actual coefficient of expansion leads to a value of about two for gamma.

Another achievement of the Einstein-Debye theory was a general formula for the melting temperature of solids. This formula was proposed by Frederick Lindemann (later Lord Cherwell), who suggested that a solid must melt when the average amplitude of vibration of each atom reaches some definite fraction (empirically about a tenth) of the diameter of the unit cell within which it is caged. One can calculate the melting point in terms of the velocity of sound in the solid (or some other measure of the elastic forces on the atom) and the atomic volume. Again the result is in surprisingly good agreement with experiment for a wide range of substances.

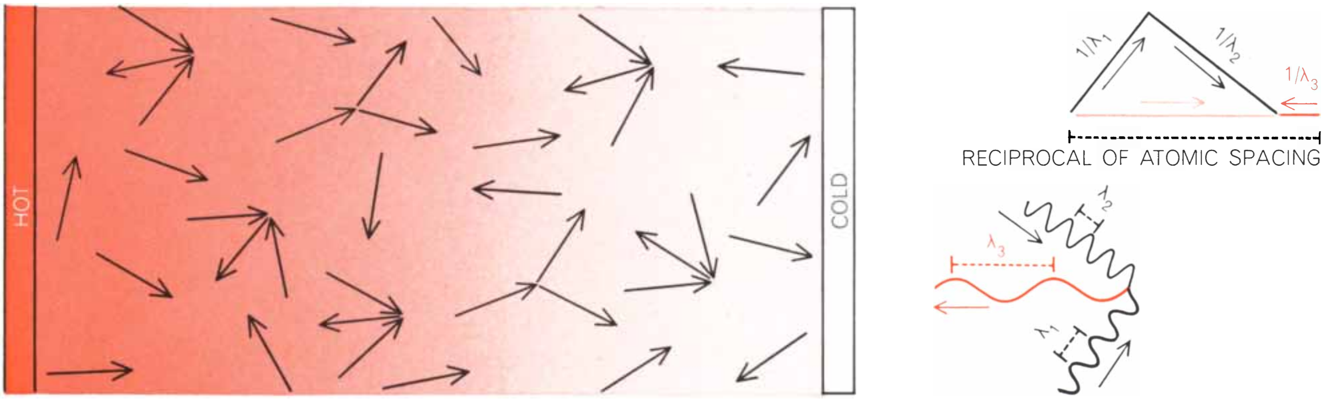
Looking back on this period just before World War I we see that a quantitative theory of the thermal properties was already firmly established. It had been achieved by adding only a few simple quantum ideas to classical mechanics. At ordinary temperatures the thermal conductivity of a nonmetallic crystal ought to be given by the kinetic formula, that is, the gas of phonons may be supposed to have the specific heat $3Nk$ and the phonons themselves an average velocity equal to the velocity of sound in the solid. The Debye, Grüneisen and Lindemann theories can then be combined to yield a rather simple formula for the phonon mean free path ($L$), which ultimately determines the rate of heat flow. After making allowances for complicated geometrical scattering, one finds that $L$ is approximately equal to $20\ T_m d/\gamma^2 T$, where $T_m$ is the melting point, $T$ is the absolute temperature, $\gamma$ is Grüneisen's gamma and $d$ is the dimension of the crystal lattice. This formula demonstrates the well-known fact that thermal conductivity falls as the temperature



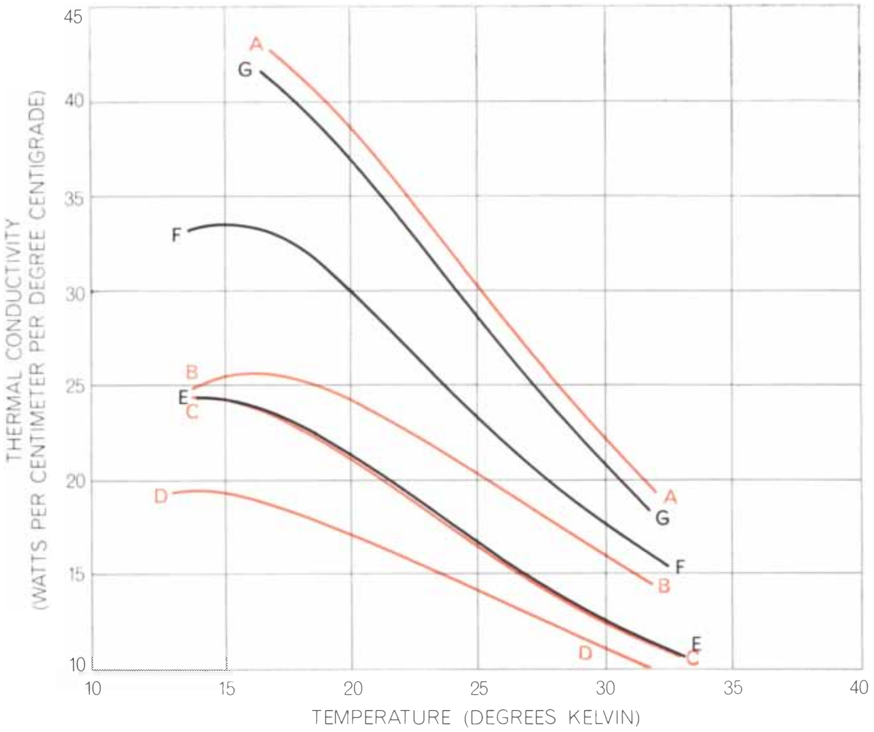
**AMBIGUITY IN WAVELENGTH** arises when the vibrations in a lattice can be assigned a wavelength that is either shorter than twice the lattice spacing (*black curve, top*) or longer (*colored curve*). The motion of the short wave to the right (*bottom*) is equivalent to the motion of the corresponding long wave to the left. Thus two high-frequency phonons can interact to produce a phonon that travels opposite to the expected direction. This "*Umklapp,*" or flopover, process appears to violate conservation of momentum.



**UNIMPEDED HEAT FLOW** would result if all interactions between phonons were normal, or *N*, processes in which crystal momentum is conserved. Phonons created at the hot end of a perfect metal crystal (*left*) would travel swiftly to the cool end. There would be no thermal resistance. The interaction of two phonons in an *N* process is illustrated at the right together with a vector diagram.



**ACTUAL HEAT FLOW** in a metal crystal (*left*) is slowed by *Umklapp,* or "*U,*" processes, which do not conserve crystal momentum and largely account for the thermal resistivity observed even in pure crystals of metal. A *U* process is represented at the right.



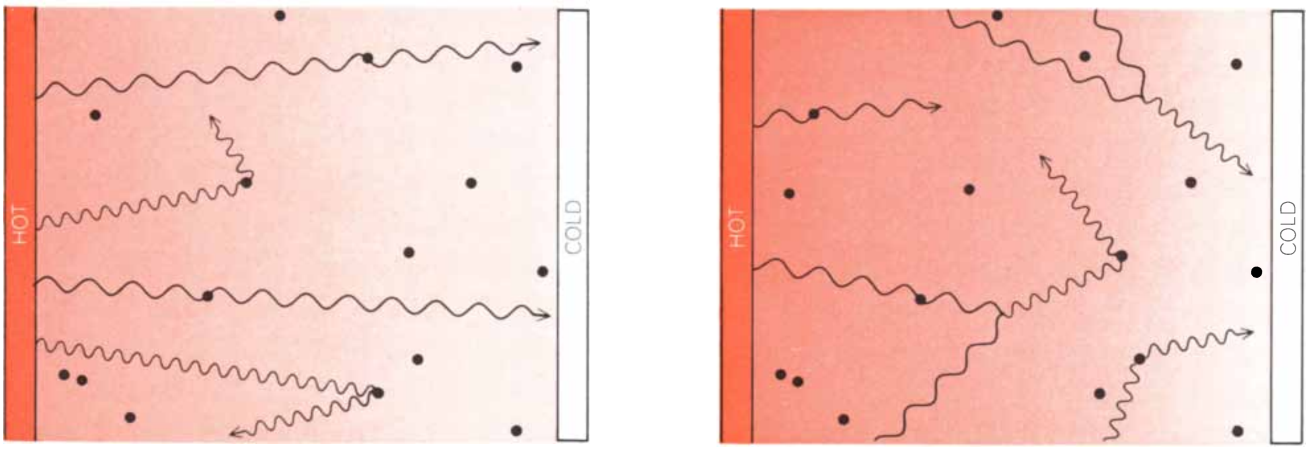
**EFFECT OF ISOTOPES** on thermal conductivity is surprisingly large in the region of a few tens of degrees Kelvin (degrees centigrade above absolute zero). These curves show the conductivity of lithium fluoride in which the percent of the rare isotope lithium 6 varies as follows: 96.25 (*A*), 90.4 (*B*), 74.7 (*C*), 50.1 (*D*), 25.0 (*E*), 7.4 (*F*), 4.7 (*G*). The balance of the lithium in each case is common lithium 7. The data were published by Robert Berman, P. T. Nettley, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson and the author.

rises. The formula also agrees with the observation that at room temperature the thermal conductivity of diamond—because it has a high melting point and permits a high phonon velocity—is comparable to that of metallic copper. For all its apparent naïveté, the formula agrees as well with experiment as anything physicists have since been able to derive by more sophisticated and vastly more complicated arguments. Nevertheless, we now know that it has grave conceptual weaknesses.

The basic objection, put forward by Rudolf Peierls in 1929, is that the "thermal" fluctuations of density that scatter the heat-carrying phonons are themselves phonon modes. We must then ask the question: What happens when two phonons meet? In an idealized "harmonic" crystal, where by definition the lattice modes are dynamically independent, there is no interaction. But in any real solid (where, for example, Grüneisen's gamma is not zero) the interatomic forces are not harmonic, and two traveling waves can interfere with each other. When this happens, the two waves can combine to produce a wave whose frequency is the sum of their individual frequencies. In quantum language we say that two phonons have collided and been destroyed, and that in their place a new phonon has been created that conserves the energy and momentum of the original particles [*see illustration on page 184*]. Conversely, a single phonon can spontaneously split up into two new ones, again conserving energy and momentum.

At first this would seem to be just what we need to make our "phonon gas" model of heat conduction even more realistic. The collisions that limit the mean free path of molecules in a real gas are mimicked by the interactions of phonons. The analogy, however, is not exact. When molecules collide, the excess energy of one of them is shared, so that eventually, after several collisions, the energy is dissipated as an increase in the energy of other molecules moving in random directions. Colliding phonons have the unfortunate property of always handing on their energy and momentum to their successors in such a way that the net current of heat is neither decreased nor deflected by the process. If all phonon-phonon interactions were of this kind, called normal processes, the thermal conductivity of a crystal would be infinite.

Peierls resolved the paradox by showing that the interference of traveling



**SCATTERING OF PHONONS BY ISOTOPES** is a function of wavelength. If the atoms of a rare isotope (*black dots*) are regarded as impurities in an otherwise perfect crystal, one finds (*left*) that long-wave phonons should be able to transport all the heat with very little scattering. Only rare short-wave phonons would be scattered. But *N* processes, which do not directly give rise to thermal resistivity, are able to convert long-wave phonons into short-wave phonons and these can then be scattered by isotopes (*right*).

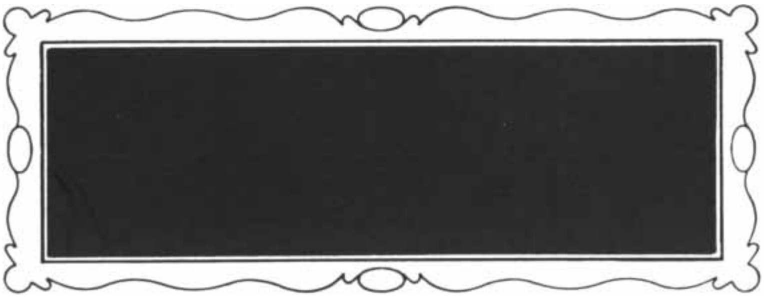
waves in a crystal lattice is not the same as it is in a continuous medium. Suppose we have two waves of short wavelength (high frequency) traveling in the same direction. Their combination wave ought to have an even shorter wavelength (higher frequency) and also ought to be moving in the same direction. But if the new wavelength is shorter than twice the lattice spacing, an ambiguity arises. The motion of the atoms in the lattice no longer tells us clearly which way the new wave is traveling. In fact, the motion of the atoms is entirely consistent with a wave of substantially longer length moving in the *opposite* direction [*see top illustration on page 185*]. In other words, the "momentum" ascribed to the phonon is only a Pickwickian "crystal momentum" and need not be conserved in phonon-phonon interactions.

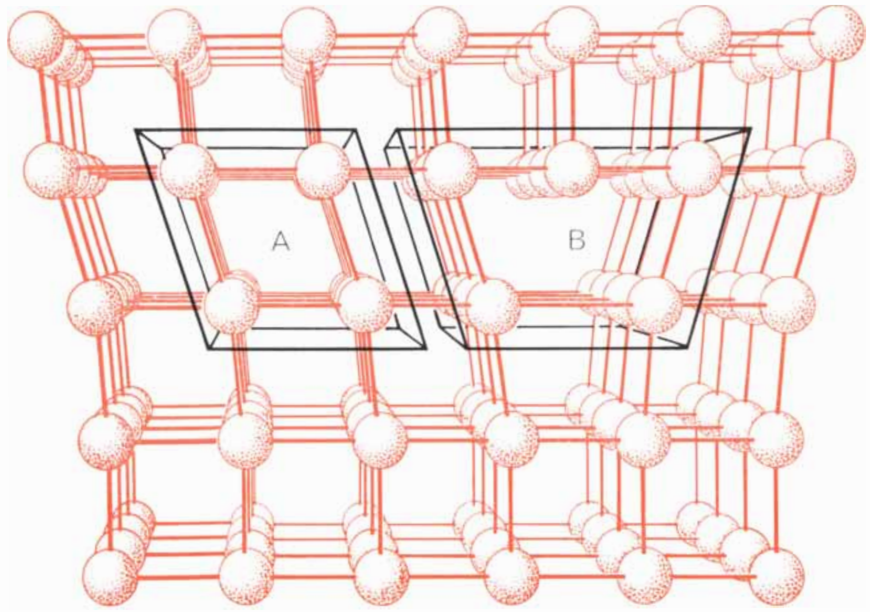
To describe such reversals in crystal momentum Peierls applied the term *Umklapp,* which in German means "flopover." Thus physicists distinguish *Umklapp* (*U* processes) from normal processes (*N* processes) in phonon-phonon interactions. The *U* processes are quite effective in reducing the mean free path of phonons. It can be shown that *U* processes occur at a rate proportional both to the absolute temperature and to the square of the strength of the nonharmonic forces, as characterized by Grüneisen's gamma. In principle, therefore, Debye's formula for the mean free path remains valid, modified only by the *Umklapp* concept.

As so often happens in theoretical physics, the gain in conceptual understanding was not rewarded by greater ease of calculation. Except in crude approximations, which are not much better than one can obtain with the simple Debye formula, the new computations have not been carried through. Accordingly many finer points governing the differences between various classes of materials are not at all well understood.

Nonetheless, one prediction of the Peierls theory has been fully confirmed by experiment. As we have seen, the thermal excitation of high-frequency lattice modes is difficult at low temperatures. It is only these modes, however, that are short enough to flop over. Cooling a crystal therefore freezes out the *U* processes. As a result the mean free path of the phonons, and with it the thermal conductivity, rises dramatically. In fact, at liquid-helium temperatures heat conduction is effected by the "radiation" of phonons.

The effect does not have much prac-





**SCATTERING OF PHONONS BY DISLOCATIONS** is due to the effects that irregularities in a crystal have on lattice waves. Their propagation is altered by local strains (*A*) and disrupted by changes in the connectivity of the lattice at the core of the dislocation (*B*).

tical significance in ordinary applications of materials science. Nevertheless, in 1956, while investigating thermal conductivity at low temperatures, Robert Berman of the University of Oxford was led to consider an important scattering mechanism that had been largely overlooked. The Peierls theory predicted that conductivity should increase exponentially as the crystal specimen was cooled. Berman found that some substances, such as solid helium and artificial sapphire (fused alumina), followed the expected law. In other substances, such as silicon and germanium, the increase of conductivity was much slower. It occurred to Berman that the deviation from theory was largest in materials with substantial concentrations of different isotopes. In potassium chloride, for example, the chlorine isotopes of masses 35 and 37 occur naturally in the ratio of three to one. Could isotope ratio be having an important effect on thermal conductivity? Berman and others soon demonstrated that such was the case [*see top illustration on page 186*].

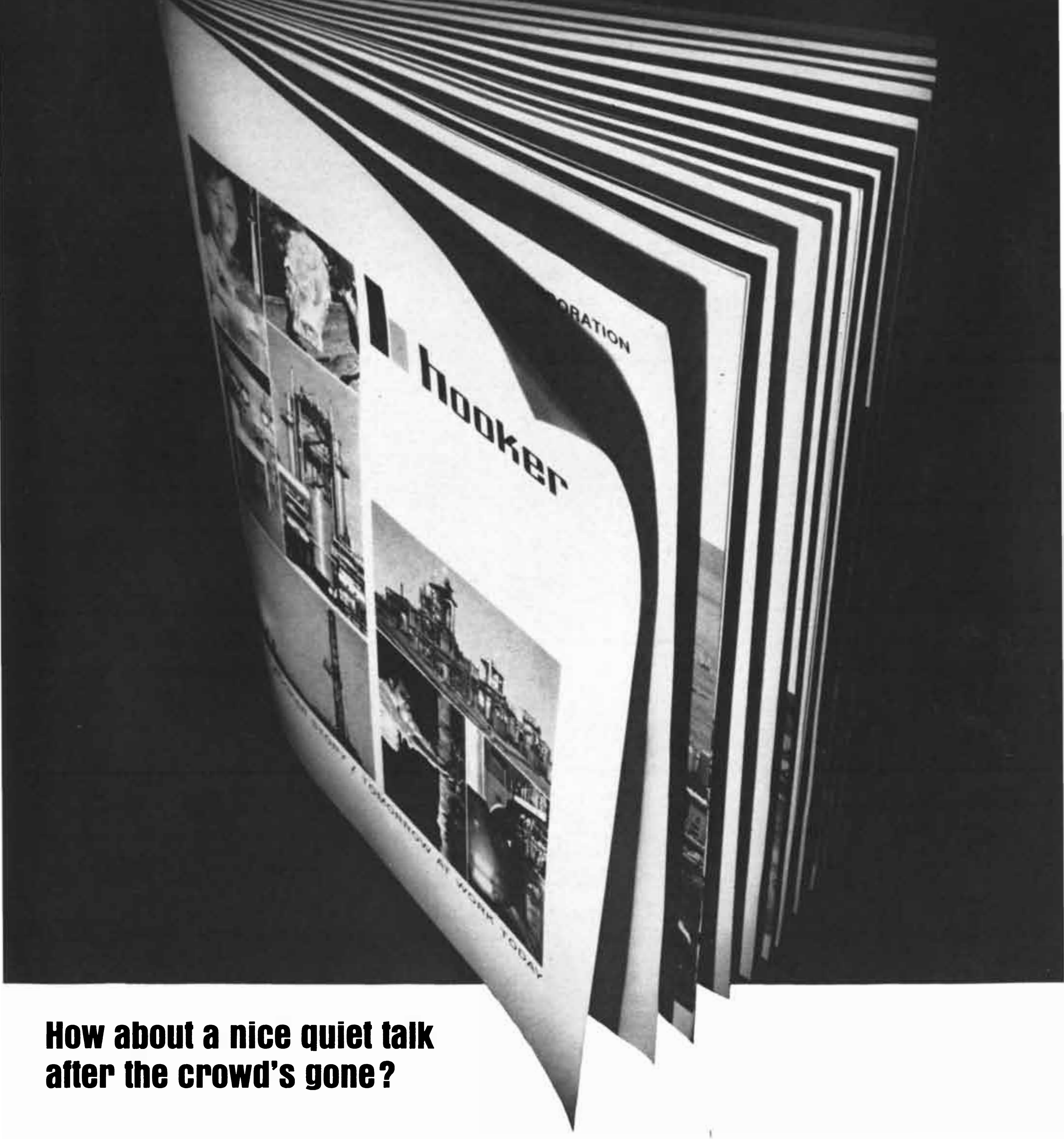
An isotope substituted as an "impurity" in an otherwise perfect crystal must scatter phonons as though it were a little local mass in an elastic medium. The scattering is proportional to the square of the difference in isotope mass and (like the scattering of light by air molecules that makes the sky blue) to the inverse fourth power of the phonon wavelength. Thus the longer the wavelength, the less the scattering. In fact, the long-wave phonons are so weakly scattered by isotopes that they seem able to transport all the heat without serious dissipation. To get a proper result one must invoke the phonon-phonon $N$ processes, which do not directly give rise to thermal resistivity but which force the long-wave phonons to combine with one another, thereby transferring the heat energy into short-wave modes that *can* be scattered [*see bottom illustration on page 186*]. In 1959 Fred Sheard and I, then working at the University of Cambridge (and, independently by a different method, Joseph Callaway, then working at the Westinghouse Research Laboratories), were able to derive formulas that matched up with the experimental results.

Actually isotopes are not an important source of thermal resistance in practical materials at ordinary temperatures, but the difficulties experienced in deriving quantitative theories of this very simple effect indicate the size of the problem of calculating the thermal conductivity of ordinary solids. We seldom have to deal with pure and perfect single crystals. What should we allow for the effect on phonons of chemical impurities, vacancies, interstitial atoms, grain boundaries, dislocations, stacking faults, magnetic-domain walls and all the other blemishes that real materials inevitably contain?

In addition to the problems of defining the physical situation, evaluating variables and trying to compute answers, the theory of the thermal properties of materials presents some difficult questions of general principle. Consider the scattering of phonons by a dislocation in an otherwise perfect crystal. It is easy to argue that the elastic strain produced around the dislocation creates changes of local density—and hence changes of the effective velocity of sound—that interact with lattice waves by the same mechanism that operates in the Debye theory of thermal conductivity. It has been found, however, that this calculation makes a much smaller contribution to thermal resistivity than is actually observed (even allowing for the fact that it is difficult to make accurate measurements). Most of the scattering, it appears, is the scattering of short-wave phonons at the core of the dislocation, where the arrangement of the atoms is very far indeed from the perfect lattice. The mere change of density is not sufficient to account for this; there must be a diffraction effect due to the actual differences in the relative positions of the atoms in this special neighborhood. Somehow or other short-wave phonons are so affronted by the unorthodox patterns of atoms at the core that they are strongly scattered.

An extreme case of the same general problem is presented by a truly amorphous material such as glass. What effect does the disordered arrangement of atoms throughout the material have on the propagation of elastic vibrations? I believe that a new mathematical technique invented by one of my colleagues, James Morgan of the Zenith Radio Research Corporation of Great Britain, may provide an entry into this subtle and hitherto intractable problem. This whole field involves classical mechanics, probability theory and a large helping of three-dimensional geometry.

In spite of these formidable mathematical difficulties, the basic physics of heat conduction is well understood. Physicists have complete confidence that it is governed by the same principle of quantum theory that rules all other solid-state phenomena. In one or two fields of materials science, such as the choice of materials for thermoelectric devices, theory has helped to guide the applied scientist and engineer. But it must be admitted that theory has a long way to go before it can design new materials to satisfy the demands of engineers employed in heavy industry. This lack of direct applicability does not detract from the study of this large and difficult topic for its own sake: for the knowledge that is acquired and the intangible rewards of traveling along a stony road.



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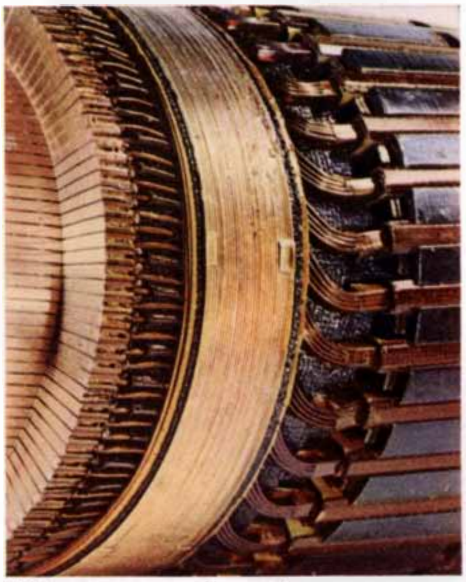
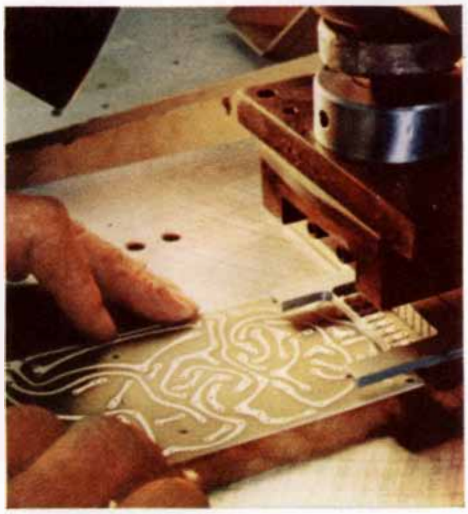


High-temperature wire coatings



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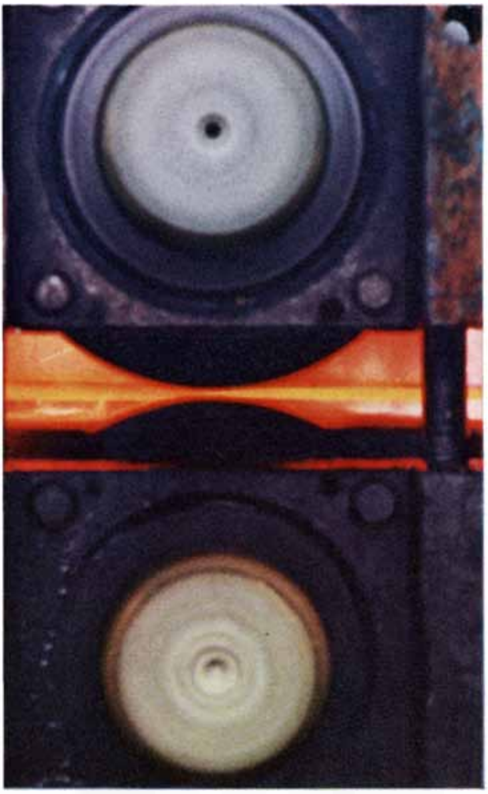

Metals plant rolling mill

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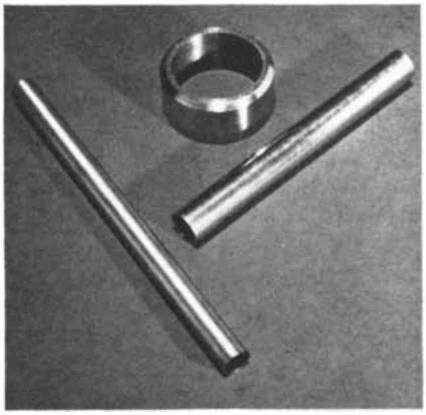
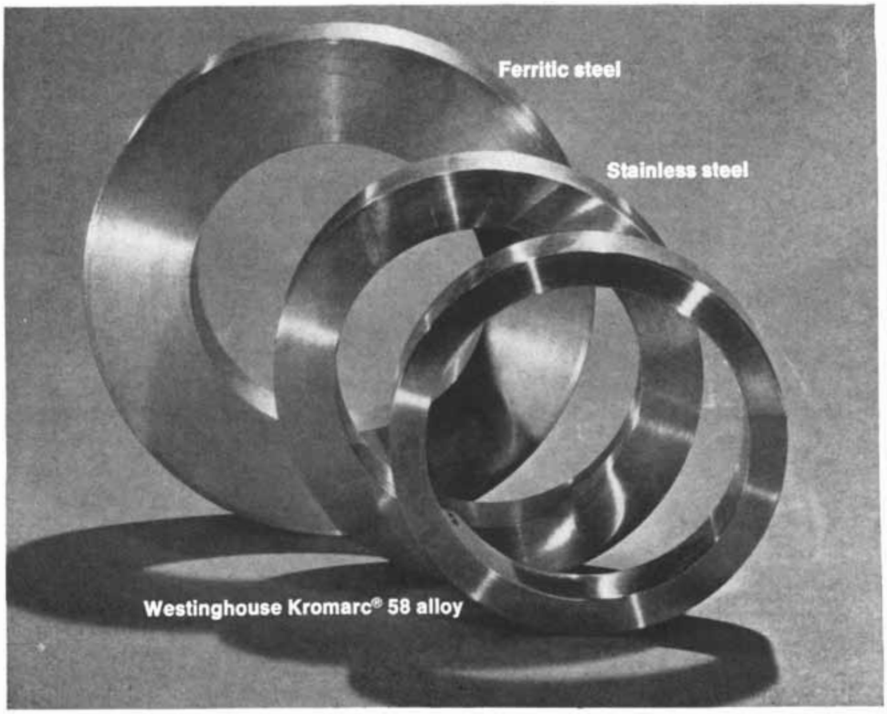


Zircaloy® alloy—low neutron absorption



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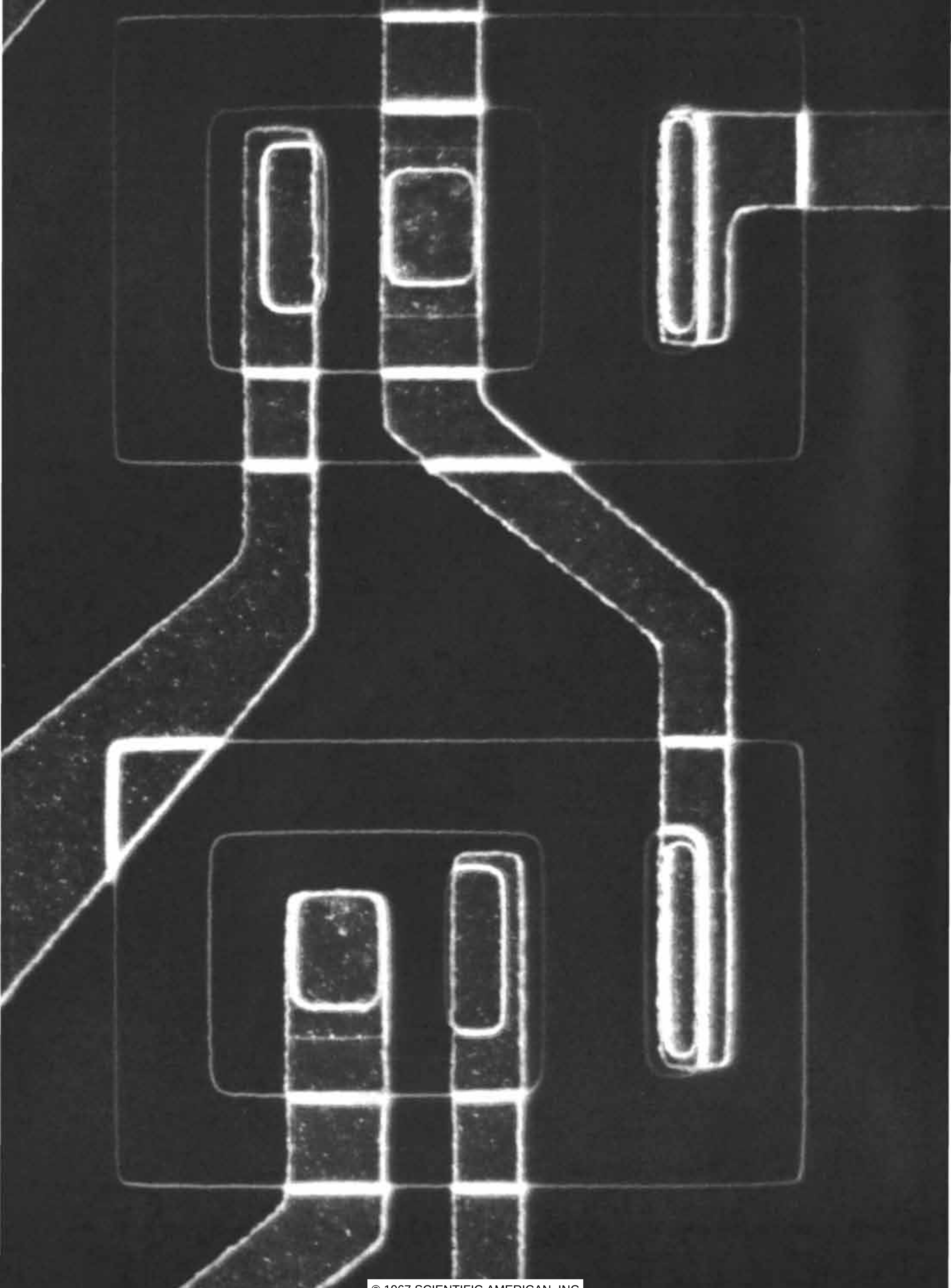


# The Electrical Properties of Materials

*Materials differ in their resistivity to an electric current by as much as 23 orders of magnitude. The insights of quantum mechanics are helping to make this full range more accessible to technology*

by Henry Ehrenreich

The electrical conductivity of materials was first demonstrated in 1729 by an English experimenter, Stephen Gray, who touched a charged glass rod to the end of a moistened cord and discovered that the cord transmitted the electricity a distance of about 1,000 feet. Today the exploration of the electrical properties of solids is disclosing much more dramatic phenomena, and these have turned out to be of fundamental significance in the understanding of matter, as well as of great technological importance.

To begin with, the wide range of electrical conductivities exhibited by materials is itself a striking fact. Between the most conductive substances (copper and silver) and the most resistive (polystyrene, for example) the difference amounts to 23 orders of magnitude [*see illustration on next page*]. To appreciate the extent of this spread, compare it with extremes in the scales of distance. One might note, for instance, that the ruler needed to measure the size of the universe is only some 23 orders of magnitude larger than the mile ruler that measures distances on the earth. Evidently, then, the electrical conductivity (or rather its inverse, resistivity, the quantity customarily used in statements of Ohm's law) is one of the most widely varying of all physical quantities.

The individual materials themselves show great variability in resistivity according to the conditions of temperature, pressure and the mixture of component substances. The addition of a minute trace of gallium or arsenic (one part per billion) to pure germanium increases its conductivity by two orders of magnitude (nearly 1,000-fold) and makes it suitable for use in transistors. A tiny further addition of the impurity can increase the conductivity 100,000-fold, converting germanium to a conductor of tunnel-diode grade. Similarly, silicon and metal oxides such as nickel oxide and titanium dioxide are lowered in resistivity by the introduction of appropriate impurities. Indeed, nickel oxide, which is an insulator in the pure state, is reduced in resistivity by 13 orders of magnitude by adding 1 percent of lithium.

Dramatic changes are also produced by changes in temperature. A semiconductor can be made a conductor by heating it to a high temperature or it can be made an insulator by cooling it to a low temperature. In contrast, the resistivity of a pure metal is much less drastically increased by heating and reduced by cooling. In some instances the change is very abrupt. For example, above 150 degrees Kelvin vanadium sesquioxide is a semiconductor; when it is cooled to just below that temperature, its resistivity suddenly jumps by six orders of magnitude and it becomes a good insulator! The best-known kind of sudden transition, of course, is the total disappearance of resistivity in certain metals (that is, their sudden transformation to the superconducting state) when they are cooled to temperatures near absolute zero.

The impact of light, like changes in temperature, also can affect electrical resistivity. Some semiconductors and insulators are extremely sensitive to light, and under illumination their conductivity may be several orders of magnitude higher than it is in the dark. This phenomenon is called photoconductivity.

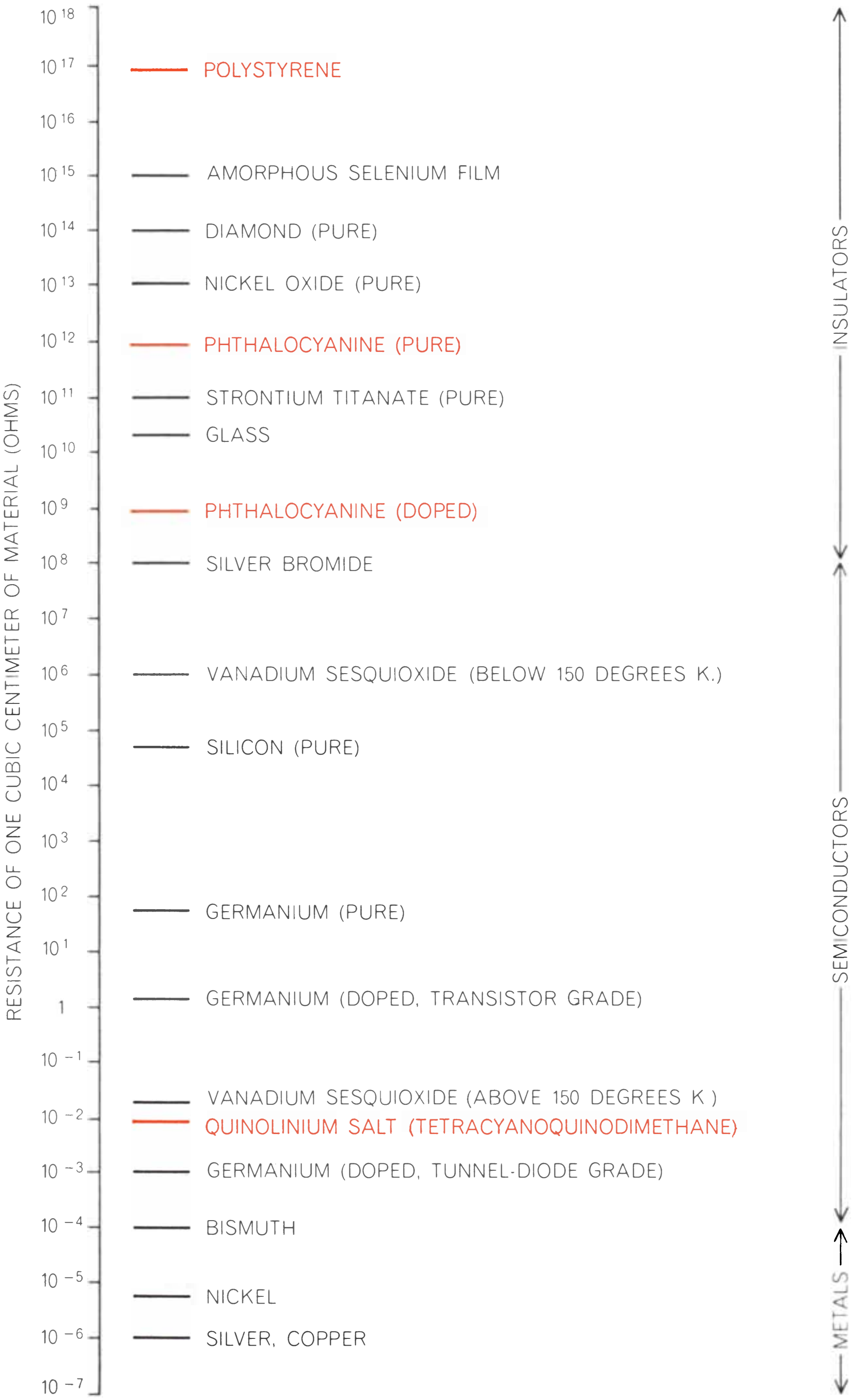
How are these facts to be explained? What principles account for the great differences in conductivity between metals and insulators, the peculiar properties of semiconductors, the abrupt transitions, the potent effects of impurities, temperature and light?

The first reasonable approach to an explanation of electrical conduction in solids was proposed in 1900 by the German physicist Paul Karl Drude. His crucial contribution was the recognition that current passing through metals must be carried by the charged particles (now called electrons) that J. J. Thomson had discovered just a few years earlier. Drude imagined conductive metals to be permeated by a gas of free electrons. An applied electric field, he suggested, accelerates the electrons along the field; because the ions they encounter in the crystal lattice deflect them and thus interpose resistance, the electrons settle into a constant drift velocity that is proportional to the strength of the applied

**TWO TRANSISTORS in the photomicrograph on the opposite page are part of an integrated electrical circuit that contains a total of 14 such transistors plus an assortment of other components and connecting circuitry on a square chip of silicon about a twentieth of an inch on a side. The circuit serves as a high-performance amplifying device in a variety of applications, including direct-current servosystems and analogue computers. The black areas are layers of silicon that have been "doped" with different impurities to produce regions that conduct by means of electrons (*n*-type material) and regions that conduct by means of electron "holes" (*p*-type material). Each of the semiconducting silicon layers is covered by a thin "passivating" layer of silicon dioxide. The slightly lighter areas are aluminum interconnections that have been vapor-deposited over the entire surface of the silicon wafer and then masked and selectively photo-etched to achieve the desired pattern. In making this photomicrograph the chip was illuminated only from the sides. The magnification is approximately 1,500 diameters. The circuit is manufactured by Fairchild Semiconductor.**

field. (The situation would be similar to the fall of an object from an airplane: the object falls with accelerating speed until the gravitational force is balanced by the force of friction with the air; thereafter the fall continues at a constant velocity.) Drude supposed the mean free path of the electrons between collisions to be only about the length of the distance between atoms in the crystal; to explain the observed conductivity of metals he assumed that all the electrons were free to act as carriers.

Drude's model successfully accounted for several observations, including the fact that in many metals the transport of heat is proportional to the transport of electricity at a given temperature, which could now be explained by assuming that electrons are involved in the transmission of heat. In certain predictions, however, the Drude hypothesis proved to be incorrect. It failed to account for the observed variations of conductivity with temperature, and since it required that all the electrons must be free, it implied that the electron gas should have a higher specific heat than was actually found to be the case; experiments showed that the amount of energy needed to raise the temperature was so small that one had to conclude only a very small fraction of the valence electrons, rather than the entire gas, was involved in conduction.

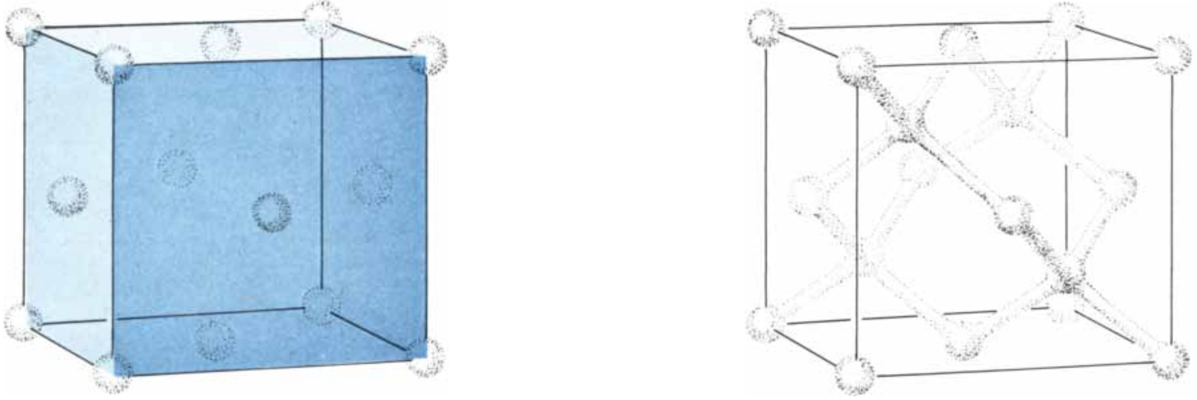


**ELECTRICAL RESISTIVITY** of materials is one of the most widely varying of all physical quantities, encompassing a range of some 23 orders of magnitude. The materials listed in this table were selected either for their familiarity, their technological importance or their scientific interest. Except for the two entries for vanadium sesquioxide, all the resistivities given here were measured at room temperature. Organic materials are indicated in color.

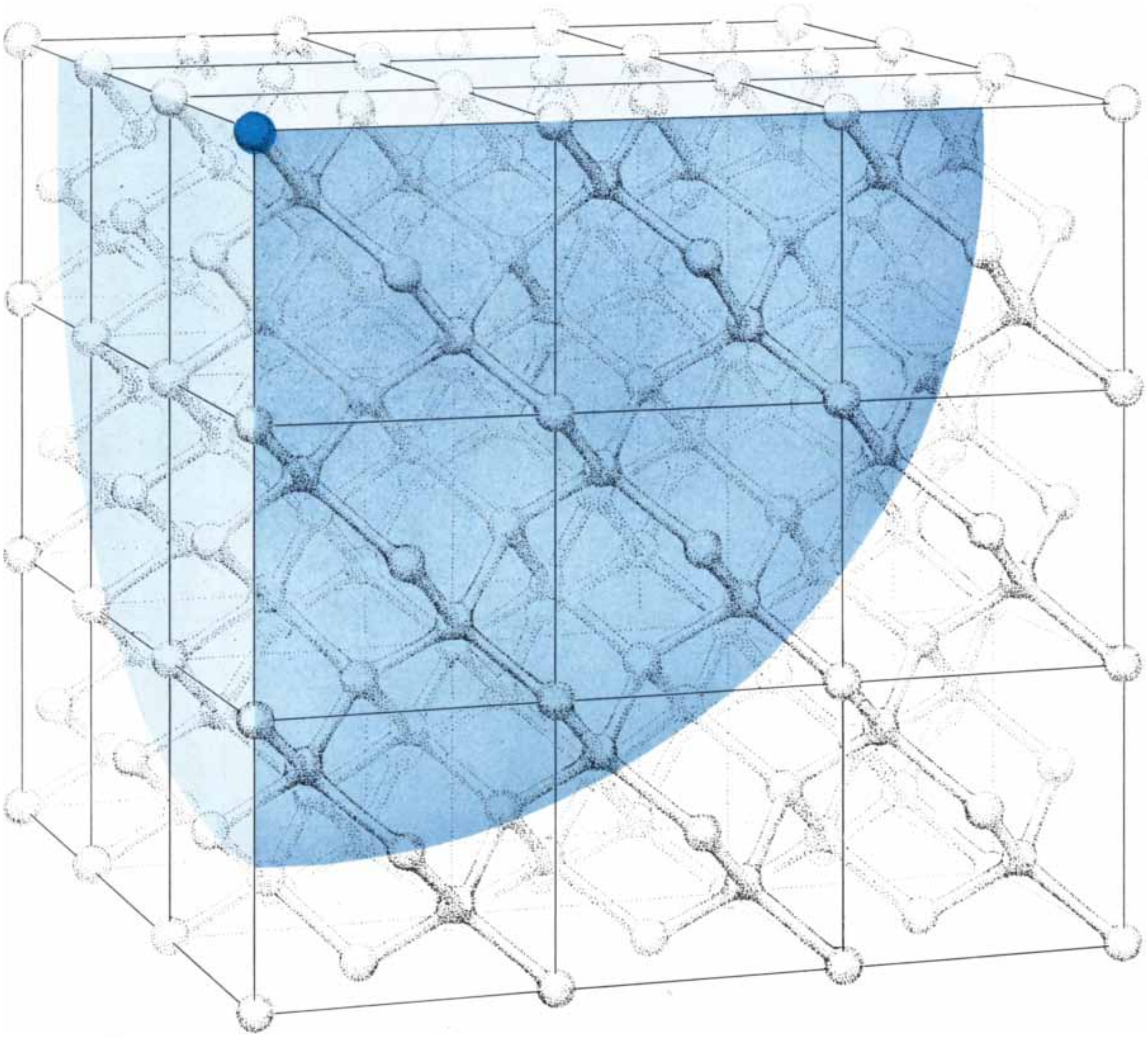
Drude's concept of mobile electrons as the agents of conduction in a metal was essentially correct, but many of the details of his model were not. The answers to the difficult questions it raised had to wait for the advent of quantum mechanics a quarter-century later. Some of the quantum-mechanical considerations affecting electrical conductivity are discussed by Sir Nevill Mott in his article "The Solid State" in this issue [*see page 80*]. Let us look into the situation in further detail.

The first requirement for conduction is a supply of carriers that are free to wander through the solid. In certain solids (such as ice and silver bromide) electricity is transmitted by ions, but in most cases, and particularly in metals, the carriers are valence electrons—electrons of the atoms' outer electronic shell. Taking a chemical view of the situation, one might describe the difference between conductors and nonconductors in terms of the relative availability of carriers. Consider the simple case of copper, a metal with a single valence electron. In the isolated atom the electron is spread out in a cloudlike orbit around the nucleus. In a crystal of copper, in which the atoms are tightly packed together, the electrons spread themselves over the entire lattice [*see top illustration on opposite page*]. They find this energetically favorable because, according to the uncertainty principle, their delocalization lowers their kinetic energy. It is this effect that causes the atoms in the crystal to stick together. Such delocalized electrons are ready candidates for acceleration in an electric field.

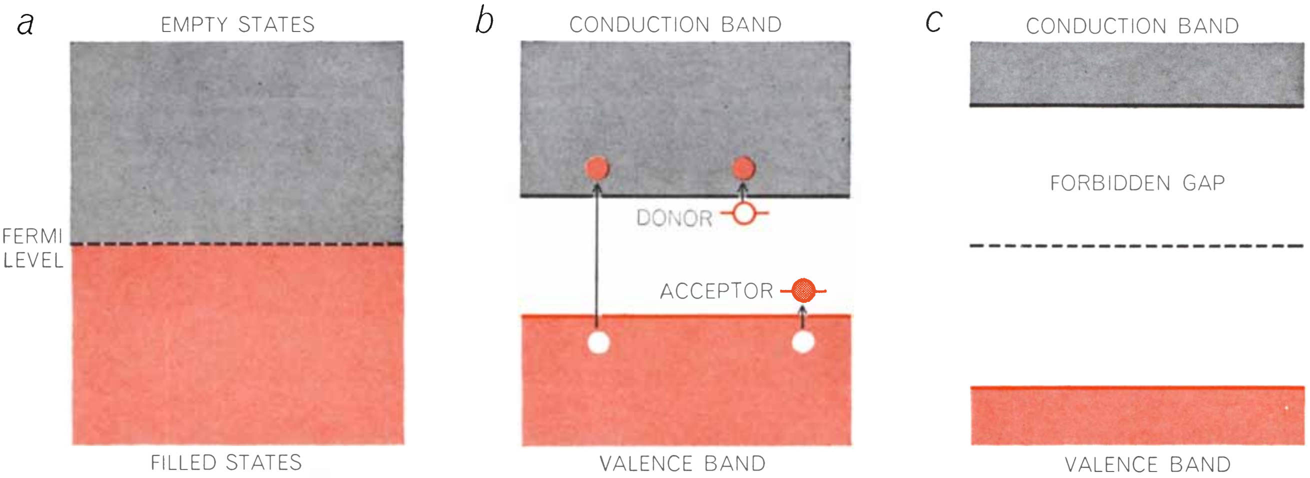
In contrast to copper, the atoms of the semiconductor germanium are cemented together more favorably by forming covalent bonds. In the resulting diamond-like structure the electrons are not free to wander through the crystal or act as electrical carriers. Accordingly at absolute zero germanium would be an in-



INTRINSIC CHARGE CARRIERS, typically valence electrons (electrons from the atoms' outermost electron shell), can conduct an electric current in pure crystals. In a metal that has one valence electron, such as copper (*left*), the valence electrons (*color*) are spread out over the entire lattice of the crystal. It is the availability of these "delocalized" electrons that makes such metals good electrical conductors. In a semiconductor, such as germanium (*right*), the four valence electrons cement the atoms of the crystal together in a diamond-like structure by covalent bonds. At absolute zero these "localized" electrons are not free to act as electrical carriers and germanium is an insulator. In order for pure germanium to become conducting, some of its chemical bonds must be broken and the bound valence electrons released; this can be done by supplying energy to the crystal in the form of heat or light.

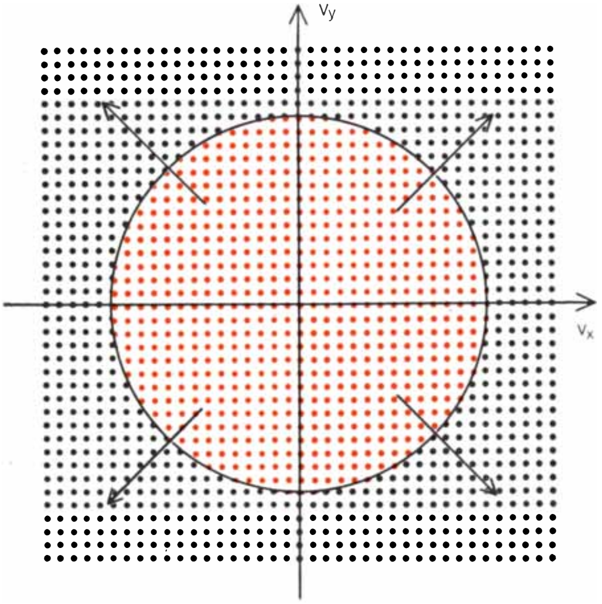


EXTRINSIC CHARGE CARRIERS can be supplied to germanium by doping the crystal with a small amount of arsenic. The arsenic atom (*color*) has five valence electrons to germanium's four. The fifth electron is only weakly bound to the arsenic atom and ranges over considerable distances from it, as indicated by the large light-colored volume. Only a small amount of energy is required to release the extra electron; as a result the doped crystal becomes conducting at much lower temperatures than pure germanium.

