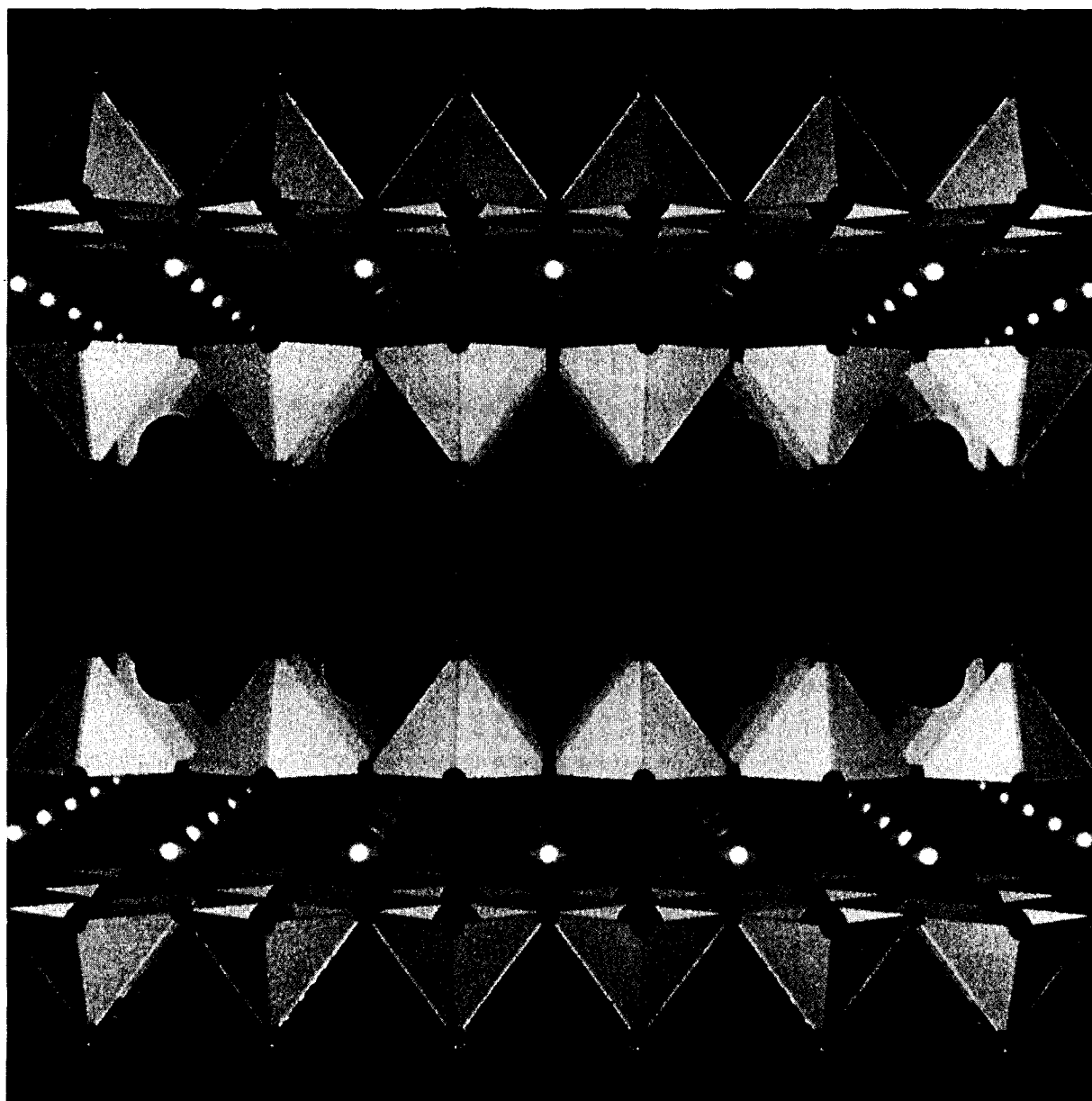#606

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High-Temperature Superconductor belongs to a family of materials that exhibit exotic electronic properties.

Perovskites

Many of the new high-temperature superconductors belong to a family of ceramics called perovskites. The adaptable perovskite structure gives rise to materials that have a wide array of electrical properties

by Robert M. Hazen

L ess than three years ago K. Alex Müller and J. Georg Bednorz of the IBM Zurich Research Laboratory discovered a material that was superconducting at higher temperatures than had ever before been achieved: it offered no resistance to the flow of electricity at temperatures as high as 28 degrees Kelvin (degrees Celsius above absolute zero). Since