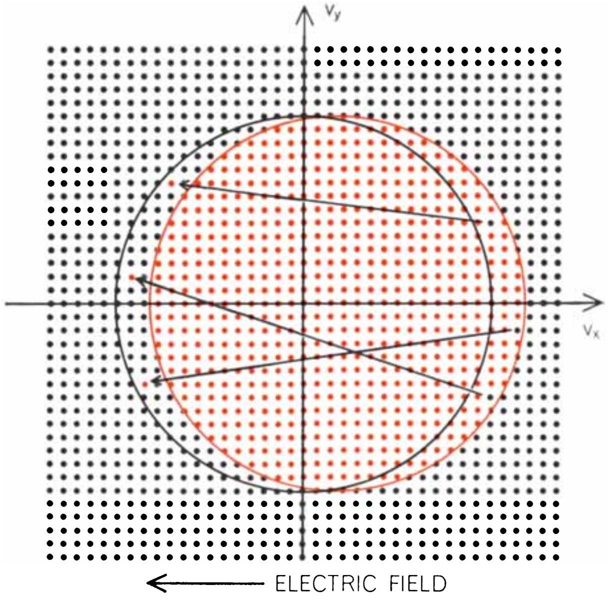


**ENERGY-BAND STRUCTURES** of a metal (*a*), a semiconductor (*b*) and an insulator (*c*) are compared in these diagrams. The electrons in all three types of solid can exist only in certain "allowed" energy bands, which are separated by "forbidden" energy gaps. The conduction band of a metal is partially filled with electrons even at a temperature of absolute zero. The highest energy occupied by the electrons is called the Fermi energy (*broken line*). In a pure semiconductor at absolute zero the valence band is completely full and the conduction band completely empty. An input of energy to the semiconductor in the form of light or heat can raise a valence electron into the conduction band. Carriers can also be supplied to the semiconductor by impurity atoms with energy levels in the forbidden gap; "donor" impurities contribute electrons to the conduction band, whereas "acceptor" impurities contribute electron "holes" to the valence band. The forbidden gap in an insulator is too large to be bridged thermally short of melting the crystal.

sulator. If, however, sufficient energy (in the form of heat or light) is supplied to break some of the chemical bonds and so release electrons, germanium becomes a conductor. Besides the electrons, the "holes" they leave at the vacated sites also become mobile electrical carriers, and under the influence of an electric field these move, like positive particles, in the direction opposite to that of the electrons. With increasing temperature the number of carriers in a semiconductor, and hence the conductivity, grows exponentially (whereas the conductivity of a metal such as copper, which has a large supply of carriers at all temperatures, is much less influenced by heat). Thus the bond-breaking requirement helps to explain why a semiconductor's conductivity increases so dramatically when it is heated.



**FERMI SURFACE** in a metal marks the division between occupied energy states (*colored dots*) in "velocity space" and unoccupied states (*black dots*). In this simplified two-dimensional diagram of a Fermi sphere each dot corresponds to an allowed electron velocity with components $v_x$ and $v_y$. According to the Pauli exclusion principle only two electrons of opposite spin can have the same velocity. The radial arrows represent the direction of increasing speed and therefore increasing energy. Conduction electrons in the solid are accommodated at the lower energies first. In the absence of an electric field there is no net velocity for the system as a whole.



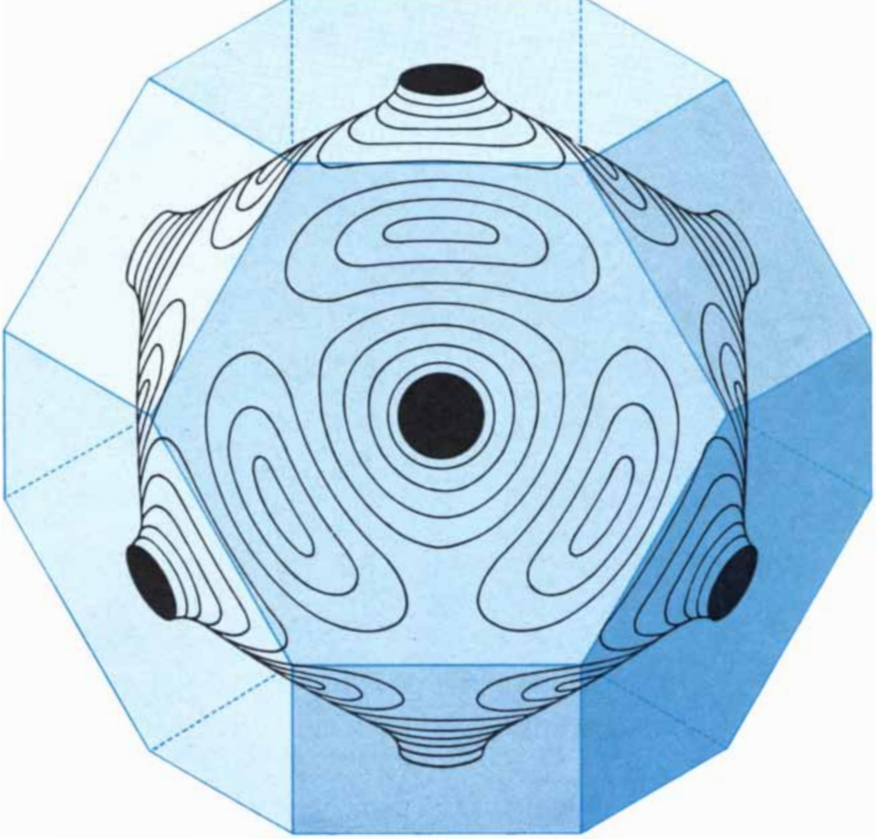
**FERMI SURFACE SHIFTS** under the influence of an applied electric field. Electrons in the metal drift preferentially in the opposite direction from that of the field. The net effect is that some electrons are transferred from the back of the Fermi surface (corresponding to velocities pointing to the left) to the front of the Fermi surface (corresponding to velocities pointing to the right). Collisions of the electrons with impurities and with atoms displaced by lattice vibrations (*arrows*) oppose this tendency, stabilizing the downfield shift of the Fermi sphere. Since all the electrons at the surface have the same energy, these transfers entail little cost in energy.

The chemical view also accounts in a general way for the ability of a minuscule amount of impurity to transform a semiconductor into a much better conductor. The impurity simply adds readily available electrons to serve as carriers. A good example is provided by the "doping" of germanium with arsenic. The arsenic atom has five valence electrons to germanium's four. The fifth electron does not enter into the covalent bonds with the germanium atoms in the crystal, and therefore its bond to the parent arsenic atom is easily broken. Since little input of energy is needed to release these electrons, the doped semiconductor becomes conducting at much lower temperatures than pure germanium. And since only a comparatively small number of carriers is required in a conductor, a minute injection of arsenic can raise germanium's conductivity to nearly that of a metal.

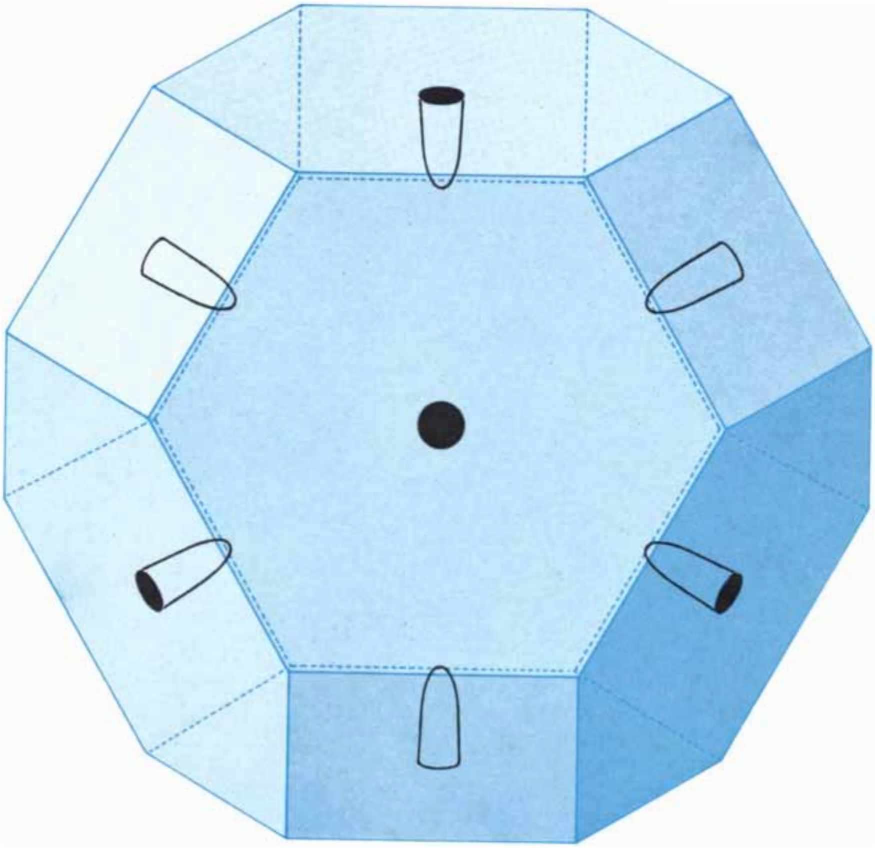
In a general way, then, the consideration of the availability of carriers furnishes a useful picture of the distinction between conductors and nonconductors. In the case of metals a very small electric field can supply enough energy to free electrons so that they can drift downstream under the influence of the field. For a semiconductor a substantial amount of energy must be applied to break the chemical bonds and release electrons. Most frequently the energy supplied is nonelectrical. If it is electrical, the crystal breaks down as a condenser does when it is subjected to too large a voltage. An insulator differs from a semiconductor simply in the strength of the chemical bonds; in insulators the bonding of electrons is so firm that they cannot be freed by heat short of temperatures that will melt or evaporate the crystal.

How can one account for the transition from the insulating to the conducting state in crystals? Is the transition generally gradual (perhaps through a progressive merging of the lowest energy state of the crystal and the higher energy states) or is it abrupt? In vanadium sesquioxide we see such a transition occurring abruptly. Perhaps in such cases an abrupt change in the crystal's mechanical or magnetic structure is responsible for the transition. Can this be taken as the general rule for all transitions? The answer is not yet known for certain. Obviously the question of the mechanism of transitions is of great theoretical and technological importance.

Such general ideas, interpreted in the light of quantum theories concerning the excitation of electrons, are helpful in



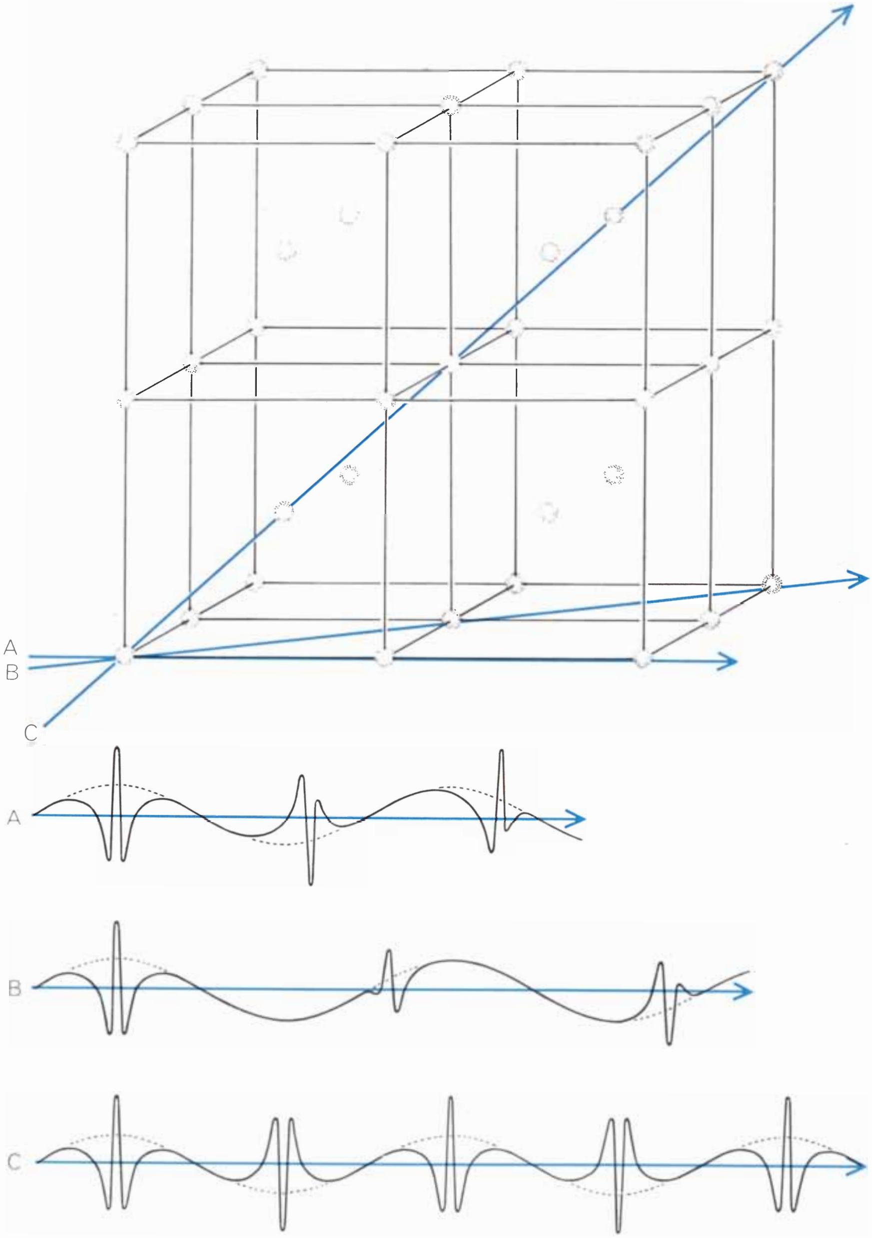
**FERMI SURFACE OF COPPER** is a distorted sphere with six "necks" pulled out to touch the boundary of the first Brillouin zone (*color*), which in three dimensions is a truncated octahedron. The faces of the Brillouin zone represent energy gaps in velocity space.



**FERMI SURFACE OF GERMANIUM,** heavily doped with arsenic to make it an *n*-type semiconductor, differs markedly from that of copper, signifying the availability of fewer electrons for conduction. The Brillouin zone for germanium is the same as that for copper.

gaining insight into some of the basic questions about the electrical properties of materials. They are only an entering wedge, however, into the major underlying question of how one describes the energy of a crystal in terms of the quantum states of its electrons. Because of the large number of electrons in a solid, this presents a many-body problem of a most difficult kind on whose understanding electrical transport theories depend. The calculations undertaken to explore the conduction process have had to depend on models that represent approximations.

The most useful approximation that has been developed to describe the distinction between the conducting and the nonconducting states of a crystal is the band model. It is based fundamentally on consideration of the quantum states allowed to electrons by the Pauli exclusion principle. According to this principle, a given quantum state cannot be occupied by more than two electrons (with opposite spins). The principle accounts for the shell structure of isolated atoms. Since electrons prefer the lowest available energy level, each successive shell is filled before higher ones are occupied.



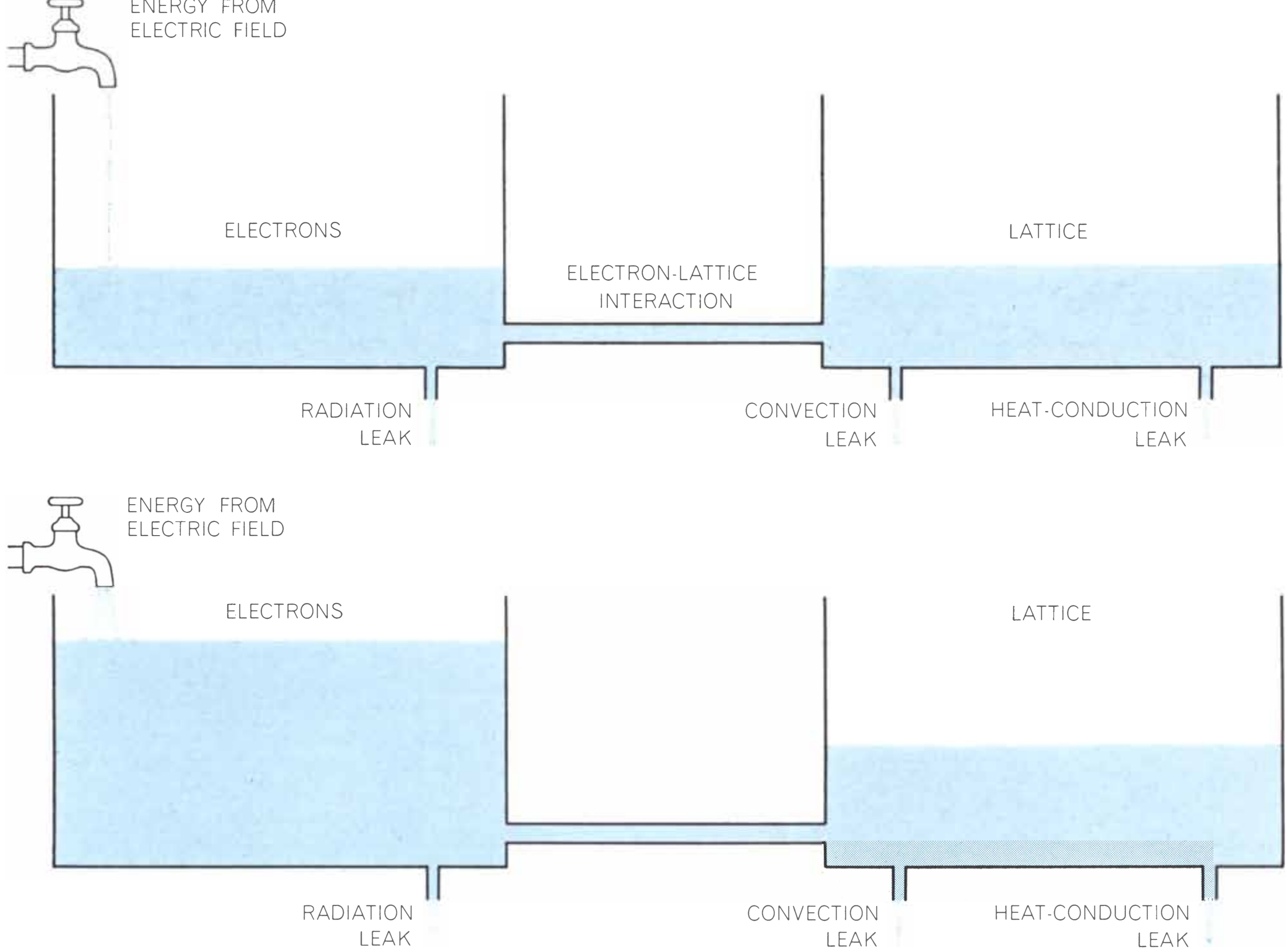
**WAVE FUNCTION** of an electron moving in a crystal lattice is modulated by the electrostatic influence of the ions it encounters. In this illustration the three different wave functions (*solid curves below*) correspond to three different directions through a body-centered-cubic lattice of sodium (*diagram above*). In all three cases the total energy of the electron (kinetic energy plus potential energy), and hence its wavelength (*broken curves below*), are the same. The rapid wiggles of the waves in the vicinity of an ion imply that the electron has a higher kinetic energy there than elsewhere. This in turn means that the electron travels very rapidly through this region and spends comparatively little time in it. As a result the influence of the ionic cores is not nearly as large as one might expect, and in many simple solids the conduction electrons can be described as if they were free particles.

When atoms are grouped together in a crystal, there is an analogous situation. The electrons wandering through the crystal have energies that fall within "bands" derived from atomic shells. Within a band the difference between permissible levels is so infinitesimal that an electron can very easily be excited from one level to the next. The bands are separated, however, by gaps that are forbidden to the electrons [*see top illustration on page 198*].

In a metal the uppermost band, called the conduction band, is only partly filled. Hence an applied voltage can excite some of the electrons to heightened energy, so that instead of drifting at random they will move in the direction of the field. In an insulator or pure semiconductor, on the other hand, the conduction band is empty, and all bands below it are completely filled. To promote an electron across the gap to the conduction band from the uppermost filled band (called the valence band) requires a great deal of energy, which must be supplied by some external source, for example the input of heat or light. (Even an insulator, with its very large energy gap, can become conducting in the presence of light. Indeed, copying by xerography depends crucially on this process in one of the best insulators, amorphous selenium.)

This picture accounts for the presence of excitable and mobile electrons in a conductor, but we still have to explain the ability of the electrons to travel along the field against the "frictional" resistance that Drude attributed (incorrectly, as it turns out) to the stationary ions in the crystal lattice. The Drude model went wrong in its two principal assumptions; first, that the stationary ions can scatter the conduction electrons, and that therefore the mean free path of such electrons in a metal is only the distance between atoms, and second, that all the electrons are involved in the conduction process. The quantum-mechanical account of conductivity explains why both postulates are incorrect.

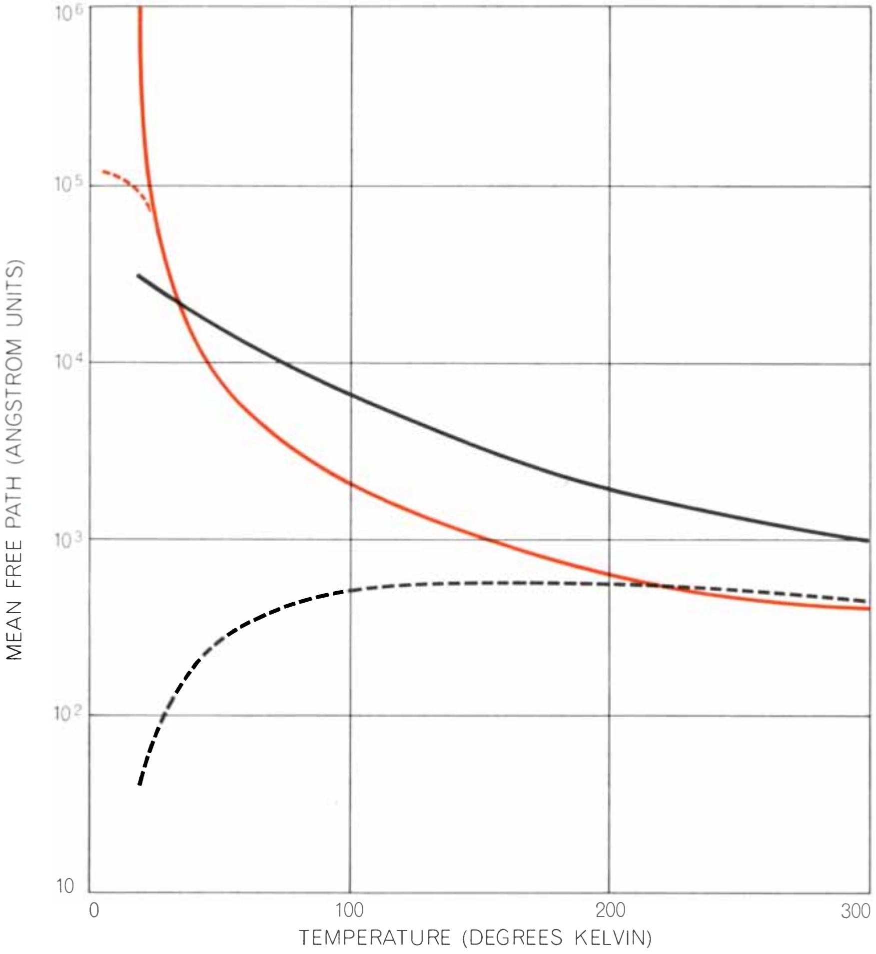
Why is the electrons' mean free path much longer than Drude supposed? The answer lies in the fact that electrons, like other particles, partake of the nature of waves. According to quantum mechanics, an electron traveling in a crystal can



**HYDRAULIC ANALOGY illustrates a characteristic of semiconductors known as the hot-electron effect, which is responsible for large deviations from Ohm's law at high electric fields. (Ohm's law states that the resistivity of a material is independent of the strength of the applied electric field.) The movement of water through the system shown here is analogous to the flow of energy in a semiconductor. The open tap corresponds to the applied electric field. Energy is transferred from the field to the electrons (*container at left*), which it accelerates. The electrons in turn transfer their energy to the crystal lattice (*container at right*). The size of the tube between the two containers represents the strength of the interaction of the electrons with the lattice. Electrons can also transfer energy out of the crystal by electromagnetic radiation, whereas the lattice can lose energy by heat conduction or convection. If the leaks to the outside are small, the containers will fill up when the tap is turned on. This retention of energy results in heating the crystal. If the tap is merely dribbling (*top*), the water in the two containers will be at the same level; in other words, in a weak electric field the effective temperature of the electrons and the lattice is the same. In the strong-field situation, on the other hand, when the tap is opened all the way (*bottom*), the electron-lattice pipe may be too small to keep the water in the two containers at the same level. The water level in the left container will then be higher and the effective temperature of the electrons will be greater than that of the lattice. As a result the resistivity of the material will depend on electric-field strength.**

be described as a wave that is modulated by the electrostatic influence of the ions it encounters. As the wave comes near an ion, it is distorted into rapid wiggles that imply the electron is accelerated to a higher kinetic energy during its passage [*see illustration on opposite page*]. This means that the electron spends comparatively little time near the ionic cores in the lattice and therefore is not greatly influenced by them. Indeed, in many simple solids the conduction electrons can be described as free particles, as Drude suggested, but with an apparent mass that may differ from that of electrons in a vacuum.

There is a crucial difference, however, between the classical picture and the one described by quantum mechanics. Whereas the Drude model implied that the mean free path of the electron between collisions should be of the order of the distance between atoms, the quantum-mechanical picture implies that the electron wave function adjusts itself to the cores in a systematic fashion. Consequently an electron can travel through a perfect crystal without ever being scattered! In other words, quantum mechanics predicts that in an ideal, fixed lattice the ions interpose no frictional force against the electrons' travel and the electrical conductivity is infinite. Of course, real solids are never perfect in this sense. Even if a crystal were completely free of impurities and defects such as dislocations, the ordinary thermal vibrations of its atoms would still cause enough irregularity to scatter the electrons to some extent. Nevertheless, the particles' wave characteristics indicate that the mean free path of the electrons must be considerably longer than the distance between atoms. (Indeed, electrons in highly purified gallium at very low temperatures have mean free paths up to 100 million times larger than the interatomic distance.) This larger mean free path in turn implies that the electrons have sufficient mobility to account for the observed conductivity of metals



**MEAN FREE PATH OF ELECTRONS** is constant in an impure metal at low temperatures and then decreases as the effects of lattice vibrations become dominant (*broken colored curve*). The solid colored curve represents the situation in an idealized pure metal. In an impure semiconductor, on the other hand, the mean free path of the electrons increases initially with temperature owing to scattering from impurities, reaches a maximum and then decreases as scattering caused by lattice vibrations gradually assumes the major role (*broken black curve*). The solid black curve represents an idealized pure semiconductor.

even though the number of contributing carriers is relatively small.

Why is it that only a small fraction of the available conduction electrons are involved in conductivity? Quantum mechanics again provides the answer. We start with the Pauli exclusion principle, which states in this context that only two electrons (of opposite spin) can have the same position in a space whose axes are the velocity components of the electrons' motion. (Velocity is defined as speed plus direction.) There is therefore a wide distribution of velocities for the conduction electrons, with speeds ranging from zero to a certain maximum. The electrons with the maximum velocity form a boundary, called the Fermi surface, that marks the division between occupied and unoccupied regions of velocity space [see "The Fermi Surface of Metals," by A. R. Mackintosh; SCIENTIFIC AMERICAN, July, 1963].

In the stable electronic configuration of the crystal there are as many electrons traveling with a given speed in one direction as there are traveling with the same speed in the opposite direction; therefore there is no net velocity for the system as a whole. If we now apply an electric field, it will accelerate the electrons (in the opposite direction because of their negative charge). In a short time each electron will have added to its velocity vector a small increment parallel to the field. This change overturns the previous balance of velocities and can be pictured as a shift of the Fermi sphere [*see bottom illustrations on page 198*]. If there were no resistance in the crystal, the Fermi sphere would continue to shift, with more and more velocities in the downfield direction and fewer and fewer upfield. However, the thermal motion of the ions and impurities that scatter the electrons from their downfield paths tend to turn some of them to velocities headed back upfield. When this resistance effect matches the accelerating effect of the applied electric field, the Fermi sphere ceases to shift. The net shift that has occurred when this steady state is reached measures the drift velocity of the gas of electrons in the downfield direction. The drift velocity can be increased by applying a stronger field or by lengthening the electrons' mean free path.

The scattering of the electrons only changes their energy by a small amount. Such a scattering will take the electron from an occupied to an unoccupied velocity state, however, and since the drift velocity is far smaller than the speed of electrons at the Fermi surface, only those few electrons very near the Fermi surface can be scattered. In fact, one can look at the entire process as if only a small fraction of all the electrons were participating in the conduction process. A similar argument shows why the electron contribution to the specific heat of a metal is as small as is observed.

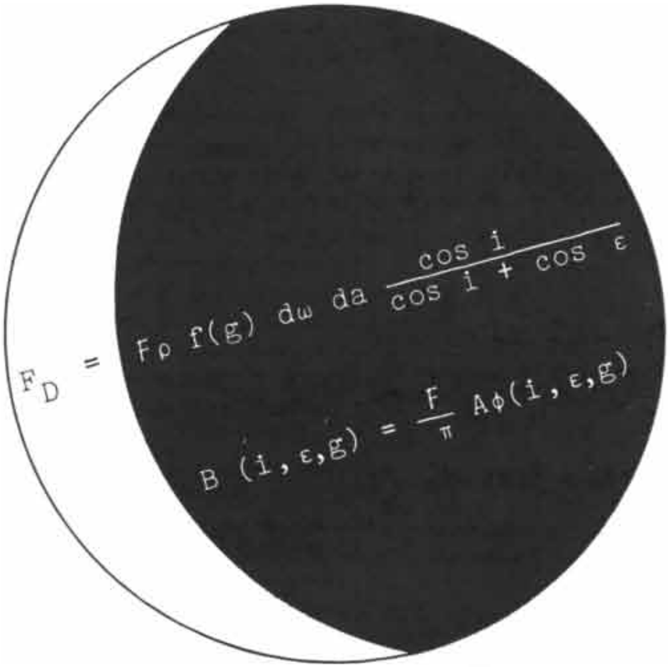
With these facts in mind, let us consider some of the important scattering mechanisms in the lattice (involving heat and imperfections) and their influence on the electrons' mobility at various temperatures. I have already mentioned the thermal vibrations of the lattice atoms in this connection. At moderate temperatures the amplitude of their oscillations around their equilibrium positions is small enough to allow the electrons a mean free path considerably longer than the distance between atoms. As the temperature rises and the oscillations become more violent the mean free path is shortened and the conductivity of the crystal of course is reduced. Conversely, a lowering of the temperature increases the mean free path and the conductivity. There are limits, however, to the conductivity that can be achieved by cooling (except in the special case of superconducting metals at very low temperatures); these limits are imposed by imperfections, which are present in all real crystals.

The most common imperfections in many semiconductors and metals are impurities (foreign atoms). Their scattering effect as a function of temperature is rather different in semiconductors from what it is in metals. In metals (where the conduction electrons have relatively high velocities at all temperatures, since their velocity is determined primarily by the Fermi surface rather than by temperature) the scattering effect of impurities is constant, regardless of temperature. In contrast, in a semiconductor the effect of impurities varies considerably with temperature. At low temperatures an electron moves past an impurity slowly, spends a comparatively long time in its vicinity and therefore is scattered more effectively. At higher temperatures, with the electrons at correspondingly increased velocities, the impurities become less effective scatterers. Hence we expect the mean free path of a semiconductor to increase with rising temperature until the lattice vibrations due to the high temperature become so violent that they have an important scattering effect. In metals, on the other hand, the mean free path is constant up to temperatures at which the scattering effect of the lattice vibrations becomes dominant.

At extremely low temperatures, oddly enough, lattice vibrations can play quite an opposite role. Paradoxically vibrations of the lattice are responsible for the infinite conductivity of superconductors. An electron traveling through the lattice at a certain velocity draws ions toward it and thereby produces an attractive region that in turn draws a second electron. This electron pairing correlates the motion of all the conducting electrons and maintains perpetual conduction of a current as long as the temperature remains low enough for the pairing not to be broken up. Interestingly enough, the metals most likely to become superconducting at low temperatures are those that are relatively poor conductors at room temperature, and the reason is the very fact that in these metals the electrons interact strongly with the lattice vibrations.

Lattice vibrations can also have a salutary effect on the mobility of carriers in certain semiconductors where most of the time the carriers are held closely to the ions in the lattice. Nickel oxide doped with a trace of lithium is such a material. At room temperature an electric field will cause the carriers to hop occasionally from one site to another, but this happens infrequently. If, however, the temperature is raised, increasing the amplitude of the lattice vibrations and thus bringing ions closer together during a portion of the vibration cycle, the chances of a carrier's hopping from one site to the next are improved; as a result the mobility of the carriers will increase exponentially with temperature.

One of the oddities of semiconductors is that they do not always obey Ohm's law, which states that the electrical resistivity of a material is independent of the strength of the applied field. It turns out that when a strong field is applied to a semiconductor, the conduction elec-



trons are speeded up from their ordinary thermal velocities to such an extent that their energy is vastly greater than the thermal energy characteristic of the temperature of the crystal. This increased electron energy can correspond to effective electron temperatures as high as 5,000 degrees K. when the crystal itself is at room temperature.

As a result the resistivity, which is ordinarily a property of the material at a given temperature, now becomes a property of the material not at its real temperature but at a higher effective electron temperature. Since the effective temperature can be changed by changing the strength of the applied voltage, the resistivity is now dependent on the voltage, in contradiction to the assertion made in Ohm's law.

This effect does not occur in metals because of the abundance of carrier electrons in them. Since there are few carrier electrons in a semiconductor, the resistance of the crystal can be made high enough to support a large voltage. Moreover, the velocities of the carrier electrons in semiconductors are so small with respect to those of the electrons at the Fermi levels in metals that it is harder for them to transfer to the lattice the energy given them by the applied field. This results from the fact that there are fewer quantum-mechanically acceptable velocity states into which the lattice vibrations can scatter the electrons if they are slow.

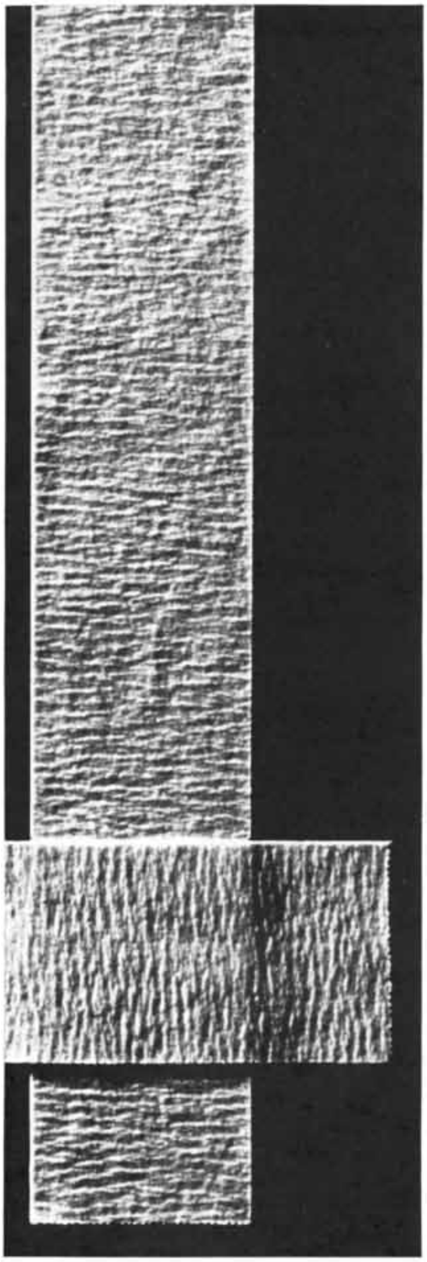
The relatively simple systems I have described in this article illustrate the new insights that solid-state research has provided into the manifold electrical properties of materials. The properties of some semiconductors are now well understood in quantitative terms, and we appear to be well on the road to a similarly precise understanding of metals. Among the fruits of this deeper understanding is the sophisticated design of solid-state electronic devices, which are becoming ever more complicated mosaics of substances. The field of applications is large and very active; I shall cite only a few of the recent developments.

One is the extensive search for new superconducting materials. Already superconducting magnets are available commercially, and the dream of lossless transmission lines for electricity seems possible for realization in the future. The central problem here is the construction of a material that will be superconducting at a reasonably high temperature. Within the past few months there has been produced a metal alloy—consisting of niobium, aluminum and germanium—that becomes a superconductor at 20 degrees K., the highest transition temperature yet found. This discovery is all the more remarkable because the previous front runner, niobium-tin with a transition temperature of 18 degrees K., maintained its preeminent position for 13 years. The new high in transition temperatures is almost (but not quite) large enough to make possible the use of liquid hydrogen instead of the more expensive helium as the coolant. There are sound theoretical arguments suggesting that 20 degrees is close to the limiting transition temperature for any superconducting material, but it is conceivable that superconductivity at room temperature might be a possibility for organic materials of appropriate design [see "Superconductivity at Room Temperature," by W. A. Little; SCIENTIFIC AMERICAN, February, 1965].

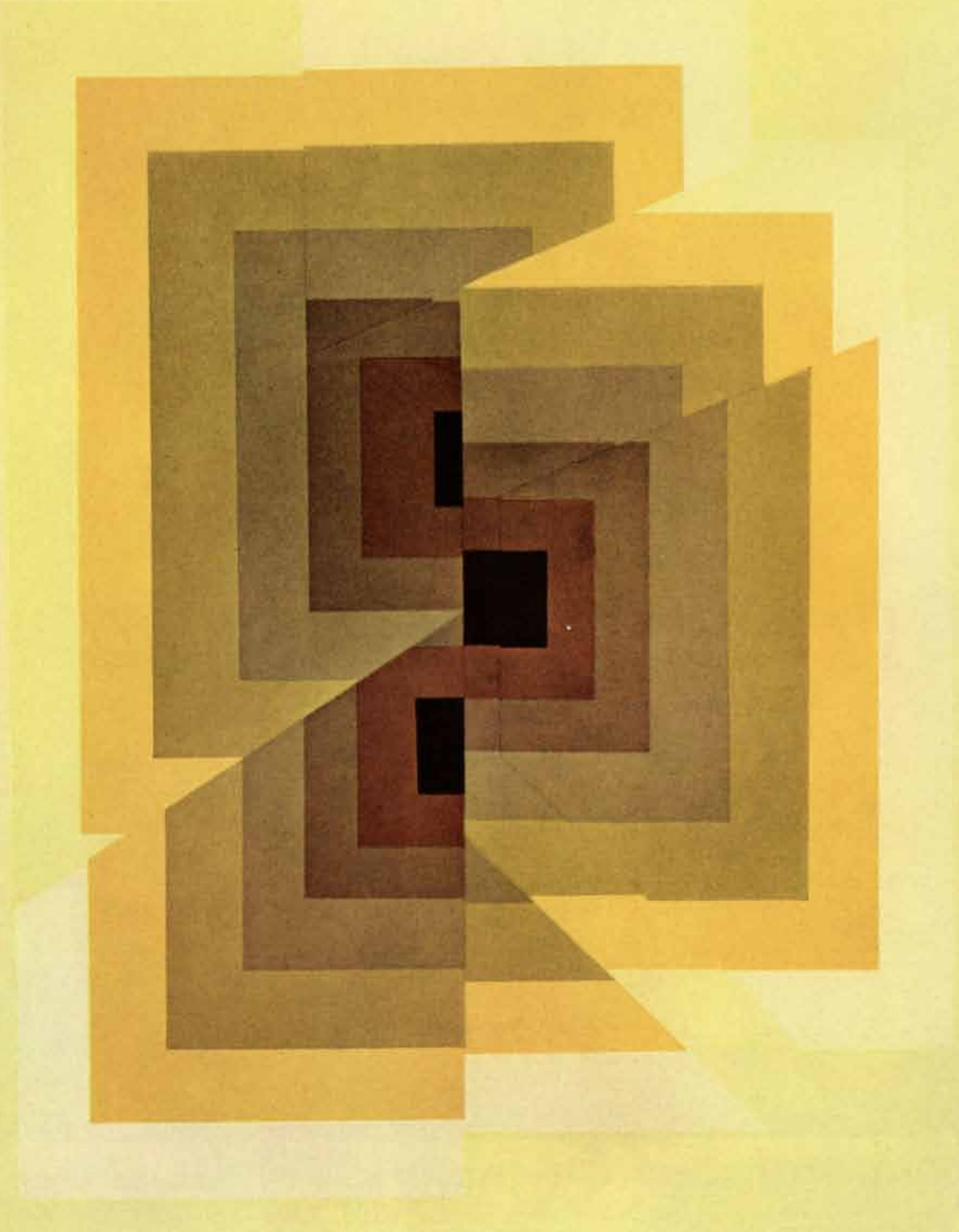
Among the exotic materials exhibiting superconductivity is strontium titanate—a superconducting semiconductor! This somewhat paradoxical nomenclature is actually not as mysterious as it seems; strontium titanate in its ordinary state is a semiconductor, but by decreasing its oxygen content it can be made metallic and superconducting.

For several reasons the electrical properties of organic materials are particularly interesting. It has been shown that the transfer of electrons from molecule to molecule plays important roles in fundamental processes of living organisms. A molecule that has been studied extensively in this context is that of phthalocyanine, a fairly simple structure that resembles the active center of the complex molecule of chlorophyll and certain other biologically active substances. The electrical properties of a number of organic materials have become important in technology. Organic dyes, for example, are used in photography. And organic chemists are investigating the synthesis of polymers with semiconducting and perhaps even metallic properties, which would make possible plastic wiring in houses and plastic transistors in television sets.

Clearly the electrical properties of materials, from pure elements to complex biological substances, depend in a fundamental way on the details of their electronic structures. It is therefore hardly surprising that the efforts of scientists to understand these properties are inextricably tied in to one of the main currents of 20th-century science: the development of quantum mechanics.



PHOTOGRAPHED AT NORAD, COLORADO SPRINGS, BY STEPHEN MICHAEL.



# The spectrum of alternatives

Today, fabricators can choose materials from an almost continuous spectrum of alternatives. By manipulating the size and bonding of molecules, industrial research has developed products from butter-soft to diamond-hard, with virtually any other physical property built in. These new substances have ushered in a new era—the era of non-metallic materials for engineering uses.

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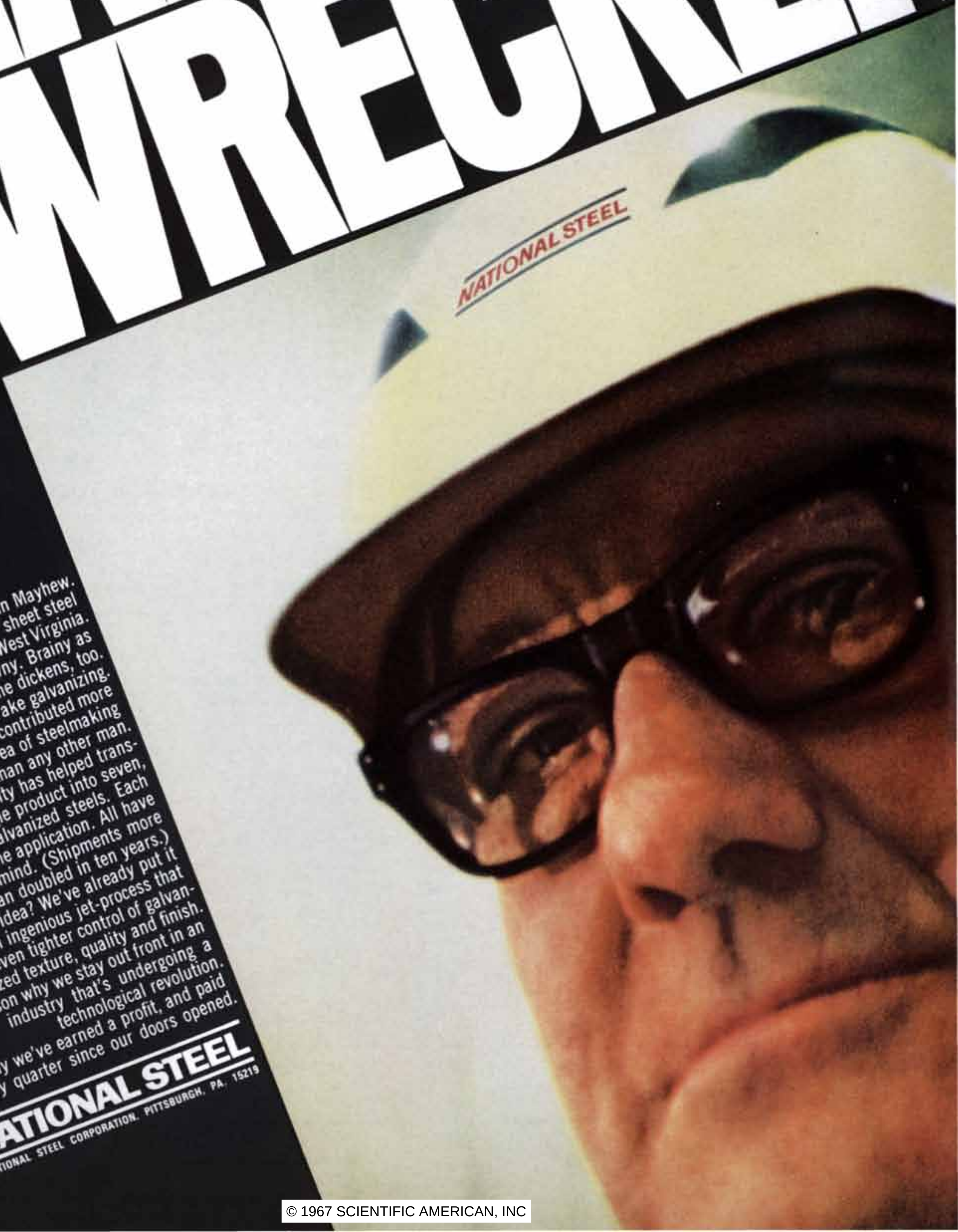
NATIONAL STEEL

# A Versatile Approach to Materials Evaluation

The megaton pressures of the ocean bottom, the micrometeorite hazards of space flight, the not-so-soft lunar landings and the 5000°F heat of re-entry are but a few of the thousands of challenges being met by materials researchers. The challenge of today's technology requires a versatile approach to materials evaluation.

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The Adsorptomat has become a member of the team of elemental, physical and thermal analysis instruments which are offered for sale and are used in our Materials Technology Laboratory to perform complete analyses for customers who do not have complete materials evaluation facilities. The demands of these customers, and the increasing government requirements for measured quality, constantly stimulate our creative effort. Our original 3,000 psi Porosimeter soon graduated to a 5,000 psi model, to a 15,000 psi model and, recently, to a 60,000 psi model.

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# The Chemical Properties of Materials

*In dealing with solid materials the chemist is concerned not only with such matters as corrosion and chemical syntheses but also with chemical events that occur inside solids, for example precipitation*

by Howard Reiss

In the study of the solid state, as in many other fields of modern scientific inquiry, it has become impossible to draw a sharp dividing line between chemistry and physics. Much of the present information about the chemical properties of solid materials has been developed by people trained as physicists, and it is an interesting fact that very few university chemistry departments offer courses in solid-state chemistry as such. Yet every discipline has its own techniques and special folklore, which, by illuminating a subject in a special way, can reveal facets not easily discoverable by other special means. Chemists have brought their own points of view to aid in the study of the physical properties of solids.

A rough distinction between the physical and chemical approaches to the study of solids might be the following: The physicist is accustomed to working with homogeneous solids in which the specific location of objects or events is of no consequence. This robs him of some opportunity to exercise physical intuition. As a result he transfers his base of operations to an abstract space known as momentum space, in which structure is recaptured. In contrast, the chemist usually deals with localized objects (for instance molecules and elements of structure) in real space. In crystals the chemist is particularly interested in localized defects or imperfections. They are mainly of two general types: point defects and line defects. The point defects include vacancies where atoms are missing, the switching of atoms out of their regular order, the displacement of atoms into interstitial spaces in the crystal, substitutional impurities (foreign atoms substituted for the regular ones), positive "holes" (where electrons are missing) and atom-like combinations of holes and electrons, called excitons, that can wander through the crystal. The line defects are principally the well-known dislocations so important to the mechanical properties of solids.

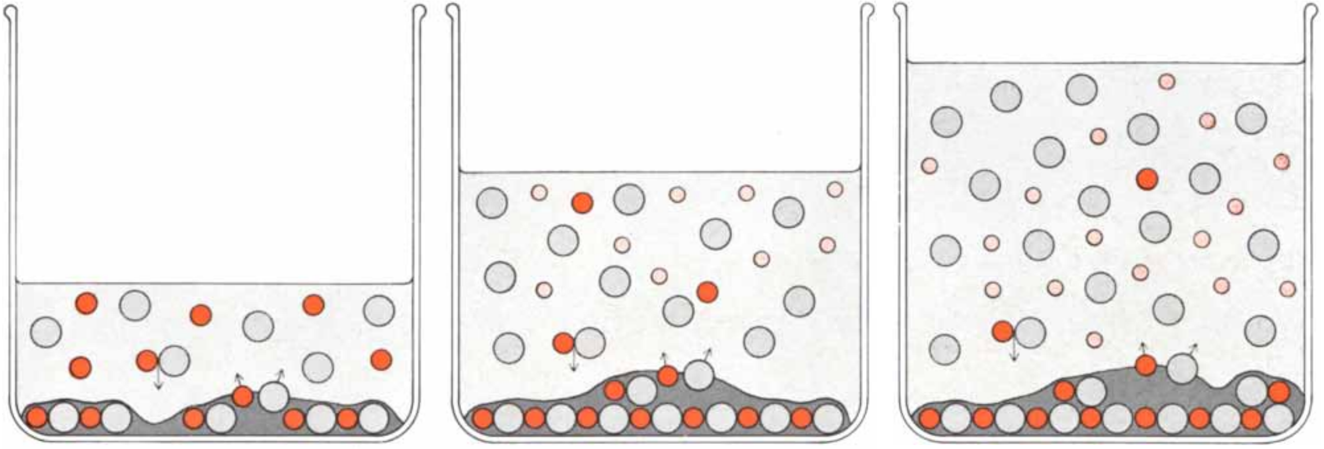
Some of the most useful properties of solid materials depend on localized imperfections as well as on the crystal regularity itself. The methods and viewpoints of chemistry have therefore been important in the development of materials technology by helping to produce defects in a controlled manner. The chemist regards each defect as a species of chemical object localized in space; he largely ignores the regular crystal background as he might the water in typical "wet" chemistry. Viewing crystal defects in this way, he is able to explain many of their effects and interactions on the basis of chemical principles, such as the law of definite proportions and the law of mass action.

As every chemistry student knows, the law of definite proportions asserts that in every sample of a given compound the constituent elements are always present in the same proportions. For example, common salt (NaCl) always contains sodium and chlorine atoms in equal number. Experiments with solid materials have shown, however, that this law can be violated. If we put solid sodium in a closed container with a crystal of sodium chloride and heat the material so that some of the solid sodium is evaporated, we find that the sodium chloride crystal soon acquires more sodium than chlorine. The regularity of the crystal lattice can be maintained only in the presence of the additional sodium ions by the simultaneous addition of vacancies occupied by negatively charged electrons rather than by negative chloride ions.

The defective crystal is said to be "nonstoichiometric." (Adherence to the law of definite proportions is called stoichiometry.) Nonstoichiometry can lead to interesting electrical properties in semiconductors and also to useful optical properties (including coloring) in various materials [see "The Electrical Properties of Materials," by Henry Ehrenreich, page 194, and "The Optical Properties of Materials," by Ali Javan, page 238]. The production of nonstoichiometric defects has therefore become an inviting field for chemists.

Now let us consider the chemical law of mass action as it applies to crystal defects. This law says simply that the rate of any chemical process depends on the products of the concentrations of the interacting species. To illustrate mass action with a simple case in ordinary chemistry, think of a saturated aqueous solution of silver chloride, with some silver chloride deposited in solid form at the bottom of the vessel. Pairs of silver and chloride ions are continually coming out of the solid into solution and, at an

**FLIGHT OF CARBON FROM SOLID STEEL is an example of chemical activity within a material. The micrograph on the opposite page shows unalloyed steel, enlarged 300 times. The lower portion shows the normal composition of the metal, intimately mixed ferrite and carbon-rich pearlite, formed during heat treatment. In the upper portion, close to the sample's surface, the carbon has been preferentially oxidized, transforming the mixture of ferrite and pearlite into ferrite alone. The micrograph was made by Lawrence H. Van Vlack of the University of Michigan and appears in his book *Elements of Materials Science*. It is reproduced by the permission of the Addison-Wesley Publishing Company.**



**SILVER IONS** are forced out of a solution of silver chloride by application of the "common-ion effect" of the law of mass action. In a beaker (*left*) partly filled with a saturated solution of silver chloride and containing a layer of solid silver chloride at the bottom, the system is in equilibrium. Positive silver ions (*solid color*) and negative chloride ions (*gray*) leave the solid and divide just as frequently as silver and chloride ions in the solution combine and reenter the solid. When sodium chloride is added to the beaker (*center: additional chloride ions are also gray; sodium ions are a tint of color*), the formerly pure silver chloride solution has more chloride ions "in common." This increases the frequency of chloride pairing with silver ions, thus reducing the number of silver ions in solution. When more sodium chloride is added (*right*), the number of silver ions in solution is further reduced.

equal rate, silver and chloride ions in the solution are pairing up and entering the solid state. This equilibrium will persist as long as the product of the ion concentrations (silver-ion concentration times chloride-ion concentration) remains unchanged. Now add sodium chloride to the solution. The addition of chloride ions increases the product of the silver-ion and chloride-ion concentrations in the solution. With more chloride ions present the chances that silver ions will encounter them are increased. As a result silver-chloride pairs will be deposited on the solid at a higher rate, and the removal of silver ions from the solution will continue until a new equilibrium is established [*see illustration above*]. Conversely, if chloride ions were removed from the solution, more silver ions would come out of the solid into solution. This "forcing" of a chemical species from one side of a process to the other is known as mass action. Another example is the dissolving of a solid acid by neutralization with a base. When a base such as sodium hydroxide (NaOH) is added to an acid solution in contact with some solid acid, the hydroxyl ions combine with the acid's hydrogen ions (forming water), destroying acid and thus reducing its concentration in solution. This causes more acid to dissolve.

In exactly the same way that the law of mass action controls ordinary chemical reactions, it can be applied to the control of defects in a crystal. We have already noted that any type of defect—a vacancy, an electron "hole" (which behaves like a positive electron), an interstitial atom, an impurity—can be treated in terms of mass action as though it were a chemical entity.

Consider a crystal of sodium chloride. We can think of each sodium ion in its normal position in the lattice as a kind of combination, or "compound," that is capable of generating two offspring: an interstitial ion and a vacancy. By jumping from its normal site into an interstice it produces both defects. A sodium ion adjacent to the vacancy can then jump into it. Therefore at temperatures high enough to agitate ions out of their sites, both interstitial ions and vacancies are able to move through the crystal lattice. Like the elements of a chemical compound, they are subject to the law of mass action, and their concentrations can therefore be controlled by the adjustment of the concentrations of other chemical-like entities.

Suppose we replace a sodium ion in the sodium chloride lattice with a calcium ion. The calcium ion carries two units of positive charge; therefore in order to conserve the crystal's charge neutrality another of the singly charged sodium ions (in addition to the one replaced) must be removed from the lattice. Thus by introducing calcium ions by adding calcium chloride to the crystal we can create vacancies. The presence of the additional vacancies can result, according to the law of mass action, in a reduction of the number of sodium ions in interstitial positions, so that the product of the two concentrations (of vacancies and interstitials) is restored to its equilibrium value [*see illustrations on opposite page*].

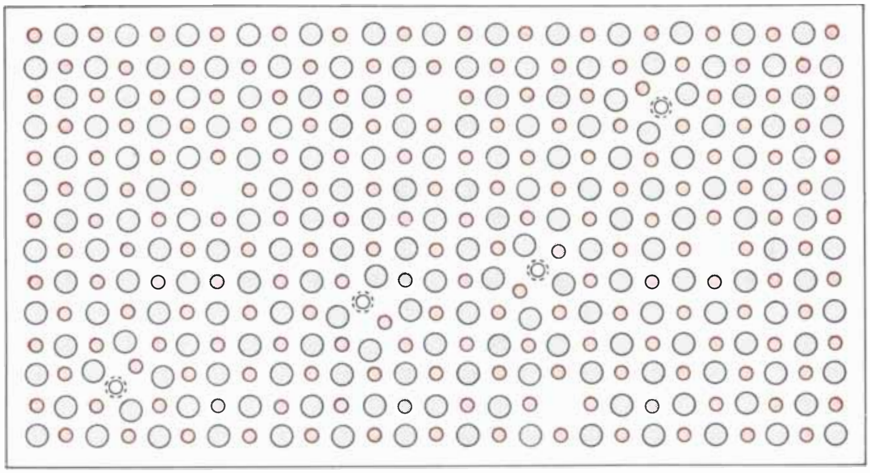
The law of mass action is applicable even to the energy states of electrons (and holes), which the physicist likes to view from the vantage of momentum space. Some of these states, as they occur in semiconductors, are actually localized imperfections. In terms of energy they are located in the forbidden band, or energy gap, between the valence band and the conduction band. Generated by chemical impurities introduced into the semiconductor crystal, these imperfections are of two types. One comes equipped with an extra electron (attached to an impurity) installed in an energy level just below the conduction band. It is said to be a "donor" because very little energy is needed to donate, or promote, the electron to the conduction band, where it may conduct electricity. Examples of donors in germanium and silicon semiconductors are lithium (an interstitial impurity) and arsenic, antimony and bismuth (substitutional impurities). The other type of imperfection comes equipped with a positive hole in an energy level just above the valence band. It is called an "acceptor" because the hole can easily accept an electron from the valence band, leaving behind a mobile positive hole capable of conducting electricity in that band. Boron, aluminum and gallium are impurities that behave as acceptors in germanium and silicon semiconductors.

Now, this phenomenon of energy bands and donor and acceptor states allows us to produce a *p-n* (positive-negative) junction in a semiconductor crystal by the introduction of impurities.

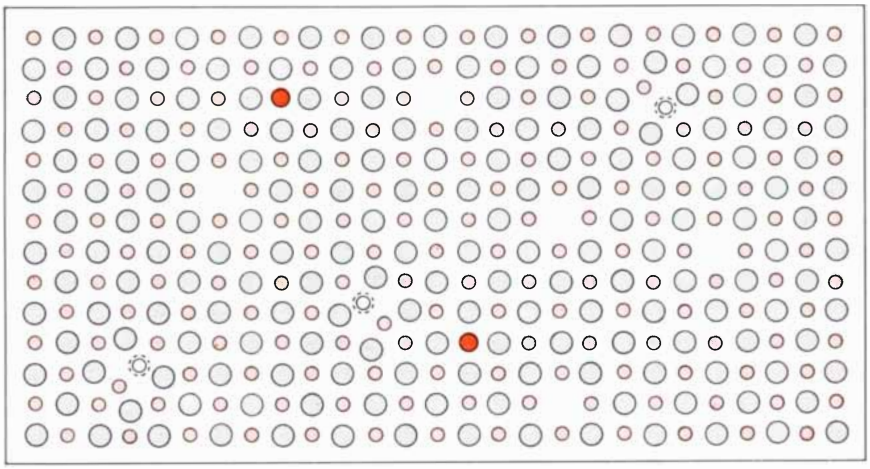
This is accomplished by "doping" one region of a silicon crystal with, say, arsenic atoms, which behave as donors and yield conduction electrons, while doping an adjoining region in the same crystal with, say, aluminum atoms, which behave as acceptors and yield valence band holes. Because of thermal agitation the mobile electrons and holes wander freely through the crystal. When electrons cross the junction between the donor and acceptor regions, they find holes on the acceptor side and "combine" with them (that is, fill the holes and go out of circulation). Similarly, holes that cross the junction to the donor side combine with electrons. The result of this two-sided process is a net removal of electrons from the donor side and of holes from the acceptor side, so that the donor side becomes positively charged and the acceptor side negatively charged. Mobile electrons are then repelled from the acceptor side, and holes are likewise repelled from the donor side. Accordingly the system comes to equilibrium with a built-in electric field at the *p-n* junction.

This built-in field makes it possible to fabricate transistors from semiconductors. A single *p-n* junction can serve as a current rectifier, because an applied voltage can drive current in one direction (holes from the *p* to the *n* side and electrons from the *n* to the *p* side) but not in the opposite direction, there being no available carriers that can cross the junction for the conveyance of current in that direction. If an *n-p* junction is paired with a *p-n* junction, so that an *n-p-n* region is created in the crystal, the system (then called a junction transistor) can act as a current amplifier.

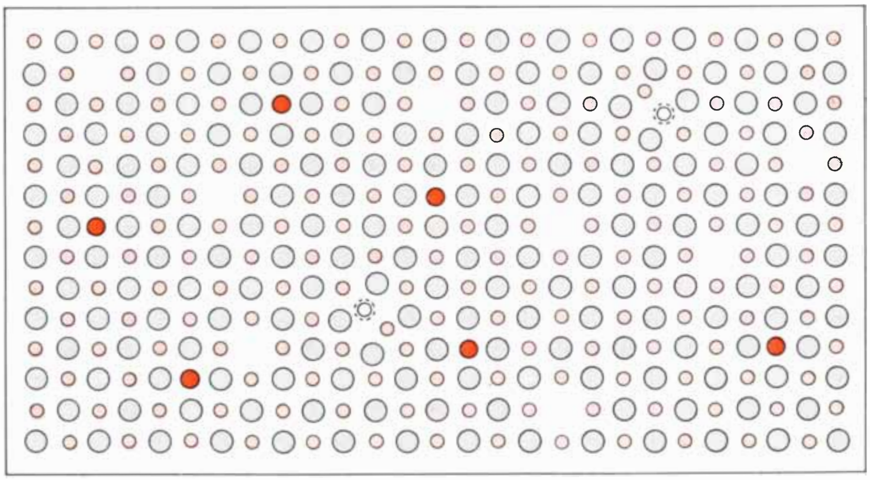
All of this—not only the production of mobile carriers but also the development of an electric field at a junction—can be discussed in chemical-like terms. The "dissolving" of lithium in solid silicon can be written $\mathrm{Li} \rightleftharpoons \mathrm{Li}^+ + e^-$, with $\mathrm{Li}^+$ standing for the donor ion and $e^-$ for a conduction band electron. Similarly, the dissolving of aluminum is represented by $\mathrm{Al} \rightleftharpoons \mathrm{Al}^- + e^+$, with $\mathrm{Al}^-$ signifying the acceptor ion and $e^+$ a positive hole in the valence band (produced when the acceptor ion traps a valence electron). Now the conduction electron donated by the lithium atom may lose energy and drop from the conduction band into the valence band, there combining with a positive hole: $e^+ + e^- \rightleftharpoons e^+e^-$. This reaction exhibits a striking parallel to the process of neutralization of an acid by a base, in which the acid's hydrogen ion combines with the base's hydroxyl ion. We can regard lithium as the counter-



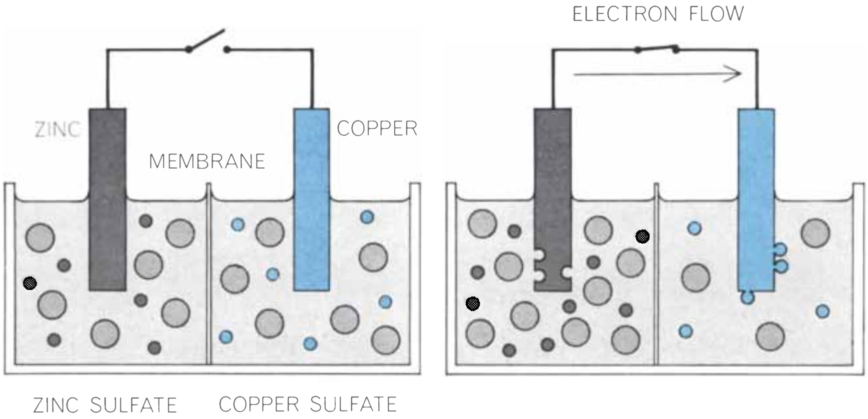
**SOLID EQUIVALENT** of the common-ion effect illustrated on the opposite page is demonstrated in the case of a salt crystal that is "doped" with calcium chloride. The lattice of sodium ions (*tint of color*) and chloride ions (*gray*) is equivalent to the fluid in the opposite illustration. Only the four sodium ions in interstitial positions (*broken circles*) and the four vacancies at the ions' former sites in the lattice are involved in the demonstration.



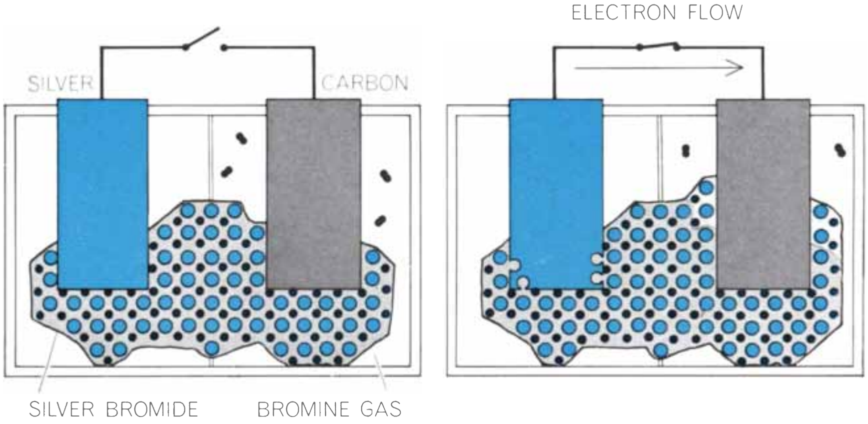
**CRYSTAL IS DOPED** by adding calcium ions (*solid color*) that add vacancies. Just as adding sodium chloride to a silver chloride solution drives silver ions out, so added lattice vacancies can capture interstitial sodium ions. Here one of the four has vanished.



**LATTICE VACANCIES** are now eight in number, whereas interstitial ions are reduced to two. Their product is identical with the product of interstitials and vacancies before the crystal was doped, thereby meeting the equilibrium requirement of the mass-action law.



**"WET" BATTERY** utilizes liquid electrolytes, separated by a membrane that is impermeable to metal ions. An electrode made of zinc is immersed in a zinc sulfate bath and a copper one in copper sulfate (*left*). When the circuit is closed (*right*), zinc atoms dissolve and enter the bath as positive ions, leaving negative electrons behind in the metal. The electrons cross to the copper electrode and join with the positive copper ions in the bath of copper sulfate to "plate out" as new atoms of copper. The cycle is completed when negative sulfate ions move from the copper bath to the zinc bath and balance the positive zinc ions there.



**"DRY" BATTERY** utilizes a solid electrolyte. Unlike the wet battery, in which the cycle of current flow is completed by the movement of negative ions, the dry battery completes its cycle by moving positive ions. Its electrodes (*left*) are in contact with solid silver bromide and the carbon electrode is surrounded by bromine gas. With circuit closed (*right*), positive ions diffuse from the silver electrode into the silver bromide electrolyte, while negative electrons move from the silver to the carbon electrode. As the diffusing silver ions reach the carbon, they combine with the bromine gas and the electrons to form more silver bromide.

part of an acid and aluminum as the counterpart of a base. Then $e^+$ becomes the analogue of a hydrogen ion, $e^-$ the analogue of the hydroxyl ion and $e^+e^-$ the analogue of the water molecule. Following this chemical reasoning, we should expect that, in accordance with the law of mass action, the removal of conduction electrons from the right side of the lithium reaction would shift the equilibrium to the right and cause more lithium to be "dissolved" in the silicon crystal. In short, the presence of the aluminum acceptor increases the "solubility" of the lithium donor. This is the same effect by which a base dissolves an acid through neutralization.

Another way to view this effect is in terms of the built-in field at a *p-n* junction. Acceptors on the negative side of the junction exert an electrical force that attracts the donors from the positive side. Accordingly the solubility of the donor is increased by the presence of the acceptor.

Experiments in the doping of semiconductors confirm with remarkable precision predictions based on the law of mass action. In fact, agreement between theory and experiment actually turns out to be better in these solid materials than it is in water solutions!

Mass-action effects have been found in insulators and metals as well as in semiconductors, and they apply to all kinds of imperfections, including the defects in nonstoichiometric crystals and even to dislocations. A dislocation may contain, along its length, atomic configurations that can be ionized; thus a linear dislocation is analogous to the chainlike protein molecule in solution, whose chemical groups can also be ionized. It has been found that the state of charge on a dislocation affects its ability to move through the crystal; hence it becomes apparent that any impurity or other defect that influences the state of charge can have a pronounced effect on the mechanical properties of the material.

Another interesting chemical phenomenon that is demonstrable in solids is the "diffusion-controlled" reaction. This concept arises when the rate of a chemical reaction depends primarily on the time required for the reacting species to diffuse to one another. Chemists have studied diffusion-controlled reactions in liquid solutions for many years. One example is the quenching of fluorescence in a liquid solution. Certain substances in liquid solution, after being raised to an excited energy state, give up their energy spontaneously in the form of light. This fluorescence is forestalled, however, if the excited molecules happen to encounter other molecules (quenchers) that absorb the excess energy in the form of heat before they can lose it in the form of light. Chemists have been able to calculate the rate at which such quenchers diffuse to the excited molecules. The mathematics of diffusion-controlled reactions has been worked out in considerable detail, and it turns out that the rate of these reactions is influenced considerably by what might be called the "experience" of the excited molecules. This means that a molecule that persists without being quenched gains information about the location of quenchers with respect to itself.

Consider a crystal of copper that has been damaged slightly by bombardment with a beam of electrons of moderate energy. The bombardment displaces a number of the copper atoms from normal sites into interstices in the lattice. Gradually the damage will heal as the mobile interstitial atoms and vacancies, diffusing through the lattice, meet one another and recombine. Hence we have a diffusion-controlled reaction in a solid. The molecules' encounters, however, are not an entirely random affair. Vacancies that survive for a considerable time do so because there were few interstitial atoms in their neighborhood. These vacancies

*(Advertisement)*

# STEEL RESEARCH AIDS PRODUCT DESIGN

***Special division makes Youngstown's complete research facilities available to the steel customer. It gives direct assistance in the design and methods of using steel in the customer's products.***

by R. H. Frazier, Manager, Research Services

Normally, research for the steel industry has two purposes:

(1) To develop new processes within the mills or to improve existing processes. For example, research in this area has led to a 50% rise in blast furnace iron production in the past ten years, and a 30% reduction in coke consumed per ton of iron production. Quality has risen, too. And all this effort has helped maintain stable, nominally low prices for iron and steel.

(2) To develop new steel products to meet more sophisticated requirements in both old and new markets. For example, new petroleum drill pipe with yield strength of more than 100,000 psi has been developed and proven. Increased depth of newer wells has seen pipe used at higher stresses, thus increasing the chance of corrosion fatigue. And the yield strength level is being increased to 135,000 psi and 150,000 psi with the expectation of equally good performance.

But at The Youngstown Sheet and Tube Company, research has a third distinct purpose — perhaps the most important one of all: to be of direct assistance to the customer.

Youngstown Steel has organized a separate division of the Research Department for the specific purpose of providing customer assistance. This division makes available to the customer the complete services of the Youngstown Research facility, not just a part.

A typical example of this service concerned the redesign of a water tank. A customer was manufacturing low-pressure water tanks by welding two drawn heads to a roll-formed body section with a welded side seam. The entire assembly was galvanized by dipping the tank into molten zinc.

The manufacturer decided to try simplifying construction by making two deep drawn sections from galvanized steel sheets and joining two sections with one circumferential weld.

Youngstown's design team played a major role in designing the tank, calculated the size and thickness of the required blank and assured a satisfactory and economical solution. Many thousands of the redesigned tanks have been made, and the customer is getting ready to make another tank, newly designed with aid from Youngstown.

If desired, Youngstown researchers make studies to suggest ways to improve the product's appearance as well as its function. And it is noteworthy that a customer's size and the size of his problems do not necessarily correlate. All companies, large or small, are served on an equal basis.

While remaining in close contact with the customer to insure that all possible assistance is always available, great care is also taken to guard against intrusion. In many cases only the customer himself knows what design characteristics best fit his entire product line. In still other cases, absolute styling secrecy is imperative. The rule is this: Youngstown research facilities are ready when needed. Proof testing or prototype copies of the product are perhaps the best methods of exactly determining the customer's needs.

At the other end of the problem, Youngstown must supply information that can help the customer realize the right forming and fabricating method.

New methods of forming, such as stretch forming, electromagnetic forming, explosive forming and combinations of cold extrusion and cold heading are being used with increased efficiency. Fabrication of a steel product by using new joining methods, such as plasma arc, laser beam, ultrasonic and friction welding, can improve quality and cut cost. Assistance to the customer in the development and application of fabricating methods is given wherever possible.

Another important factor in determining whether or not a product can be produced profitably from steel is material handling. Increasing labor costs make it imperative to handle material mechanically. Using steel's magnetic properties can help reduce handling costs. The steel manufacturer does it in his own plant to transfer large tonnages of steel. The steel user has employed magnetic methods in some of his handling problems, but further economies can often be worked out. Helping improve material handling methods is just one of the Research Services Division's function.

Value Analysis, a method of determining the total cost of putting a product on the market, is used by Youngstown to help the customer reduce overall costs. For often most of the cost of a finished product is contained, not in the raw material, but in the many processes along the line.

Youngstown Steel's Research Services Division is dedicated to establishing a cooperative effort with the customer to maintain a complete exchange of all information helpful in building product quality and efficiency. Its benefits include assistance from Youngstown's Operating and Sales Departments as well.

This article gives a glimpse of what's happening in steel research at Youngstown. It's just a part of the continuing research effort going on 24 hours a day at Youngstown's research center.

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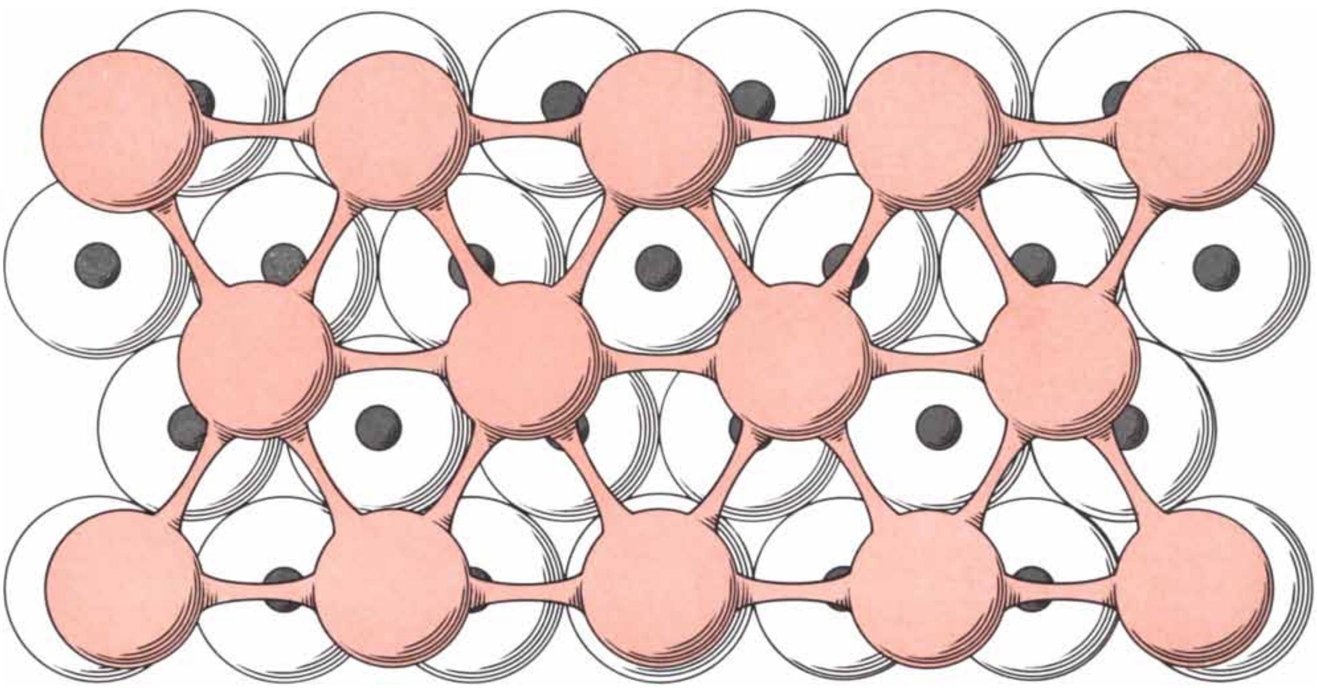


**GEOMETRIC RELATIONSHIPS** appear to play a key part in the chemistry of surface reactions. In this diagram of epitaxial growth a layer of silicon atoms has been "grown" on a substrate of close-packed beryllium oxide. The geometry of the silicon array (*color*) does not match that of the beryllium oxide, but it is close enough to permit the growth of the silicon crystal on the alien surface.

therefore gained some "information" about the distribution of interstitial atoms in their vicinity, so that their recombination is not with a random environment. This "knowledge" on the part of the reacting species plays a part in the rate of recombination.

The physicists who studied the healing of radiation damage in crystals dealt with the matter at first as if the rate of healing depended simply on the law of mass action in a straightforward way, ignoring the nonrandom aspects mentioned above. Collaboration with chemists who were familiar with the effect led to the proper corrections. This is an instance in which the combination of chemical and physical approaches provided a more satisfactory solution to a problem than either approach did separately.

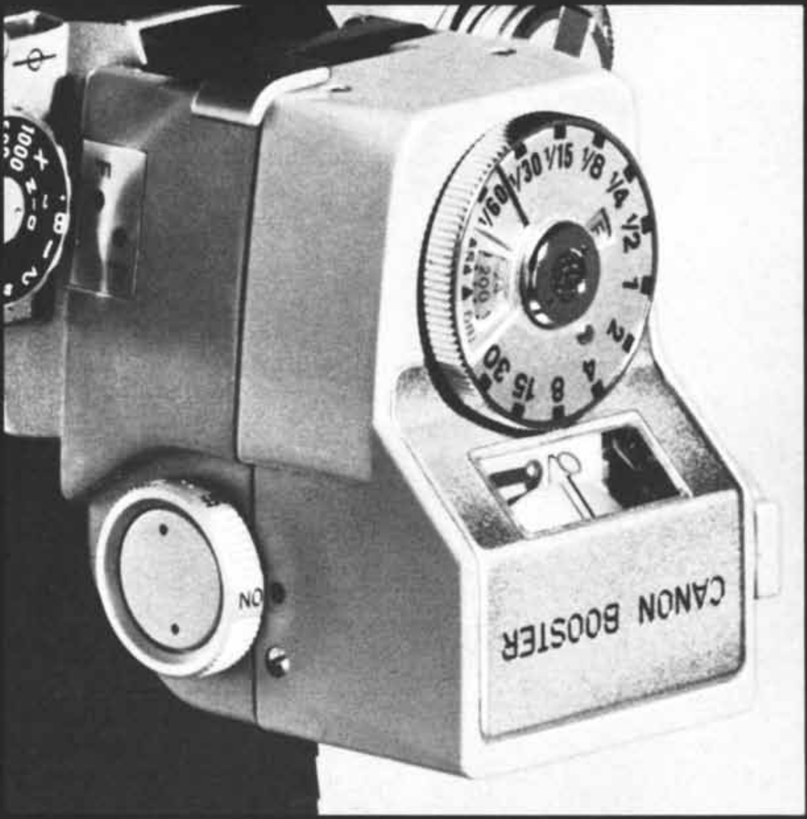
It should not be supposed that chemical-like reactions in solids are generally of such an esoteric nature. More familiar reactions occur. Precipitation, for example, is a common phenomenon within solid materials. Precipitates usually take the form of small particles—aggregates of atoms that come out of solution in the solid and are deposited at various places in the crystal. They can exert a strong influence on the properties of the solid.

If to a solution of lithium in solid silicon one adds another electron-donating substance, the lithium's solubility will be reduced. Lithium atoms therefore precipitate out of solution by diffusing through the crystal until they collect in sizable aggregates (perhaps containing some silicon atoms as well). The formation of the aggregates is a diffusion-controlled reaction. Another interesting precipitate occurring in silicon involves oxygen. Precipitated oxygen atoms form aggregates by joining with silicon atoms in chainlike "polymers." Some of these aggregates are electrically active and donate conduction electrons to the crystal. In the early days of the silicon transistor an unwanted excess of conduction electrons sometimes developed mysteriously; the phenomenon was eventually traced to the presence of precipitated oxygen.

In addition to influencing the electrical properties of semiconductors, precipitates can produce other effects in solids. For example, they can alter the brittleness or strength of a crystalline material by interfering with the movement of dislocations.

Solids can be the seat of another chemical process that is better known in connection with liquids. This is the familiar wet-cell electric battery phenomenon. Such a battery might consist of a zinc plate immersed in a water solution of zinc sulfate and a copper plate in a solution of copper sulfate, the two solutions being placed in contact [*see upper illustration on page 214*]. Atoms from the zinc plate dissolve in the zinc sulfate as positive ions. The electrons left behind on the solid zinc travel by way of an external circuit to the copper plate; there they combine with positive copper ions from the copper sulfate solution, and the copper atoms thus formed are deposited as copper metal. The circuit is completed by the movement of negative sulfate ions from the copper side to the zinc side of the solution, thereby balancing the added zinc ions. The overall chemical reaction is simply the reaction of zinc with copper sulfate to produce copper and zinc sulfate. The sulfate solutions serve as electrolytes for the transport of the current, and energy to drive the current is provided by the chemical reaction.

Now, this type of process can take place in a system with a solid compound, instead of a liquid solution, serving as the electrolyte. Consider an arrangement in which the electrodes are solid silver on one side and carbon in contact with bromine gas on the other, and the electrolyte is solid silver bromide [*see lower illustration on page 214*]. Silver ions can diffuse rather rapidly through solid silver bromide. As atoms from the silver electrode dissolve in the silver bromide (becoming positive ions) the electrons remaining behind in the silver electrode travel by way of an external circuit to the carbon. Meanwhile silver ions, having crossed to the carbon through the bromide, combine with the electrons and the bromine gas to form silver bromide.



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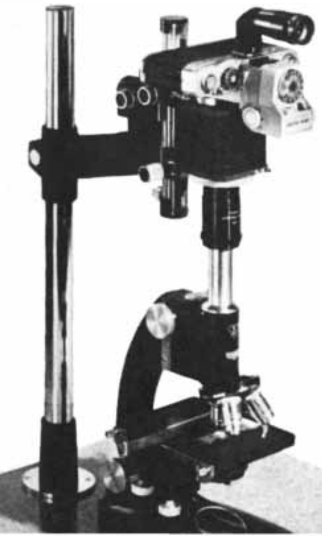

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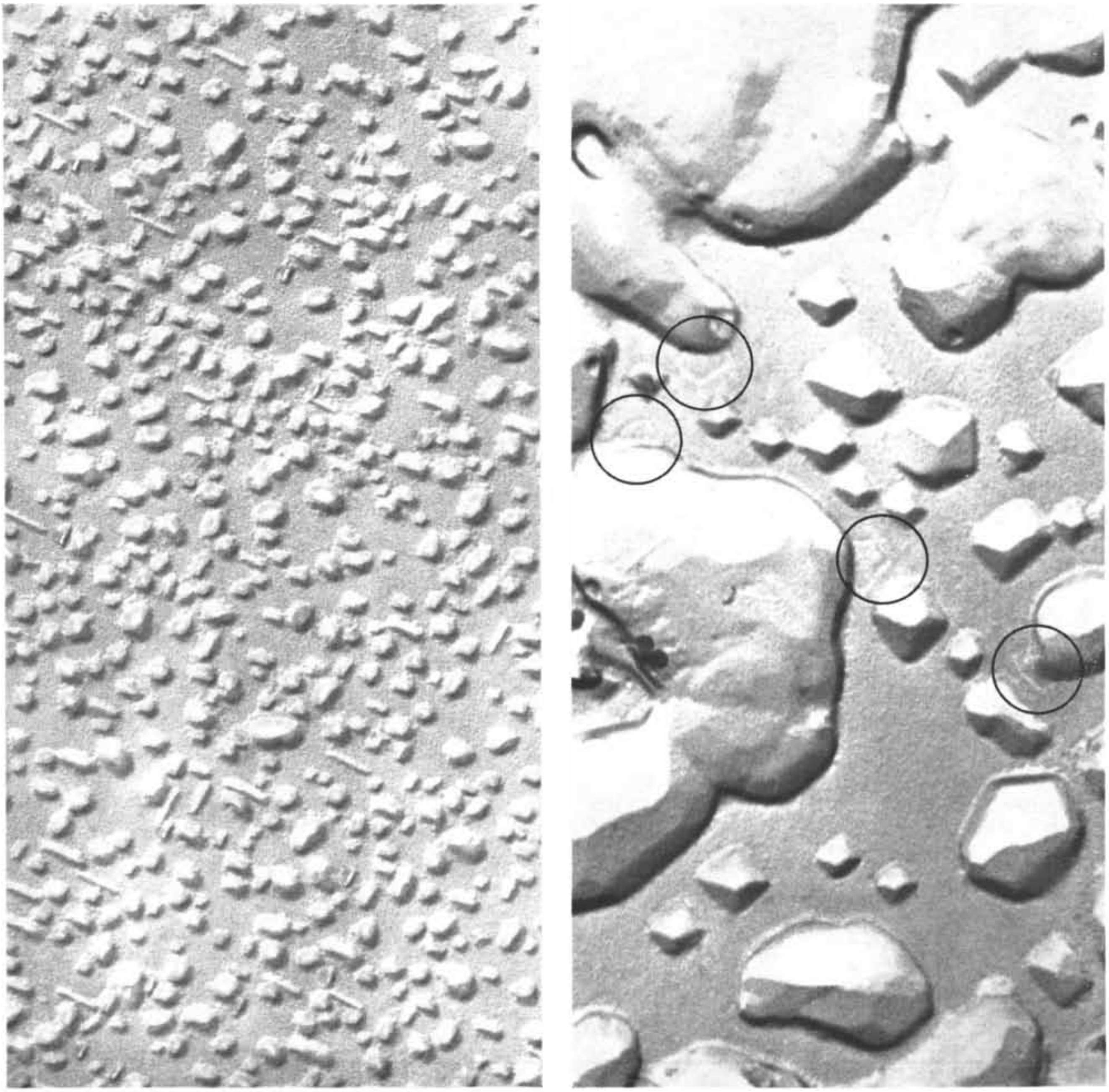
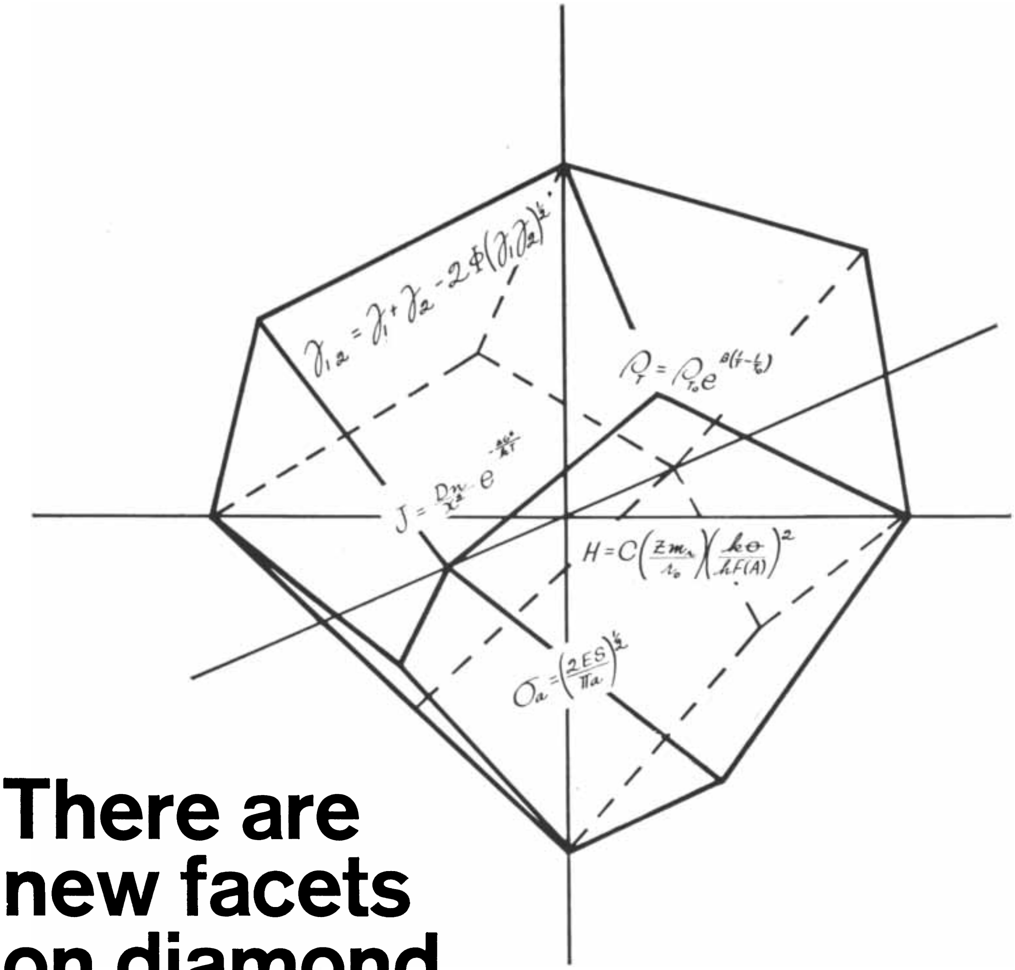
Hence the circuit is completed: current is carried by electrons in the external part of the circuit and by positive silver ions in the electrolyte. Note that the electrolyte must be a nonconductor of electrons; if electrons could travel through it, they would cross from the silver electrode to the carbon by that route and thereby short out, or bypass, the external circuit.

Again, as in the wet sulfate battery, the solid-state version is energized by a simple chemical reaction: the combination of silver with bromine to form silver bromide (a solid that does not conduct electrons). Solid-state batteries are now receiving a great deal of attention, particularly for use in space vehicles and possible use in automobiles. Among the encouraging recent developments is the discovery of solid electrolytes in which ions can diffuse about as rapidly as in some liquid electrolytes. These discoveries were made independently and almost simultaneously at the University of Essex in England and at North American Aviation, Inc.

Still another important field of research on solid-state materials is their surface chemistry. Most solid surfaces, even when they seem very smooth, are riddled with submicroscopic defects—atomic vacancies, kinks, ends of dislocations, dangling chemical bonds and so forth—that make it easy for foreign atoms to



**EPITAXIAL GROWTH** of silicon on a substrate is seen in two intermediate stages in these micrographs. The sample at the left, derived from an extremely dilute silane source, shows early growths that exhibit crystallographic symmetry. The early growths soon coalesce into larger, unsymmetrical islands. The sample at the right, derived from a silicon tetrachloride source, has initial nuclei shaped like small pyramids. The circles outline the traces left by some of the pyramids after they were absorbed by the adjacent islands. Both replica electron micrographs were made by R. L. Nolder of the Autonetics Division of North American Aviation, Inc.


$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi(\gamma_1\gamma_2)^{\frac{1}{2}}$
$\rho_T = \rho_{T_0} e^{\alpha(T-T_0)}$
$J = \frac{Dn}{\lambda^2} e^{-\frac{\Delta G}{kT}}$
$H = C\left(\frac{Zm_1}{r_0}\right)\left(\frac{k\theta}{hF(A)}\right)^2$
$\sigma_a = \left(\frac{2ES}{\pi a}\right)^{\frac{1}{2}}$

become attached to the surface. Layer on layer of contaminating material may build up in this manner. A familiar example, of course, is the corrosion of metal surfaces. When an oxide film covers a metal, it is likely to contain oxygen-atom vacancies or metal atoms displaced into interstitial spaces or both. Oxygen atoms can be added to the oxide lattice at the oxygen-air interface, forming metal vacancies in much the same way that sodium added to sodium chloride forms chloride vacancies. Metal atoms can jump into these vacancies and by this process are able to diffuse through the film. Thus metal from the interface between metal and metal oxide is transported to the air interface, where it combines with oxygen to form more oxide.

Electrochemical mechanisms exist that can inhibit the oxidation of a metal surface. These have been studied by immersing a metal electrode in an oxidizing electrolyte solution and applying a voltage to the electrode; when the flow of current falls off, it signals a decline in the rate of oxidation. This phenomenon has often been observed; the electrochemical reaction begins at a rapid rate and then slows substantially. Two mechanisms that can bring about such a state of "passivity" have been identified. When a metal electrode is immersed in moderately concentrated nitric acid ($HNO_3$), the acid molecule, reacting with an electron, gives up a negative oxygen ion (and becomes nitrous acid: $HNO_2$). Consequently a layer of negative oxygen ions is laid down on the metal surface; these pull positive metal ions from the surface and form a layer of oxide. As the film grows it becomes difficult for metal atoms to pass through the film to the oxygen, and the oxidation therefore falls to a negligible rate. Another passivating mechanism involves carbon monoxide. If a metal electrode is immersed in a solution of hydrochloric acid containing carbon monoxide, a layer of carbon monoxide is often adsorbed on the metal surface. In this case, however, the carbon monoxide layer apparently has no tendency to grow but acts as a film that electrically insulates the metal from the electrolyte solution. The electrochemical reaction therefore comes to a halt and the metal is "passivated."

Surface defects are believed to account for the reaction-promoting properties of some solid catalysts. One hypothesis concerning the mechanism of catalytic activity, which is supported by some experimental evidence, assumes that the molecule about to undergo chemical reaction is adsorbed on the catalyst surface by the attachment of its atoms to dangling chemical bonds. As a result of this attachment some bonds within the molecule are weakened and break as the molecule becomes detached from the catalyst. The molecule thereupon splits in two and completes the reaction. Such a mechanism depends, of course, on a fit between the configuration of the molecule and the atomic arrangement in the catalyst's surface. It also depends on the strength with which the molecule is adsorbed on the surface: if the adsorption is too strong, the molecule will simply remain attached; if it is very weak, there may be no catalytic action. A reaction that is thought to proceed by this mechanism is the removal of hydrogen atoms from the hydrocarbon cyclohexane over a zinc oxide catalyst.

Surface geometry plays a key role in another surface process. This is the process in which one crystal is grown on another—the phenomenon known as hetero-epitaxy [*see illustration on page 218*]. For example, the geometric arrangement of atoms at the surface of beryllium oxide is such that single crystalline layers of silicon atoms can be laid down on it [*see illustration on page 216*]. Such an arrangement, with a semiconductor laid on an insulating base, is used in the fabrication of compact integrated circuits.

A particularly interesting phenomenon is the ability of doped semiconductors—for example a *p*-type material—to act as catalysts. The more valence band holes there are in the solid, the more effective is its catalytic action. This implies that some step in the catalytic process involves the donation of electrons from the reacting system to the catalyst. The transfer of electrons may occur during the process of adsorption or during the chemical process itself. In any event, the phenomenon is interesting because it illustrates how a bulk property of a catalyst (the degree of its *p*-typeness) can influence a surface reaction. Doping the catalyst to make it more or less *p*-type (that is, controlling the concentration of electrons) can change its properties.

At the surface of a semiconducting catalyst there is usually a built-in electric field very similar to the field at a *p-n* junction. Work must be done to move holes or electrons through this field, and this shows up in the energy required to advance the catalyzed reaction. Indeed, energy considerations dominate all chemical reactions and the physical properties—electrical, magnetic and optical—of all materials.

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# The Magnetic Properties of Materials

*Why atoms are magnetic is well understood, but why some materials are magnetic is less so. Nonetheless, advances in magnetic materials have made possible devices from refrigerator latches to computer memories*

by Frederic Keffer

Magnetic materials provide a good illustration of how man's practical reach can exceed his theoretical grasp. The peculiar properties of magnets have been known since lodestones were recognized 3,000 years ago. Every day in the U.S. alone magnetic materials are used to generate three billion kilowatt-hours of electric power. Magnetism also works to distribute electric power efficiently, to energize electric motors, to reproduce sound and visual images, to store information, to latch doors and turn speedometers. Until 40 years ago, however, no one understood why certain materials were magnetic. Even today there are more basic questions about magnetism than there are answers.

Almost everything that is known about the magnetic properties of materials has been obtained from experimental discoveries—some intentional but many the result of lucky accidents—and from a few bold inductive insights. Little progress has been made deductively. Although no one seriously doubts that all magnetic properties flow naturally from quantum mechanics and electromagnetic theory as it is applied to many-atom systems, the systems themselves have generally proved to be too complex for analysis by reasoning from the general to the particular.

Three basic magnetic properties of materials have called for explanation since they were first noticed. The first is the fact that some materials are magnetic in the absence of any applied magnetic field. Associated with this property is the fact that the same materials generally become more magnetic when a comparatively weak magnetic field is applied to them. This dual property is what we call ferromagnetism. The second property, which is characteristic of the same materials, is the disappearance of the ferromagnetism when the material is heated above a specific temperature. Above that temperature ferromagnetism is replaced by a comparatively weak magnetism that varies in proportion to the intensity of any applied magnetic field and is along the direction of the field. This property is termed paramagnetism. The third property that requires explanation is exhibited by *all* materials and is a magnetic response in a direction opposite to that of any externally applied field. This property, called diamagnetism, is much too weak to be of any practical value; it is scarcely noticeable in materials that are ferromagnetic or paramagnetic.

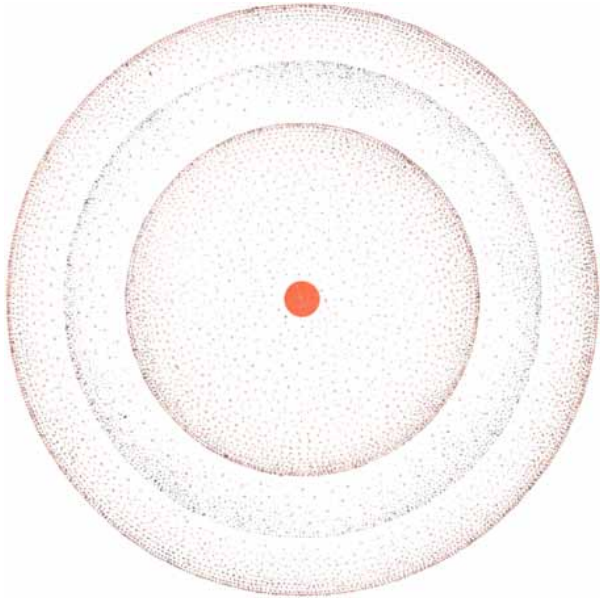
The lodestone, which is the mineral magnetite ($Fe_3O_4$), is the principal natural magnet. It is presumably magnetized when it cools from the molten state in the presence of the earth's magnetic field, even though that field is extremely weak (about .5 oersted). Metallic iron, however, is the magnetic material par excellence. Freshly smelted iron is rarely magnetic, but if the iron is drawn into the shape of a bar (as William Gilbert demonstrated at the end of the 16th century), the earth's magnetic field will magnetize it. So will any other magnetic field, such as a lodestone's, and the bar will remain magnetized after the field has been removed. The critical temperature at which the spontaneous magnetism of magnetite changes to paramagnetism is 585 degrees centigrade; the critical temperature for iron is 770 degrees C. The critical temperature of a ferromagnet was named the Curie temperature after Pierre Curie, who was a pioneer student of paramagnetism.

In 1907 another French physicist, Pierre Weiss, provided the first inductive insight that came anywhere near accounting for the behavior of magnets. Even those scientific workers who frequently accept the role of speculative leaps might boggle at Weiss's flight of fancy. There appeared to be not the slightest theoretical justification for two new concepts he introduced: the "domain" and the "molecular field."

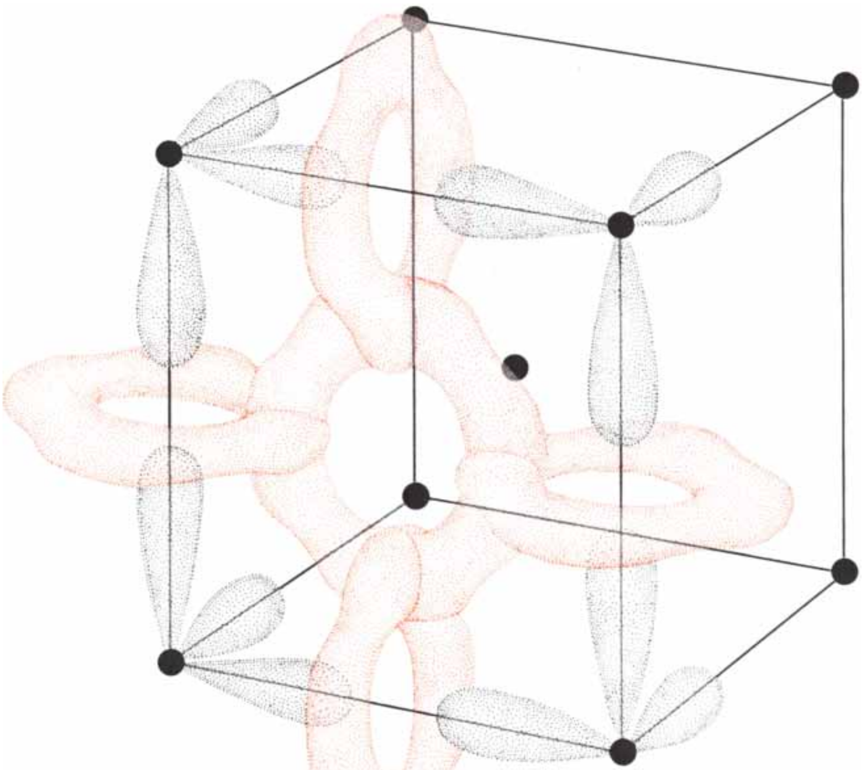
According to Weiss, a ferromagnet that is below its Curie temperature is made up of small, permanently magnetized regions—domains. The total magnetic strength of the material is simply the sum of the magnetic strengths of all its domains. If the magnetic axes of the various domains happen to point in many different directions, the material's total magnetic strength will be very small, even zero. The application of an external magnetic field, Weiss held, aligns the magnetism of the domains much as the wind will align a group of weather vanes, thus greatly increasing the material's total magnetic strength. The applied field need not be particularly strong; a light breeze turns weather vanes as effectively as a gale does. Weiss visualized his domains as being small but macroscopic. We now have direct evidence that the domains exist; they are usually between .1 and .01 centimeter across.

Compared with the dimensions of atoms and molecules, Weiss's domains were enormous. Accordingly they were not closely related to any particular

**MAGNETIC DOMAINS appear as a pattern of zigzags on the surface of an alloy of manganese and bismuth in the micrograph on the opposite page. The domains are visible because the plane of polarized light reflected from a magnetized surface is rotated in proportion to the degree of magnetization. The micrograph was made by the metallographic unit at the Research and Development Center of the General Electric Company. Other domain micrographs, in which a magnetic powder outlines the domain walls, appear on pages 231 and 232.**



**IRON ATOM** consists of a nucleus surrounded by clouds of electrons arrayed in concentric shells. The shell that forms the outermost cloud contains two electrons. These have opposite spin and form a magnetically neutral pair. Most of the 24 electrons in the other shells also pair opposite spins; nine such neutral pairs form the inner cloud. Of the six electrons in the middle cloud, two form a neutral pair. The remaining unpaired four make iron magnetic.



**LATTICE CELL,** one portion of an iron crystal, consists of nine atoms (*black*) in a cubic array, one at each corner and one in the center. Stippling in black indicates areas of strong positive magnetization associated with the unpaired electrons in the four atoms that form the face of the cube. Stippling in color indicates areas of weak negative magnetization along the face of the cube. Positive and negative areas elsewhere are omitted. C. H. Shull of Massachusetts Institute of Technology and H. A. Mook of Harvard University determined the distribution of the areas by scattering magnetically polarized neutrons from an iron target.

theory of atoms and molecules. His second concept—the molecular field—was intended to explain at the atomic level why domains are present in ferromagnets below the Curie temperature but absent above that temperature. Weiss rested his molecular-field hypothesis on the assumption (prevalent at the time but not confirmed by experiment until much later) that the atoms of certain materials were themselves infinitesimal magnets. Below the Curie temperature, Weiss proposed, an intrinsic magnetic field kept these atomic magnets in alignment. Above the Curie temperature thermal agitation was strong enough to overcome the aligning power of the intrinsic field. The material then lost its ferromagnetic properties and exhibited paramagnetism only.

The intrinsic field that Weiss postulated was not only strong but also mysterious. He assumed that it was related in some way to the material's state of organization at the atomic or molecular level; hence his name for it. The thermal energy required to overcome the field could be estimated from the temperature at which it disappeared, and so its strength could be estimated. For iron this proved to be on the order of 10 million oersteds—greater than the strongest steady magnetic fields produced today with many megawatts of power.

Weiss, of course, had not the slightest notion of the origin of the hypothetical field. The mystery remained unsolved until 1928, when Werner Heisenberg of Germany and Y. I. Frenkel of the U.S.S.R. independently suggested that the field probably arose from large electrical forces at the atomic level that were masquerading as magnetic forces because of a subtle quantum-mechanical effect. Hence both of Weiss's hypotheses, proposed well in advance of any supporting theory or evidence, have proved to be generally correct.

Why is it that some, rather than all, atoms are infinitesimal magnets? Today we know that atomic magnetism is almost entirely the result of an imbalance of an atom's electrons [*see top illustration at left*]. Some atomic nuclei are also little magnets, but because the strength of their magnetism is inversely proportional to their mass it is weaker than the magnetic strength of electrons by a factor of about one to 2,000. Electron magnetism is of two kinds: the magnetism associated with the angular momentum of the electron's spin and the magnetism associated with the angular momentum of the electron's orbital motion around the nucleus. In either case

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the direction of the resulting magnetism is along the axis of rotation.

In most kinds of atoms—or at least in most assemblages of atoms in molecules and solids—there is a tendency for both the spin and orbital angular momentums of adjacent electrons to cancel each other by the formation of antiparallel pairs. In such a pair the spin of one electron, for example, will be clockwise and the spin of the other counterclockwise. Their total momentum is therefore zero, and so is their total magnetism. It is this tendency—or rather its slight variability—that accounts for the extremely weak magnetism of "nonmagnetic" materials. When the application of a magnetic field slightly unbalances the orbital pairing of electrons, the result is diamagnetism; when it slightly unbalances the spin pairing (which it can do only in metals), the result is a very weak form of paramagnetism.

The Pauli exclusion principle requires that no two electrons occupy the same state, by which is meant both the same region of space and the same spin and orbital momentums. It is possible, however, for the two electrons to occupy the same region if they are an antiparallel pair. In quantum mechanics the stricture against occupying the "same" region simultaneously is overcome because the two electrons behave like superposed, smeared-out charge distributions. It is this behavior, together with the attractiveness of the nucleus for electrons, that gives rise to the antiparallel pairing tendency of all atoms. It rather resembles the way in which space is saved in a sardine can by packing the fish head to tail (except that even more space could be saved if antiparallel sardines, like electrons, completely interpenetrated one another).

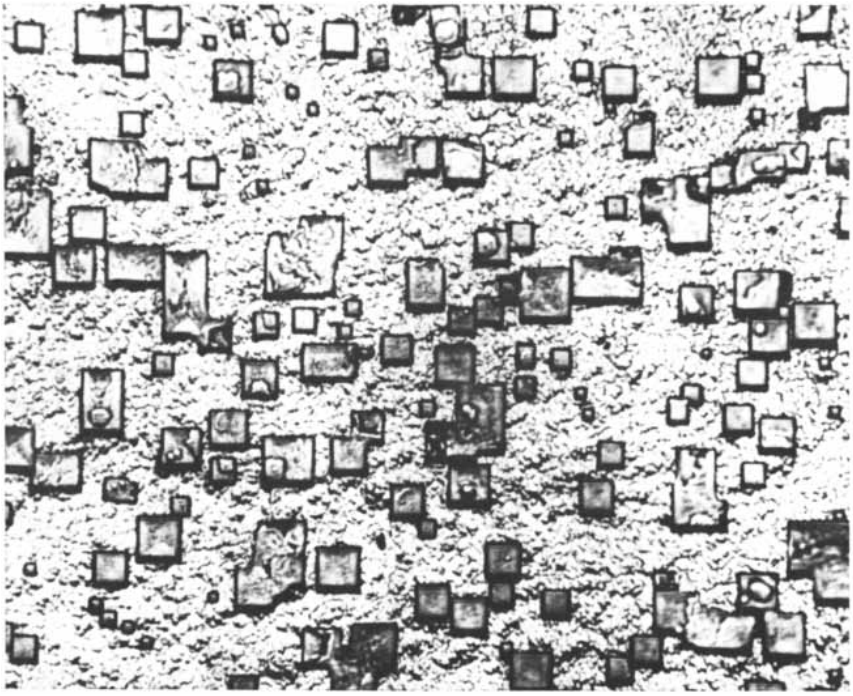
The antiparallel tendency must, of course, overcome the mutual repulsion of the two interpenetrating electrons. It usually does. The outstanding exceptions are found in the "transition" metals and the rare earths [*see periodic table on pages 76 and 77*]. These elements are characterized by atoms in which some electrons have not formed antiparallel pairs. In reality any atom that has an odd number of electrons is magnetic, and many kinds of atoms have outer electrons that are unpaired. These outer electrons, however, usually form antiparallel pairs with the outer electrons of neighboring atoms on coming together in a solid. What gives the magnetic atoms in the two groups of elements their unique property—and thereby gives rise to strongly magnetic materials—is that the unpaired electrons are located not in the outermost electron cloud but in the inner ones, where they are not able to form pairs with electrons in other atoms.

The atoms of ferromagnetic materials are tiny magnets because of their unpaired inner electrons. These electrons, however, are more or less screened from the adjacent atomic magnets by outer electrons. How, then, can we account for ferromagnetism? In a ferromagnetic material neighboring atoms tend to be magnetically aligned. The picture is complicated in its details, but it is evident that Weiss's concept of a long-range molecular field, coupling each atomic magnet with equal strength to all other atomic magnets, was partly mistaken. Instead the coupling effect is a short-range one, being sharply limited by electron screening.

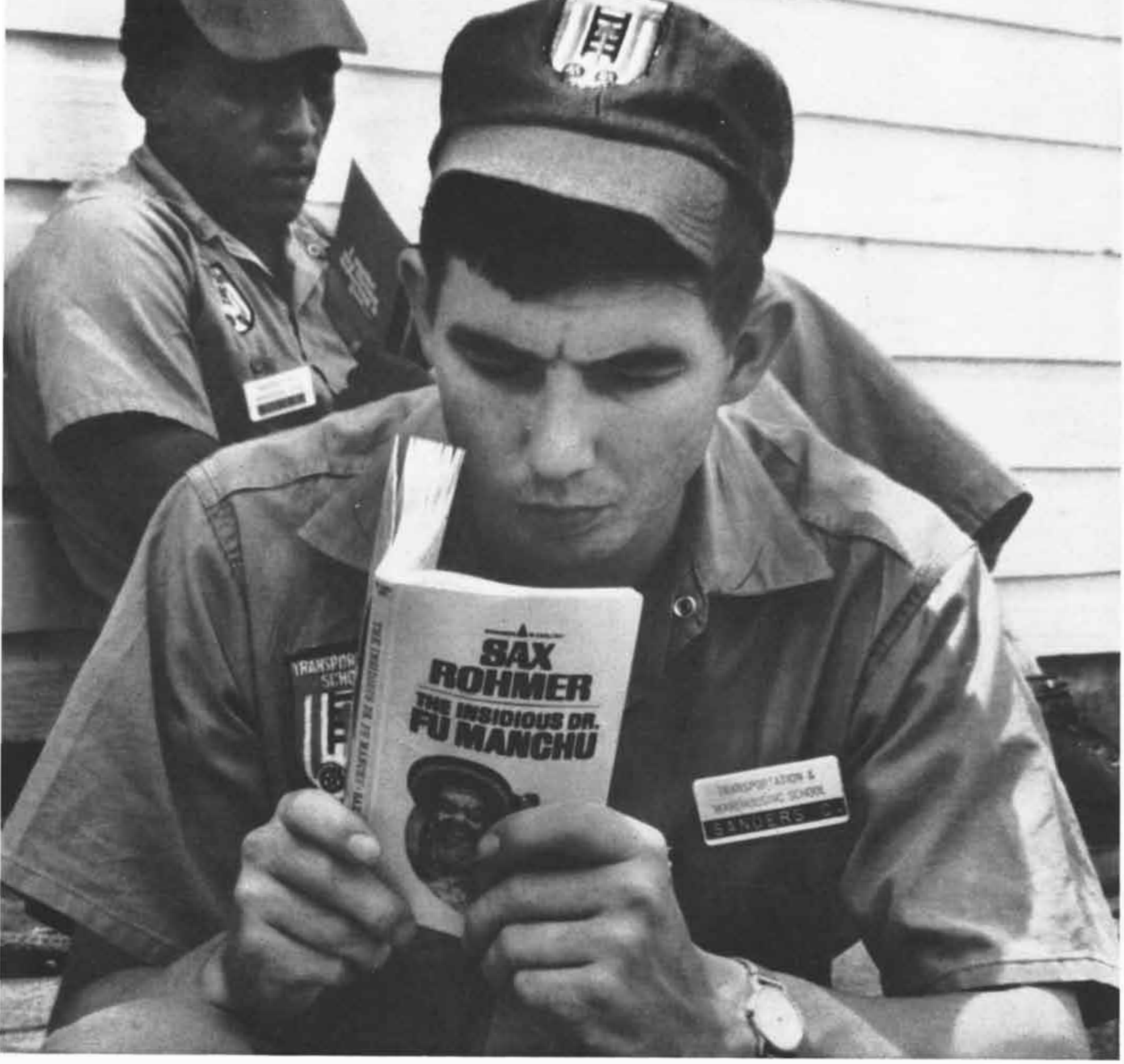
Short-range coupling nonetheless exerts a powerful influence. Consider the example of a ferromagnetic material that has been heated above its paramagnetic threshold and then allowed to cool. As it approaches its Curie temperature, the energy of thermal agitation gradually becomes less than the coupling energy. At this point each atomic magnet begins to line up with its nearest neighbors, and those with their nearest neighbors and so on, as if all the atoms were being guided by the kind of long-range field visualized by Weiss. One is reminded of the situation when, as the quiet of evening descends, suddenly all the dogs in a town get to barking together, although each dog responds only to the neighboring dogs.

The coupling effect can also produce antiparallel alignments. Manganese fluoride, for example, is paramagnetic at temperatures above minus 206 degrees C. Below this transition temperature (which is analogous to the Curie temperature of a ferromagnet) each manganese atom that, so to speak, points upward is paired with one that points downward, and no overall magnetism is observed. This property is called antiferromagnetism. The transition temperature between the antiferromagnetic and the paramagnetic state has been named the Néel temperature after the French physicist Louis Néel, who with his colleagues first clarified the phenomenon.

There are other coupling arrangements, the most notable of which produces ferrimagnetism (not to be confused with ferromagnetism). When magnetite is cooled below its Curie temperature, for example, the short-range coupling is such that two out of the three iron atoms in the material are aligned by pointing upward and the third points downward, so that there is a net magnetism due to one atom in three. Thus the oldest of magnets is not a ferromagnet at all. The macroscopic properties of ferrimagnets, however, are generally



**CUBE-TEXTURED STEEL, enlarged 500 diameters, has crystal grains oriented so that the face of each cube lies parallel to the surface of the metal sheet. This orientation avoids one source of energy loss when the metal's magnetization is reversed, thus reducing hysteresis.**



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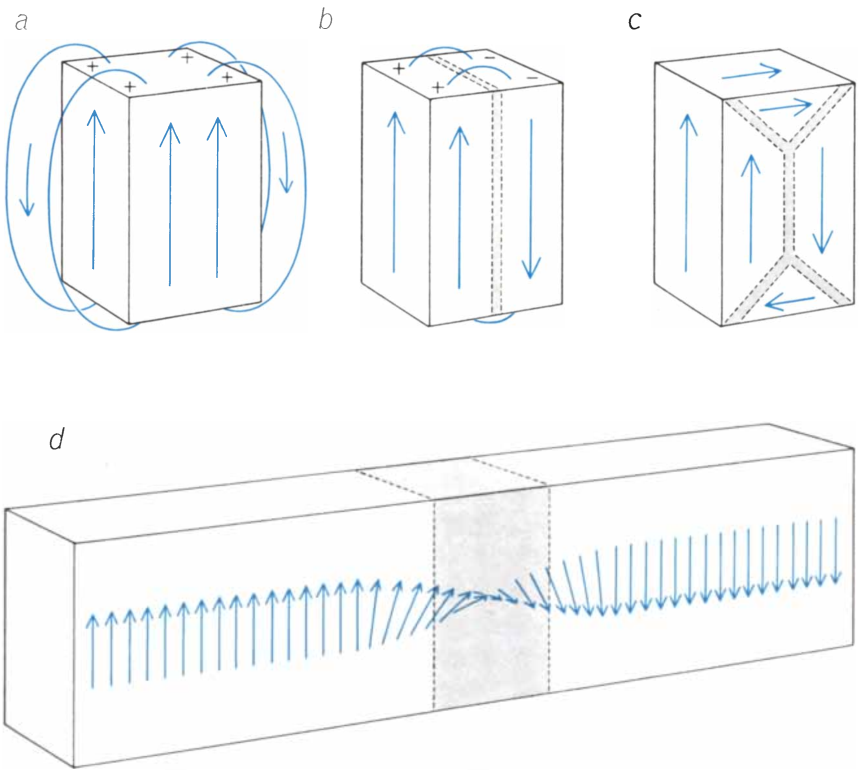


**DOMAIN FORMATION** is caused by the spontaneous subdivision of a uniformly magnetized material (*a*). Division into two domains (*b*) lowers the external field energy of the material, as is evident from the shortened external magnetic lines of force (*color*) in this example. The next division, from two to four domains (*c*), eliminates all external lines of force. The zone between domains, known as a Bloch wall, is shown in detail at bottom (*d*). In this zone some "north" poles in the material, which are turning through 180 degrees, come to the surface of the material and cause the lines seen in the photograph on the opposite page.

similar to those of ferromagnets. Among the man-made ferrimagnets are the technologically important ferrites and iron garnets. The ferrites were developed in the 1940's by J. L. Snoek and his associates at the Philips Research Laboratories in the Netherlands. The iron garnets were first made in the late 1950's by Néel's group in France and by workers at the Bell Telephone Laboratories.

Coupling forces that favor antiparallel alignments sometimes extend an appreciable distance, to the point of affecting neighboring atoms twice removed. Since it is obviously impossible for each atomic magnet to line up antiparallel to very many distant neighbors, some second-nearest and third-nearest atomic magnets tend to end up parallel with respect to one another in spite of the coupling energy. One compromise, resulting in a stable situation, is made when adjacent atomic magnets form a helix. In a crystal of manganese dioxide below a temperature of minus 189 degrees C., for example, there is a turn angle of nearly 129 degrees in each plane of atoms, so that the helix makes five revolutions in the process of crossing 14 planes. This compromise property, known as helimagnetism, was discovered simultaneously in 1959 by A. Yoshimori of Japan, J. Villain of France and T. A. Kaplan of the Lincoln Laboratory of the Massachusetts Institute of Technology. The existence of helimagnetism immediately suggests an interesting generalization. Antiferromagnetism, for example, could be defined as helimagnetism with a turn angle of 180 degrees and ferromagnetism as helimagnetism with a turn angle of zero degrees!

It is relatively easy to see how the domain hypothesis explains ferromagnetism. Not until some three decades ago, however, was it realized how domains too could be explained by means of a fundamental principle of physics. This is the principle that at low temperatures all systems tend toward a state possessing minimum energy. The external lines of force of a uniformly magnetized material are shrunk and the energy of the external magnetic field is reduced whenever the sample is subdivided by increasing the number of its domains [*see illustration above*]. The Russian physicists L. D. Landau and Eugene M. Lifshitz were the first to note this effect in 1935. They pointed out that, whereas the multiplication of domains within a ferromagnetic material would reduce the energy of the external field, it would simultaneously raise the short-range coupling energy, because the number of atomic magnets with antiparallel alignment along domain boundaries would be increased. Eventually the process of subdivision reaches a state of equilibrium; the addition of further domains would increase the coupling energy more than it would reduce the field energy.

The antiparallel alignment of the atomic magnets on opposite sides of a domain boundary is not abrupt but a gradual transition that occupies a zone named the "Bloch wall" after Felix Bloch, who investigated domain boundaries in the 1930's. The "turnover" within the Bloch wall is much more gradual than the twisting in helimagnetism; the zone is some 300 atomic planes thick compared with a few planes at most. Both helices, however, are the result of a similar compromise in the sharing of coupling energy.

In 1931 the late Francis Bitter, working at the Westinghouse Research Laboratories, proved the existence of domains by making them visible. As later refined, the Bitter technique consists of polishing the surface of a magnetic material, spreading a colloidal suspension of magnetic iron oxide particles over the surface and placing a microscope cover glass on top. The particles collect along the lines where the atomic magnets in each Bloch wall point toward the surface, making the domain boundaries plainly visible through a microscope [*see upper illustration on opposite page*]. The shifts in domains under the influence of external magnetic fields that could be observed with Bitter's technique made it possible to investigate such properties as reversible and irreversible magnetization.

From the technological viewpoint an ideal magnetic material should possess one or the other of these properties. It should either be "soft," meaning easy to magnetize and demagnetize, or "hard," meaning the opposite. Hard materials come into play whenever permanent magnets are required; soft ones are needed for electric generators, motors and transformers. There was a practical means of telling soft and hard materials apart long before there were theories explaining the two properties. A material was placed in a magnetic field, the intensity of the field was varied and the resulting magnetization of the material was plotted as a curve.

Using this technique in 1885, the British physicist J. A. Ewing noted that after the external field was reduced to zero the specimen continued to show net magnetization. When Ewing reversed the field, he found that net magnetization in the reverse direction persisted after the field was reduced to zero. He named this tendency for induced magnetization to remain after the applied field was removed "hysteresis," after the Greek word meaning "to lag."

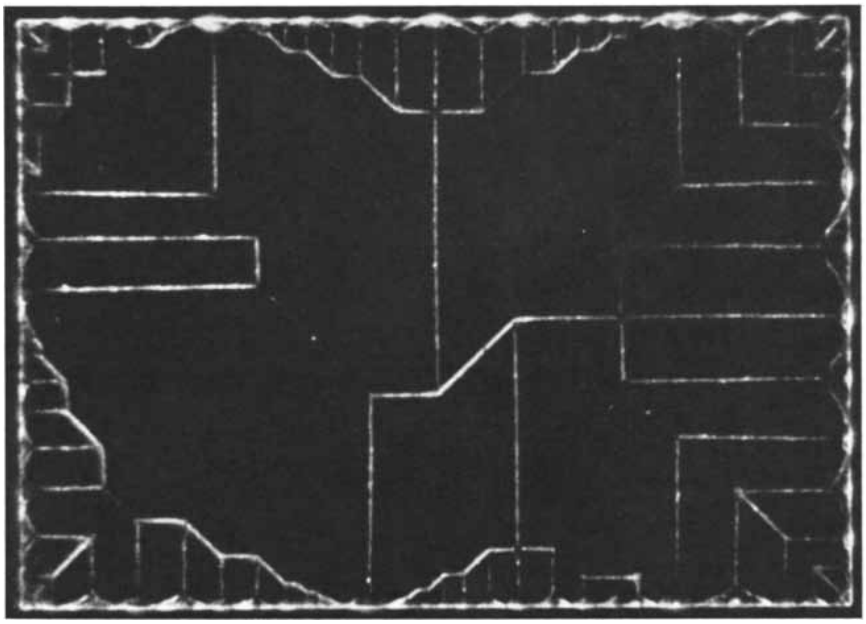
Any generator, motor or transformer would operate with maximum efficiency if no magnetization remained after the applied external field dropped to zero. Because of hysteresis a vast treasure is wasted each year. The underlying cause of the phenomenon has been revealed by the study of domains.

When a weak external field is applied to a magnetic material, the material's domain walls are seen to move. The motion is in a direction that increases the size of the domains whose magnetization is parallel to the applied field and reduces the size of domains whose magnetization is antiparallel. These increases and reductions are reversed when the applied field is reversed. When a stronger external field is applied, however, the domain walls are often pushed past obstacles, thereby rendering some of the specimen's magnetism irreversible. Obstacles exist at the boundaries between the material's crystal grains, at places where nonmagnetic inclusions are present and at imperfections.

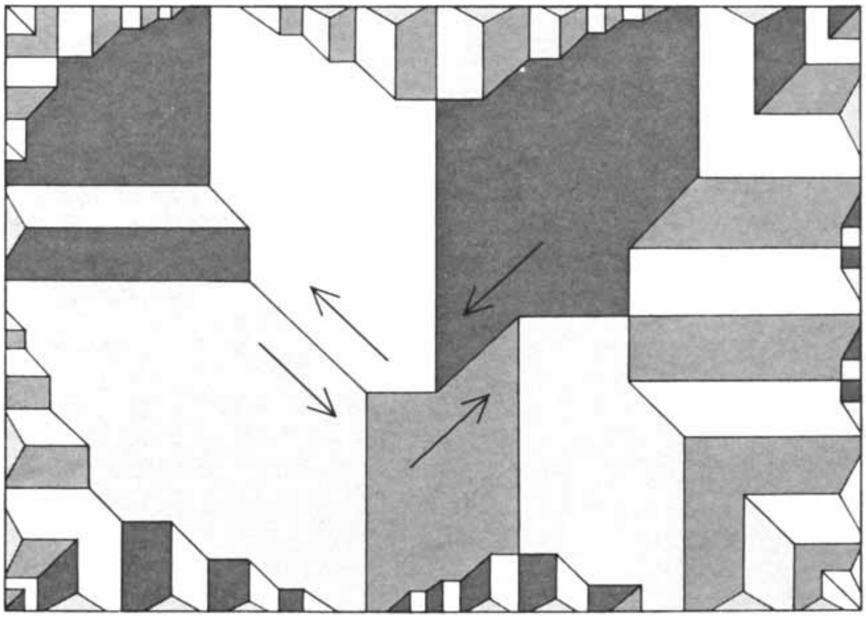
Irreversible magnetism is trapped behind an energy barrier, so to speak, when the external field is reduced to zero. It cannot be changed unless an external field of opposite polarity and exceeding some threshold is applied. If the energy state in which the material has been left is not the lowest state possible, the system is said to be metastable. Most ferromagnets contain imperfections that act as obstacles. As a result they exist in a large number of metastable states, and the immediate behavior of any ferromagnet depends markedly on the particular metastable state into which it was last maneuvered. This is one reason why the study of magnetic materials, if not an art, is certainly a science that depends heavily on good luck.

Irreversible magnetization means that the plot of a material's demagnetization path does not overlap its magnetization path. The figure described by the two paths is known as the hysteresis loop; it is narrow for soft materials and wide for hard ones [*see bottom illustration on next page*]. The inexpensive fabrication of soft magnetic materials is difficult because the ferrous materials that are most easily made are full of such obstacles as crystal boundaries and randomly oriented crystal grains, all of which give rise to hysteresis. The ideal soft magnet would be a ferrous material that was cheap to make and in which the crystal grains were all oriented in the same or nearly the same direction.

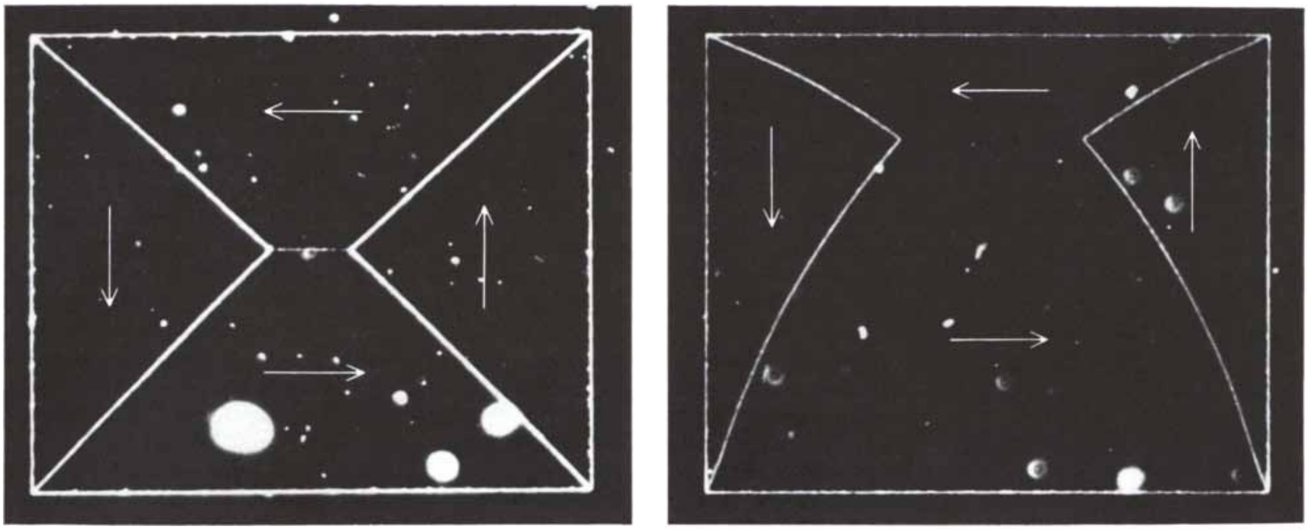
In 1934, after thousands of experiments, N. P. Goss of the Cold Metal Process Company perfected an orientation process using steel with a 3 percent content of silicon. He subjected the steel to a moderate cold-rolling followed by an annealing, another moderate cold-rolling and a high-temperature annealing. The theoretical basis of the very exacting Goss recipe is not well understood. It appears that impurities, usually manganese sulfide, keep all but similarly oriented crystal grains from growing and that the



**DOMAIN WALLS** in a single crystal of nickel are made visible under the microscope by a coating of magnetized iron oxide. The powdered oxide gathers along the lines at which poles in the Bloch wall point to the face of the crystal (*see illustration on opposite page*).



**ANALYSIS OF DOMAINS** in the nickel crystal in the top illustration is shown in this diagram. Most domains prove to have one or another of four directions of magnetization, comprising two sets with opposite polarity (*arrows*). Both the micrograph and the diagram were prepared by R. W. DeBlois of the General Electric Research and Development Center.



**WALL MOTION** in a magnetized material is produced by application of an external magnetic field. The domain walls in a single crystal of nickel-cobalt alloy (*left*) have been shifted (*right*) by applying a 3.6-oersted field favoring the growth of the lower domain.

pinch of sulfur is critical—there can be neither too much nor too little.

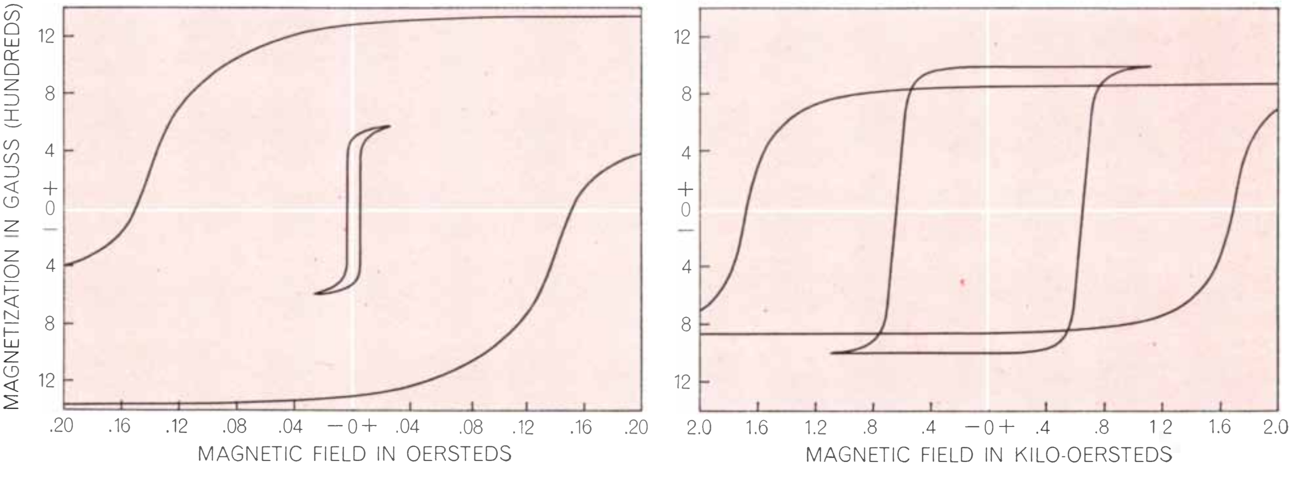
The percentage of silicon in the recipe represents a compromise. The addition of silicon increases steel's electrical resistivity (usually a desired characteristic) but makes the metal brittle. Where mechanical strength is required, as in the rotating parts of generators and motors, steels that contain 1 to 3 percent silicon are used. A higher silicon content can be tolerated in transformers, but steels with more than 4.5 percent silicon are at present too brittle for normal use.

Many metallurgists are nonetheless working toward a reasonably ductile 6.5 percent silicon steel. At this percentage, for some entirely mysterious reason, the metal loses the property of magnetic materials known as magnetostriction. An electrostatic interaction that physically stretches each iron crystal slightly in the direction of magnetization, magnetostriction adds to hysteresis losses. It also appears to be the reason transformers make a humming sound.

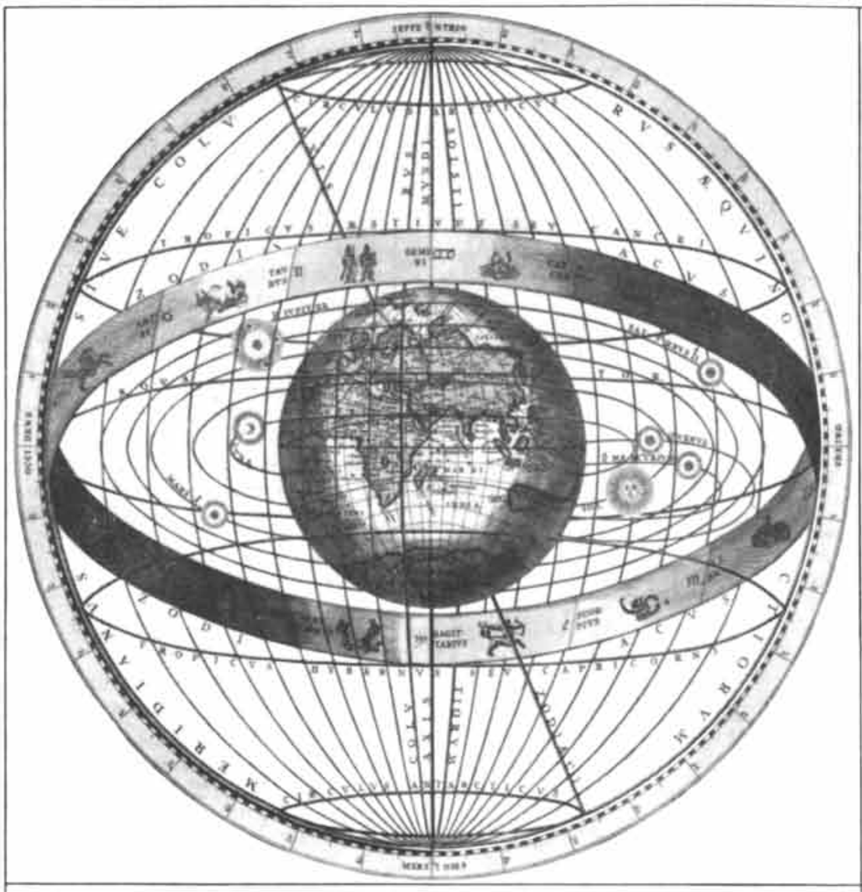
An improvement over Goss steel, made according to an even more exacting formula, is "cube-textured" steel. In this material the cubic face of each crystal grain lies parallel to the surface. This minimizes the energy spent in overcoming another source of hysteresis loss, unfavorable anisotropy: a nonsymmetrical distribution of the crystal's energy field.

In some applications the cost of a material is secondary to the reduction of hysteresis loss. An example is the inductive loading of submarine cables. Permalloy, a mixture of 78.5 percent nickel and 21.5 percent iron in which both magnetostriction and anisotropy are minimal, was perfected for cable telegraphy. The anisotropy of iron is opposite in direction to that of nickel and the two nearly cancel each other. Subsequent research showed that adding a third element to the alloy—usually molybdenum—can drive both magnetostriction and anisotropy to zero. The improved combination has been christened supermalloy. Consisting of 79 percent nickel, 15.7 percent iron, 5 percent molybdenum and .3 percent manganese, it shows an extraordinary ability to become magnetized in almost negligible fields.

Ferromagnetic materials exposed to changing external fields are subject to energy losses besides those caused by hysteresis. One such important loss in conducting materials arises from eddy currents, which are induced by field changes and which increase as the frequency of the charges increases. Any enhancement of electrical resistivity—for example by the introduction of impur-



**EXTREME DIFFERENCE** between "soft" (*left*) and "hard" (*right*) magnetic materials requires an increase by 10,000 in the horizontal scale of graph at right if hysteresis loops typical of both are to be compared. The large loop at left is for Goss 3 percent silicon steel; the very small one is for supermalloy. The smaller loop at right is for Alnico No. 5. The much larger loop is for Alnico No. 9.



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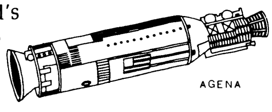

Polaris. Now undergoing extensive alterations, this submarine fleet ballistic missile remains the Free World's foremost deterrent force. To extend its deterrent capabilities further, considerable engineering challenges must be overcome.

Poseidon. State-of-the-art engineering problems never before encountered in an ICBM must be solved during development of this eventual successor to Polaris.

Information systems. Projects under way will help hospitals, corporations and governments efficiently manage exploding masses of information.

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Deep Quest. This research vehicle is part of Lockheed's corporate commitment to pioneer in the undersea world. Among its missions will be a detailed exploration of the ocean floor. Specifications call for a payload capacity of 3½ tons, and a submergence duration of up to 48 hours.

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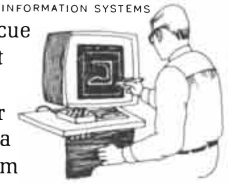

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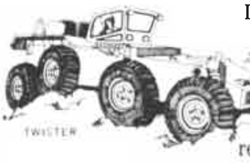

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ities—will lower eddy-current losses. The reduction of the area through which the currents travel also cuts losses; this is done by building the magnet out of alternate layers of metal and insulation.

Some ferrites have an electrical resistivity 100 billion times greater than the resistivity of metals, which makes them immune to eddy currents As a result these ferrimagnetic materials are often used in high-frequency devices. Their major application at present is in the "flyback" transformers of television picture-tube scanning systems, but ferrites also have important uses as elements in microwave circuits. Because not all the atomic magnets in ferrimagnetic materials point in the same direction, the maximum magnetization of ferrites is limited. They are therefore ruled out for most generator, motor and transformer applications.

Logically enough, the first efforts to produce hard magnetic materials for industrial use emphasized the addition of various internal obstacles. One early process involved the rapid cooling of steel containing about 1.2 percent carbon. Iron carbide normally starts to precipitate at 870 degrees C.; rapid cooling of the steel kept the finely divided material suspended throughout the crystal lattice, which also underwent many internal strains because of the sudden reduction in temperature. The process brought about a "martensitic" transformation in the steel. Unfortunately martensitic steel is magnetically unstable. Its magnetization is easily altered by shock, vibration or even variations in temperature. Instability remains a disadvantage in the vastly improved martensitic alloys perfected in the 1920's by the Japanese metallurgist K. Honda.

Recent years have seen the development of an entirely new class of permanent magnets. The theory underlying them was first stated by Néel, who found that a small enough particle of magnetic material cannot contain more than a single domain and thus cannot support any Bloch walls. In iron, he found, the critical size was a diameter of roughly .000002 centimeter. It has since been demonstrated that elongated single-domain particles, when they are magnetized in the direction of their elongation, are magnetically extremely stable.

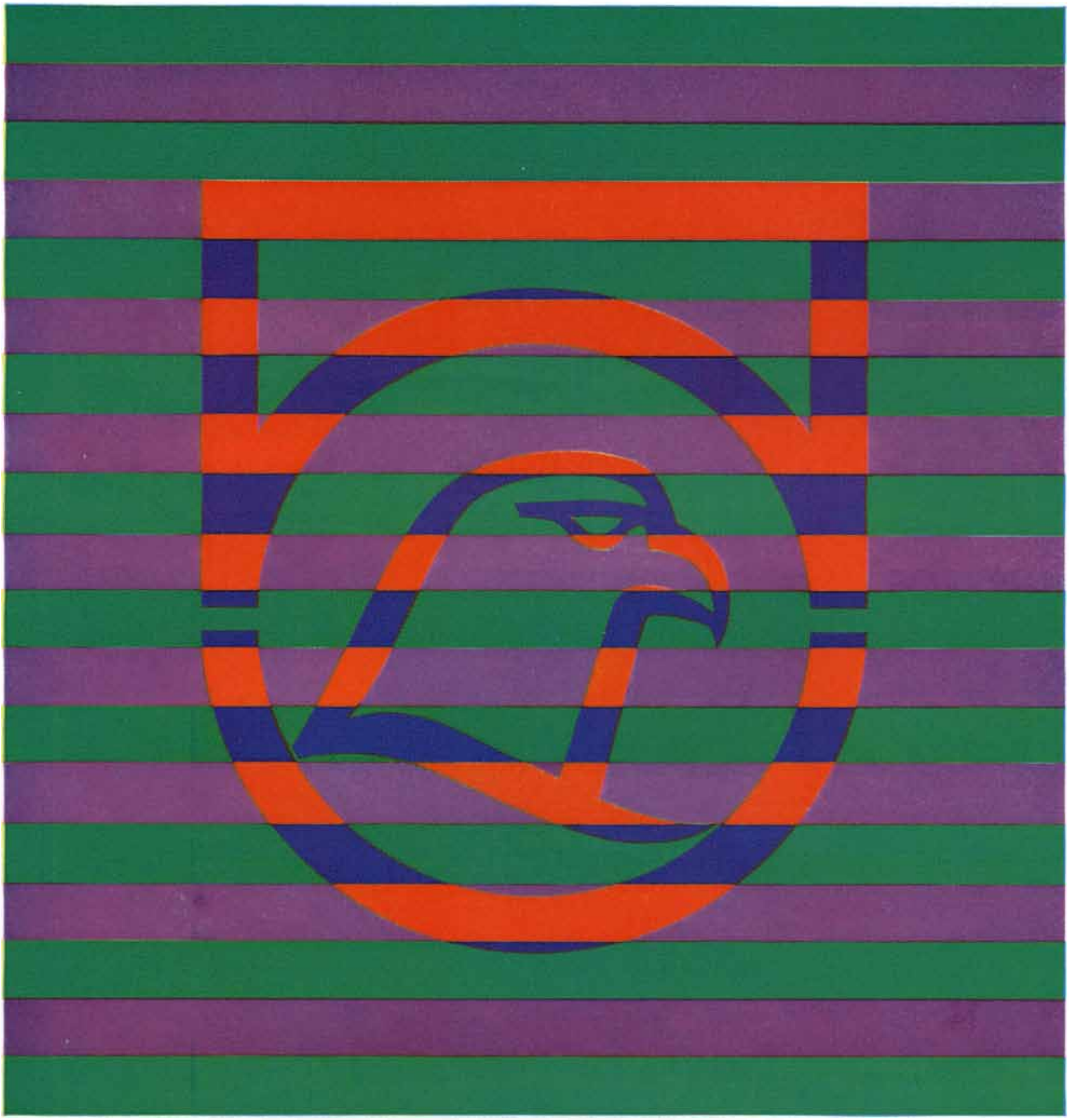
The first, and still the most widely used, of these materials are the precipitation alloys, of which Alnico is probably the best known. T. Mishima of Japan invented the prototype and called it MK steel; its formula was approximately $Fe_2NiAl$. G. D. L. Horsburgh and F. W. Tetley of Britain further improved the alloy by adding cobalt and copper. Alnico magnets are fabricated in columnar form by pouring the molten alloy into a cylindrical mold with a cold bottom and hot walls. The upward freezing of the metal produces elongated particles. At the same time the alloy decomposes into a magnetic component rich in iron and cobalt and a nonmagnetic component rich in nickel and aluminum.

Some ferrites with very large anisotropy have also proved to be good permanent magnets. One of them, marketed by the Westinghouse Electric Corporation under the name Westro, is made by aligning the individual crystals in powdered strontium ferrite, usually by means of a magnetic field, and then pressing and sintering the powder. This ceramic material has found many applications and has even been mixed with rubber to make flexible magnets, such as gaskets for refrigerator doors.

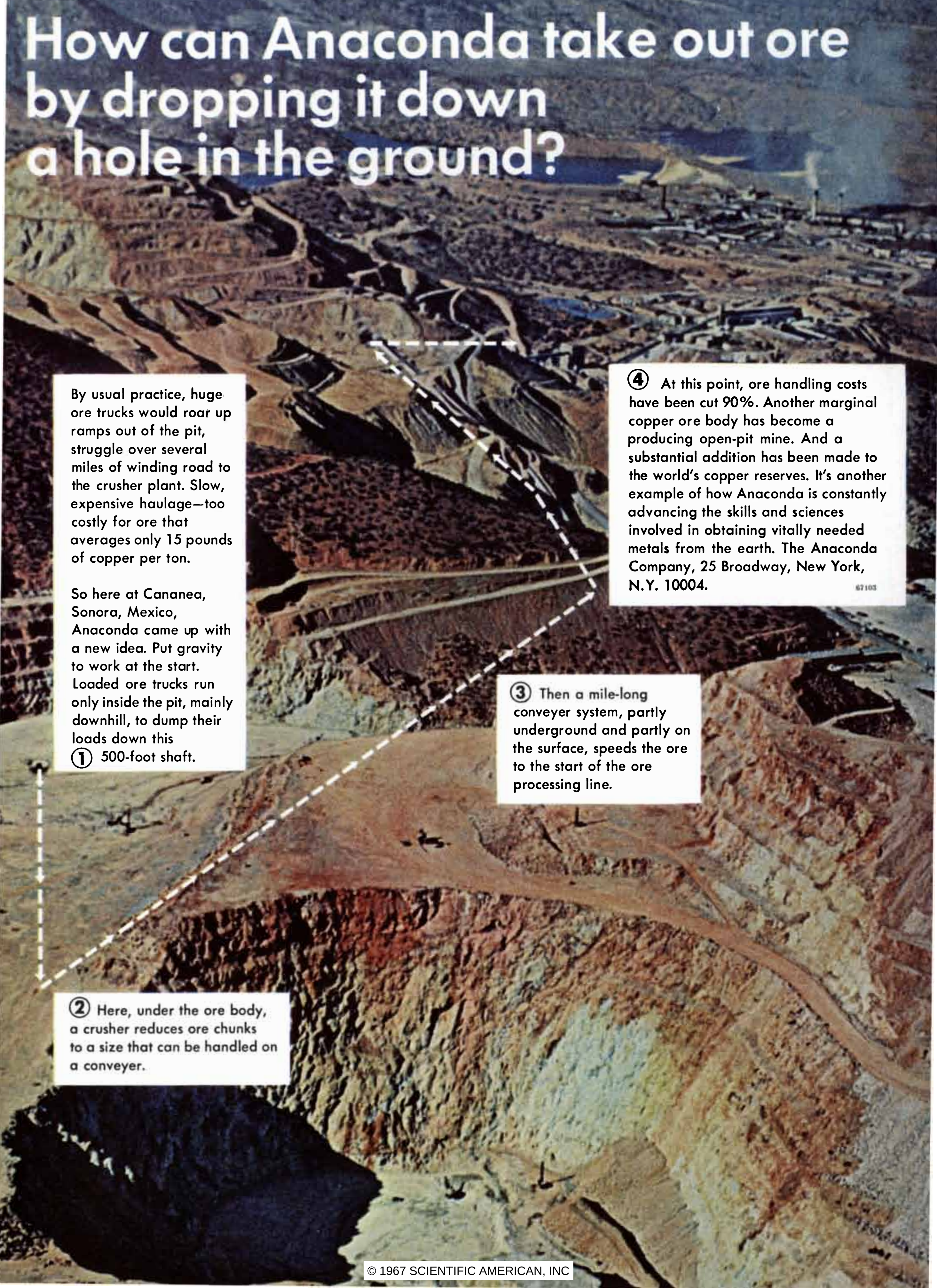
Another elongated, single-domain material is marketed by the General Electric Company under the name Lodex. Iron alloyed with 30 or 35 percent cobalt is electrodeposited in mercury. The particles are removed from the mercury, coated with antimony and placed in a lead matrix that is then ground into a powder. Each grain of the powder is a tiny magnet. The softness of the lead matrix allows the material to be cold-pressed and stamped into unconventional shapes that find application in such dissimilar devices as speedometers and hearing aids.

One application of magnetic materials calls for properties that lie halfway between hard and soft. The magnetic-memory element in a digital computer must be hard enough to retain its forward or reverse magnetization—the states corresponding to 0 and 1 in the binary system—indefinitely on being stored. It must also be soft enough to switch states cleanly and rapidly when a small external field is applied in the course of information read-in or read-out. Tiny ferrite cores are being replaced today by thin magnetic films in the interest of faster switching.

William Gilbert wrote in 1600 that it was "by good luck" that "smelters of iron or diggers of metal" had discovered magnetite perhaps as early as 800 B.C. Luck has played no less central a role in the development of the theories by which we explain magnetic properties. In recent years systematic application of these theories has begun to yield planned materials. The recipe still calls for a large measure of luck, however, and will no doubt continue to do so.



# How can Anaconda take out ore by dropping it down a hole in the ground?



By usual practice, huge ore trucks would roar up ramps out of the pit, struggle over several miles of winding road to the crusher plant. Slow, expensive haulage—too costly for ore that averages only 15 pounds of copper per ton.

So here at Cananea, Sonora, Mexico, Anaconda came up with a new idea. Put gravity to work at the start. Loaded ore trucks run only inside the pit, mainly downhill, to dump their loads down this ① 500-foot shaft.

② Here, under the ore body, a crusher reduces ore chunks to a size that can be handled on a conveyer.

③ Then a mile-long conveyer system, partly underground and partly on the surface, speeds the ore to the start of the ore processing line.

④ At this point, ore handling costs have been cut 90%. Another marginal copper ore body has become a producing open-pit mine. And a substantial addition has been made to the world's copper reserves. It's another example of how Anaconda is constantly advancing the skills and sciences involved in obtaining vitally needed metals from the earth. The Anaconda Company, 25 Broadway, New York, N.Y. 10004.

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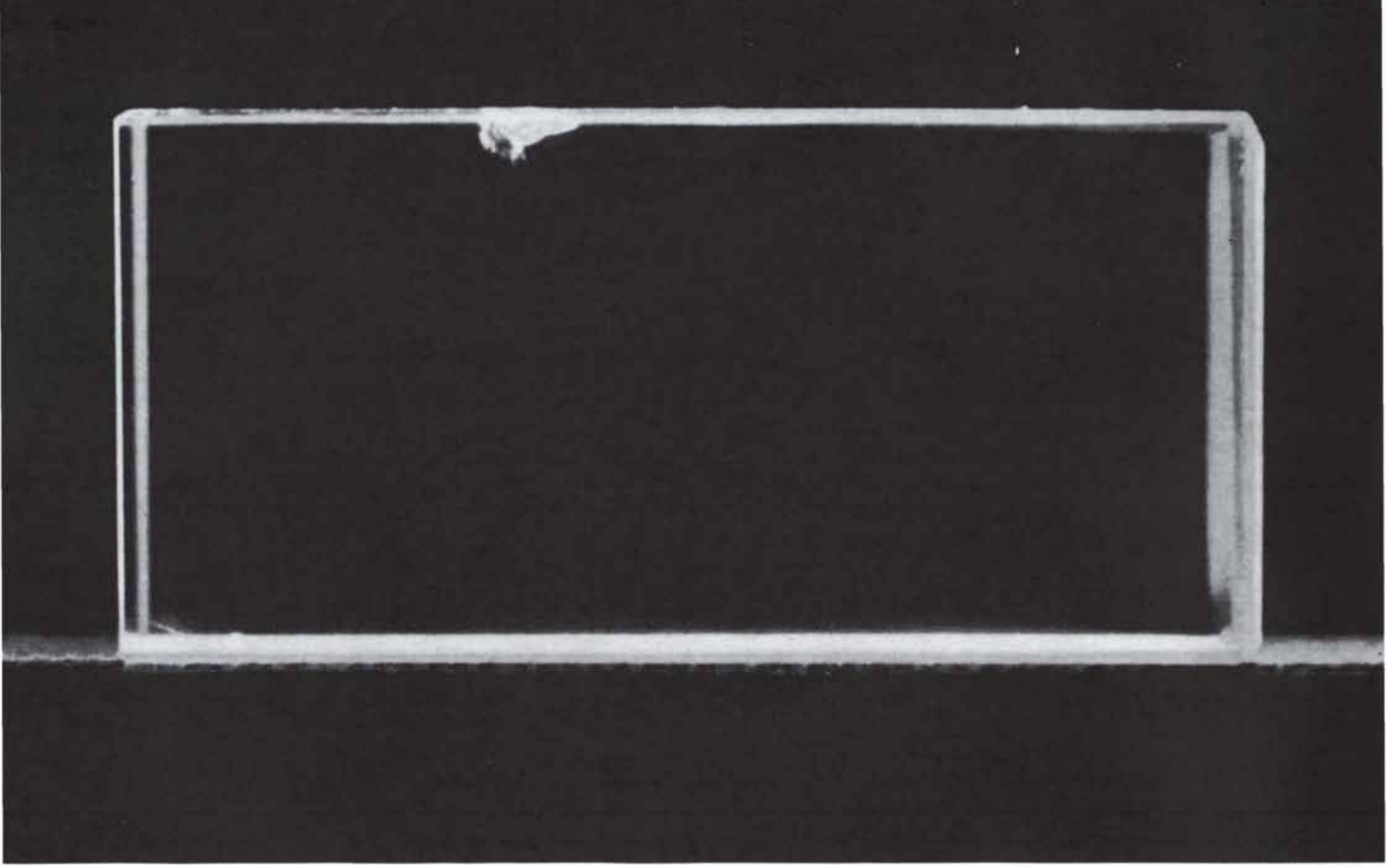
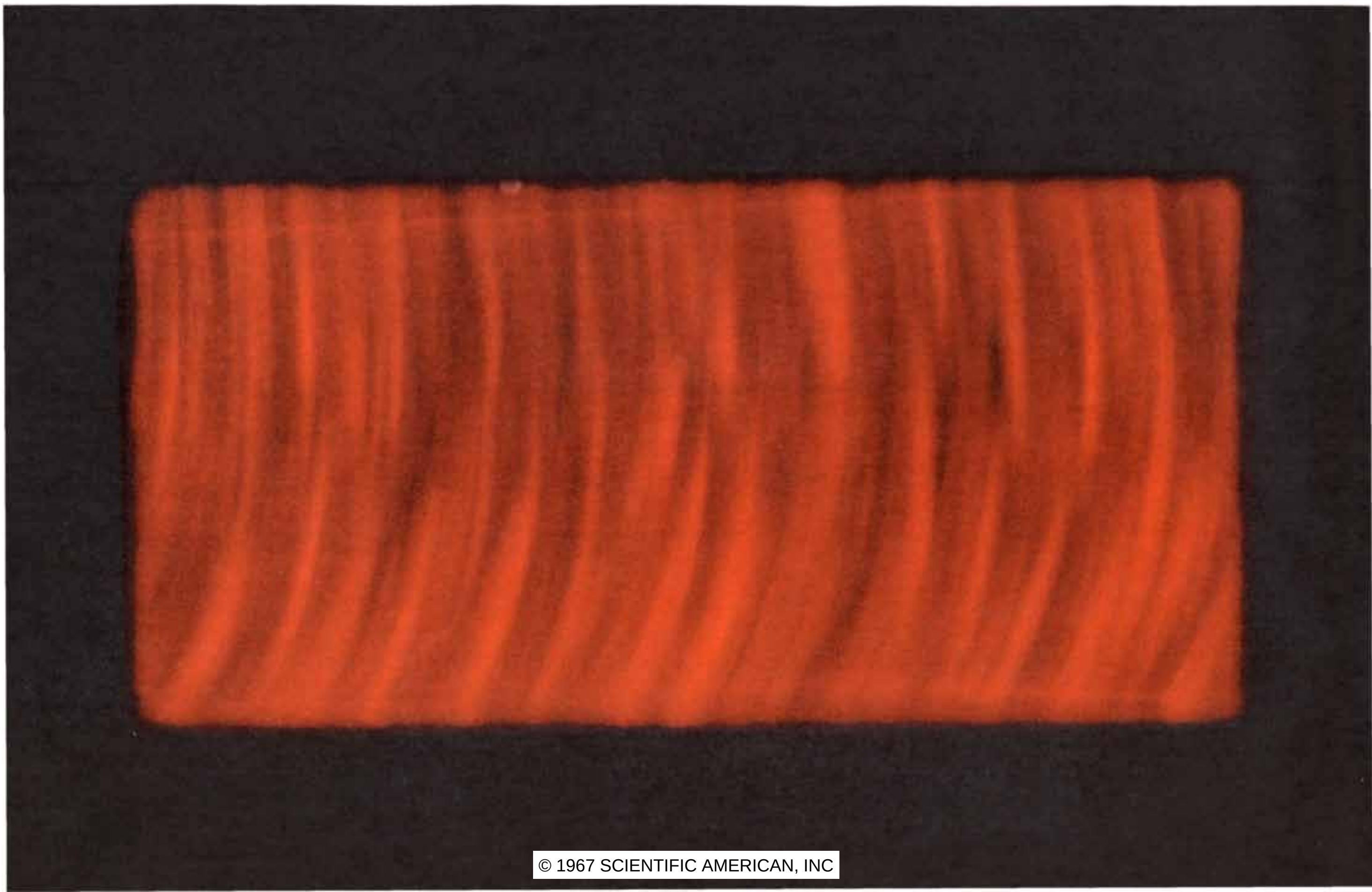


FLUORESCENCE EFFECT can be produced in a normally clear crystal of sapphire (*top*) by subjecting the crystal to an intense beam of blue light from an argon gas laser (*bottom*). The red fluorescence is emitted by traces of excited impurity atoms of chromium in the sapphire's crystal lattice. The unevenness of the red color indicates the nonuniform distribution of chromium atoms in the crystal. The highly collimated laser beam, which passes from right to left across bottom photograph, is invisible to the camera.



# The Optical Properties of Materials

*The quantum-mechanical interpretation of the spectroscopic characteristics of the elements has made possible a number of technological advances such as the development of lasers*

by Ali Javan

Before the advent of quantum physics one could give only very crude answers to such elementary questions as: Why do materials have characteristic colors? Why do all materials glow when they are heated? What makes one material transparent and another opaque?

We now know that all these optical properties are intimately related to the way electrons are deployed in a material. This article explains how the modern theory of quantum mechanics accounts for the optical properties of materials in terms of their electronic structure, and shows how this knowledge is being used in the development of new materials for optical applications. For historical as well as expository reasons I shall begin by describing the optical behavior of isolated atoms, such as one finds in a gas, and then proceed to show how this comparatively simple picture is related to the complex many-body problem presented by a typical solid material.

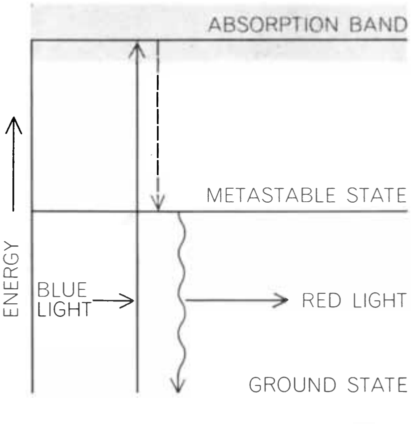
The insights of quantum mechanics have come in large part from spectroscopy, which began more than 300 years ago with the experiments of Isaac Newton. In his *Opticks* Newton wrote: "In a very dark Chamber, at a round Hole, about one third Part of an Inch broad, made in the Shut of a Window, I placed a Glass Prism, whereby the Beam of the Sun's Light, which came in at that Hole, might be refracted upwards toward the opposite Wall of the Chamber, and there form a colour'd Image of the Sun." It was this experiment that led Newton to discover that his observed solar spectrum did not originate in the glass prism but was a property of the sunlight itself. The prism merely refracted the different colors at different angles. This simple arrangement was the first spectroscope, and Newton's experiment marked the first application of spectroscopy to the study of the interaction of light and matter.

It is now common knowledge that the colors observed by Newton correspond to electromagnetic waves of various frequencies, each with a specified wavelength: the higher the frequency, the shorter the wavelength, and vice versa. For example, the frequency of visible light extends from about 4,300 to 10,000 trillion cycles per second, corresponding to wavelengths of about 7,700 to 3,900 angstrom units (ten-billionths of a meter). The angle of refraction of a particular colored ray through a piece of glass is a unique function of its wavelength: the shorter the wavelength, the larger the angle of refraction. Although Newton did not advocate a wave theory of light, he described the various colors by their "degree of refrangibility" as they passed the prism of his spectroscope.

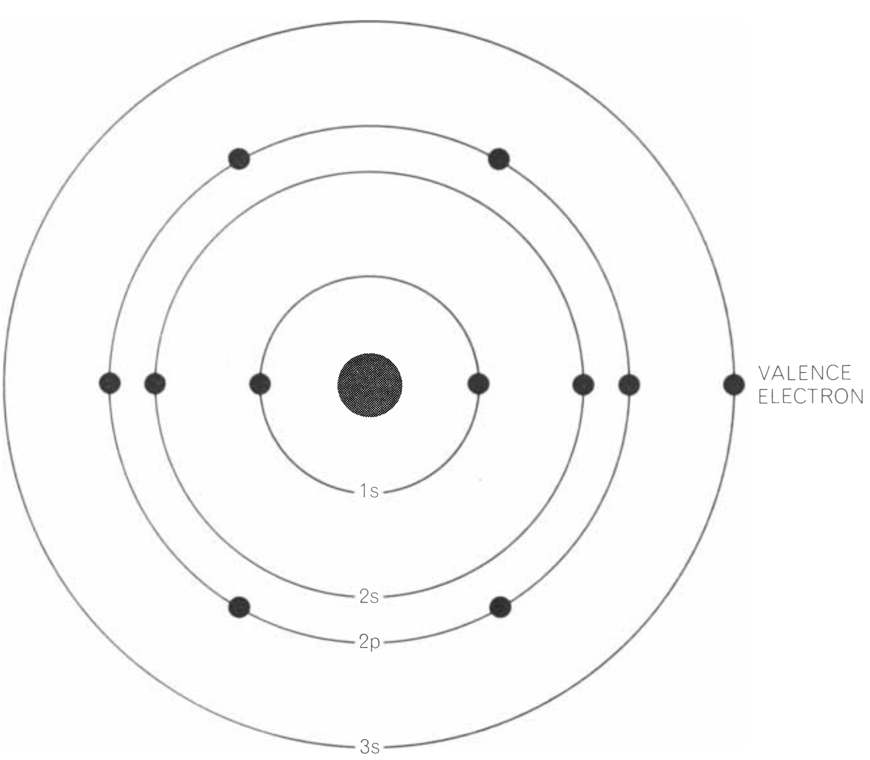
A great deal of useful information is contained in the characteristic spectra associated with the various species and states of matter. Indeed, one might say that matter communicates with us by means of the spectrum of light that it emits and with which it interacts. Consider the visible spectrum of the sun as seen through Newton's prism. The dominant feature of the solar spectrum is a color continuum extending over the entire visible range from red to violet. The distribution of intensity among these colors is governed by the temperature of the emitting surface of the sun. The particular color combination that appears to us as white sunlight indicates a surface temperature of about 6,000 degrees centigrade.

In fact, at a given temperature all hot bodies, regardless of their composition, emit a continuous spectrum of rays with an identical distribution of intensity. As the temperature of the body is increased, this distribution changes: the color being emitted at maximum intensity shifts toward the violet end of the spectrum. Thus stars that have higher surface temperatures than the sun appear blue against the night sky. Similarly, as the filament of an incandescent electric light bulb is gradually heated, its dominant color changes from an initial dull red to a bright yellowish white.

If Newton had made a very narrow slit instead of a hole in the "shut" of his window, he would probably have discovered that his solar spectrum also contained a sprinkling of narrow, dark lines. A century passed, however, before these delicate features came to the attention of Joseph von Fraunhofer, a German master of optical devices. Fraunhofer



**ENERGY-LEVEL DIAGRAM** of an isolated chromium atom shows how the red fluorescence effect originates in a clear sapphire. The chromium atom absorbs a photon of blue light, causing an electron in the atom to be excited from its ground state to a broad upper absorption level. A nonradiative process involving an exchange of energy with the crystal lattice then causes the electron to decay to a lower metastable energy state, from which it decays spontaneously to the ground state, emitting a photon of red light.



**SODIUM ATOM** has 11 electrons, one of which—the valence electron—occupies the atom's outer boundary and is responsible for the chemical behavior of sodium as an alkali metal. The distinct quantum states of this single valence electron are also responsible for the optical properties of an isolated sodium atom. The rest of the electrons form closed inner shells and are tightly bound to the nucleus. In spectrographic terminology the electron shells of the elements are designated 1, 2, 3, 4, 5 and so on. The subshells are designated *s*, *p*, *d* and *f*.

mapped hundreds of these dark lines, lettering eight of the most prominent *A* through *H*. Another 50 years passed before Fraunhofer's work led to the exciting discovery that many elements found on the earth also exist on the sun. It then became clear that the Fraunhofer lines were caused by the passage of solar rays through the sun's outer atmosphere. Layers of gas in this atmosphere contain isolated atoms of certain elements, which characteristically absorb the sun's rays only at sharp and well-defined wavelengths. For example, a pair of closely spaced dark lines in the yellow region of the solar spectrum—Fraunhofer's *D* lines—are due to the absorption of sunlight by sodium atoms.

The absorption lines of sodium and other elements can be reproduced in the laboratory by means of a simple absorption spectroscope. When one views an ordinary incandescent lamp through a prism spectroscope with a narrow slit, one sees a continuous spectrum of color extending from red to blue. Now, if one places a flame containing sodium atoms between the lamp and the slit, the continuous spectrum is altered in the yellow region, where the Fraunhofer *D* lines are located. In fact, the intensity of the light is diminished by an appreciable amount precisely at the wavelengths of the two *D* lines. This reduction in intensity is caused by the absorption of light by the sodium atoms in the flame. An element that strongly absorbs an incident light ray at a definite wavelength may become entirely transparent at a slightly different wavelength. The width of such an absorption line is defined by the range of wavelengths within which strong absorption takes place.

The existence of characteristic absorption lines is an important aspect of the optical properties of matter in all three of its states: gas, liquid and solid. Isolated atoms or molecules in a gas at moderate pressure yield sharp, narrow absorption lines, which become somewhat broader as the pressure is raised. In liquids and solids these absorption lines become very broad, in some cases encompassing sizable regions of the visible spectrum. Thus red glass examined through an absorption spectroscope shows a strong absorption band covering the green and blue regions and leaving the red region transparent, whereas blue glass shows a strong absorption band in the red and yellow regions and is transparent in the blue region. A completely transparent glass of course shows no absorption bands in the visible region of the spectrum.

The absorption characteristics of materials are not restricted to the visible region of the spectrum. A crystal transparent to visible light may be completely opaque in the infrared and ultraviolet regions. Metals, on the other hand, reflect visible light and hence are opaque in this region, but they are often transparent at short ultraviolet wavelengths.

Simultaneous with the discovery that elements have characteristic absorption lines, it was found that elements are also capable of emitting characteristic radiation at well-defined wavelengths. These emission lines were first observed in flames and later in electrically excited gases. In recent years they have also been produced by electrically or optically excited impurity atoms in certain solids, a situation that is quite similar to that in a gas. When the spectra of such light sources are analyzed in a prism spectroscope, a series of sharp bright lines is obtained. The wavelengths of the emission lines for a particular element coincide exactly with that element's characteristic absorption lines. Sodium, for example, which strongly absorbs at the Fraunhofer *D* lines, also emits radiation at these wavelengths.

During the 1850's it was further recognized that some of an element's emission lines could be strongly "reabsorbed" by the same element. A related optical property has been added to this list in our own century. Under appropriate conditions matter is capable of amplifying instead of absorbing an incident light ray. This property—the basis of the modern laser—will be discussed later in this article.

Toward the end of the 19th century there was collected a vast body of data on the precise wavelengths of the absorption and emission lines in the spectra of a great many elements. Moreover, curious regularities were recognized in some of these spectra. The interpretation of these regularities became a major challenge of the time. The precision with which the spectral lines were charted provided one of the keys to quantum mechanics—the ultimate interpretation of the optical properties of matter.

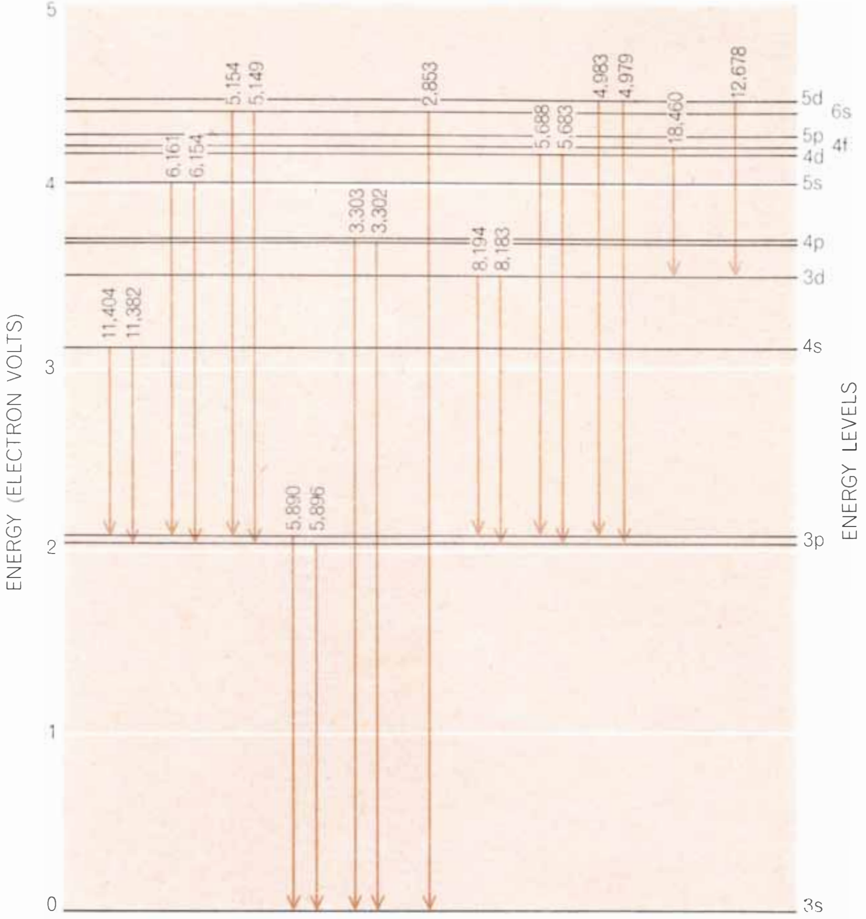
In the initial formulation of quantum mechanics hydrogen played a decisive role. Its simple atomic structure of one electron bound to one proton produced a line spectrum that revealed the quantum nature of an atom's electronic structure in its barest essentials. These laws were then generalized and applied to the optical properties of more complex atoms containing many electrons and finally to atoms in the liquid and the solid states.

In their present form the laws of quantum mechanics in principle embrace all the optical properties of gases, liquids and solids. The mathematical manipulation of these laws becomes exceedingly intricate, however, when one is dealing with many-body interactions, particularly in solids. For the purposes of this article, therefore, the hydrogen atom will serve as a starting point for further generalization about more complex systems.

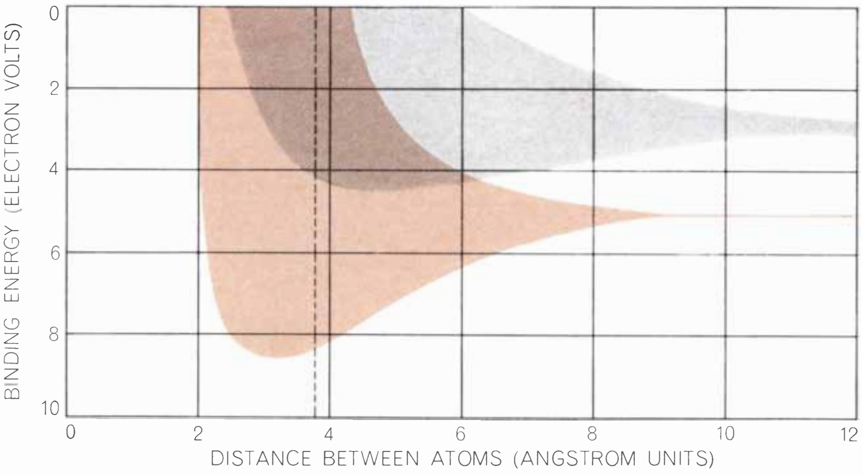
The hydrogen atom can be described in quantum-mechanical terms as an electron "cloud" surrounding a single proton nucleus, the volume of the cloud being much larger than that of the nucleus. Although the electron behaves in some respects as a pointlike particle with a definite charge and mass, in other respects its position can be regarded as being spread over an extended volume whose size and shape depend on the electron's motion. The density of this cloud at each point around the nucleus represents the probability of finding the electron at that point. The total internal energy of the atom is uniquely determined by the configuration of the electron cloud, and the configuration is in turn is governed by the wavelike behavior of the electron.

An atom can exist in only one of a number of quantized energy states, each state corresponding to an electron cloud of a different size or shape. Accordingly an atom can change its energy only in distinct quantized steps, each step a transition from one energy state to another. The various states, arranged in order of increasing energy, constitute the energy-level diagram of the atom.

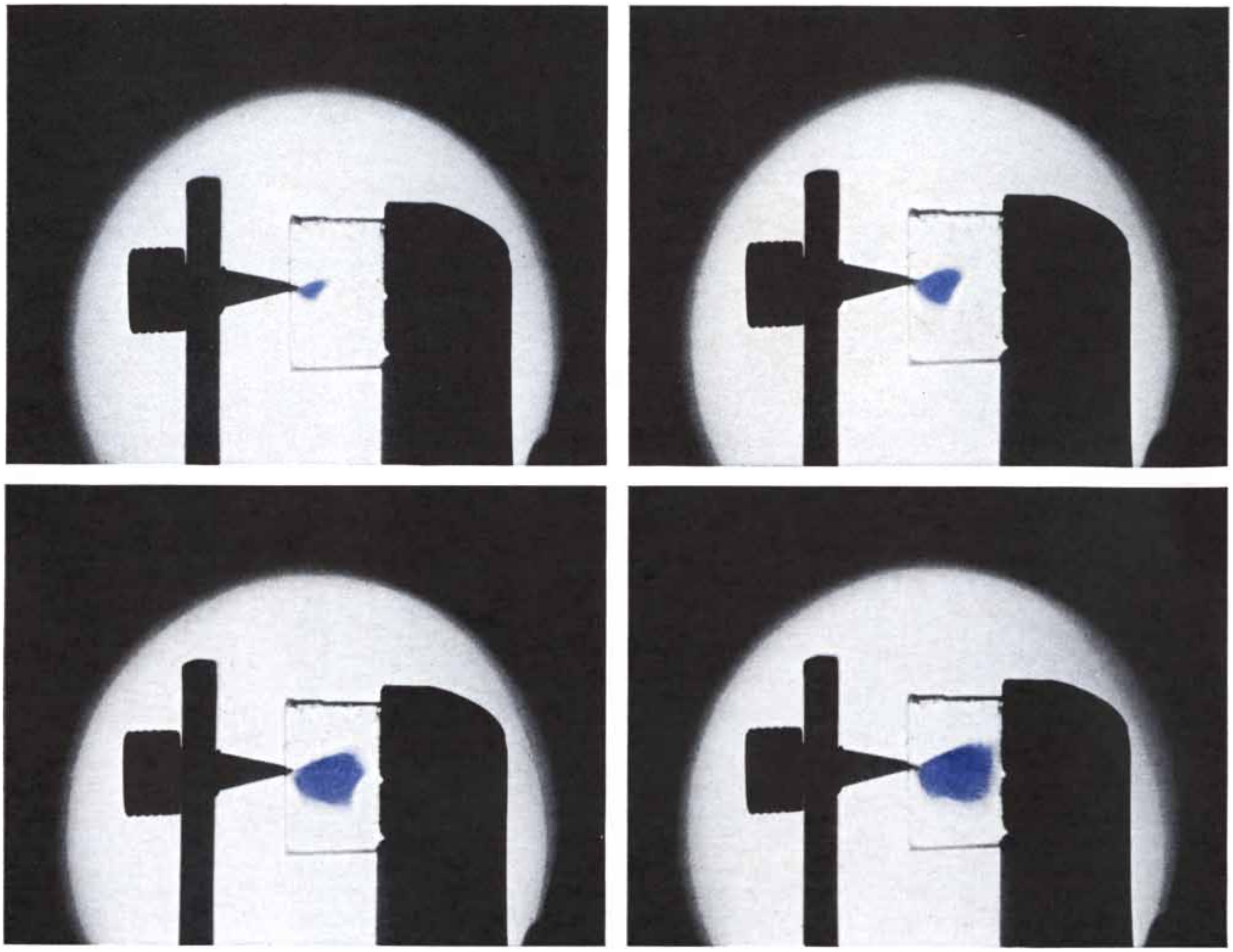
Atoms that have more than one electron can be similarly described. In that case, however, the different electrons occupy different quantum states, and the internal energy arises from electron-electron interactions as well as from electron-nucleus interactions. Most of the chemical and optical properties of an atom are determined by the quantum states of its valence electrons, which occupy the atom's outer boundary. The rest of the electrons form closed inner shells and are tightly bound to the nucleus. An atom of sodium, for example, has 11 electrons, one of which is the valence electron responsible for the chemical behavior of sodium as an alkali metal [*see illustration on opposite page*]. The distinct energies associated with the various quantum states of this single valence electron are responsible for the optical



**ENERGY-LEVEL DIAGRAM OF SODIUM ATOM** shows some of the upper energy levels to which the valence electron (normally at the 3*s* level) can be excited by the input of energy to the atom. An excited electron can return to the 3*s* level by a variety of routes (*colored arrows*); for each transition from an upper level to a lower one the atom emits a photon of light with a characteristic wavelength, which is indicated in angstrom units on the arrow representing that transition. The two transitions from the split 3*p* level to the 3*s* level are responsible for the characteristic yellow *D* lines in the spectrum of sodium.



**QUANTUM STATES OF SOLID SODIUM** can be traced back to their origin as energy levels in the isolated sodium atom. This is done by assuming that the atoms of the solid are arranged on a fictitious crystal lattice with interatomic separations many times larger (*right*) than those found in the actual solid. As the interatomic separation is gradually reduced toward the value corresponding to that for the actual crystal lattice of sodium (*broken vertical line*), the energy levels of the atoms split into broad bands (*left*). The overlapping of the various bands in metals is responsible for their distinctive optical properties, such as color and opacity. Only the 3*s* (*color*) and 3*p* (*gray*) bands of sodium are shown here.



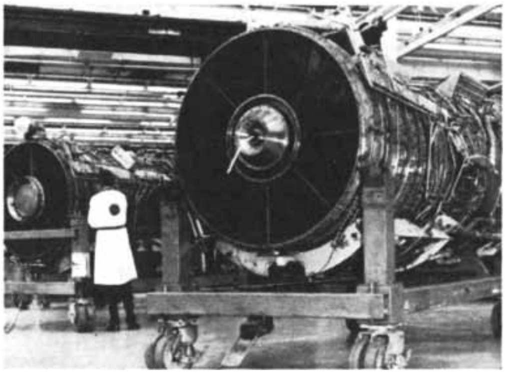
**DIFFUSION OF COLOR CENTERS** in a normally clear crystal of potassium chloride is demonstrated in this apparatus devised by R. L. Wild of the University of California at Riverside. The transparent crystal contains an equal number of positive and negative vacant lattice sites. A color center is an electron in one of the negative vacant lattice sites that is capable of absorbing light in the visible region of the spectrum. The extra electrons are injected into the crystal by means of a pointed stainless-steel electrode. A voltage of about 300 volts is applied to this electrode. The crystal and the electrodes are located in an oven maintained at about 550 degrees centigrade. At this temperature the color centers appear deep blue; at room temperature they would be purple. The interval between pictures in this sequence is about one second. The crystal is about 10 millimeters square and three millimeters thick.

properties of isolated sodium atoms in the gaseous phase.

There are several ways of looking at the system of quantum states in a solid. One of these views—the energy-band model—traces the quantum states of the solid back to their origin in the isolated atom. This is done by assuming that the atoms of a given solid are perfectly arranged on a fictitious crystal lattice with interatomic separations many times larger than those found in an actual solid. The quantized states of this fictitious solid are simply duplicates of the states of an isolated atom that undergoes negligible interactions with its neighbors. As the interatomic separation is gradually reduced toward the value corresponding to that for an actual crystal lattice, however, the energy levels of the atoms split into broad bands [*see bottom illustration on preceding page*]. This splitting occurs when the valence electron clouds of adjacent atoms begin to overlap appreciably, giving rise to strong interactions among the atoms. The overlapping of the various bands in metals is at the root of both their electrical conductivity and their distinctive optical properties, including such absorption characteristics as color and opacity. On the other hand, in an insulator such as sodium chloride or calcium fluoride the valence electrons occupy nonoverlapping bands and the crystals are generally transparent.

In addition there exist a variety of colored materials that derive their optical properties from the quantum states of impurity atoms embedded in the crystal lattice of an otherwise transparent solid. The width of the energy level of the impurity atom depends on the extent of its interaction with the host lattice. For a strongly interacting state the level is broad and forms a band similar to that of a pure solid; otherwise the level is narrow and resembles that of an isolated atom. For example, sapphire is a transparent ionic crystal consisting of aluminum oxide with traces of titanium and chromium, whereas ruby has the identical composition but with a few percent of the chromium. The absorption spectrum of a ruby shows wide absorption bands in the blue region, resulting in the ruby's characteristic pink color. The chromium ions, which substitute for aluminum ions in the crystal lattice of the ruby, are solely responsible for this absorption spectrum. The width of the bands shows that the chromium atom interacts quite strongly with the lattice.

A closely associated substitution can

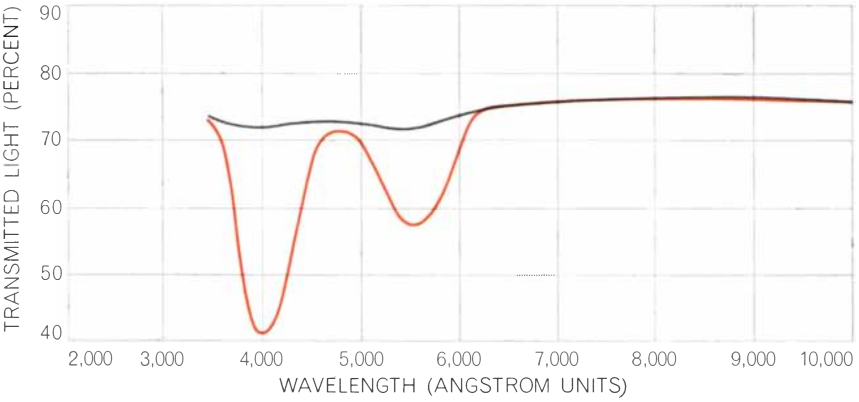


take place in certain ionic crystals such as potassium chloride. In this case missing chlorine atoms in the crystal lattice are replaced by free electrons, creating "color centers" with a characteristic absorption spectrum that gives the normally transparent crystal a purple or blue color depending on the temperature.

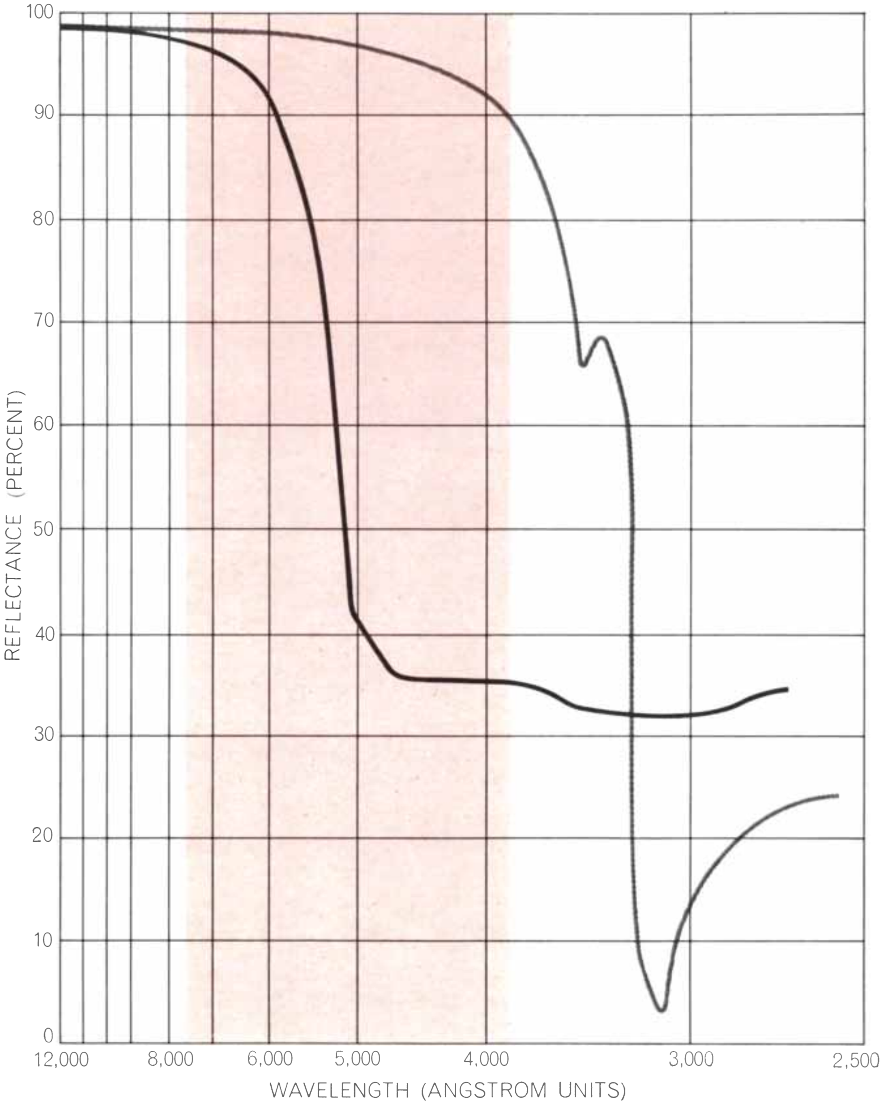
When an atom is in its lowest energy state, it prefers to stay there for an indefinite time unless it is disturbed by some external means. Such a disturbance can take the form of a collision with an external electron, causing the atom to be excited suddenly to a higher energy state. Once the atom is in an excited state, it tends to decay spontaneously to a lower energy level. The decay is accompanied by the emission of a light wave at a frequency that is uniquely and universally proportional to the change in the energy of the atom. This universal relation of energy change to frequency defines a resonance frequency for each pair of levels. In fact, whenever a spontaneous transition from a higher to a lower level occurs, an electron in the atom exhibits a decaying oscillatory motion at the resonance frequency of the corresponding pair of levels. The oscillation, in turn, is responsible for the light wave radiated at that frequency. When the emission ends, the emitted energy in the light wave precisely equals the change in energy of the atom. Thus the energy in the emitted light wave is also universally related to the frequency of that wave. Here the quantized nature of the atom goes hand in hand with the quantized state of the radiation field; one photon, or quantum of light, is emitted when one atomic transition occurs. The laws of quantum mechanics make it possible to calculate exactly the probability of spontaneous emission from one level to a lower one. The probability is high for some pairs of levels and exceedingly low for others.

In brief, the quantum states of an atom are defined by a set of energy levels, with a resonance frequency associated with each pair. An atom can decay with a predictable probability from a higher to a lower level by spontaneously emitting a photon at the corresponding resonance frequency. It must be emphasized that the exact energies of an atom's quantized states are predictable theoretically; one merely needs to know the number of electrons in the atom and the nature of its nucleus. The rest follows from the universal laws of the interactions of the electrons with the nucleus and with other electrons.

The emission line spectra of isolated



**ABSORPTION SPECTRA** of a clear sapphire (*gray curve*) and a pink ruby (*colored curve*) are compared. Both are ionic crystals of aluminum oxide with traces of certain impurities. The only difference between the crystals is that ruby has considerably more chromium, amounting to a few percent. As a result the absorption spectrum of the ruby shows strong absorption bands in the blue region, and this gives the ruby its characteristic pink color.



**REFLECTANCE SPECTRA** of gold (*black curve*) and silver (*gray curve*) are compared. Gold reflects red and yellow light strongly at the surface but allows some penetration by green rays, which are then completely absorbed within a small thickness of the bulk of the metal. Silver, on the other hand, strongly reflects incident light over most of the visible region of the spectrum (*color*) but allows considerable transmission in the ultraviolet.

atoms can now be interpreted in terms of this quantum-mechanical picture. For instance, the energy-level diagram of a sodium atom contains two closely spaced levels immediately above its lowest energy state. The spontaneous transitions from these two levels to the lowest energy state are responsible for the emissions at the two closely spaced Fraunhofer *D* lines. Precise measurements of the difference in wavelength between these two lines reflect the difference in energy between the two excited levels. This "level-splitting" is a manifestation of an important property of the electron known as spin. In a crude sense an electron can be visualized as a spinning entity with a fixed angular momentum. In the more sophisticated theory the electron spin and its resulting interaction are shown to be necessary consequences of the laws of quantum mechanics when they are formulated in a manner consistent with the theory of relativity. These fundamental insights have all emerged from delicate experimental observations of the optical line spectra of the elements.

The structural detail of an atomic nucleus introduces additional minute features in the energy-level structure of an atom; these generally appear as further level-splittings or small energy shifts. The study of these effects in optical emission-line spectra has yielded a wealth of information about atomic nuclei, including their size, charge distribution and spinning behavior.

Let us turn now to the interaction of an isolated atom with an incident light wave. This interaction is particularly strong if the wavelength of the incident light is close to that of one of the atom's emission lines. In other words, strong interaction occurs when the incident light frequency is near or at the resonance frequency of a given pair of energy levels. When the atom is found in the lower level, it undergoes a transition to the upper level by absorbing energy from the incident light ray. The amount of absorbed energy is exactly the amount gained by the atom. The opposite happens when the atom is found in the upper level: the atom decays to the lower level by giving its energy change to the incident light wave. The latter process is an emission act induced by the applied field and drastically different from the spontaneous emission described above. In the induced emission the emitted light wave cannot be distinguished from the incident light. Spontaneous emission, however, is independent of an incident light ray and generally occurs isotropic-

ally—the emission probability is the same in any direction in space.

The induced emission probability, which is proportional to the intensity of the incident light, is exactly identical with the probability of the absorption process of an atom initially found in the lower level. An induced emission, however, must compete with the act of spontaneous emission, and at a low intensity spontaneous emission may predominate. Finally, the induced emission (or absorption) probability diminishes considerably if the frequency of the incident radiation is appreciably different from the resonance frequency of the atomic transition.

Induced emission by atoms in the upper level enhances the incident light, whereas absorption by atoms in the lower level attenuates it. Accordingly when the average number of atoms in the lower level exceeds that in the upper one, the absorbing transitions would prevail and a total attenuation of the light wave would result. The reverse process, called population inversion, occurs if the average number of atoms in the upper level is larger than the number in the lower—the incident light is then amplified as it passes through the medium. This kind of amplification, "light amplification by stimulated emission of radiation," is the underlying principle of the laser.

There exist a host of nonradiative processes that also cause transitions among atomic energy levels. These play an important role in determining the average number of atoms in each level and therefore establish the main absorption and emission characteristics of an ensemble of atoms. For instance, the impact of a free electron with an atom or the collision of two or more atoms can induce transitions among various atomic energy states without requiring either the emission or the absorption of a light wave. In such cases the quantized change in the internal energies of the atoms is determined by the kinetic energies of the collision partners.

For matter in thermal equilibrium the exact number of atoms in each level is uniquely determined by the temperature of the system. It is a general property of this thermal distribution that the average number of atoms in a lower level is always larger than that in an upper one. Because of this, matter in thermal equilibrium always attenuates an incident radiation at a frequency on or very near any atomic resonance frequency.

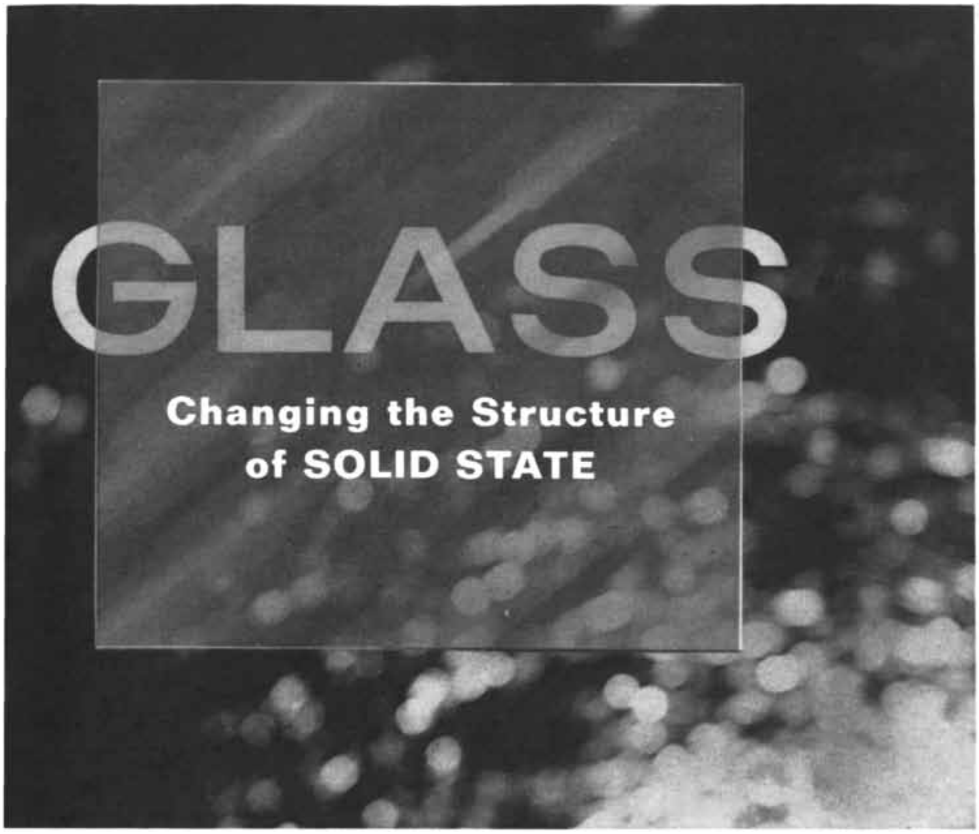
A broad class of systems exist that, though in a steady state, are not in thermal equilibrium and therefore cannot be described in terms of temperature. Most of the universe is composed of such nonthermal systems. In these cases the average number of atoms may be larger in a lower or an upper level, depending on their excitations and decays. These systems allow amplification of an incident radiation when an upper level is more populated than the lower one.

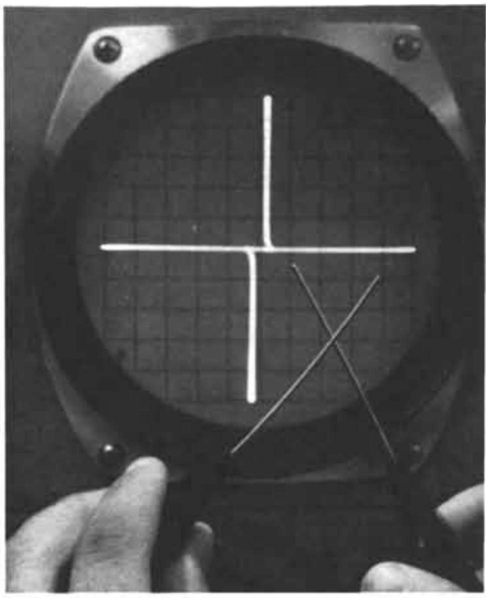
Consider an ordinary neon lamp, essentially a glass tube filled with neon gas at low pressure. An electric voltage applied across a pair of electrodes at opposite ends of the tube causes the ionization of a small fraction of the neon atoms. This results in a stream of free electrons—an electric current—passing through the tube. The electrons collide with neon atoms and excite them into higher energy levels. The spontaneous emission from the various excited levels is responsible for the color of the lamp.

In such an electrically excited gaseous discharge the atomic population distribution is completely nonthermal. Under the proper conditions it could allow population inversion among some level pairs and amplification of light waves at the corresponding resonance frequencies. It was an oversight in scientific history that this possibility passed unrecognized in the late 1920's, since by that time quantum mechanics had successfully formulated the principles of induced emission and absorption of light, and the excitation processes in electrically excited gas discharges were also fairly well explored. All the necessary theoretical and technical information for the achievement of light amplification in an electrically excited gas was close at hand. However, physicists of the time were so preoccupied with the emission and absorption line spectra and the characteristics of matter in thermal equilibrium that they missed this exciting possibility. Thus laser amplification, based on the principle of population inversion in a gas discharge, was achieved some 30 years late.

A medium capable of a sufficient light amplification becomes unstable if it is placed between a pair of parallel mirrors. The light wave, propagating at right angles to the mirrors, will be reflected back and forth and enormously amplified by the medium. This process can be initially triggered by the spontaneous emission of a light ray in the amplifying medium itself. Output coupling can be provided by allowing a small beam of light to be transmitted through the surface of a mirror. This system, commonly called the laser, generates an intense directional light with a minute frequency spread. Several general types of laser

> "It seems good for philosophers to move to fresh ways and systems; good for them to allow neither the voice of the detractor, nor the weight of ancient culture, nor the fullness of authority, to deter those who would declare their own views. In that way each age produces its own crop of new authors and new arts . . ."
>
> Fernel,
> 16th Century

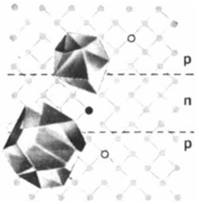




**Simplest Switch** ever made by man is an active thin film of OVONIC semiconductor material vacuum deposited between two wires. Oscilloscope trace shows inherently symmetrical E-I characteristic. Switching speed is less than 150 picoseconds.

# OVONIC

## BULK-EFFECT SEMICONDUCTORS*



YOU'VE SEEN drawings of crystal lattice structures like this before. Over the past 20 years they've become the classic way of illustrating the basic precepts of present-day solid state physics and semiconductor technology. In fact, the theories and materials represented are so widely known now that most scientists have come to assume that periodicity, controlled diffusion of impurity atoms in high purity crystals, and rectifying p-n junctions are the fundamental basis for semiconduction and solid state switching.

That may have been a fair assumption once. But it's not any more. For the past seven years, we at ECD have been "moving to new ways and systems" for solid state control of electricity. We've taken some common elements—mixed and melted them in a variety of compositions—and come up with a whole new family of semiconducting devices having many unique characteristics:

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Regarding electrical characteristics, OVONIC bulk-effect semiconductors are inherently symmetrical with respect to current flow. They respond identically to both polarities; switching speed is less than 150 picoseconds ($10^{-12}$ sec.); and conduction occurs as a carrier multiplication effect throughout the material. In addition, they can tolerate levels of X-ray and fast neutron radiation several orders of magnitude higher than p-n junction devices without transient or permanent effect on their performance.

**State of the art:** At the present time we're producing OVONIC Threshold Switches as discrete components for use in a wide range of applications. For example: They can perform all circuit functions in digital computers, generate and switch microwaves, control electroluminescent displays, amplify analog signals by pulse width modulation techniques. We're also developing mass arrays and large scale all film integrated circuits—plus unique non-volatile memory devices and sensor amplifiers.

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exist, each of them using a different method to prepare level pairs with inverted populations. Among the major types are gas-discharge lasers, chemical lasers, semiconducting-diode lasers and homogeneous optically pumped liquid and solid-state lasers. These devices, useful in many practical applications, have also provided a new tool for research into the nature of matter.

Consider now an atom in its lowest energy level interacting weakly with a light ray whose energy does not correspond to the separation of any upper level from the ground state. It is no longer appropriate to describe this interaction in terms of absorption and emission accompanying a real atomic transition, since the frequency of the light is appreciably different from the resonances of atomic transitions. Actually the atom serves to weakly scatter the incident light in all directions while essentially remaining in its unperturbed energy state. The incident radiation will force an atomic electron to oscillate at the frequency of the light wave itself; the electron, in turn, radiates the scattered light wave in all directions at its oscillating frequency. The intensity of the reemitted light is generally a function of the incident light frequency and the proximity of this frequency to various atomic resonances.

When a collection of atoms is subjected to such an incident light wave, the atoms' reemitted waves interfere with one another. The propagation pattern of the resultant sum of the reradiated light waves depends on the density and spatial distribution of the scattering atoms. This effect is responsible for the index of refraction of a transparent material, giving rise to the reflection and refraction of light. The reflection of an incident light by a transparent solid with a uniform density comes from the superposition of reemitted light waves by atoms at the surface boundary of the medium. The refracted light ray results from this superposition of reemitted light by atoms in the bulk of the solid.

In metals the reradiation at the boundary interface is so strong that most of the incident radiation is reflected over a wide range of the spectrum. This phenomenon differs, however, from the partial reflection of light at the boundary of a transparent dielectric crystal. The conduction electrons in metal behave collectively as a highly dense plasma, and cause total reflection of long-wavelength incident light; at shorter wavelengths there is partial transmission. Gold, for example, reflects red and yellow light strongly but allows some penetration by green rays, which are then completely absorbed within a small thickness of the bulk of the metal. Silver, on the other hand, reflects strongly over most of the visible spectrum but allows considerable transmission in the ultraviolet [*see bottom illustration on page 244*].

There are in addition a number of light-scattering processes in which an incident ray at one frequency is absorbed by an atom and then reemitted at an entirely different frequency. When the absorption and reemission occur simultaneously as part of a single transition, the phenomenon is called the Raman effect. Here the difference in frequency between the two light waves must exactly equal a resonance frequency between a pair of atomic levels; the individual light frequencies, however, are not required to be near any of the atomic resonances. Raman scattering, which can take place in gases, liquids or solids, is usually weak unless the intensity of the incident light is very high.

Light absorption at one frequency and light emission at another frequency can also take place in two separate steps. An incident ray at the resonance frequency of a pair of levels is first absorbed in the usual way, causing an atomic transition from a lower level to an upper one. After a certain delay the atom spontaneously undergoes a transition involving a third level, emitting a light ray at the appropriate frequency. In some cases the delay may be as short as a microsecond or less, in which case the phenomenon is called fluorescence. In other cases the delay can be for seconds or even days, allowing the emitted light to be observed after the incident light is turned off; this phenomenon is called phosphorescence.

The absorption and emission characteristics of matter outlined in this article of course extend far beyond the visible region of the electromagnetic spectrum. On the long-wavelength side there are the infrared, far-infrared, microwave and radio-wave regions, and on the short-wavelength side the ultraviolet, X-ray and gamma-ray regions. The optical properties of materials in all these regions are similar to those in the visible region in their basic relation to the quantum-mechanical interactions of electrons, but they are vastly different in detail. In these ranges spectroscopy requires a diversity of experimental techniques, ranging from Newton's prism to radio-wave and gamma-ray spectrometers.

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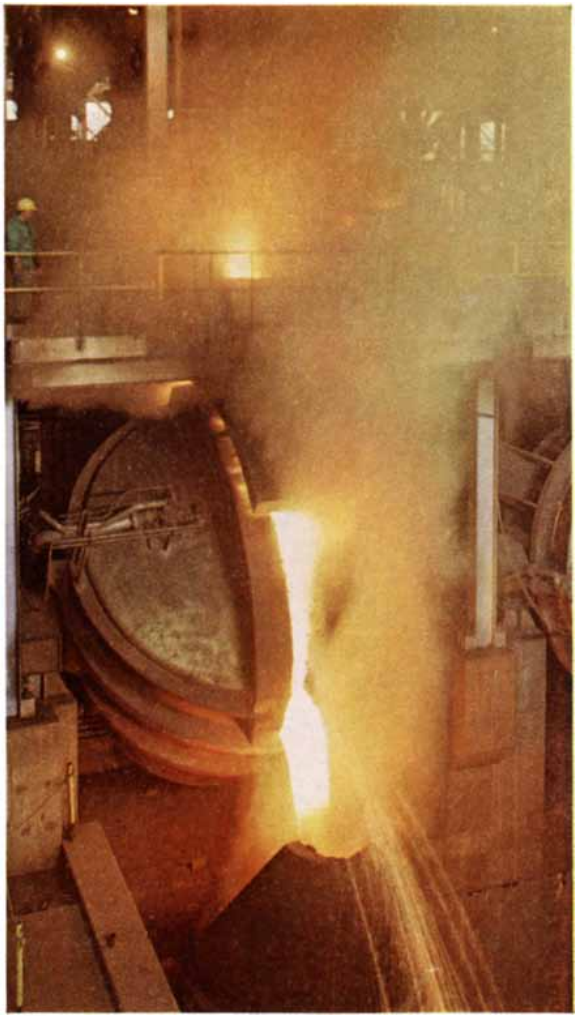
# Allegheny Ludlum is the story of fire and imagination



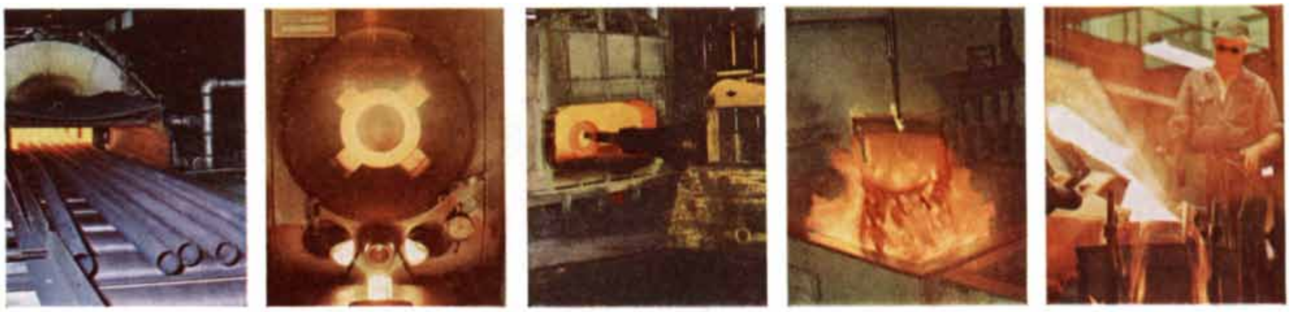
## *Out of this combination has come a remarkable assault on the limits of metals technology.*

Since its inception, decades ago, Allegheny Ludlum has explored and exploited the endless phenomena which result when metals and heat are brought together. It has concentrated on the "special metallurgy" of high alloys involving chrome and nickel—on developing and perfecting metallurgical combinations and processing techniques which hold greatest promise of technological progress.

Out of this infinitely variable yet single-minded concentration has come an exceptional series of crucial developments. Forty years ago, or more, came A-L valve steels which made internal combustion engines truly practical. A-L's other contributions to the technology of stainless steels and high-temperature alloys are immeasurable. The latest are several special machining grades, two low-cost grades (MF-1 for mufflers and AM 363 for certain structural applications) and Almar 362, the first mar-aging stainless steel, offering very high strength and corrosion resistance without sacrificing formability.

Similarly, A-L has made significant contributions in silicon electrical steels, especially in grain-oriented variations, and in a great many magnetic materials. A-L is also a major producer of tool steels; deep experience with the machining characteristics of its other products leads logically to the continuous development of optimum techniques and materials for the forming of special alloys.

Out of this cohesive experience, too, have come other, related achievements: consumable electrode and vacuum melting techniques which have become standard; advancements in the art of extruding, casting and forging alloy steels; impressive accomplishments in dimensional control, in surface finishes, in heat treating, in cladding and bonding dissimilar metals. And the process still goes on. Continuing, intensive research, on a very large scale, uncovers new problems and promises which fire the imagination.



## *As time has passed and experience has grown, A-L has extended its own capability in several important directions.*

A-L's metal-producing subsidiaries comprise independent operations, yet the products of each bear a close relationship to those of A-L itself. The subsidiaries provide, in a sense, an extension of capabilities deeper and farther into certain specialized fields. A continuing interchange of knowledge and experience gives customers the benefit of synergy at work.

**Wallingford Steel Company** produces welded pipe, tubing and strip, frequently down to .001-inches, in stainless, electrical and specialty steels. Early and continuing development of precision rolling and gaging equipment assures exacting gage control in the firm's many strip products.

**Special Metals Corporation** pioneered vacuum induction melting on an industrial scale in the United States. It is now the world's largest producer of vacuum induction melted alloys, specializing in ultraclean nickel base alloys for such critical applications as gas turbine parts. The company developed such grades as Udimet 500, Udimet 520 and Udimet 700.

**The Arnold Engineering Company** specializes in magnetic materials, such as Alnico and hard ferrite permanent magnets, Silectron and tape-wound cores, powder cores and transformer laminations. Recent developments include soft ferrite cores for radio and TV applications, hard ferrite motor magnets and the chemical milling of ultra-thin nickel alloy materials of which Arnold is an important producer.

**Carmet Company**, a wholly integrated producer of cemented carbide products for metal-cutting, metal-forming, mining and wear-resistant parts, was the developer of special 700-series grades for machining steel, a significant advance. Carmet also pioneered close-tolerance preforming of tungsten carbide blanks and made continuous mining practical through the introduction of carbide-tipped cutters and bits.

**International Powder Metallurgy Corporation** brings to A-L an outstanding capability in its specialized field. With equipment which includes a 1,000-ton multi-motion automatic hydraulic press, IPM can produce powder metal parts weighing up to 50 pounds. IPM extends A-L's overall capability in a unique way, especially in developing combinations of metals which cannot be achieved through liquid-state metallurgy.

**Ajax Forging and Casting Company**, recently organized as a subsidiary through the combination of Ajax Steel & Forge Company, Extrusion Machine Company and A-L's Forging and Casting Division, provides a ready-made platform for new advancements in the forging, casting and forming of special steels.

**True Temper Corporation** is A-L's newest subsidiary, the first to be concerned primarily with consumer products rather than metals production. True Temper is a very successful producer of hand tools and implements for garden, lawn, agricultural, construction and household uses, golf club shafts and heads, and rail anchors. It also makes fishing tackle and will soon introduce skis and ski poles.

Between them, Allegheny Ludlum and its subsidiaries offer an impressive history of experience with the potentialities of fire and imagination. Allegheny Ludlum Steel Corporation, Oliver Building, Pittsburgh, Pa. 15222. 5260

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# The Competition of Materials

*Now that the properties of all materials are better understood, it is clear that quite different materials can be used for the same purpose. This calls for subtle choices involving both technology and economics*

by W. O. Alexander

The engineer necessarily takes a greater interest in the properties than in the composition of the materials he chooses to meet the requirements of his design. Nowadays he is likely to find at least two and in some cases three or four radically different kinds of material ready to serve in each end use. In such industries as aerospace and electronics, where cost has not been a ruling consideration, designers have produced numerous dramatic demonstrations of the interchangeability of materials that is a recurrent theme of the preceding articles in this issue of *Scientific American.* This trend in technology has gained economic significance in western Europe and the U.S. over the past decade as producers in one primary materials industry after another have developed capacity in excess of the demand for their product. Now producers as well as users are promoting the competition of metals, ceramics, glasses, plastics, rubbers, concrete and timber, each defending its traditional markets as it seeks entry into the markets of others.

Here is a set of new and knotty questions for the business economist. The plotting of supply-demand curves for a given commodity no longer suffices to explain or predict its movement. Simple comparison of the cost per pound of steel, aluminum and plastics tells little about their true relative competitive positions. Economics must reckon at closer range with technology in order to estimate the viability of one material against other materials. The detailed investigations necessary to establish the ruling criteria of the many-cornered rivalries of materials technology remain to be made. The preliminary considerations presented in this article suggest, however, that a useful index of the competitiveness of a material is its cost per unit of property required.

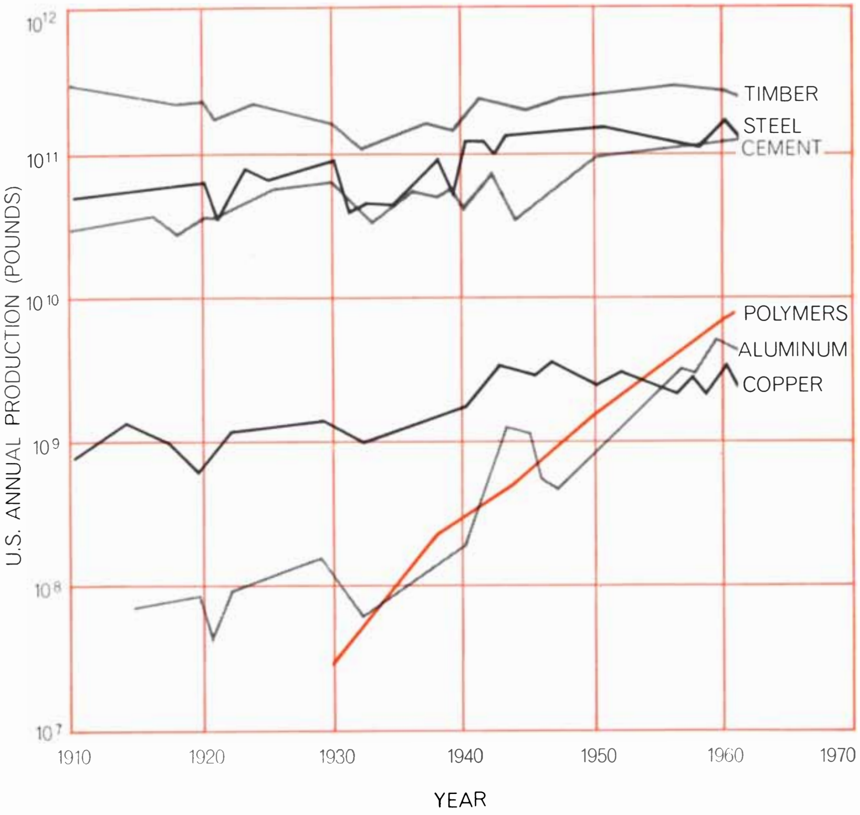
Cost in this formulation is the cost of the material in the job. To the cost of the material at the mill, plant or warehouse is added the cost of fabrication and incorporation in the final product. As for properties, those that determine the usage of the vast bulk of materials can be listed as strength and rigidity, space-filling and the quality and durability of the surface. The last requirement may be met by a number of accessory materials or treatments, so that it is not usually a critical element in the choice of the primary material. The space-filling requirement can be met in many applications by leaving the member hollow, so that this is not critical either, unless great rigidity is required. Strength remains as the property most sought. The index of competitiveness may therefore be expressed as cost per unit of strength.

There are, of course, applications where high electrical conductivity or extreme rigidity or high corrosion resistance may be of transcendent importance. Such requirements, however, dominate the selection of only a minor portion of all the materials that are used commercially. The principal exception is copper, for which high conductivity dictates more than half the usage.

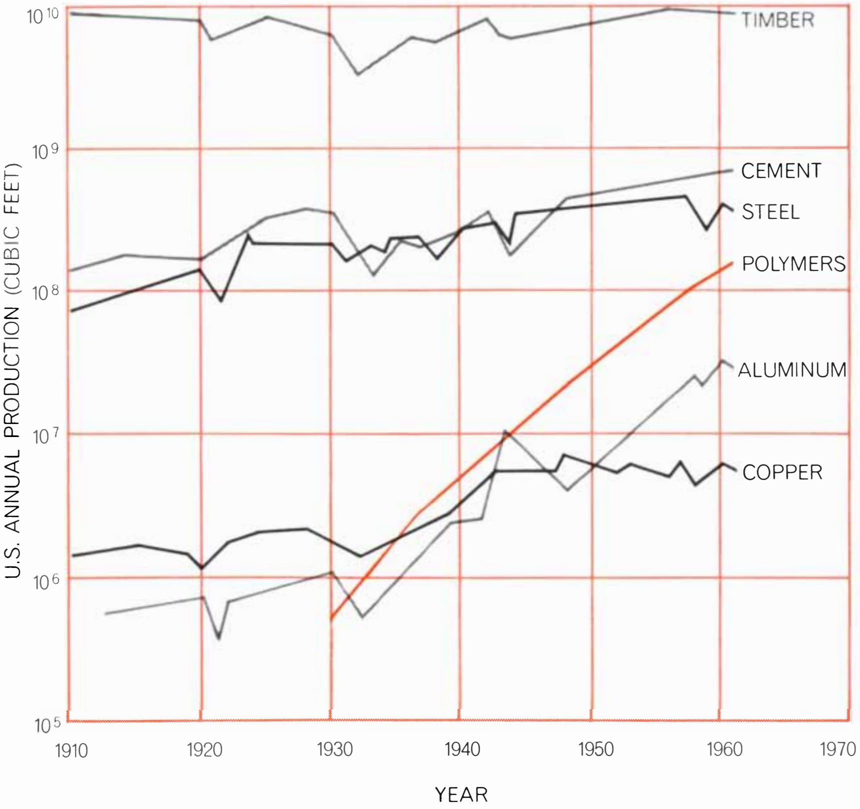
The national accounts of the industrial countries customarily reckon the costs of materials at three stages on their way to market. The first stage is extraction: the cost of ores at the mine (which may include a charge for beneficiation) or the cost of timber at the forest (which in the future must include the cost of afforestation). The second stage is at the conversion of the raw material into purified or concentrated form, for example a metal in the pig or ingot. Finally there is the cost at which, in the case of metals, the plate, sheet or shape is delivered to the manufacturer of the end product. At each stage cost is incurred for the energy involved in the conversion or processing, for labor and for selling, administration and other costs, all of which go to build up the final price.

In the production of metals some credit can be taken for the reprocessing of scrap, offset in part by the loss in value of worked metal that must be scrapped and recycled in the mill. The production of plastics begins at the oil or gas well. To the fabricator a plastic is usually delivered in the monomer state, to be polymerized in the same operation that yields the end product. Plastics typically yield a low order of scrap, usable only in such secondary products as toys, that is a burden to the solid-waste disposal system. The felling of timber and dressing of lumber produce waste in vast quantities, useful for by-products such as chipboard and fiberboard but so cheap that its utilization is usually a question of transportation costs. Cement and concrete involve the simplest production cycle: the calcining of limestone rich in silica, alumina and iron oxide, and grinding the sinter with a small amount of

**OPEN-PIT COPPER MINE of the Kennecott Copper Corporation in Bingham Canyon, Utah, appears in the vertical aerial photograph on the opposite page. The largest producer of copper ore in the world, it symbolizes a typical modern instance of the competition of materials. Copper has traditionally been the leading material for the conduction of electricity. It still is, but for long-distance power-transmission lines, in which lower cost and lighter weight offer special advantages, it is giving way to aluminum. The concentric rings that appear in the photograph are the terraces of the mine, which are excavated by power shovels.**



**COMPETITION OF SIX MAJOR MATERIALS** in U.S. is reflected in curves of poundage that are based on similar ones plotted by C. G. Suits of the General Electric Company.



**RELATION OF CURVES IS CHANGED** by using cubic feet instead of pounds, correcting for lighter weight of newer materials. On this basis polymers begin to approach steel.

gypsum. This is followed by mixing the cement with aggregate and sand, usually on the site, and pouring the slurry into molds that contain the steel reinforcing bars. Concrete has little or no value at the end of service.

In the past a producer of one of these commodities could gauge his efficiency merely by keeping his eye on other producers of the same commodity. Now he must operate against the unfamiliar economics of entirely different kinds of materials. It is important for the steel producer, with costs at the ingot or raw steel running at $85 per ton, to know that the pig cost of the aluminum producers is around $500 per ton. Any substantial reduction in the cost of aluminum pig is bound to make this metal a more formidable competitor to steel. The costs at the purified metal stage reflect the large differences in the geology and chemistry of the various metals and the corresponding differences in the costs of mining and smelting them. Costs thereafter tend to converge because the operations involved—rolling, forging, casting and so on—are more or less the same for all. Over the past 25 years, as producers of aluminum, magnesium, beryllium, titanium and the other new or relatively new metals have perfected their primary and secondary technologies, costs of purified metals have been the determining factor in the development of markets for these metals.

The general price trend for most materials has been upward. In the U.S. the slope is about the same as that of the economic inflation. In western Europe metal prices have risen somewhat more slowly since the end of World War II, reflecting efficiencies gained in new plant. The marked exception to the rule on both sides of the Atlantic has been the prices of the major plastics; these are still decreasing, and plastics are therefore becoming correspondingly more competitive.

Statistics for output divide the principal materials into two classes. In the U.S. the older materials show a rather slow increase [*see top illustration at left*]. Aluminum and the plastics, in contrast, rise steeply from low levels of output, increasing at 10 percent and 10 to 15 percent per annum respectively. The same trends, trailing the U.S. by two to five years, appear in the western Europe statistics. At about five million tons in 1962, the U.S. plastics output might seem negligible compared with that of steel, at about 100 million tons. An important property of plastics, however, is their low density. The cubic-foot curve

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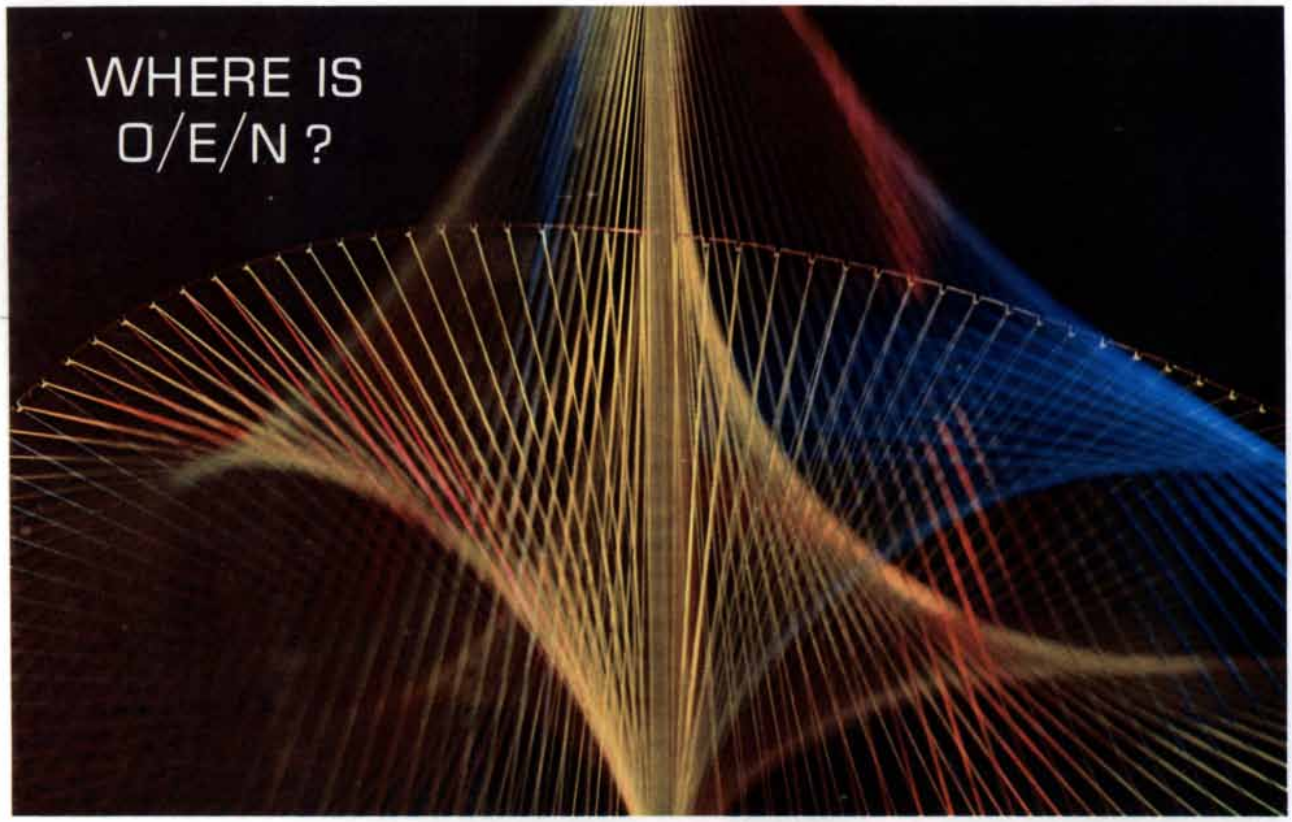
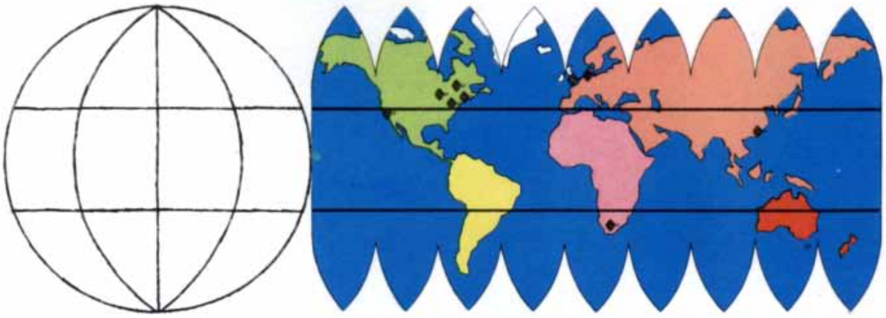


# WORLDWIDE



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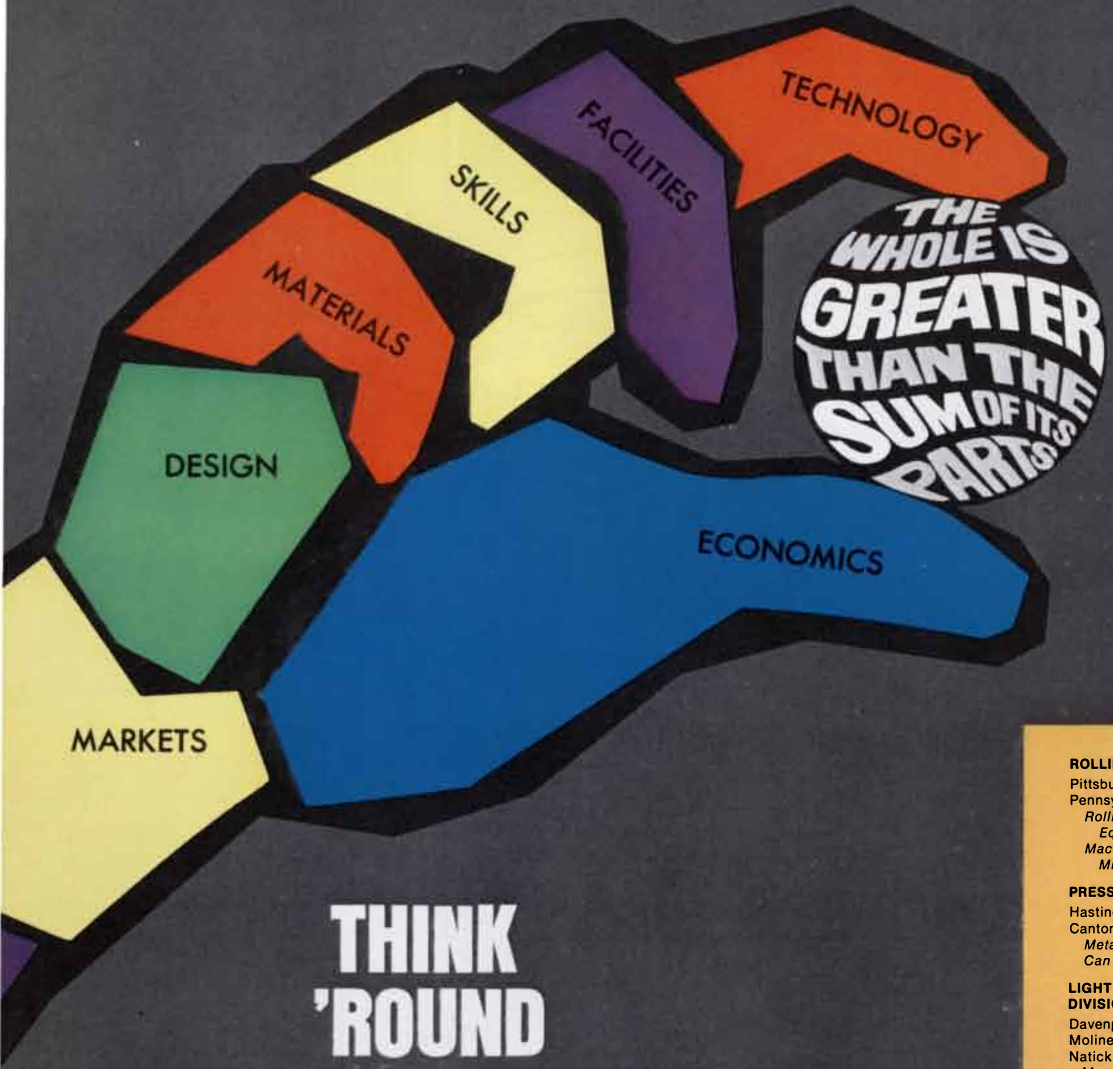

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plotted by C. G. Suits of the General Electric Company, shows the plastics beginning to bulk at the same order of magnitude as steel in the U.S. economy [*see bottom illustration on page 256*]. Even bigger than steel, and by a huge margin, is concrete. The tonnage for any year can be derived by multiplying the cement output by six; for volume, the multiplier is eight.

The retardation in the continued growth of output curves for the older metals undoubtedly reflects the competitive inroads made by aluminum and the plastics. It also reflects increasing efficiency in the engineering of metals and in some cases a disproportionately lower use of them in major applications. For the generation of electric power, which is increasing 8 to 10 percent per annum, the use of copper in generators has been reduced from 200 pounds per megawatt to 56 pounds per megawatt during the past decade. The increase in speed and payload from the Boeing Stratocruiser to the Boeing 707 has reduced the use of metal from 7.7 to three pounds per passenger mile [*see illustration on page 266*]. To a less spectacular degree, increase in the efficiency of design has reduced the metals requirements of the automobile industry and the heavy construction industry, particularly in factory buildings and bridges.

A summary economic expression of these developments in technology is provided by the technique of input-output analysis developed by Wassily Leontief of Harvard University. Putting the input-output tables of the U.S. economy for the years 1947 and 1958 to the task of producing (in the computer) the same 1958 gross national product, Leontief's colleague Anne P. Carter found a net reduction of 10 percent in the materials inputs required by the 1958 technological order. The metals showed the biggest losses in usage, with a 27 percent drop in the requirement for steel [see "The Economics of Technological Change," by Anne P. Carter; SCIENTIFIC AMERICAN, April, 1966].

It appears, therefore, that the industrial nations have arrived at a significant turning point; their per capita consumption of metals has reached a peak and is now on the decline. Before one applies this finding to a projection of the future growth of the metals industries in the world as a whole, however, it is well to consider one or two contingencies. The per capita consumption of metals for two-thirds of the world population has yet to approach that of western Europe, America and Japan. Should money and technical staff be redeployed to increase the rate of development of the poor nations, the present spare capacity in the industrial nations would be quickly overfilled. One has only to think of the 760 million people in China, who consume 90 pounds of steel each year compared with the half-ton consumed per capita in the U.S., to appreciate that a mere trebling of the rate of consumption in China would soak up most of the world's unused steel-producing capacity. If the people of India and China were to open one can per week, that would be some 60 billion cans, or about

| | TENSILE STRENGTH (TONS PER SQUARE INCH) | DENSITY (GRAMS PER CUBIC CENTIMETER) | COST (£ PER TON) | COST (PENCE PER CUBIC INCH) | COST (PENCE PER TON PER UNIT OF STRENGTH PER SQUARE INCH) |
|---|---|---|---|---|---|
| **CAST IRON** | | | | | |
| GRAY | 10–14 | 7.3 | 70 – 120 | 1.98–3.39 | .20–.24 |
| HIGH DUTY | 14–24 | 7.3 | 90–150 | 2.54–4.25 | 28–.29 |
| **WROUGHT STEEL** | | | | | |
| STRUCTURAL | 37–43 | 7.8 | 80–100 | 2.4–3 | .065–.07 |
| SHEET | 25 | 7.8 | 40–58 | 1.3–1.75 | .05–.07 |
| STAMPINGS AND FORGINGS | 35–45 | 7.8 | 140–200 | 4.22–6 | .12–.13 |
| WELDMENTS | 25 | 7.8 | 260–800 | 7.6–23.5 | .29–.95 |
| **ALUMINUM CASTINGS** | | | | | |
| SAND CASTINGS | 9–11 | 2.7 | 300–480 | 3.12–5.02 | .35–.45 |
| LM 24 ALLOY DIE CASTINGS | 16 | 2.7 | 270–320 | 2.82–3.34 | 18–.21 |
| **WROUGHT ALUMINUM** | | | | | |
| EXTRUDED | 12–18 | 2.7 | 355–390 | 3.7–4.1 | .23–.31 |
| SHEET | 13–19 | 2.7 | 260–600 | 2.7–6.3 | .2–.3 |
| WELDMENTS | 17 | 2.7 | 800–1,200 | 8.3–12.5 | .49–.73 |
| **POLYETHYLENE (MOLDED)** | 1 | 0.9 | 260 | .9 | .9 |
| **POLYVINYL CHLORIDE (PIPE)** | 4 | 1.4 | 200 | 1.08 | .25 |
| **RESIN-GLASS LAMINATES** | | | | | |
| WITH GLASS MAT | 10–12 | 1.4 | 360 | 1.9 | .16–.2 |
| WITH GLASS WEAVE (MOLDED) | 25–70 | 1.87 | 3,000 | 21 | .3–1 |
| EPOXY AND GLASS WEAVE (MOLDED) | 32 | 1.87 | 4,000 | 29 | .91 |

**COSTS OF MATERIALS IN BRITAIN, which do not differ greatly from those in the U.S., are given in these figures assembled by the author. Here an adjustment is made not only for weight ("*Cost per cubic inch*") but also for strength (*column at right*). Accordingly whereas some of the newer materials cost far more per ton than the older ones, their cost per unit of strength is much less out of line.**

| | STEEL | ALUMINUM | COPPER |
|---|---|---|---|
| ORE | | | |
| RAW | 9.39 | 7.15 | |
| BENEFICIATED | 12.46 | 58.00 | |
| PIG IRON | 56.07 | | |
| RAW METAL (INGOT, BILLET OR BAR) | 85.00 | 500.00 | 748 00 |
| SHEET | 131.34 | 810.00 | 1,410.00 |
| STRUCTURAL | 129.36 | 760.00 | 1,415.00 |
| WIRE | 213.56 | 640.00 | 1,030.00 |

**SAMPLE PRICES FOR THREE METALS in the U.S. (in dollars per ton) show the wide variation in the costs of converting the ores of different metals into raw metal and finished products. The prices of copper ores are not given because such ores are not available on the market; they are mined by the companies that make the raw metal and the finished products. The figures were assembled by Jack R. Miller of the Battelle Memorial Institute.**

two million tons of steel strip, a year.

For the present, excess capacity in the metals industries sharpens the competitive struggle. One significant conflict engages modes of fabrication rather than kinds of metals. In the metal trades it has been axiomatic that the properties and dimensions of metals in the wrought form are universally superior to those of metals in castings. Inaccuracy and uncertain reproducibility in the making of the molds and poor surface appearance and low mechanical properties in the castings have nullified the economies inherent in moving directly from the molten metal to the finished product. In recent years, however, technology has been moving faster in the foundry than in the metal-stamping and forging shops. Such techniques as vacuum-pressure die-casting and the automatizing of investment casting have been reducing costs and improving the product. Whereas wrought steel continues to come in at lowest cost, casting brings in products made of nonferrous metals at a lower cost than products made of these metals in the wrought condition. In the United Kingdom the cost-per-unit-strength criterion finds wrought steel at .05 to .13 pence per ton of tensile strength per inch compared with aluminum castings at .18 to .45 pence and wrought aluminum at .20 to .31 pence [*see illustration on preceding page*].

Engineers and metallurgists in the wrought-metal field have missed significant opportunities for progress as a result of their predilection to go automatically for larger and larger initial ingots to feed bigger and bigger breakdown mills, presses and forges. An elementary analysis of the cost of working metal by rolling shows that a great amount of energy is required to break the ingot down to slab or billet and then roll it to finished dimensions. Energy costs are bound to become dominant with continued increase in the price of energy and rising production per man-hour. Already energy accounts for about a third of the total cost of converting raw metal to finished intermediate products, with direct labor and overhead each accounting for a third. Although gigantism secures some marginal economies, it can be justified in the future only in the rolling of wide plate and sheet and in the forging of heavy single pieces. The alternative approach, just gathering momentum, is continuous casting. For small cross sections of steel and aluminum, continuous casting has already demonstrated its feasibility and economy. In addition to reducing energy charges, the technique involves smaller plant costs and greater freedom in plant location, and its high speed makes it possible to keep inventories to a minimum.

The heavy construction industry presents an arena in which steel is pitted against concrete. At present the situation in this tug-of-war varies from country to country. It appears to depend less on the objective qualities of the two materials than on the ingenuity and prestige of the architects and engineers committed to the one material or the other and on the

# Probing the puzzles of polyethylene

Western Electric has been tracking solutions to problems of processing plastic for some years now. Our experiments have required thousands of pounds of polyethylene, a computer, and what is probably the world's most highly instrumented plastics extruder. But all of this showed us better ways to insulate and jacket telephone cables for the Bell System.

What's more, from all the data we collected, our engineers gained basic knowledge about what happens to plastic inside the extruder. They started with a mathematical model assembled from various published theories. As the experiment progressed, they improved the model and developed new theories (see SPE Journal Vol. 21, Nos. 10, 11, and 12).

The information gained aids us in predicting the effects of three operating and four machine design variables. Now we can design extrusion screws that will produce high-quality coatings more economically.

Western Electric is one of industry's largest users of polyethylene. Most of it is used to protect telephone circuits from shorts and corrosion. With our improved extrusion processes we help the Bell System continue to give you the world's most reliable telephone service at low cost.

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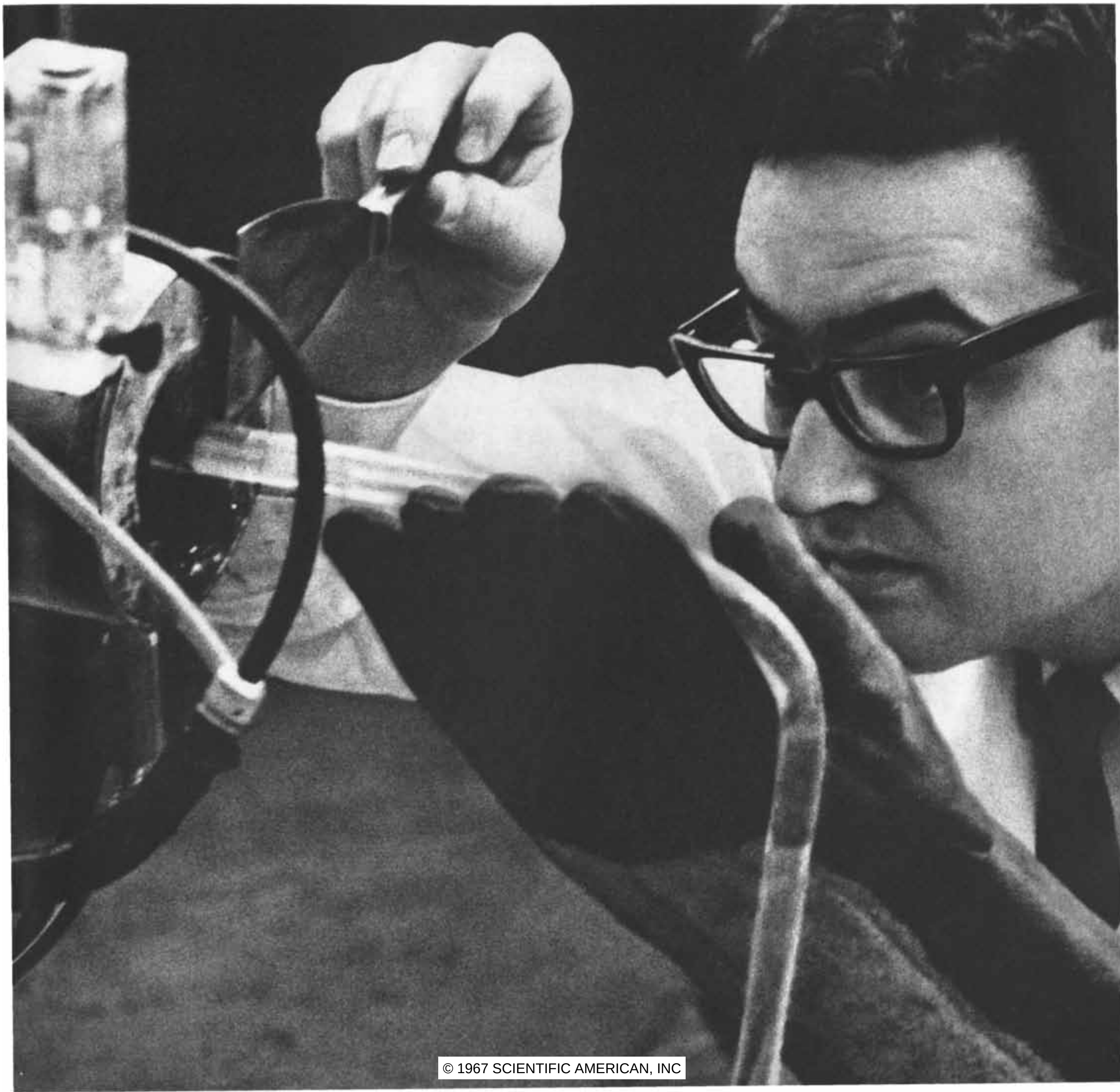

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competitiveness and marketing flair of the producers in the two industries. Judging by North America, it would seem that steel has won in vertical structures whereas concrete has taken over horizontal structures, except for the very biggest bridges. In the United Kingdom the competitive position of steel is compromised by building codes that recognize only 45 percent of the 100 percent improvement in the strength of structural steel achieved since 1877. Regulations require, in addition, heavy fireproofing of steel structural members, a measure usually secured by cladding the member in concrete with a consequent considerable increase in the dead load of the structure. Americans minimize this requirement by insisting on a low fire rating for the entire contents of the building.

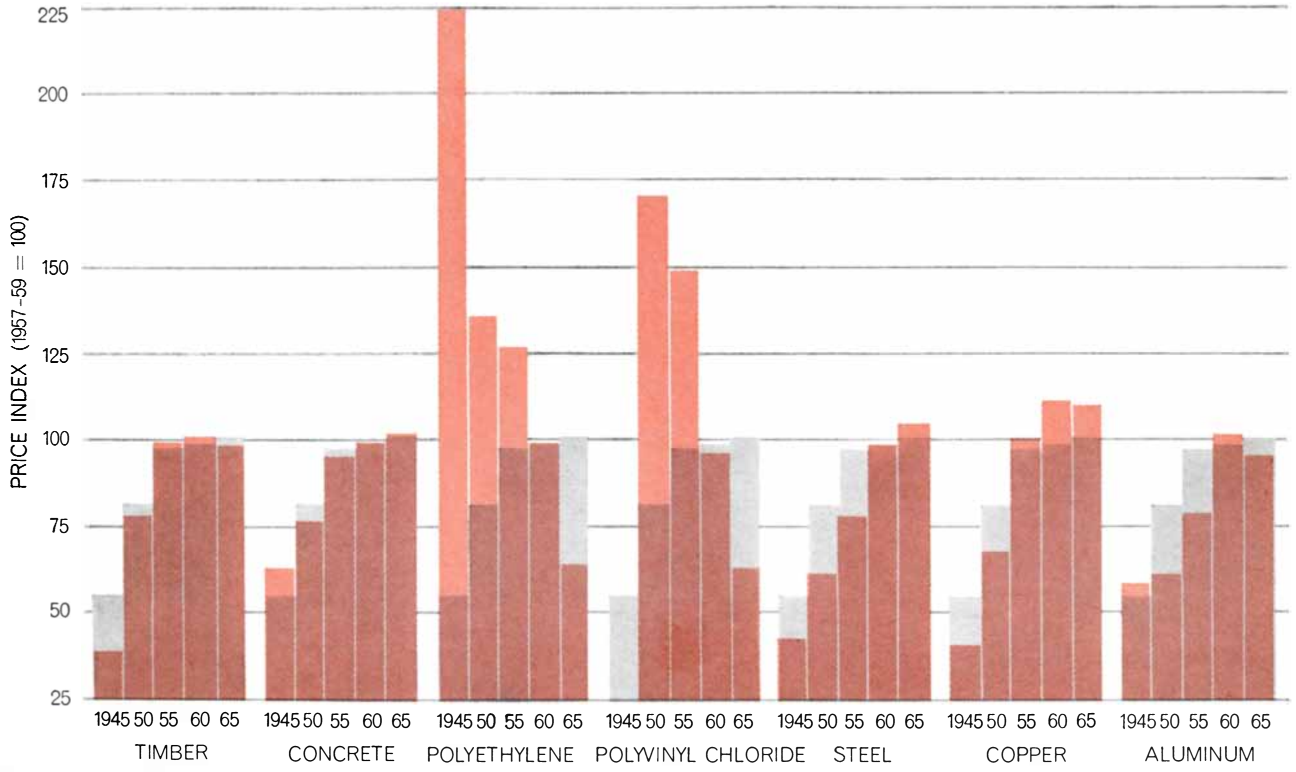
On the other hand, the proponents of steel in both Britain and America must contend with a 600 percent improvement in the performance of reinforced concrete achieved in recent years. On the cost-per-unit-strength basis structural steel appears evenly matched with reinforced concrete. It is no wonder that relatively small multistory buildings can be built of concrete at costs 25 to 35 percent below that of steel.

On its lighter flank, steel has been losing other markets to aluminum. Although the output of aluminum in the U.S. economy comes to only 5 percent of the tonnage of steel, it should be noted that this amounts to 15 percent by volume. Moreover, 50 percent of the aluminum goes into identified steel markets. Aluminum made an easy entry into many of these markets during the war and in the immediate postwar years, when steel was in short supply. But aluminum has continued its encroachment and competition has sharpened, particularly in the U.S., as both industries have gone out to sell excess capacity. On the basis of cost per unit strength, experience in the United Kingdom places steel well ahead of aluminum, at .05 to .13 pence compared with .20 to .31 pence per ton of tensile strength per inch. Secondary criteria, such as lightness, rigidity and better corrosion resistance, must therefore enter into economic design considerations to qualify the rule of the primary criterion.

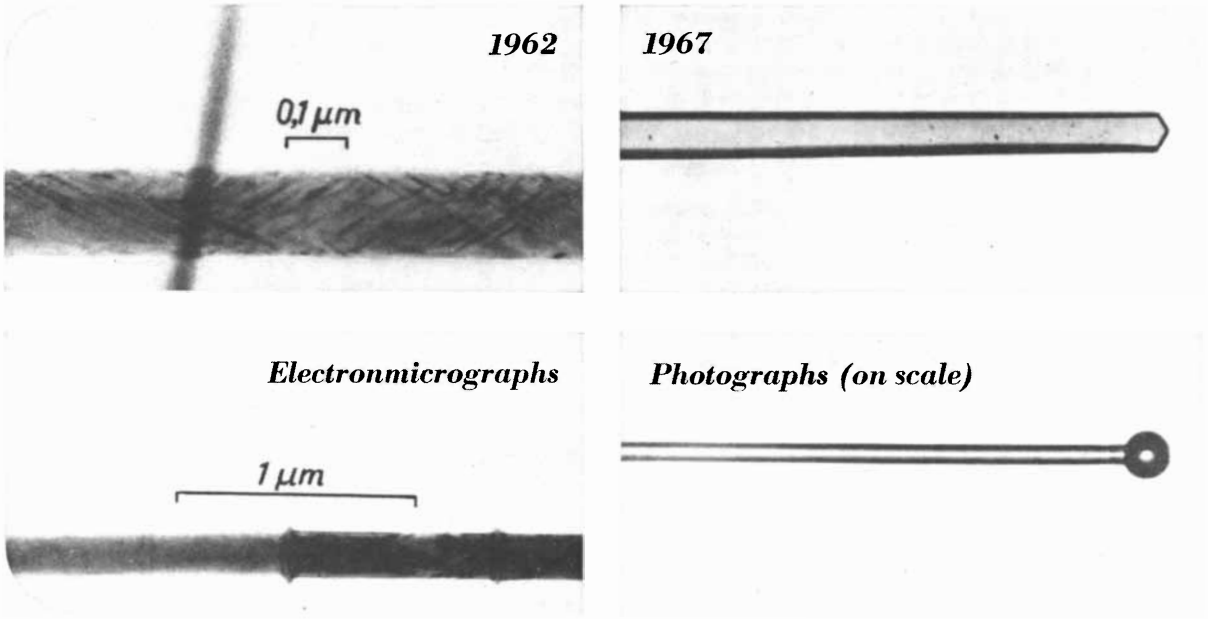
In the U.S. the competition of aluminum has induced major steel producers to establish research and product-engineering laboratories that they never seemed to require for competition with one another. Toward recovery of the substantial portion of the container industry lost to the light weight, easy formability and corrosion resistance of aluminum, they have reduced by two-thirds the thickness of strip rolled for cans and are looking for ways to eliminate the expensive tin and tinning process. In the construction industry, steelmakers turned back a challenge from aluminum alloys for short-span highway bridges, but they had to share this victory with reinforced concrete. Conversely, it appears that steel has lost the skyscraper curtain-wall market. Here the properties desired are lightness, appearance and constancy of surface. Aluminum, anodized to various colors and finishes, has proved more desirable than even stainless steel and much less expensive.

In the shipyards of the United Kingdom, on all new passenger ships and on the vast majority of cargo vessels, the use of aluminum alloys is reducing the weight of top hamper—deckhouses, lifeboats and the like—and hence the weight of metal per ton mile of cargo moved. This use of aluminum also brings improvement in the stability of the ship.

Aluminum has grown at the expense of another traditional metal: copper. The latter has now been displaced from long-distance electrical transmission lines. What aluminum lacks in conductivity it makes up in cheapness and lightness. Use of the metal as a specially shaped rod, rather than in a twisted wire



**MATERIALS PRICES** (*color*) **are compared with all prices** (*gray*) **in this chart based on U.S. experience from 1945 to 1965. In general the prices of older materials such as concrete and steel have kept pace with the rise of all prices. The prices of newer materials such as polyethylene and polyvinyl chloride have shown a decline not only with respect to all prices but also in absolute terms.**



# *SiC - a promise and a problem*

Though many materials have been hailed for their ”great potential value”, few have retained - or are likely to retain - this tag for as long as silicon carbide.

With a hardness which is second only to that of diamond in the Mohs' scale it didn't require much brainstorming to come up with the idea of using silicon carbide as an abrasive. In fact this application has been around since 1890, when Acheson found a method (still in use in an essentially unaltered form) for producing silicon carbide in a grade suitable for cutting and grinding.

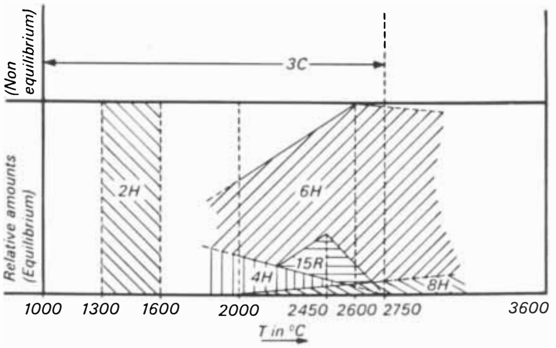
But silicon carbide promises more. As a semiconductor it has unique properties which make it particularly suitable for high temperature diodes and transistors, and also for opto-electronic devices. However, there are problems of producing silicon carbide in the right form for these applications.

One must realise that silicon carbide is a bit of a *prima donna*, with strong whims and fancies about the crystalline form in which it chooses to appear and with marked preferences for the way it wants to incorporate foreign substances. A great deal of longwinded research and technological experiments have been undertaken to make it pure and doped exactly as required, and to unravel the intricacies of its crystalline structure. Though the underlying principles are now understood and over 50 polytypes have already been discovered, the preference of silicon carbide for the 6H(33) structure still remains a mystery (see graph).

Pure single crystals of various structures can now be made with definite band gaps and charge carrier mobilities. With the right dopings we are able to produce light-emitting diodes which together cover the whole spectrum. But the full potentialities in these fields have yet to be realised.

Elsewhere, however, we are really getting to grips with the stuff. Since silicon carbide is a material which has great strength even at high temperatures, dislocation-free, hair-like single crystals (whiskers) should be ideal for reinforcing high temperature materials. In 1962, we were making these whiskers in the micron range; now we can grow them *en masse* in lengths of up to 10 cm or more, in a variety of cross-sections - triangular, hexagonal, circular and in ribbons.

So we've made this *prima donna* of a substance give us a chance to fulfill yet another of its many promises. In spite of its quirks, we are continuing our courtship in an attempt to woo out its promising properties, particularly in the semiconductor field.



***The Philips Research Laboratories carry out research in many fields of fundamental science. Among these: Acoustics, Chemistry, Cryogenics, Perception, Plasma, Material testing, Nuclear physics, Solid state physics, Telecommunications, Television.***

***The laboratories are an integral adjunct to the International Concern whose simple slogan is:***

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PHILIPS

| YEAR | TYPE OF AIRCRAFT | BASIC DATA | POUNDS PER HOUR PER PASSENGER MILE |
|---|---|---|---|
| 1930 | HANDLEY PAGE 42 | 29,400 LB.<br>95 M P H<br>39 PASSENGERS | 8 |
| 1940 | EMPIRE FLYING BOAT | 48,000 LB<br>145 M P H.<br>30 PASSENGERS | 11 |
| 1950 | BOEING STRATOCRUISER | 146,000 LB.<br>315 M P H<br>60 PASSENGERS | 7.7 |
| 1960 | BOEING 707 | 312,000 LB.<br>600 M P H<br>173 PASSENGERS | 3 |
| 1963 | SUPER VC10 | 322,000 LB.<br>625 M P.H.<br>180 PASSENGERS | 2.8 |
| 1970 | CONCORDE | 292,000 LB<br>1,450 M P H<br>160 PASSENGERS | 1.1 |

**SHIFT IN THE MATERIALS REQUIREMENT** of a given technology is revealed in figures assembled by author, showing decrease in pounds of metal used per passenger mile flown.

cable, produces a conductor with much greater efficiency on the criteria of cost and weight per kilowatt of power transmitted. Aluminum holds its advantage down to 11 kilowatts and even lower, leaving copper to be used in central-station and substation gear.

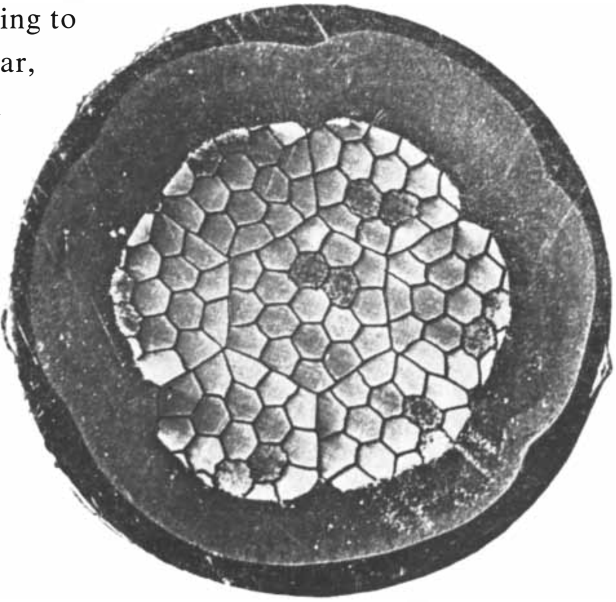
In every one of their markets the metals producers encounter competition from plastics. What makes this competition difficult is that no catalogue of the costs and properties of the various plastics indicates very clearly what their advantages are. On the basis of cost per unit strength, the most competitive of these materials—polyvinyl chloride and resin and glass fiber laminates—show the comparatively high values of .9 to 8.0 pence respectively. Polyethylene, which has now swept to first place among plastics, costs in molded form as much as .9 pence per unit strength. The answer is, of course, that the vast bulk of plastic materials is not now purchased for performance on this criterion. On the contrary, their great attractions are falling price, low density, the facility with which they can be worked into intricate finished shapes, and the wide range of hardness and softness, stiffness and flexibility, color, transparency and opacity in which they can be specified. When all is said and done, however, the position of plastics in the materials marketplace can be epitomized by the view of a plastic engineer I know, who says he always likes to sell plastics but he would prefer to buy metals any day.

It is not surprising that plastics should dominate the toy business or should now be on the ascendant in the packaging industry. From copper, lead, zinc, tin, steel and cast iron, however, polyethylene and polyvinyl chloride have taken large volumes of pipe and tube for domestic, municipal and industrial plumbing. Glass-filled nylon is used instead of zinc, magnesium or aluminum in precision die castings. In the U.S. resin-glass laminates have made the manufacture of small boats into a big business. These are reasonably high-specification products, and the success of plastics in such uses is a portent of further developments. In the case of metals, limits and properties are now well defined and no significant new metals are in the offing. In plastics, where new molecules remain to be synthesized, polymerized into chains of new configuration and aggregated into structures with novel combinations of properties, there is always a chance of an overnight revolution. As Herman F. Mark shows [see "The Nature of Polymeric Materials," page 148], if a plastic could be developed with suitable mechanical properties at 150 degrees centigrade, this could completely alter the competitive situation in such huge metal markets as automobiles and construction. This is the biggest development impending in the technology and economics of materials.

NEWCOMER COMING ON FAST IN MATERIALS

# WHITTAKER CORPORATION

When this
special issue
of SCIENTIFIC AMERICAN
went to press, advancing technology had already outpaced today's materials—the Whittaker research team focuses on the development and tailoring of tomorrow's materials. Research programs currently underway range through polymeric, metallic, ceramic, and refractory materials. For example, Whittaker scientists have developed advanced high-modulus fibrous composites utilizing sophisticated fibers such as boron and graphite imbedded in Whittaker-developed high-temperature resinous matrices. Precision extrusion techniques have led to the development of metallurgically bonded composites combining such dissimilar metals as stainless steel and titanium. Whittaker products represent the tangible results of Whittaker advanced research capabilities, including applications relating to automotive, architectural, marine, nuclear, aviation, missile, spacecraft and launch vehicle technologies. Perhaps our advanced materials capabilities or products can help you. Our address is 9229 Sunset Blvd., Los Angeles, California 90069, Whittaker Corporation. Ask us.



*Macrophotograph of a high-strength-to-weight beryllium / titanium composite material.*

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# MATHEMATICAL GAMES

## *Double acrostics, stylized Victorian ancestors of today's crossword puzzle*

by Martin Gardner

In modern set theory two sets are said to intersect if they have one or more elements in common. The crossword puzzle, the Double-Crostic and games of the Scrabble type can be thought of as combinatorial play in which 26 elements (letters) are arranged into sets (words) that intersect in the manner dictated by the rules and the geometric pattern on which the elements are placed. Of the hundreds of varieties of word puzzles that exploit intersection, few have been more elegant in a literary way, or have had as interesting a history, as the double acrostic. It is almost forgotten today, yet it was the ancestor of the crossword puzzle and the most popular form of wordplay in English-speaking countries throughout the last quarter of the 19th century and until the end of World War I. In London in 1915 eight newspapers ran a daily double acrostic. *The World* had carried the feature since its first issue in 1874, *The Queen* since the 1860's.

The double acrostic was a highly stylized form, usually written in verse. Here, for example, is a short specimen by Tom Hood, son of the English poet Thomas Hood:

We are words that rhyme,
And we're both in time.
One is a season, the other a song;
If you guess them rightly,
  you can't be wrong.
1.
It is very good fun,
If it's properly done.
2.
A beast with two toes,
How slowly it goes!
3.
The sun's overhead—
There's no more to be said!
4.
The sun's going to sink;
This is coming I think.

The first stanza gives clues for two words, called the uprights, that are spelled vertically by the initial and final letters of the words to which clues are given by the numbered stanzas. The two uprights must be of equal length and in some way related to each other. In this instance the first upright, known as the primal, is JUNE. The second upright, called the final, is TUNE. The horizontal words, defined in the numbered stanzas, are called the cross-lights or simply the lights. The complete answer is:

JesT
UnaU
NooN
EvE

The cross-lights could vary in length, as in this instance. It was permissible on occasion to do such things as spell them backward, use only parts of them or even scramble their letters, provided that the required operations were specified by hints in the stanzas. If the middle letters of each cross-light formed a third upright, known as the central, the puzzle was called a triple acrostic.

Henry Ernest Dudeney, in a little book called *The World's Best Word Puzzles* (1925), which will be reprinted this fall by Scribner's, attributes the invention of the Victorian double acrostic to Queen Victoria! The evidence for this is in a rare volume called *Victorian Enigmas; or, Windsor Fireside Researches: Being a Series of Acrostics Enigmatically Propounded* (1861), by Charlotte Eliza Capel. Miss Capel wrote that her original double acrostics had been inspired by a puzzle given to her five years earlier by a friend at Windsor Castle who told her it had been written by the Queen for the royal children. Although the Queen's puzzle, which Miss Capel reproduced, is not in rhyme, it is certainly a double acrostic. Nine geographical words are defined (Naples, Elbe, Washington, Cincinnati, Amsterdam, Stamboul, Torneå, Lepanto, ecliptic), the initials of which spell NEWCASTLE and the finals of which, read in reverse, spell COAL MINES.

Going back five years from 1861 places the date of the Queen's puzzle at 1856. It was in the *Illustrated London News* for August 30 of that year, writes Dudeney, that the first double acrostic was printed. It bore the by-line of Cuthbert Bede, the pen name of Rev. Edward Bradley. Bradley called his puzzle an "acrostic charade" and said it was a novel type of wordplay "lately introduced." The clues to its uprights, LONDON and THAMES, were given by these lines:

A mighty centre of woe and wealth;
  A world in little, a kingdom small.
A tainted scenter, a foe to health;
  A quiet way for a wooden wall...

(Apparently the problem of river pollution is not a new one.)

The term "double acrostic" was firmly established by 1860, when puzzles of that type were included in a book, *Charades, Enigmas and Riddles,* collected by someone calling himself A. Cantab. "The Double Acrostic," Cantab writes, "is a very recent invention." By 1884 the double acrostic craze had reached such proportions in England that an *Acrostic Dictionary* of 256 pages was compiled by Mrs. A. Cyril Pearson, whose husband wrote a number of puzzle books. It listed 30,000 common words, alphabetized by first and last letters.

Of the hundreds of thousands of double acrostic poems published in Victorian newspapers, magazines and books, none were more charmingly written than those by Thomas Hood, the younger. Like his father, he was a skillful and prodigious writer of humorous verse, much of it published in *Fun,* a comic weekly he edited, and later in his own periodical, *Tom Hood's Comic Annual.* He turned out hundreds of puzzle poems of all types. The double acrostic on page 270 is from a children's book, *Excursions into Puzzledom,* by Hood and his sister, published in 1879, five years after Hood's death. Can the reader discover its uprights and cross-lights before they are given next month?

It is no surprise to learn that Lewis Carroll, who enjoyed all kinds of puzzles, was addicted to the double acrostic and was the creator of many splendid specimens. His best is one that first appeared in his 1869 book *Phantasmagoria* [*see illustration on page 272*]. An entry in Carroll's *Diary* for June 25, 1867, reads: "Blore [one of Carroll's mathematics students at Christ Church, Oxford] brought his niece Miss Kyser to see photographs —I took a couple of her as well. Sat up

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Ruler of all things, for a space his hand
Is traced in sparkling lines throughout the land:
Painting each pane and jewelling each tree,
Checking the brooks and rills that trickled free;
Tasting the roots and fruits all stored away,
Withering the garden blooms that were so gay.
Such is my First,—the boys alone delight
To see his silent traces over night.
And greet him well, for long they all have reckoned
Upon his aid to help them to my Second.

*1*

Where the fairies come, we grow,
Their most secret haunts we know.
Our fringed fans are tall and green,
Pavilions for the elfin queen.
Those that with all careful heed,
Sow at night our mystic seed,
May her sportive revels see
Underneath the greenwood tree!

*2*

When a frisky fancy takes
The jovial Land of Cakes,
She calls for her piper to play her a tune,
Till the very roof-tree shakes!
And then ere it grows too late,
A perplexing figure of eight
Is danced by the lads and lasses all
At a most astonishing rate!

*3*

When Pierre meets Marie in the lane,
  And slyly steals a kiss,
He asks a question clear and plain,
  To which she answers—this!

*4*

No traveller of modern times
  Such wondrous tales narrated;—
As of this ancient mariner
  Have been most gravely stated.

*5*

When the storm king rises
  From his cloudy lair,
And his muttered anger
  Grumbles in the air;
Doors and windows rattle,
  Sign-posts creak and groan.
And from roof and rafter
  This is roughly blown.

***A typical double acrostic by Tom Hood***

listening to the music of the Christ Church Ball and wrote, at Miss Kyser's request, another one of those acrostic ballads of which I had given Blore some before."

This is how Carroll later introduced the ballad in *Phantasmagoria:* "[It] was written at the request of some young friends, who had gone to a ball at an Oxford Commemoration—and also as a specimen of what might be done by making the Double Acrostic *a connected poem* instead of what it has hitherto been, a string of disjointed stanzas, on every conceivable subject, and about as interesting to read straight through as a page of a Cyclopedia. The first two stanzas describe the two main words, and each subsequent stanza one of the cross-lights."

Carroll did not disclose the solution, but in 1932, when Macmillan issued *The Collected Verse of Lewis Carroll* (there is a Dover reprint called *The Humorous Verse of Lewis Carroll*), an anonymous editor appended to the poem what he believed to be its two uprights, COMMEMORATION and MONSTROSITIES, without supplying the cross-lights. The answer, which has dogged the poem ever since, is unquestionably wrong. As far as I know, the first printing of the correct uprights was in "The Best Acrostics," an article by H. Cuthbert Scott in *The Strand Magazine*, Vol. 50 (December, 1915), pages 722–728, with answers on page 109 of the next issue. The primal upright is QUASI-INSANITY, the final COMMEMORATION. Readers should enjoy searching for the cross-lights; there is little doubt about any but the fourth and the ninth. I shall discuss the complete solution next month, and I shall be pleased to hear from anyone (although I cannot reply to all letters) who can shed new light on the two doubtful words.

It is easy to see how the double and triple acrostic, with its two or three vertical words, evolved into more complicated forms, including the crossword puzzle and such later variants as the Double-Crostic. The first crossword deserving the name was constructed by Arthur Wynne of Liverpool, who came to the U.S. around the turn of the century to begin a career in journalism. He was the editor of *Fun*, a Sunday supplement of the *New York World*, when he published in it on December 21, 1913, his first "Word-Cross Puzzle." (The interested reader will find it reproduced in Clark Kinnaird's *Encyclopedia of Puzzles and Pastimes*, 1946, page 80.) It was such an immediate success that

Wynne began composing similar puzzles in all shapes and sizes.

In 1924 two young men, Richard Simon and Max Schuster, opened a book-publishing office in New York but were in need of something to publish. Simon's aunt had a sick friend who was addicted to the *World's* crosswords. Was there a book of such things, she asked her nephew, that she could give her friend? There was not. Simon and Schuster made arrangements to reprint 50 of the *World's* crosswords ("The worst idea since prohibition," the *World's* editors said) and persuaded the Venus Pencil Company to donate 50,000 pencils to be attached to the book's cover as a promotional stunt. The first 50,000 copies of *The Cross Word Puzzle Book,* under the imprint of the Plaza Publishing Company, sold out in three months, touching off a craze that spread quickly to England and France (*"les mots croisés"*) and other countries. In Canada a bilingual form became popular, with English words going one way and French words the other. During the next 20 years the sale of more than two million copies of crossword books firmly established the house that became Simon & Schuster.

Most newspapers in the U.S. began to publish a daily crossword in 1924. The

THERE was an ancient City, stricken down
With a strange frenzy, and for many a day
They paced from morn to eve the crowded town,
And danced the night away.

I asked the cause: the aged man grew sad:
They pointed to a building gray and tall,
And hoarsely answered "Step inside, my lad,
And then you'll see it all."

*1*

Yet what are all such gaieties to me
Whose thoughts are full of indices and surds?
$x^2 + 7x + 53$
$= \frac{11}{3}$

*2*

But something whispered "It will soon be done:
Bands cannot always play, nor ladies smile:
Endure with patience the distasteful fun
For just a little while!"

*3*

A change came o'er my Vision—it was night:
We clove a pathway through a frantic throng:
The steeds, wild-plunging, filled us with affright:
The chariots whirled along.

*4*

Within a marble hall a river ran—
A living tide, half muslin and half cloth:
And here one mourned a broken wreath or fan,
Yet swallowed down her wrath;

*5*

And here one offered to a thirsty fair
(His words half-drowned amid those thunders tuneful)
Some frozen viand (there were many there),
A tooth-ache in each spoonful.

*6*

There comes a happy pause, for human strength
Will not endure to dance without cessation;
And every one must reach the point at length
Of absolute prostration.

*7*

At such a moment ladies learn to give,
To partners who would urge them overmuch,
A flat and yet decided negative—
Photographers love such.

*8*

There comes a welcome summons—hope revives,
And fading eyes grow bright, and pulses quicken:
Incessant pop the corks, and busy knives
Dispense the tongue and chicken.

*9*

Flushed with new life, the crowd flows back again:
And all is tangled talk and mazy motion—
Much like a waving field of golden grain,
Or a tempestuous ocean.

*10*

And thus they give the time, that Nature meant
For peaceful sleep and meditative snores,
To ceaseless din and mindless merriment
And waste of shoes and floors.

*11*

And One (we name him not) that flies the flowers,
That dreads the dances, and that shuns the salads,
They doom to pass in solitude the hours,
Writing acrostic-ballads.

*12*

How late it grows! The hour is surely past
That should have warned us with its double knock?
The twilight wanes, and morning comes at last—
"Oh, Uncle, what's o'clock?"

*13*

The Uncle gravely nods, and wisely winks.
It *may* mean much, but how is one to know?
He opes his mouth—yet out of it, methinks,
No words of wisdom flow.

***Lewis Carroll's most difficult double acrostic***


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Plain Old Thinking
Concepts
Theories
Imagination
Breakthrough
Hypothesis
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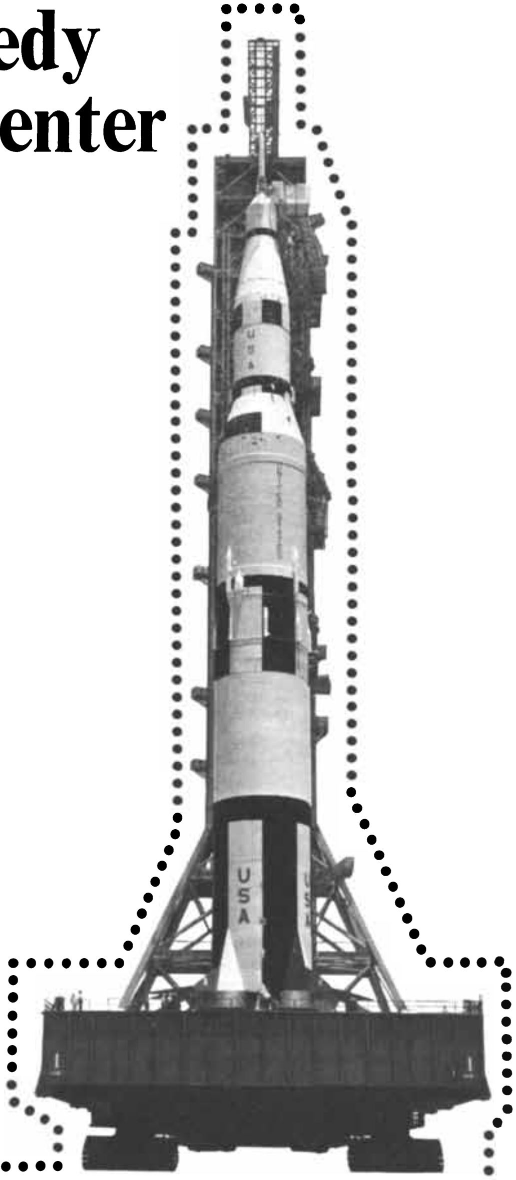
# Boeing openings on Apollo/Saturn V at Kennedy Space Center



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My *first* is a garment that fastens behind;
   My *second* applies to a lush little lake;
My *third* in your *Handwörterbuch* you will find
   May mean whilst or because; my *fourth* is a fake:
The Association of Impotent Old Apoplectic Parties;
   My *fifth* is the steamship *Nigerian Royal Highness;*
My *sixth* a confection of musical art is;
   My *seventh* an organ remote from the sinus;
My *eighth* is a painter fantastic and French;
My *ninth* is exclaimed at a wrench or a stench;
And my *tenth* is a nimble but mythical wench.

*Five-by-five word-square poem by Edmund Wilson*

astonished *World* announced late that year that its first daily puzzle would be composed by Gelett Burgess, of purple-cow fame, and added:

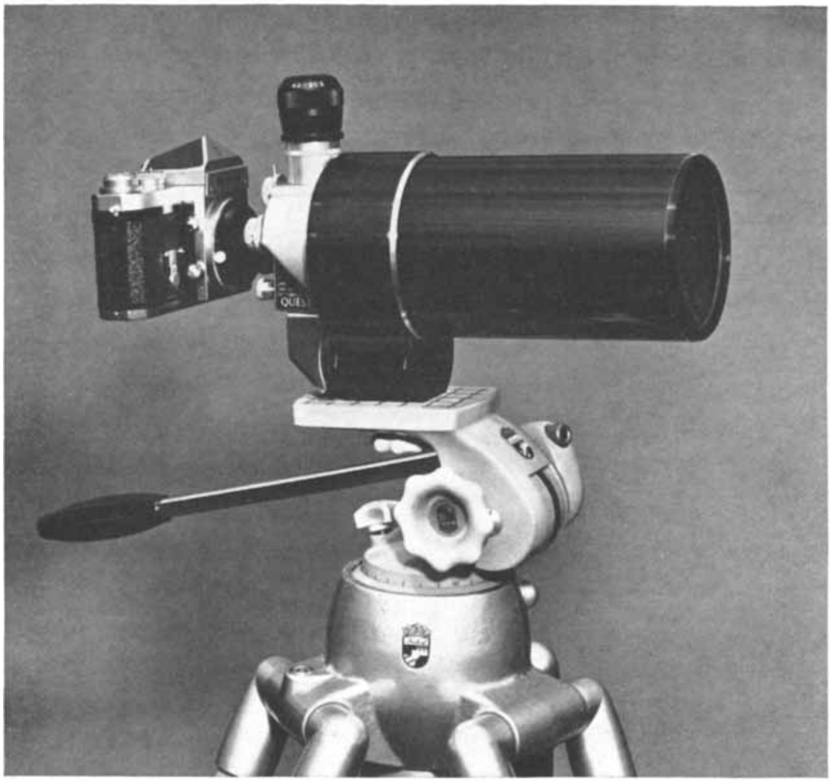
The fans they chew their pencils,
   The fans they beat their wives,
They look up words for extinct birds—
   They lead such puzzling lives!

*The New York Times* was the last major paper to succumb. In 1942 it instituted its Sunday puzzle, edited by Margaret Farrar, the wife of the publisher John Farrar and still the crossword puzzle editor of the *Times* and the nation's leading authority on the topic. (As Margaret Petherbridge she had been one of the three editors of Simon & Schuster's first puzzle book.) More than 90 percent of the nation's newspapers now have a daily crossword, and millions of crossword books are sold annually. It is the most popular type of puzzle in all parts of the world except in countries, such as China and Japan, where the language does not have individual letters and therefore is not suitable for intersecting word patterns.

The Double-Crostic, in which the words of a literary quotation and the name of the author and his work are derived from words clued by cryptic definitions, was invented by a Wellesley College graduate and Brooklyn high school English teacher, Elizabeth Seelman Kingsley. Mrs. Kingsley's first Double-Crostic appeared in *The Saturday Review of Literature* in March, 1934, to be followed by a large output of Double-Crostics for that magazine, other magazines and numerous Simon & Schuster books. When she retired in 1952, five years before her death, the work was continued by her assistant, Doris Nash Wortman, until Mrs. Wortman's death in June. The term "Double-Crostic" is a registered trademark, but the puzzle form appears regularly under other names, such as *The Reporter*'s Acrostickler and the *National Review*'s Trans-O-Gram. Kinnaird, in his *Encyclopedia,* calls them literary anacrostigrams.

One of the earliest and hardest-to-compose variants on the double acrostic is the word square, which can be thought of as a kind of ultimate acrostic because every letter in it marks an intersection of two words. A set of $n$ horizontal words, each of $n$ letters, intersects with another set of $n$ vertical words of $n$ letters that are read down. The uprights are sometimes identical with the horizontals, sometimes a different set entirely. Dudeney says in his book on word puzzles that he was the first to put the definitions for such squares into verse, and he gives a number of examples. Edmund Wilson, who shares with his literary antagonist Vladimir Nabokov a liking for wordplay, has more recently tried his hand at versifying word squares. In an amusing example from Wilson's *Night Thoughts* (1961) the five horizontal words are given first, followed by clues to five different words that form the uprights [*see illustration above*]. Can the reader construct Wilson's square before it is revealed next month?

The missing center digit in the diamond-shaped factorial shown last month is easily found by recalling that every multiple of 9 has a digital root of 9; if one keeps summing the digits of the number, casting out 9's as he goes along,



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the final digit must be 9. Every factorial higher than 5! is a multiple of 9 because 6! has 3 and 6 as factors and 3 times 6 is 18, a multiple of 9. Therefore to find a missing digit in any factorial greater than 5! one simply obtains the digital root of the mutilated factorial and subtracts it from 9 to get the missing digit. If the mutilated factorial has a digital root of 9, the missing digit could be either 0 or 9, but in this case the digital root of the mutilated diamond factorial is 3 and so there is no ambiguity. The missing center digit must be 6.

$A! + B! + C! = ABC$ has the unique solution $1! + 4! + 5! = 145$.

To find the number of different minimum-length routes from one corner of a rectangular section of city blocks to the diagonally opposite corner, consider that if the rectangular section is $a$ blocks long and $b$ blocks wide, the minimum path that connects diagonally opposite corners is $a$ plus $b$. Call this sum $n$. Every $n$-length path from corner to corner can now be expressed as a chain of $n$ symbols, of which $a$ symbols will be identical (indicating a block's travel lengthwise toward the goal) and the remaining $b$ symbols will be identical (indicating a block's travel widthwise to the goal). If we let a penny stand for a movement of one block lengthwise and a dime for a movement of one block widthwise, then the number of different routes will equal the number of different ways that $a$ pennies and $b$ dimes can be arranged in a row. Every distinct route can be put in one-to-one correspondence with a permutation of the $n$ coins, and every permutation of the coins corresponds to one of the routes. The hint given last month was the formula $n!/a!b!$ for the number of ways of arranging $n$ objects in a row, of which $a$ are identical and the remaining $b$ are identical. The rectangle is six blocks long and four blocks wide, therefore the problem of determining the number of different routes is isomorphic with the problem of finding the number of different ways six pennies and four dimes can be placed in a row. The answer is $10!/(6! \times 4!) = 210$.

The problem ties in with the discussion of Pascal's triangle (December, 1966), as the reader will discover if he labels each intersection with the number of different minimum-length routes from the upper left corner to that intersection. The answer, 210, is found on the triangle simply by starting at the top of the triangle, moving six (or four) steps down one side, then turning and going down four (or six) steps in the other diagonal direction.

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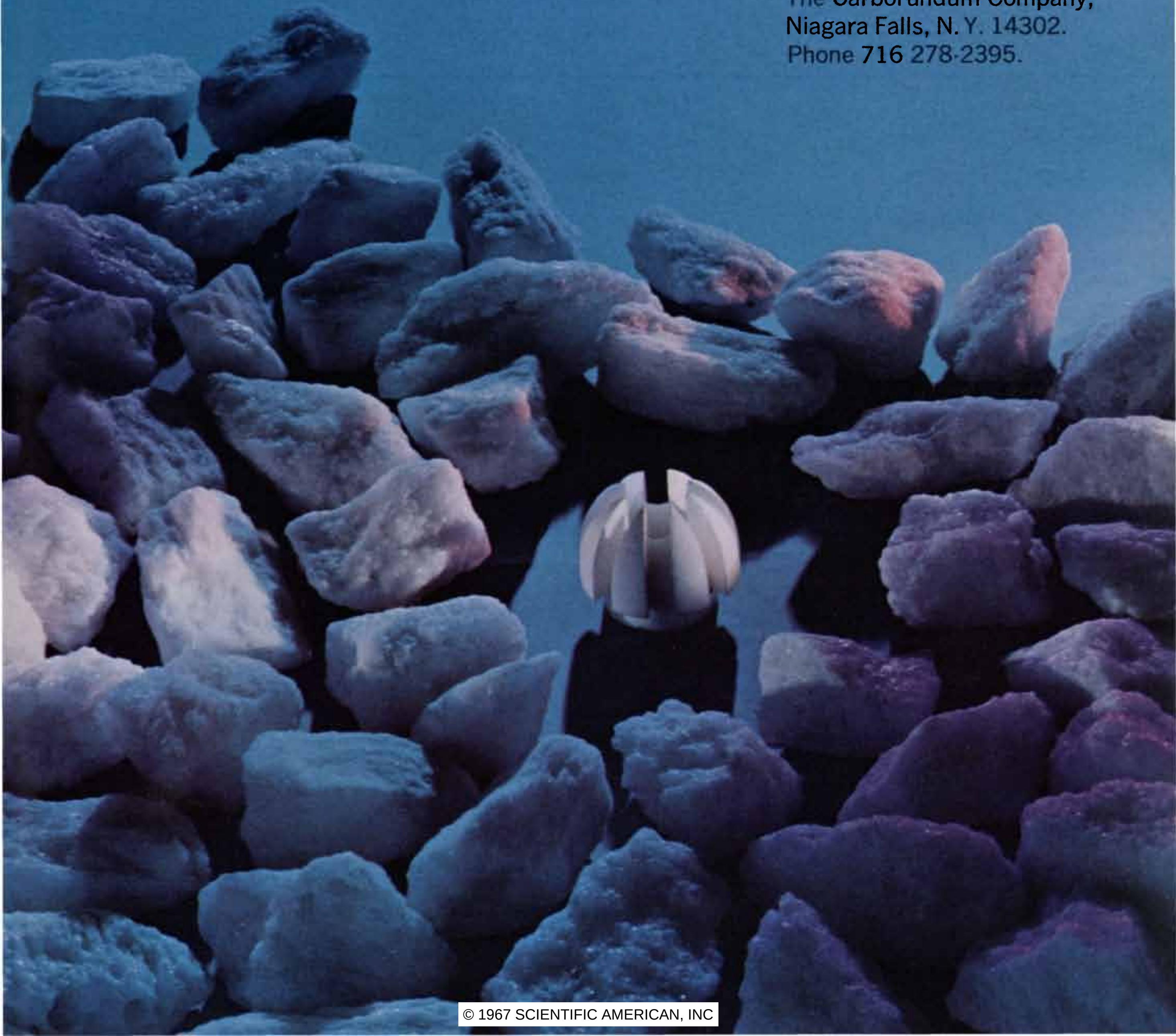

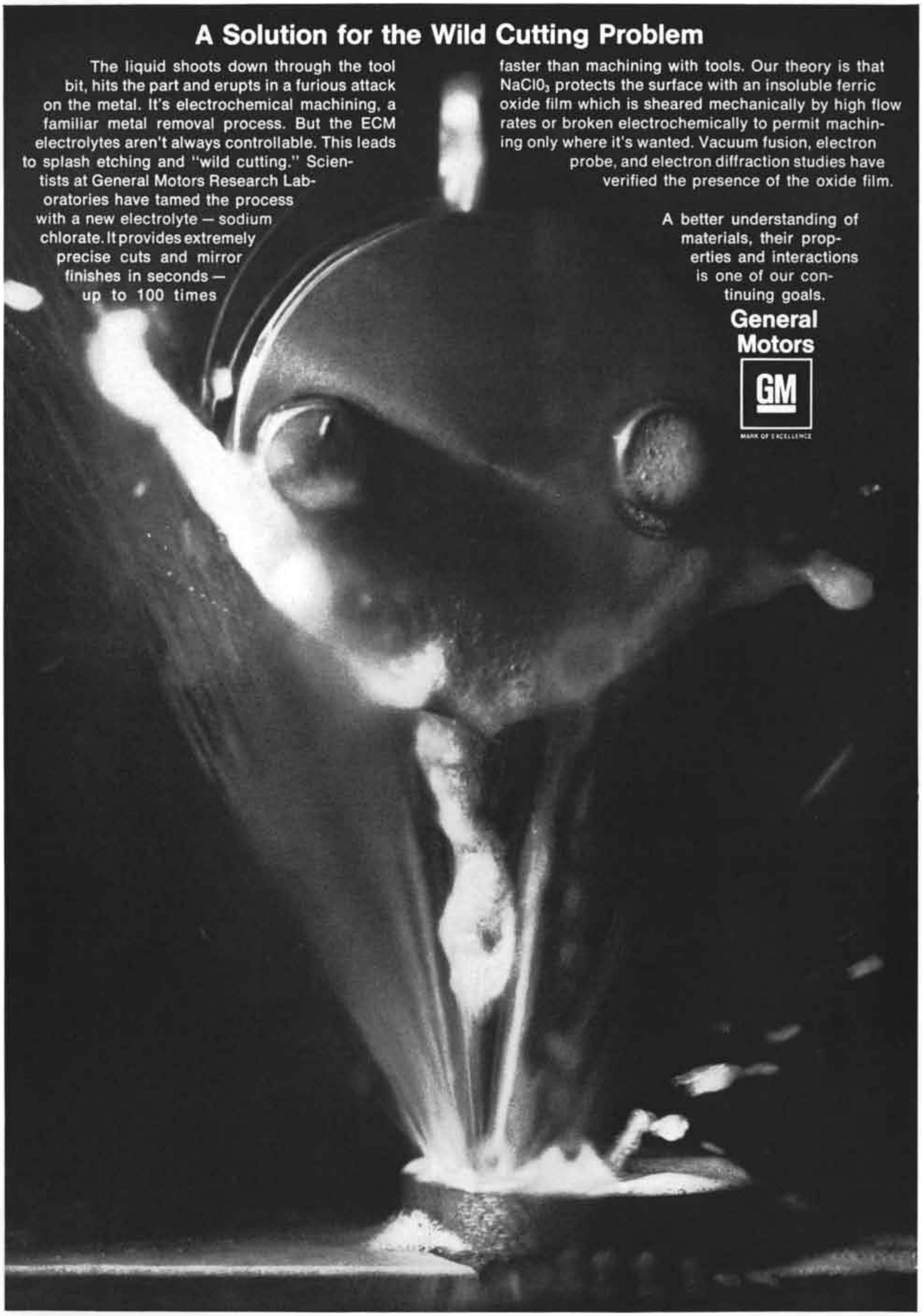

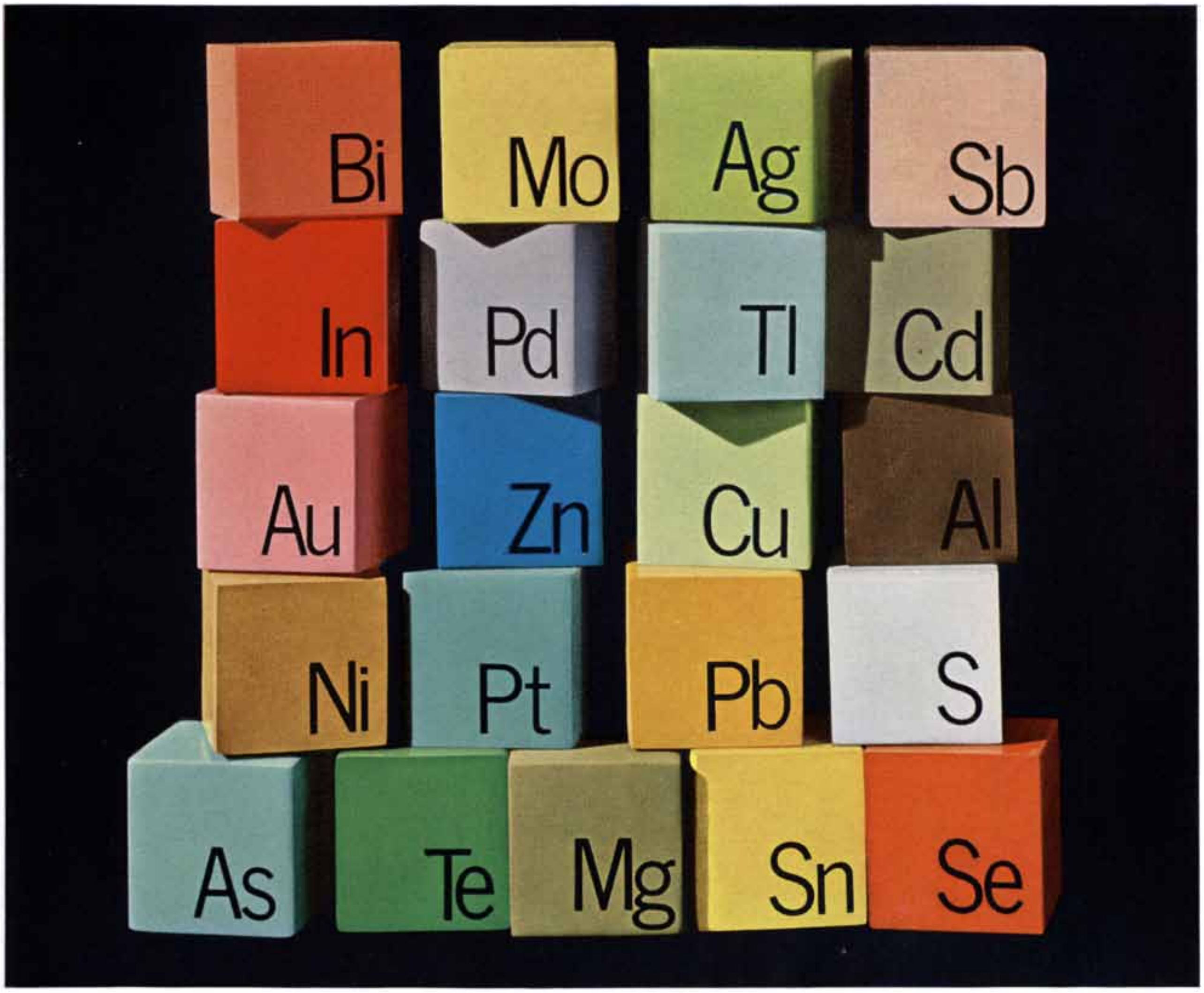

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# materials of Man

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There is a vast number of different protein molecules in a complex organism like man; nevertheless, each one (in normal circumstances) is unerringly reproducible. Such "hereditary replication" of proteins is thought to be governed by the cellular compounds, desoxyribonucleic acid (DNA) and ribonucleic acid (RNA). A postulated DNA-RNA-protein system is to some extent schematized in the accompanying photograph—a model reconstructing microscopic events on a very large scale and in three dimensions.

Specifically, the model portrays a puff on a chromosome as seen microscopically in certain insect cells, and also the involvement of DNA and RNA in the production of proteins. The puffing of fibers in such species signals activation of a gene. While puffing has not been observed in human cells, an analogous event is believed to occur when human RNA is produced.

At the top of the model may be seen an unpuffed portion of the chromosome (that is, an inactive gene) and a representation of the protein histone, which is thought to hold DNA in the compact, twisted form it assumes when not active. When a gene becomes active, present knowledge suggests, a hormone or other substance combines with histone, thereby canceling its inhibitory effect.

This model, a byproduct of The Upjohn Company's active interest in the field of molecular biology, has been and will continue to be exhibited at scientific (chiefly medical) meetings in various cities.

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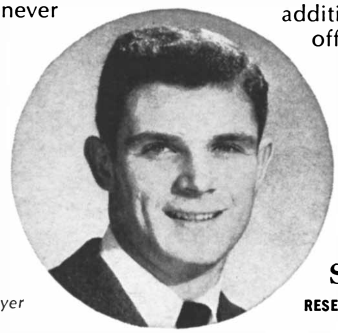

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# THE AMATEUR SCIENTIST

## *How to construct a gas chromatograph that can measure one part in a million*

Conducted by C. L. Stong

If one ounce of ethyl ether has been dissolved in 248 barrels of water and one drop of the mixture has been divided into 50 equal parts, how can the ether in one of the minute droplets be quickly identified? Robert Van der Kloot, a schoolboy in Skokie, Ill., makes such determinations by means of a gas chromatograph he has built at home. His instrument separates mixtures of unknown gases and vapors as they flow through a fractionating column—a slender pipe packed with coated granules—and detects the separated fractions as they emerge serially through a tiny flame of burning hydrogen.

Van der Kloot built the instrument with the help of his father, Albert P. Van der Kloot, who is a chemist. The two of them set out to construct an instrument of high sensitivity and the greatest possible simplicity. The first goal was achieved with impressive success: the apparatus easily detects dilutions of one part in a million. The second objective proved to be more elusive, according to Albert Van der Kloot, who writes:

"The experimenter who designs instruments as a pastime soon discovers that striving for maximum simplicity runs counter to human nature. Part of the fun comes in devising convenient features and amusing gadgets that are not strictly essential to the operation. Bob and I yielded to this temptation more than once. We built several versions of the apparatus and shall describe two of them. One version is comparatively insensitive but useful for demonstrating the principles of gas chromatography. The second version, when it is operated properly, is capable of matching the performance of professional instruments. We shall identify the features that can be omitted as they come up in our discussion.

"Our instruments are similar in principle to the gas chromatograph described previously in these columns by Steve Langhoff and Glen Martin [see 'The Amateur Scientist,' SCIENTIFIC AMERICAN; June, 1966]. That article is an excellent introduction to the technique of gas chromatography and should be consulted by beginners who undertake the construction of our apparatus. Our design differs from the Langhoff and Martin one principally in the provision of a heated inlet fixture for injecting small specimens into the fractionating column, the use of more effective materials in the fractionating column and the substitution of a flame-ionization detector for the incandescent filament that Langhoff and Martin used for sensing the separated materials.

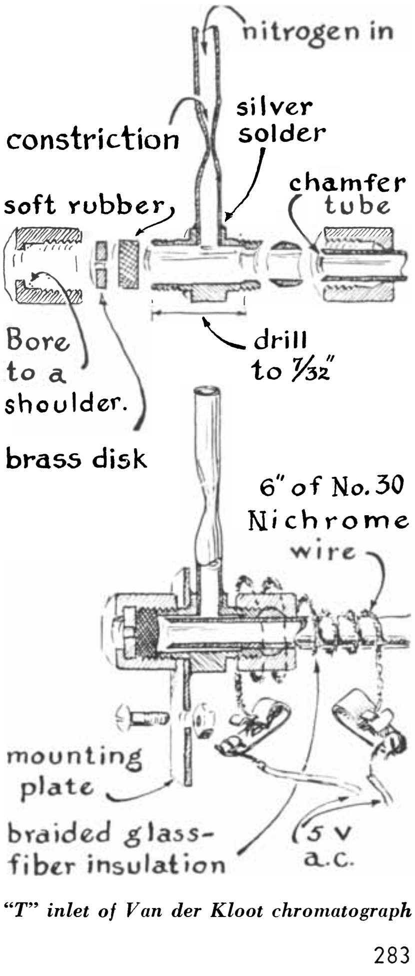
"The inlet of our system is essentially a *T* fitting. Specimens are injected into the inlet with a hypodermic syringe, the needle of which pierces a rubber septum that closes one end of the crossarm of the *T*. The opposite end of the crossarm is joined to the fractionating column.

"We made the *T* fitting by drilling a 1/8-inch hole in the side of a tubing connector 1/8 inch in diameter and silver-soldering a 1/8-inch copper tube into the hole. This formed the leg of the *T*, through which nitrogen gas flows into the system and sweeps the specimen through the column. A constriction was made in the leg of the *T* by inserting a piece of spring-steel wire .009 inch in diameter and squeezing the tube between the jaws of a vise. The wire was then removed. The constriction thus formed helps to control the flow of nitrogen and prevents the volatilized specimen from backing up into the nitrogen inlet. A ready-made compression *T* would have served our purpose but none was handy.

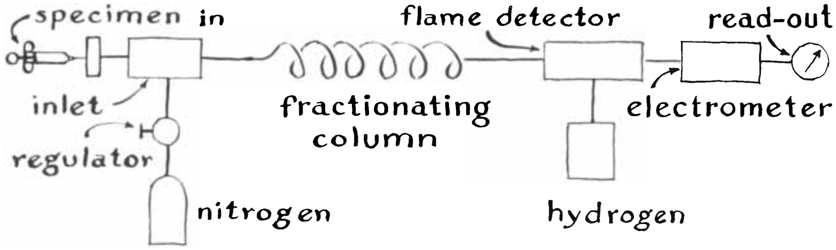
"To encourage the smooth flow of specimen materials into the column we drilled the fitting lengthwise and slipped a length of 1/8-inch copper tubing inside. The insert extended to within 1/8 inch of the outer end. Prior to assembly we reamed the outer end of the insert to a taper resembling a small funnel.

"The septum, which consists of a disk cut from a sheet of rubber about 1/16 inch thick, is clamped between the compression nut of the fitting and the threaded end of the crossarm. We also silver-soldered a disk of brass inside the nut and drilled a hole 1/16 inch in diameter through the center of the disk. The centered hole serves as a guide for the hypodermic needle when specimens are injected into the system [*see illustration below*]. This arrangement is one of the nonessential elements in the design of our gas chromatograph, but it is convenient for preventing damage to the point of the needle, which might otherwise be accidentally thrust into the metal.

"The fractions constituting a specimen



*"T" inlet of Van der Kloot chromatograph*



*Schematic arrangement of the chromatograph*

separate most distinctly if the specimen enters the chromatographic column as a compact 'plug' of gas or vapor. To transform liquid specimens quickly into vapor we heat the entire inlet assembly electrically. In applying the heating unit the fitting was first wrapped with glass-fiber insulation. We then wound six inches of 30-gauge Nichrome heating wire around the insulation to form a single-layer coil of widely spaced turns. The turns of the coil were bound in place by a second layer of glass-fiber braid. The electrical resistance of the coil is 3.2 ohms. It operates from the five-volt tap of a transformer.

"The design of fractionating columns varies with the nature of the materials to be analyzed. Normally columns consist of copper tubing 1/4 inch in diameter filled with a loosely packed inert granular substance known as the support. The granules of the support are usually coated with a thin film of liquid called the partitioner. The partitioner largely determines the performance of the fractionating column. Demonstration columns can be packed with an uncoated material such as Tide, the detergent, but the performance of such columns is comparatively poor. If Tide is used, it should be heated to a temperature of 150 degrees centigrade for several hours to drive off perfume and other volatile components.

"Diatomaceous earth was used as the support in the first gas chromatograph. This material is produced by the Johns-Manville Corporation under the brand name Celite. The material must be screened by an 80-mesh sieve to separate from the powder the granular particles that might otherwise clog the column. Crushed firebrick can be used as the support; it too must be screened.

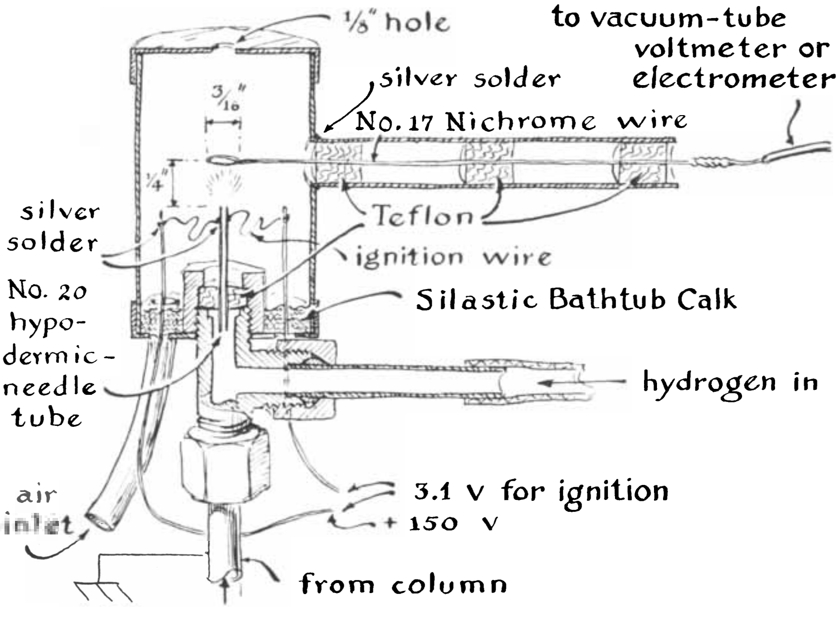
"The effectiveness of supports depends strongly on the uniformity of the particle size. The technology of support materials is developing rapidly. A wide variety of special types is now stocked by companies that deal in supplies for gas chromatographs. Some of the new materials are surprisingly costly. We use the support known as Gas Pac W, which is available from Chemical Research Services Incorporated of Addison, Ill. The serious experimenter will find it worthwhile to use a good support. The very best and most expensive types are not essential, but good separations cannot be made with inferior supports.

"Partitioners are equally important. We used three: glycerine, squalene and polyethylene glycol 600. This last chemical is available from the Jefferson Chemical Company of Houston, Tex. Columns can be made simply by mixing the liquid with the solid. Coatings of more uniformity can be prepared, however, by dissolving the liquid in a suitable solvent, stirring the mixture thoroughly into the solid and then evaporating the solvent. We used lacquer-thinner and stirred the batch occasionally as it dried. Be sure to do this work outside and avoid inhaling the vapor. In general we use 12 to 15 grams of liquid partitioner to 100 grams of support. Usually we make up batches of 25 grams, an adequate amount for packing a tube eight feet long and 1/4 inch in diameter.

"To the eye the coated material after drying appears similar to the uncoated support. It flows freely. To pack a column we stand the tubing vertically and plug the bottom end with a wad of glass wool. The coated support is poured into the upper end of the tube through a funnel. During this operation we hold a vibrating sander against the tube to make the powder fill the voids.

"Freshly packed columns should be coiled, placed in the oven of the instrument, heated somewhat above normal operating temperature and flushed with compressed nitrogen to eliminate traces of solvent and other volatile substances. The column should not be connected to the detector during this conditioning procedure. A few minutes of flushing is adequate in the case of columns intended for demonstrations or other low-sensitivity applications, but those designed to work at the highest sensitivity may have to be flushed continuously for several days.

"The rate at which materials travel through the column is partly determined by the temperature of the packing materials; therefore the temperature must be carefully controlled. The oven we used for maintaining the temperature of our low-sensitivity instrument is identical with that described by Langhoff and Martin. It houses the inlet, fractionating column and detector. We made it from a wooden box a foot square and nine inches deep. The top of the box is closed with a removable lid. The inner surfaces are lined with sheets of cement board

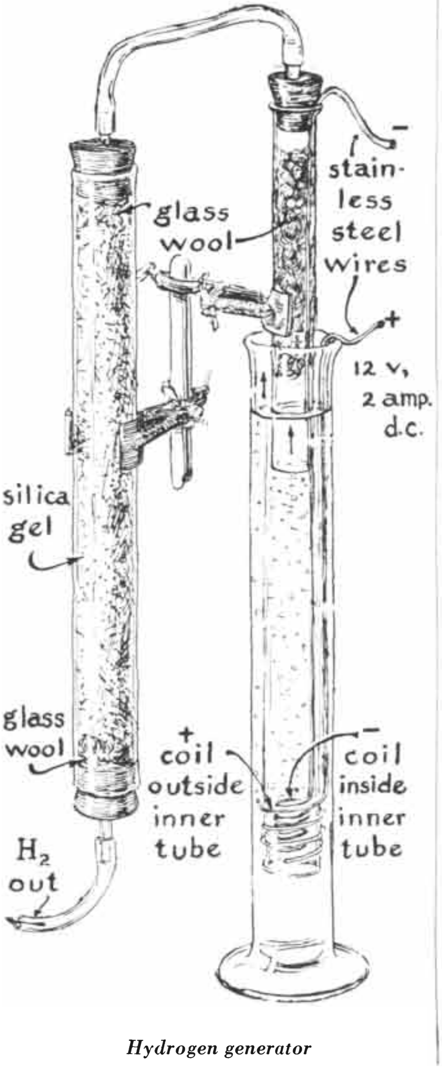


*Details of the burner housing*

fastened in place with Silastic Bathtub Calk, which is available in hardware stores. Oven temperature is regulated by means of a variable autotransformer that energizes a 300-watt heating unit inside the box.

"The oven used in the high-sensitivity unit is designed for higher operating temperature and consists of a metal box lined with Marinite, a product of the Johns-Manville Corporation. It is equipped with a system of electronic temperature control. Actually a minimum system for making demonstrations does not require an oven. Interesting separations can be made at room temperature with fractionating columns ranging in length from six inches to three feet.

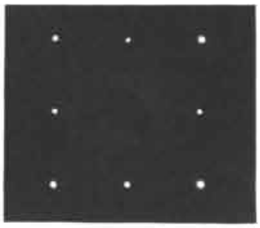
"The heart of our detector is a tiny flame of hydrogen, mixed with gases from the fractionating column, that burns invisibly on the tip of a hypodermic needle. The point of the 20-gauge needle was ground off to make a right angle to the axis of the tube. The tube is



*Hydrogen generator*

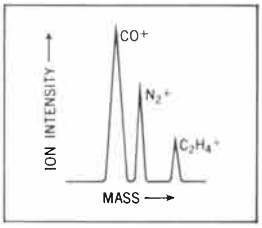
# Materials Research at the Aerospace Corporation

*Too often, materials survive laboratory tests only to fail in the real environment. For this reason, the Materials Sciences Laboratory (MSL) of the Aerospace Corporation is using a number of approaches in research on metals, ceramics and composites to better relate experimental results with actual performance. Three examples are studies involving Low Energy Electron Diffraction (LEED), thermal stress fracture analysis and mass spectrometry.*



**A LOW ENERGY ELECTRON DIFFRACTION PATTERN FROM A (100) MOLYBDENUM SURFACE.** The innermost spots result from the adsorption of a half monolayer of oxygen. The outermost spots represent the clean Mo surface. This sensitive technique is being employed to study the physics of surface reactions and related physical and mechanical properties in simulated space environments.

**ARRESTED THERMAL STRESS CRACK IN A COMPOSITE OF ZIRCONIUM CARBIDE WITH GRAPHITE.** The lamellar eutectic structure of an arc-cast carbide alloy dissipates mechanical energy promoting discontinuous fracture. Energy dissipation is enhanced by major crack diversions and blunting that take place when the crack encounters a proeutectic graphite flake. A major improvement in resistance to thermal stress failure induced by a simulated reentry environment is attributable to a basic alteration in fracture mode.



**MASS SPECTRUM OF $C_2H_4$, $N_2$, AND CO AT m/e = 28.** This spectrum depicts the high degree of mass resolution achieved with a double-focusing mass spectrometer used at MSL to study the response of materials to very high temperature. Vaporization of refractory materials is studied under both Langmuir and Knudsen conditions. In related studies, DTA and TGA systems are coupled to the mass spectrometer for an investigation of mechanisms and rate of decomposition of high temperature polymers. Results of these studies find application in development of ablation models for advanced thermal protection of missiles and manned reentry vehicles.

MSL's broad research program includes the following fundamental and applied areas of investigation: degradation of satellite materials in space environments, gas-surface interaction mechanisms, particulate and electromagnetic radiation effects in solids, kinetics of formation of carbonaceous species during graphite vaporization, high strain rate loading of structures, performance of materials and sub-systems in an enemy induced environment, controlled solidification of composites, elastic properties of ceramic composites, and mechanisms of stress corrosion in high strength alloys. Early application of results to advanced space and reentry programs is found through close interaction of the Aerospace Corporation with the U.S. Air Force. These and other important materials problems provide a challenge to scientific ingenuity in a stimulating research environment. Staff members are encouraged to communicate with the scientific community through professional societies and publications. If you are interested in contributing your talents and participating in research of this nature, please send your resume to:

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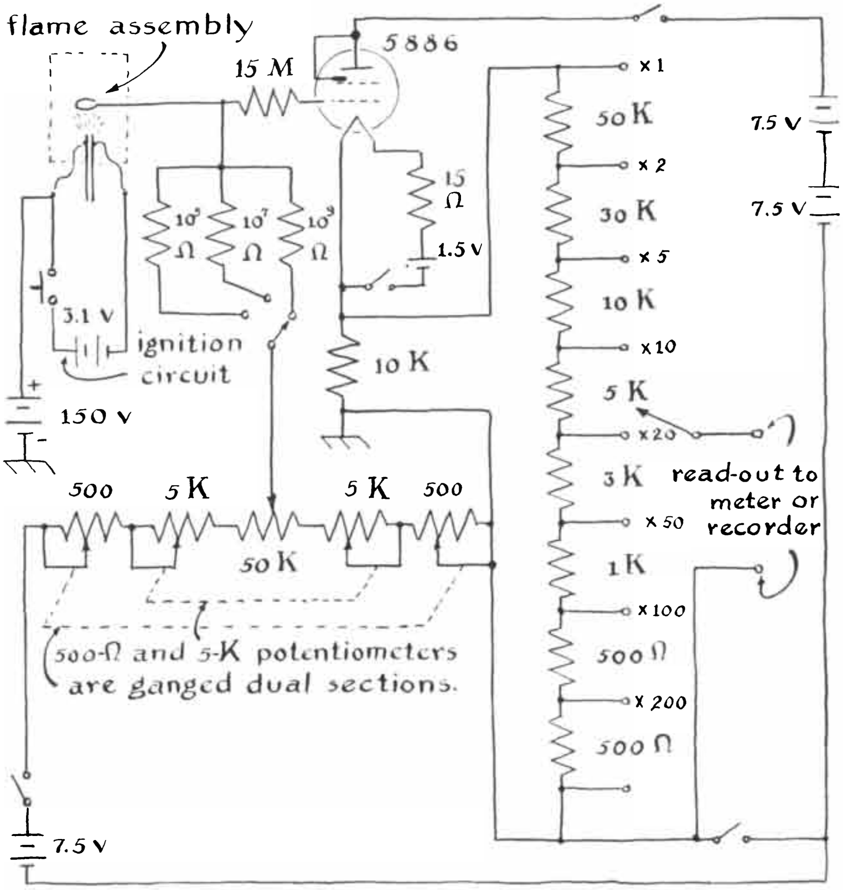

*Electrometer for the chromatograph*

clamped vertically in the end of a *T* fitting by a Teflon bushing, which insulates the tube electrically from the fractionating column. A loop of 20-gauge Nichrome wire, about 3/16 inch in diameter, is centered horizontally about 1/4 inch directly above the flame. This wire, which functions as a negative electrode, is also insulated from the fractionating column by Teflon bushings; they are supported by a metal housing that shields the flame both electrically and from drafts.

"During operation a potential of 150 to 200 volts is applied between the flame and the loop. The heat of the tiny flame breaks some of the molecular bonds of the gases and thereby ionizes the substances more or less, depending on their nature. The electrical conductivity of the path between the flame and the loop varies in proportion to the ionization of the burning materials. Conductivity of the path is measured continuously by a meter, the movements of the pointer indicating the passage of each substance through the flame. The response of the meter does not identify the substance but merely indicates its passage. Substances must be identified by passing known materials through the fractionating column and observing the rate and sequence in which they emerge. Known materials can then be added to unknown specimens; identification is established by comparing the performances.

"The housing of our burner was made of brass tubing 3/4 inch in diameter. The ends were closed by caps made of slightly larger tubing that telescoped over the 3/4-inch stock. Disks cut from sheet brass were silver-soldered to 1/2-inch lengths of the larger tubing to complete the caps.

"The base of the housing involves a bit of fussy construction. Openings must be made for admitting an air supply, the burner assembly and electrical connections [*see bottom illustration on page 284*]. A brass compression *T* clamps the Teflon bushing, which in turn supports the hypodermic tubing, as previously mentioned. The fractionating column is connected to the opposite end of the crossarm of the *T*, and the hydrogen supply enters the burner through the leg of the *T*. The burner is inserted into the housing through a centered hole in the bottom, and the air supply occupies an adjacent hole.

"We equipped the burner with an ignition wire—a handy but nonessential

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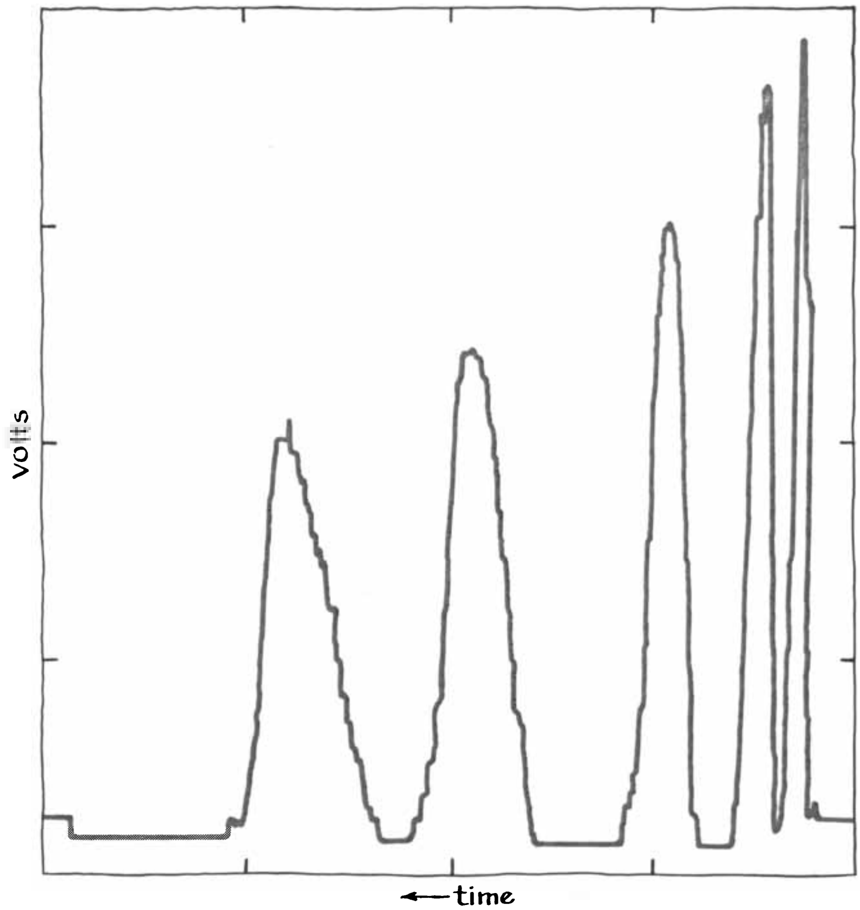


*Instrument's analysis of mixed solvents*

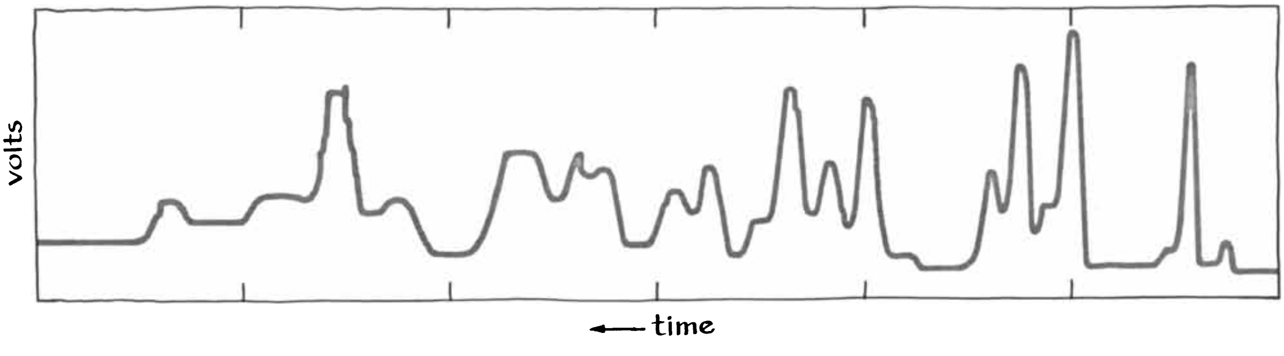
feature. The gadget consists of a two-inch length of 24-gauge Chromel wire, silver-soldered at its center to the hypodermic tubing about 1/8 inch below the tip. Gas is ignited by connecting the heater wire momentarily to a source of three volts. The flame could be ignited almost as conveniently by lifting the top of the housing and using a match, but Bob thought it would be fun to devise the ignition circuit. It was. The polarizing voltage required between the burner and the wire electrode above the flame can be connected to either lead of the ignition wire. The leads are supported by a layer of Silastic Bathtub Calk in the bottom of the housing. The calk also serves as electrical insulation. Teflon insulation was used exclusively in the construction of the burner for our high-sensitivity instrument.

"Special care must be taken to insulate the wire-loop electrode. In effect it picks up the weak signal generated by the flame. Spurious electrical leakage between the loop and the ground can generate 'noise' that may mask the desired signals. The loop for our low-sensitivity instrument was made from a short length of Nichrome wire that we stripped from a discarded 1,000-watt heating unit. Insulators were made of three 1/4-inch lengths of 1/4-inch Teflon rod. The plastic pieces were drilled axially and slipped over the wire like widely spaced beads. The assembly was then inserted into a length of 1/4-inch brass tubing that we had previously silver-soldered into a 1/4-inch hole in the side of the housing at a point that brought the loop 1/4 inch above the flame. For our high-sensitivity instrument we substituted a loop of platinum wire for the Nichrome.

"A supply of compressed hydrogen for the burner can be bought in a cylinder, but we prefer to generate our own gas by the electrolysis of water. Gas so obtained is less expensive, more convenient and much safer than compressed gas. A small leak in a supply of compressed hydrogen can be ignited accidentally, and the fire may escape notice because the resulting flame is almost invisible. Yet the heat is so intense that an accidental fire can lead to disaster. Leaks that do not catch fire may collect in pockets of potentially explosive gas that is both odorless and colorless.

"The design of the hydrogen generator can be varied according to the materials available. The construction requires a container, preferably of glass, for holding 25 ounces or so of electrolyte, which consists of a 15 percent solution of potassium hydroxide in distilled water. (A solution of this strength is caustic and may cause a painful burn if it comes in contact with the skin.) Two electrodes of stainless steel are immersed in the caustic solution and energized from a source of 12 volts, direct current. Our generator draws about two amperes and is energized by a battery charger.

"The negative electrode, at which hydrogen is liberated, is enclosed by a glass tube about 3/4 inch in diameter. Oxygen is liberated at the positive electrode, which is located outside the glass tube, and escapes into the air. The top of the 3/4-inch glass tube is connected through a rubber stopper to a filter containing



*Analysis of gasoline*

silica gel, which separates the gas from a fine mist that rises above the electrodes [*see illustration on page 285*]. The filtered gas is fed directly into the burner of our low-sensitivity instrument.

"We used a one-liter graduate for the container, but any slender bottle with a wide mouth could be substituted. Electrodes were made by winding, with stainless-steel wire, a pair of single-layer coils two inches long. One coil fits inside the 3/4-inch tube near the bottom and the other is wrapped around the outside of the tube, also near the bottom. Electrodes of similar size and shape could be made of stainless-steel sheet.

"We insert a loose tuft of glass wool inside the 3/4-inch glass tube just below the stopper to retard the mist that forms above the bubbling electrolyte. We cover the top of the graduate with a mat of the same material to protect neighboring apparatus from the mist.

"If hydrogen is admitted directly to the burner from the generator, the flame will flicker imperceptibly because of bubbles that rise to the surface of the electrolyte and burst. The electrometer of our high-sensitivity instrument responds to the flickering flame as though it were detecting noise. We suppressed the wavering flow by inserting a constriction in the supply line from the generator. The constriction was made by inserting a piano wire about .01 inch in diameter into a length of 1/8-inch tubing and squeezing the tubing in a vise. The wire was then pulled from the tubing, which was inserted into the supply line.

"The rate at which hydrogen is generated varies with the voltage applied to the stainless-steel electrodes. We control the rate by a rheostat made of a short length of Nichrome wire and a battery clip. The Nichrome wire is connected to one lead of the battery charger; the clip is connected to one of the stainless-steel electrodes. The rate of gas production is adjusted by attaching the clip to selected points along the wire. The proper voltage depends on the geometry of the electrodes. If the voltage appears to be too low to generate an adequate supply of gas, reduce the spacing between the electrodes.

"The burner must also be supplied with air. In the case of our low-sensitivity instrument we couple the output of an aquarium pump directly to the inlet of the burner housing. Any oil-free pump of similar capacity should be adequate. The rate of flow is controlled by a needle valve. For operation at high sensitivity in a laboratory where organic fumes may be present we pass the air

first through a drying tube packed with silica gel and then through a similar tube packed with Linde 5A, a material that functions as a molecular sieve. It is manufactured by the Linde Division of the Union Carbide Corporation, 270 Park Avenue, New York, N.Y. 10017.

"Gas flow into the burner should be regulated to approximately 25 milliliters of hydrogen per minute and 500 milliliters of air per minute. A simple meter for measuring the rate of gas flow is described in the account by Langhoff and Martin. The optimum rate of gas flow through the fractionating column depends on the size of the column. Normally it varies from 10 milliliters per minute in columns of 1/8-inch diameter to 40 milliliters per minute in 1/4-inch columns.

"The output of the flame-ionization detector can be observed most readily by connecting a vacuum-tube voltmeter across the output. Clip one lead of the meter to the fractionating column and the other to the wire-loop electrode of the burner. We used an old meter that was calibrated for a maximum potential of three volts with an input resistance of 11 megohms. A meter designed for lower full-scale voltage indication or with a higher input resistance would in effect have increased the sensitivity of the gas chromatograph. Even so, the old meter worked well for demonstrations and simple analytical work.

"The accompanying graph [*top of page 288*] shows a typical analysis. The graph displays voltage peaks that were generated by the detector when a specimen consisting of 10 microliters of mixed solvents was injected into the instrument. The solvents, in order of elution, were ethyl acetate, ethyl alcohol, n-propyl alcohol, n-butyl alcohol and isoamyl alcohol.

"Plotting output voltages and time recordings simultaneously can be a busy and frustrating job. If a number of test runs are to be made, the experimenter will soon become aware of the advantages of an automatic pen recorder. Commercial pen recorders are priced beyond the reach of most amateurs, and the best expedient might be to build a recorder of the type described in this department by Thomas W. Maskell [see 'The Amateur Scientist,' SCIENTIFIC AMERICAN; July, 1966]. The instrument is relatively inexpensive.

"Maximum advantage of the high sensitivity of our instrument can be realized only if the output of the flame-ionization detector is measured by an electrometer. The electrometer need not be elaborate, because it is not required to measure currents lower than 10 trillionths of an ampere. We use a cathode-follower electrometer with a single vacuum tube [*see illustration on page 286*].

"Care must be taken with certain details of the construction. All insulation on the input side of the electrometer should be of Teflon and all related components must be clean. Avoid touching the insulation or the vacuum tube with unprotected fingers. The tube must be shielded against light, moisture and mechanical shock. All contacts must be clean. We found it important to use switches and wire-wound resistors of the highest quality. All components except special resistors in the megohm range can be bought from large electronic suppliers. We got the special resistors from the Victoreen Instrument Company of Cleveland, Ohio.

"As explained by Langhoff and Martin, the instrument is placed in operation by first turning on the nitrogen, air and hydrogen supplies. Heating current is then applied to the inlet and the burner is lighted. Finally the oven is brought up to a predetermined temperature, say 80 degrees C. in the case of a column filled with Gas Pac W coated with polyethylene glycol 600. After all units of the system have reached normal operating temperature, 10 microliters of a selected specimen are injected into the fractionating column. The analysis will be complete within a matter of minutes.

"Interesting initial experiments usually include the analysis of 'pure' solvents. Exceptionally high sensitivity is not required for detecting impurities in most volatile reagents, although the products are not as impure today as they were a few years ago before manufacturers began monitoring their processes with gas chromatographs. Our high-sensitivity instrument can also be used to analyze volatiles created by the fermentation of yeast. Many interesting features of fermentation can be investigated because the nature of the volatiles depends on such factors as the type of yeast, the composition of the mediums and the temperature of growth.

"Gas chromatography has attracted the interest of workers in several branches of biology, notably for the rapid identification of bacterial cultures, an application that shows great promise. Again, many variables await investigation. The gas chromatograph is among the recent developments in instrumentation. Opportunity for adding to its power as an analytical tool and for using it as an instrument to probe the unknown is by no means closed to the persistent and enterprising amateur."

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# BOOKS

## *Cosmology before and after quasars and the cosmic black-body radiation*

by Dennis Sciama

THE MEASURE OF THE UNIVERSE, by J. D. North. Oxford University Press ($11.20).

I have often wondered what it must have been like to be a nuclear physicist in the early 1930's, particularly in 1932—that *annus mirabilis* which saw the discovery of the neutron and the positron and the first splitting of the nucleus by artificially accelerated particles. Now I think I know. As a cosmologist I have seen in the 1960's a similar stream of discoveries following one on another at an almost indecent rate. The years 1963 to 1965 stand out, beginning with the discovery of quasars, followed by the measurement of the fantastic red shifts possessed by some of them and culminating in what is perhaps the greatest discovery of them all: the cosmic black-body radiation. I should say at once that the evidence is not yet decisive that any of these discoveries has cosmological significance, but it is good enough to have reduced most cosmologists, who are traditionally starved for basic observations, to a state of bewildered euphoria.

These reflections are prompted by the publication of an interesting book called *The Measure of the Universe,* written by J. D. North, an Oxford philosopher. It is a history of modern cosmology that ends just before the new period begins. It barely mentions quasars and does not mention the cosmic black-body radiation at all. This is no criticism, because the book was written too early for it to have done so. It was therefore written at the right time to take stock of the first great period in cosmology. That period, which had only the expansion of the universe to explain, we might justly call the geometrical period. Today we are well and truly launched into the astrophysical period.

To be fair to the early theorists, they did predict the expansion of the universe before it was discovered. By the early 1920's it was clear to Willem de Sitter, Alexander Friedmann and Hermann Weyl that Einstein's field equations of general relativity had as solutions homogeneous and isotropic model universes whose material substratum was in a state of expansion, the relative velocity at which two particles moved apart simply being proportional to their distance (except for refinements for very widely separated particles). Moreover, if the debatable cosmical constant was dropped from the field equations, as Einstein later urged, then *all* the homogeneous and isotropic solutions exhibited expansion (or contraction if one cared to reverse the sense of time). It was not until 1929 that the Hubble law, that the observed red shift is proportional to the distance of a galaxy (as estimated by various more or less dubious criteria), was first stated.

North's book gives a thorough account of this classical phase of theoretical cosmology. There were many controversies at the time about the properties of the various models. That phase is now over, and the correct results are enshrined in standard theory. There were also controversies of a different nature; not everyone accepted the view that general relativity was uniquely fitted to deal with the universe as a whole. Various "heretical" theories were proposed, notably by Sir Arthur Eddington, E. A. Milne, P. A. M. Dirac and Pascual Jordan, and they are described too. I deliberately mention separately the steady-state theory of Herman Bondi, Thomas Gold and Fred Hoyle, because I think it is fair to say that of all the heretical theories this is the one that has irritated and excited the most people, has provoked the most good astrophysics and has more or less survived to the present day.

I say "more or less" because one of the consequences of the new turn of events—of cosmology becoming astrophysical—is that if the red shifts of the quasars are cosmological in origin, and if the universe is filled with black-body radiation, then the chances of the steady-state theory surviving are very small indeed. I want to make clear why this is so, and to discuss what further information we can hope to extract from the new results and their likely future extensions. I must add that for me the loss of the steady-state theory has been a cause of great sadness. The steady-state theory has a sweep and beauty that for some unaccountable reason the architect of the universe appears to have overlooked. The universe in fact is a botched job, but I suppose we shall have to make the best of it.

One of the botches is the existence of a singularity, that is, a moment when the density of the universe was infinite. To be more precise, this is what general relativity requires for the homogeneous and isotropic models to which I have referred. It has sometimes been suggested that the singularity would go away as soon as one admitted that the real universe was neither exactly homogeneous nor exactly isotropic; in such circumstances the galaxies would not move quite radially, and so the matter they are made of would not all have emerged from exactly one point in the past. It has recently been shown by Stephen Hawking and others, however, that the orthodox theory of general relativity, without on the one hand a cosmical constant and on the other assumptions of exact symmetry, still requires the physical properties of the universe to have been singular at some time or times.

It was to avoid such an unpleasant singularity (and for other reasons too) that Bondi, Gold and Hoyle proposed in 1948 a deviation from orthodox general relativity that would allow the continual creation of matter at a rate just compensating for the expansion of the universe. The resulting mean density of the universe (and indeed all its other average properties) would then be independent of time, leading to a steady state that would automatically persist forever. It is this magnificent conception we must now reluctantly abandon.

The first evidence against the steady-state theory came from counts of celestial radio sources, conducted notably by Sir Martin Ryle and his colleagues in Britain, but also by B. Y. Mills and J. G. Bolton in Australia and by M. Ceccarelli in Italy. These counts showed that the number of faint radio sources was far too large compared with the number of bright sources to be compatible with the steady-state theory. This evidence has given rise to much controversy, mainly because the majority of sources concerned have not yet been identified optically. Accordingly inferences drawn from these counts have been surrounded by an aura of uncertainty. A straightforward interpretation, stressed by Ryle and studied in detail by William Davidson and by Malcolm Longair, requires that the radio sources exhibit intrinsic evolution. That is to say, the faint sources, which are mostly at great distances and so are now being seen as they were a long time in the past (because of the time their radio waves take to reach us), must have average properties different from the bright sources, which are mostly relatively near and so are being seen almost contemporaneously with ourselves. Such evolution is of course incompatible with a steady-state universe, but it would be expected in a universe evolving from a dense state to a dilute one, a universe to which one can attach the concept of an age.

Needless to say, there have been several implausible attempts to evade Ryle's argument. My own attempt has turned out to be correct, but not in the way I intended. I proposed before the discovery of quasars that the radio sources in Ryle's catalogue consisted of two different populations. One population was to be the radio galaxies that had already been identified optically and were well known. For the second population I proposed the existence of radio stars in our galaxy, whose distribution between bright and faint sources would explain the anomalous counts but would have nothing to do with cosmology. It has turned out that a second population of starlike (that is, unresolvable) radio sources does exist. Moreover, they are just the ones responsible for the excess of faint sources (as has been shown independently by Philippe Véron and Longair). But these quasi-stellar radio sources, or quasars, have large red shifts and are therefore not the objects I had in mind.

It is true that a few physicists and astronomers (James Terrell, Geoffrey and Margaret Burbidge, Hoyle) hold, with differing degrees of assurance, that these large red shifts are not cosmological in origin, and that the quasars are within, or relatively close to, our galaxy. This would be in tune with my proposal, but I find their arguments unconvincing. If the red shifts have a Doppler origin, that is, if the quasars are receding from us rapidly as a result of a local explosion, the question arises of why we do not see any blue shifts from quasars fleeing from neighboring galaxies toward us. Of course, if quasar emission is a sufficiently rare process, the nearest such galaxies would be too far away for their quasars to be visible, but then why should we be privileged to witness such a rare event so close to us? Clearly this is possible but unlikely.

On the other hand, if the red shifts do not have a Doppler origin but arise, say, from the Einstein gravitational effect, and if the sources are distributed uniformly in space with the ones observed so far quite close to us, then we would not expect the source counts to manifest an excess of faint objects. The relative number of bright and faint sources should be the same as if there were no red shift (that is, the same as for a uniform distribution of stationary sources) and this is not what is observed. We conclude that the red shifts are most probably cosmological in origin. On this basis Martin Rees and I have carried out an analysis of the red shifts of the quasars, and we find again that there are too many faint sources with large red shifts to be compatible with the steady-state theory.

In weighing the significance of what I have said so far it is important to understand how accidental it is that we should be able to observe such large red shifts so easily. Objects with these large red shifts are so distant that the different cosmological theories make substantially different predictions about them, but such objects are visible only because quasars happen to be a hundred times brighter than galaxies. In contrast, the existence of cosmic black-body radiation, which also serves to distinguish among different theories, is intimately bound up with the development of the universe itself.

The detection in 1965 of excess radiation at microwave frequencies (that is, at wavelengths of a few centimeters) and the evidence that it has a black-body spectrum (that is, is in thermal equilibrium characterized by a single temperature) has been described in a recent issue of *Scientific American* [see "The Primeval Fireball," by P. J. E. Peebles and David T. Wilkinson; June]. The temperature observed is about 3 degrees absolute. I should like to make the following comments on this result:

1. No plausible noncosmological explanation has yet been proposed (and not for want of trying).

2. A natural cosmological explanation does exist if the universe was once very dense.

3. A temperature significantly greater than 3 degrees would not be compatible with our general knowledge of radio astronomy and high-energy astrophysics.

I shall say no more about the first point, but I should like to discuss the second and third in a little more detail. As in the case of the expansion of the universe, the existence of cosmic black-body radiation was predicted before it was observed. Around 1950 it was proposed by George Gamow and his associates that the early, dense stages of the universe were very hot, a state of affairs often described as the "hot big bang." Their reason for making this proposal was that in such conditions thermonuclear reactions could occur at an appreciable rate, converting primordial hydrogen into helium and possibly heavier elements. By choosing the right early conditions Gamow was able to account approximately for the abundance of helium with respect to hydrogen that is observed today. This helium problem is actually in a very confused state at the moment, but the important point here is that if the early, dense stages were hot, unquestionably there was ample time for matter and radiation to come into thermal equilibrium. At that time, then, the radiation would have had a black-body spectrum. Moreover, at all times thereafter the spectrum would remain that of a black body, the radiation simply cooling down as the universe expanded. Gamow's original calculations of helium formation led him to predict for the present temperature of the black-body radiation a value of about 30 degrees absolute, but modern calculations are compatible with a lower temperature, in particular with a temperature of 3 degrees absolute.

As I have mentioned in my third point, we now know that a temperature as high as 30 degrees can be ruled out. Cosmic ray protons and electrons interacting with such radiation would produce effects that could be observed, and they are not. Three degrees is about the highest permitted temperature from this point of view, and 3 degrees is just what has been found. The connection between the microwave observations and Gamow's theory was made by Robert H. Dicke and his colleagues at Princeton University. In fact, they had the bad luck to be setting up apparatus to look for the excess radiation when it was discovered accidentally down the road by Arno A. Penzias and Robert W. Wilson of the Bell Telephone Laboratories.

Can the steady-state theory account for the excess radiation? It would be reasonable to propose that along with the newly created matter there comes into existence newly created radiation; indeed, some such effect would be expected as a result of the creation process itself. But why the observed spectrum should be that of a black body over a wide range of wavelengths is totally obscure. It is therefore critically important to establish without doubt that the actual spectrum is that of a black body. The present evidence is strong but not decisive. Further work is being done, and this point should be settled fairly soon.

There is one final property of the radiation that I want to discuss because it is in some ways its most exciting feature, and that is its degree of isotropy—its uniformity with respect to direction of arrival. Just a few months ago R. B. Partridge and Wilkinson announced that any anisotropy is less than a few tenths of a percent. I have heard cynical scientists comment that this result throws doubt on the whole phenomenon, on the grounds that noise generated internally by the observing instruments would be more "isotropic" than externally generated noise, even noise coming from a highly isotropic universe. To silence this cynicism it is necessary to show that the universe is likely to be isotropic to the required degree. A first step in this direction has recently been taken by Charles W. Misner, who has shown that for a certain class of model universes any initial anisotropy would be rapidly removed by a rather exotic form of viscosity involving the pairs of neutrinos that would be excited by the high temperatures then prevailing. Misner's program is to allow the universe to start out as irregularly as it wishes and then to show that all irregularities would be damped out by the action of accepted physical processes, except for those irregularities we actually observe (such as clusters of galaxies).

Another intriguing aspect of the isotropy measurements is that they can be used to determine our "absolute" velocity, that is, our velocity with respect to the distant matter that last effectively scattered the radiation. Because of the Doppler effect such a velocity would reveal itself by leading to a slightly higher temperature for the radiation ahead of us and a slightly lower temperature for the radiation behind us. The present limit on the anisotropy corresponds to a velocity limit of 300 or 400 kilometers per second. One contribution to the expected velocity comes from the sun's known rotation around our galaxy of about 250 kilometers per second. Even this, however, depends on the correctness of Mach's principle [see "Inertia," by Dennis Sciama; SCIENTIFIC AMERICAN, February, 1957]. According to Mach's principle, the local nonrotating frame of reference as determined dynamically coincides with the frame in which distant matter is not rotating. The well-known rotation of our galaxy, with which is associated the galaxy's dynamical flattening, would then be a rotation with respect to distant matter, and therefore to the effective sources of the black-body radiation.

To obtain our net motion relative to these sources, however, we must also allow for the peculiar motion of our galaxy in the local group of galaxies (which has been estimated to be about 100 kilometers per second) and a possible systematic motion of our galaxy in the local supercluster. This supercluster is believed by some astronomers (Vera Rubin, Gérard de Vaucouleurs, K. F. Ogorodnikov) to be a flattened system of galaxies rotating around the Virgo cluster. I have recently rediscussed our possible motion in the supercluster and arrived at a tentative rough estimate for our net motion through the black-body radiation of about 400 kilometers per second in the general direction of the center of our galaxy.

Future observations of the black-body radiation should be able to test this prediction, and in view of the uncertainty surrounding the notion of a local supercluster I would not be at all surprised to find that it is wrong. My point is simply that yet another new range of problems has been opened up for the cosmologist by the existence of the black-body radiation. We have come a long way in a few years from the geometrical considerations described in North's book, and we can rejoice. Cosmology has at last become a science.

## Short Reviews

THE DOLPHIN SMILE: TWENTY-NINE CENTURIES OF DOLPHIN LORE, by Eleanore Devine and Martha Clark. The Macmillan Company ($7.95). Herodotus himself, the father of history, began the record, and his passage appears at the beginning of this dolphin anthology. He tells of the matchless harpist Arion, threatened with being thrown overboard by the sailors whose ship he had chartered for a return to his own Corinth,

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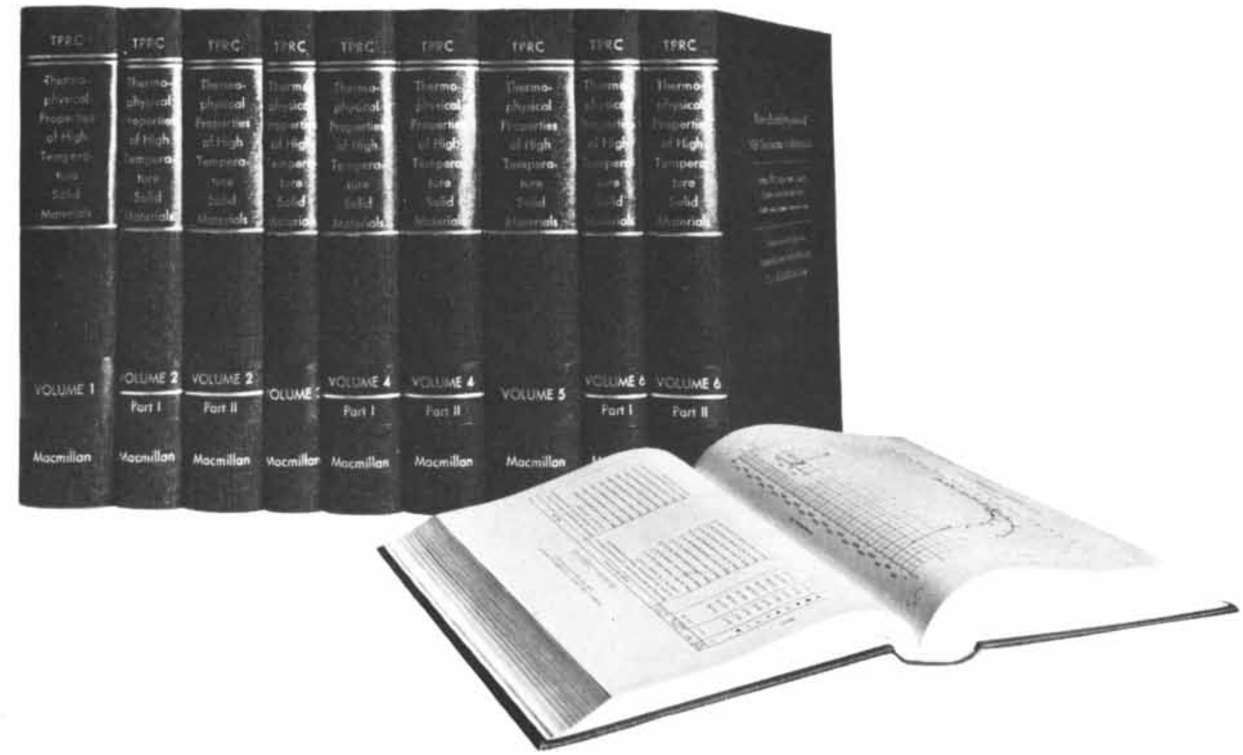

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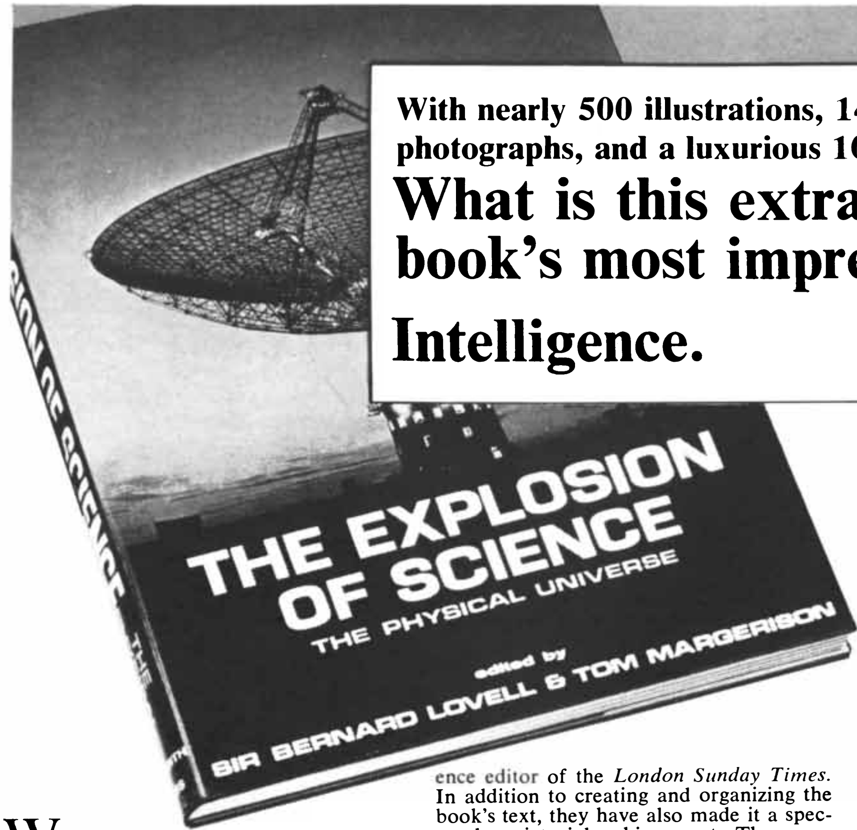
who flung himself into the sea. A dolphin carried him ashore safely. One of the anthologists begins the book by telling of her first dolphin-tow—not, to be sure, in a time of peril but in a pool at Islamorada, all in play. Then you can read of the modern instances, of Pelorus Jack, a beakless Risso's dolphin that for more than 20 years met and accompanied the steamers that crossed Cook Strait on the run between Wellington and Nelson, New Zealand, frequenting a stretch of sea near Pelorus Sound. He would stay alongside the ship for some 20 minutes, always alone, riding the bow wave and rubbing the side. His appearance was not invariable, but it became so regular as to be a successful tourist attraction. Pliny tells of a boy who rode a dolphin at Hippo, the Algerian town of which much later Augustine became the bishop. And in 1955 a dolphin followed small boats, and even took a 13-year-old girl named Jill Baker for short rides in the beautiful harbor of the New Zealand North Island resort of Opononi. The Hippo dolphin was killed by the state; the visitors who came to see were a drain on the treasury. The Opononi dolphin was welcomed for its effect on tourism, but it died within the year, trapped somehow in a shoal pool. There are 100 extracts in this captivating collection, with authors ranging from Homer to Leo Szilard and fact mixed with fancy. The imagist poet Amy Lowell describes the dolphin precisely; that built-in smile and playful movement wins all human watchers to the dolphin. The U.S.S.R. made dolphin-killing a crime in 1966, "for the sake of science"; in the same year the Israeli Fisherman's Union declared "total war" on its coastal dolphins, because they cause great damage to fishnets along that Mediterranean shore. But all sides agree on the cunning and the humor of the dolphin. For those who enjoy the short takes of a well-made anthology, this is a book of wonder and pleasure. One complaint: all the sources are not precisely identified.

DIVISION STREET: AMERICA, by Studs Terkel. Pantheon Books ($5.95). The ethnographers have found a new method in the last few years: the long and intimate interview, tape-recorded and presented in selections of the original language. By a brilliant use of this exacting scheme, Professor Oscar Lewis has built for us out of the testimony of a few people in the slums of Mexico and Puerto Rico a convincing view of an entire culture—the culture of poverty. In this book a gifted semiprofessional—a man whose career has been spent before the announcer's microphone, the disk jockey's turntable and the master of ceremonies' television camera—has tried the same method on a far more complex subject: the whole American urban culture in the year 1966, described by 70-odd Chicagoans. Here they speak, drawn into reflective self-appraisal, into profound commentary on our life and times, by the gentle questions of a patient and opportunistic interviewer, not putting questions but "making conversation." "My world was my city—guerilla journalism." Here are hog butchers and copy chiefs, here the drifters, the nostalgic, the alienated, the smug. The flavor of the word, skillfully transcribed from tape by a real craftsman, Cathy Zmuda, is pungent on the pages.

A house painter: "What did you do before you had a TV set?" "Oh, that's easy. She played a guitar. I played a harmonica.... We got to know each other pretty well. I haven't talked to her since we got the television set.... I don't think it's been detrimental to the kids. ... They know there's more to the world than what's across the street...." A master baker and trained engineer in an automated bakery: "We need skilled pastry chefs badly, because we have to make these cakes originally by hand.... We call this experimental baking.... There are lots of applicants, but nobody can fill the job.... Very few people want to become bakers, craftsmen. If they have the intelligence and dexterity, they try to become engineers." A young editor of a neighborhood paper, a draft-Goldwater man: "No, I wouldn't eliminate war.... Man's got to have hardship and he's got to have drives.... I'm not gonna lose any sleep over the Bomb...." A retired teacher of Greek language and ways: "When I lived in Greek Town here, sometimes ...I would take a trip...to stay a month or so, and then I felt the *nostos* for Chicago. I wanted to come back.... Now, in this neighborhood, to come back to what?" A lady with town and country houses: "I've had the privilege of visiting the Strategic Air Command headquarters. General Power was in command. Seeing that perfectly marvelous nerve center...you feel that we are protected.... Well, I'll tell you...one little remark. Somebody said, 'Do you think Red China will attack?' And he said, 'We should be so lucky.' "

PRINCIPLES OF PHYSICAL OCEANOGRAPHY, by Gerhard Neumann and Willard J. Pierson, Jr. Prentice-Hall, Inc. ($22.50). THE ENCYCLOPEDIA OF OCEANOGRAPHY, edited by Rhodes W. Fairbridge. Reinhold Publishing Corporation



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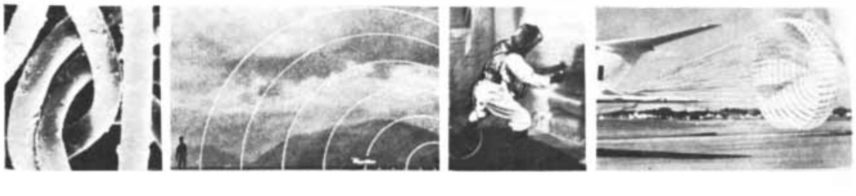

($25). The ocean is vast, and books that set out to present an up-to-date account of our knowledge of the ocean are proportionately large. The first book, by two professors at New York University, is a comprehensive and modern text, aimed at seniors and beginning graduate students. Its domain is the ocean as a physical system: its motions, its energy budget, its surfaces, its quality as a substance and its epistemology—how we learn these facts, deep and dark though they lie. Like any such work, it demands from the reader some mathematical preparation; the laws of mechanics and the differential calculus of hydrodynamics are in the arena. Vectors will help; the authors are careful to include straightforward derivations, or at least plausible arguments, for the considerable mathematics beyond what they call on, notably Fourier integrals. The book is not, however, a mathematical text; the abundant maps of sea and land, the photographs of the FLIP (a horizontal ship in motion and a vertical manned buoy at rest), of the freighter in the Bay of Fundy resting on the bottom at the dock at low tide, give it a scent less of the lamp than of the salt. One striking result can be cited. The heat engine of the sea, unlike that of the air above it, is fed with solar energy not at its level of highest pressure but at its lowest. Such an engine is only inefficiently driven by expanding and contracting fluid. Thus the wind can drive the turbulent surface waters, but the deep ocean—most of the mass—is stirred little by the wind. Much of what does move in it is sinking extra-salty water and rising water of less salinity. The energy is still provided by the sun.

*The Encyclopedia of Oceanography* consists of a couple of hundred rather brief articles covering not only the physical ocean but also the biological one. In addition it covers specific areas in profusion: the Persian Gulf and the English Channel are described from the bottom up. Such topics enter the Neumann-Pierson textbook only as examples. The tides are treated in the textbook with care; the equations are developed and long-series solutions are given. The encyclopedia perforce gives a much briefer and more elementary account, but then it includes a summary table of the tides at many ports.

HELICOPTER AND AUTOGIROS: A CHRONICLE OF ROTATING-WING AIRCRAFT, by Charles Gablehouse. J. B. Lippincott Company ($4.95). The helicopter goes back to the ancient sources: a toy in China, a dream sketch by Leonardo. A model driven by a little steam engine flew in London by 1842. (Wrote George Cayley in 1843: "Very great power in proportion to weight . . . is necessary.") In the days of the Wrights there were plenty of tries at the helicopter. Some more or less flew, if not always forward or higher than a man's head. Control and genuine free flight were not attained until about 1935, partly under the interim influence of the highly successful autogiro, a wingless airplane with a free-spinning rotor. Hundreds of autogiros were built and used all over the world. Trading on the earlier work, the Luftwaffe produced and used practical helicopters by the dozen. It hoped to produce thousands, but bombing canceled its plans. American helicopters—Sikorsky, Bell and Hiller—came into marginal use by the end of World War II. By the time of the Korean war they had achieved military maturity with the "counterinsurgency" tactics that today make the U.S. Army a very large air force. This ugly role—the gunship circling the clearing, firing its modernized Gatlings at the jungle around—is paralleled by a humane tradition of rescue. Perhaps 100,000 lives have been saved, it is reckoned, by helicopters. There is a photograph of the small freighter *Tanda Maru* sinking in a boiling sea with a helicopter hanging overhead, which commemorates a 1955 rescue celebrated in verse: "Thus 14 Japanese seamen were saved./Ah, calm and heroic Lieutenant Gates."

It was not an easy task, either. A helicopter pilot works like an organist, except that his errors are even more apparent. In a typical machine the pilot steers to the left and the right with foot pedals, which control the pitch of the small rear-mounted propeller. His right hand works the cyclic control, a joy stick that moves in all directions, followed by the axis of the large overhead rotor. His left arm controls a collective pitch stick, so that he can climb or descend by pushing or pulling it forward and back to steepen or flatten the pitch of all the rotor blades at once. In that same hand he grips the twist handle that gives quick access to the engine throttle. There is nowadays a servomechanism to link throttle and pitch, but the pilot still exercises a fine control. The final chapters of the book give a good account of helicopter mechanics; the severe strain on the rotor hub, which must from a small central shaft control the forceful motions of the big blades, is made clear. Here is the origin of the high maintenance costs of the present-day helicopter, a topic not ade-

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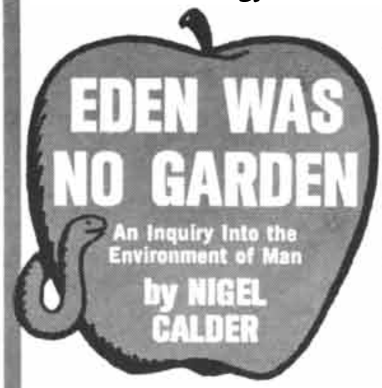

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quately discussed in this otherwise satisfying account.

The Plastids: Their Chemistry, Structure, Growth, and Inheritance, by J. T. O. Kirk and R. A. E. Tilney-Bassett. W. H. Freeman and Company ($17.50). The green of the summer landscape and the reds and yellows of tomato or of tiger lily are not the result of pigment held diffusely in the cells of the plants. On the contrary, all higher plants photosynthesize, and store their carotene and starch, inside certain small organelles within each cell called plastids. The plastid containing chlorophyll is the prototype, the chloroplast; all the others too can be seen to come from a single little layered subcell, handed down at cell division all complete. The plastids are present in the seedling grown in the dark, without their green pigment. They sometimes lose their greenness during plant growth, and the white and green leaf patterns of many a garden ornamental is the result. Plastids are known to make DNA and RNA; they have their own genetics, complete with mutation and some features of independent evolution. Nevertheless, they are by no means independent of the nucleus of the cell they inhabit; their properties are frequently under the control of the nuclear genes. This book is a modern review, containing both a thorough account of the older literature about plastids and a great deal of up-to-date work. Much of it was done by the two authors, whose impetus comes largely from the University of Oxford school of C. D. Darlington. Beautiful electron microscopy, elaborate biochemistry and complex genetics span the study of plastids. In view of the current strength of biology at the cellular level and below it, these important entities, something like symbionts and something like organs of plant cells, are likely to receive keen attention. It is quite possible that one day they will be cultured freely like the bacteria they somewhat resemble. This book does not much concern itself with the molecular biology of photosynthesis or of the other functions of the plastid; it tends rather to deal with the system as a whole. On those terms it is a production of expertise and thoroughness.

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ALGEBRA, by Saunders MacLane and Garrett Birkhoff. The Macmillan Company ($11.95). Late in the 1930's this same pair of authors more or less formed the curriculum in algebra for American mathematics students with their work *A Survey of Modern Algebra,* whose third edition is now a couple of years old. In that work the idea of algebra was taken up on the basis of a general and axiomatic approach, and the student learned that discrete elements that could be combined according to several rules of combination formed the essence of this realm of mathematics. Groups, rings, fields and algebras became common currency; vectors and matrices began to appear as mere portions of a broader topic. The style is quite abstract; one recalls the dismay with which a physics student would find the whole of the algebra of the Dirac matrices as a single exercise in one chapter of MacLane and Birkhoff. This book is a fresh start at the same task, aiming at advanced undergraduates, hoping to introduce them to the still more powerful generalizations of algebra in the 1960's. The old topics are there, taking their places in turn as special cases. Now the generality is contained in concepts as

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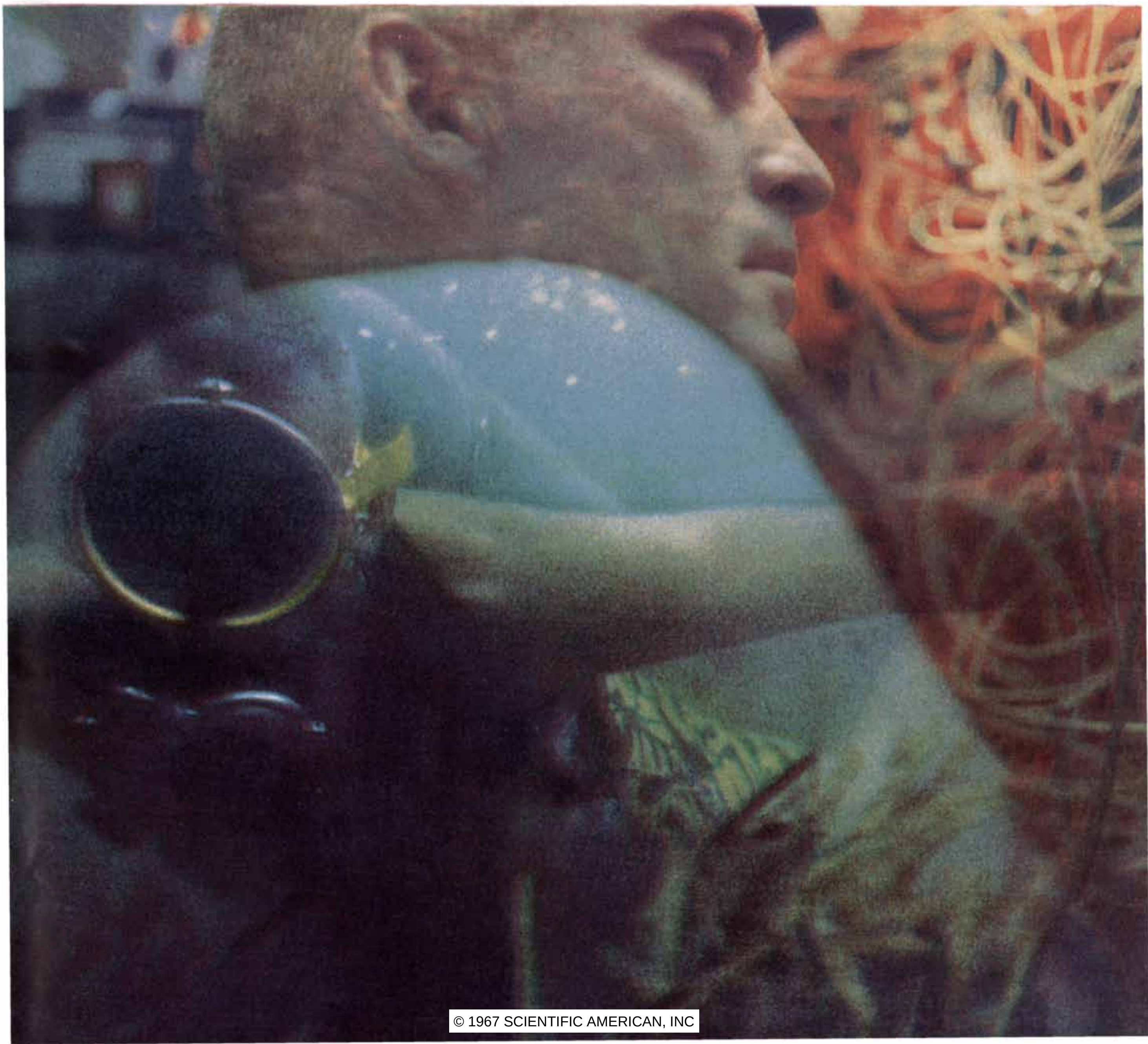

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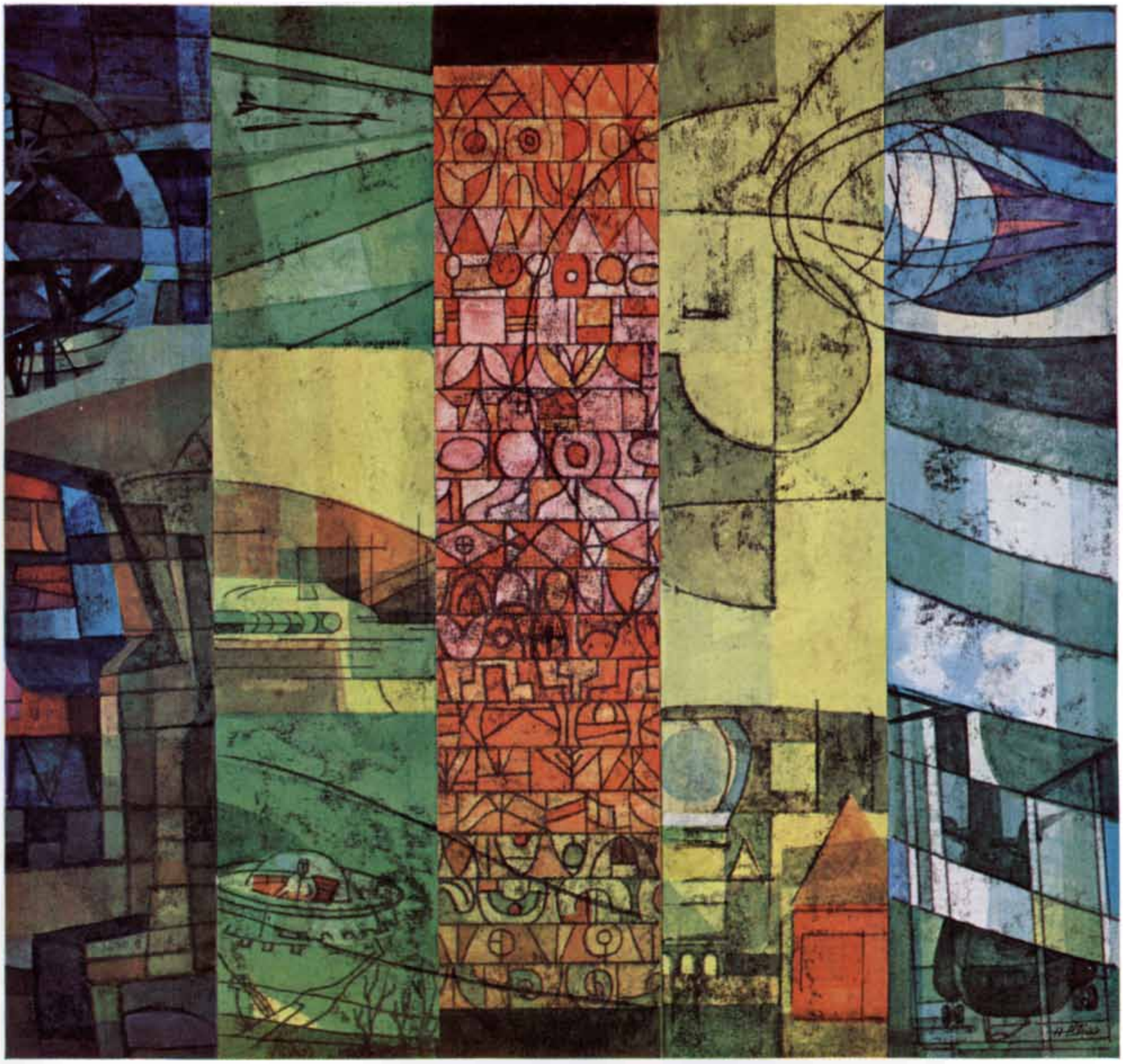

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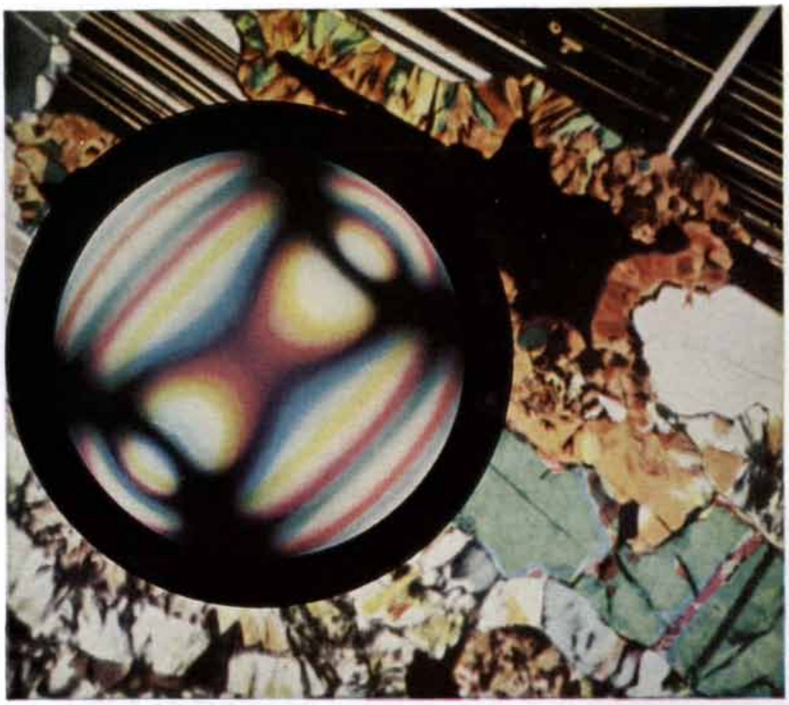

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powerful as that of category—a category is a class of objects together with two particular functions mapping them in certain ways. There is a category of all sets, one of all groups, of all rings and so on. Another powerful concept is functor; such a construction builds sets from given sets and functions from given functions. It acts on all sets and all functions. The study of algebra can be seen once again as a multiple exemplification of a certain essence. Again this is likely to become a widely used text. There are problems every few pages. The algebras of the physicist are fading into special cases of the problems.

INFRA-RED PHYSICS, by J. T. Houghton and S. D. Smith. Oxford University Press ($9.60). The electromagnetic frontier has for more than a decade lain on the short-wave side of the millimeter microwave band and on the long-wave side of the photographic plate. Indeed, physical and analytical chemists have already built a kind of frontier city in the near infrared, populous if a little wild, depending on semiempirical study of the vibrational similarities of polyatomic molecules. Even more remarkable applications, still more or less secret, have come from military explorers seeking to detect distant sources of heat. Room-temperature radiation rises to a peak around a wavelength of 15 microns, the far infrared lies between that region and the microwaves. The best near-infrared detectors are transparent semiconductors, such as lead sulfide, whose conduction levels happen to lie very close to filled bands, so that small quantum energies will set them free. Liquid-helium cooling is a commonplace. There are a variety of ingenious image-forming techniques, used for target pictures and guided missiles, one expects, more than for locating deep tumors.

This volume is a clear summary of the entire field, at the level of a graduate student. It devotes perhaps half of its space to the physics of molecular motions, lattice vibrations in solids and the theory of semiconductors. The other half is given over to a discussion of sources, detectors and applications, and above all to the clever means of dispersive spectrometry necessary in this new optics. The general reader can profit from the more descriptive chapters, but only the reader trained in physics will grasp the relatively complete account of energy levels and phonons and oscillator strengths. The unusual unity of the volume, which treats both molecular and solid-state physics, both instrument design and physical analysis, is its strength and its charm.

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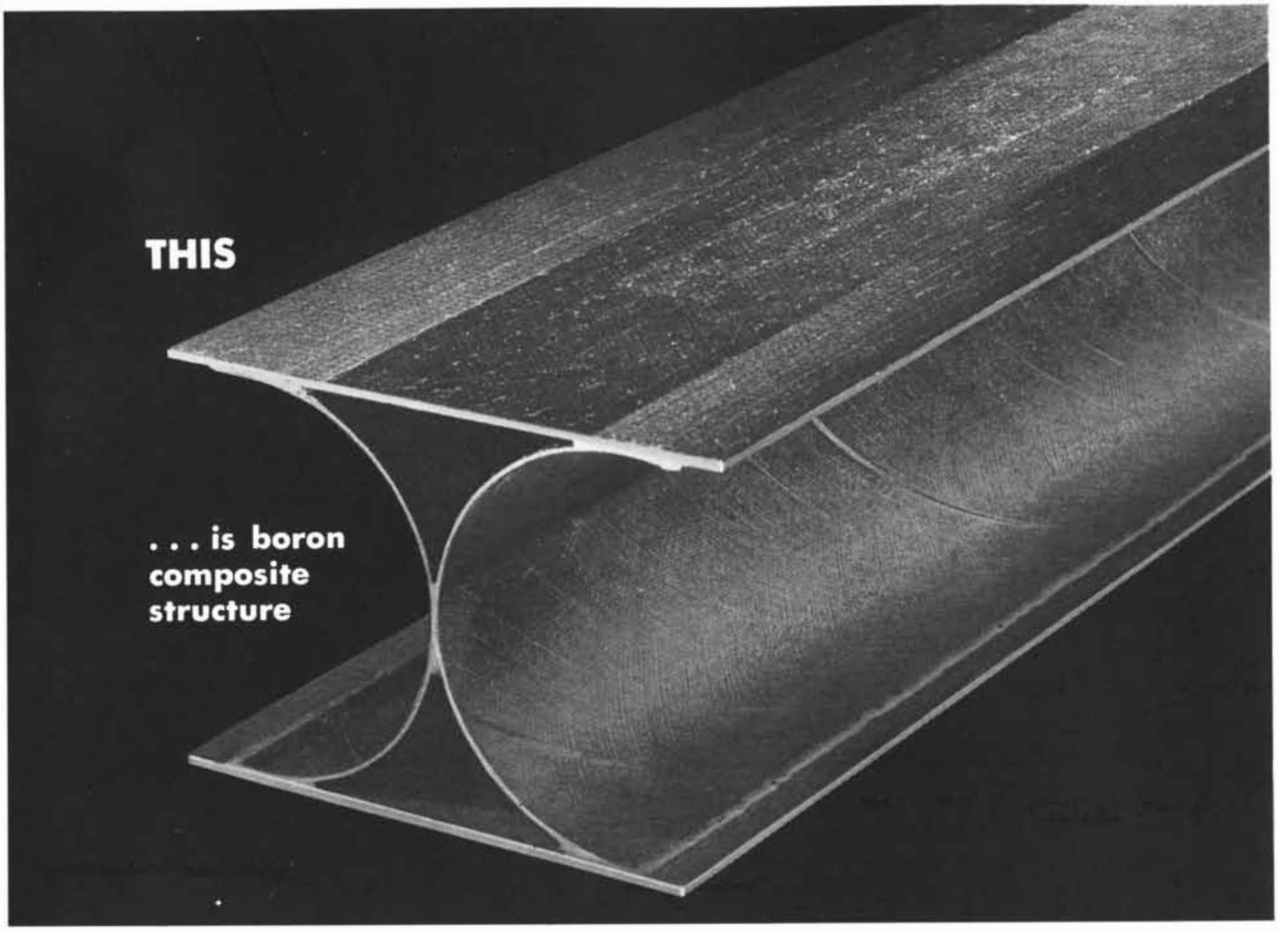
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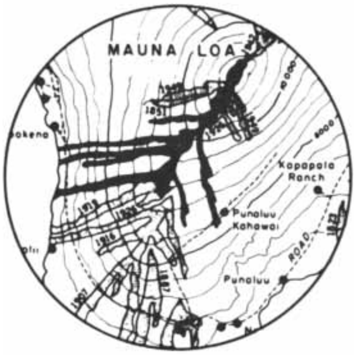

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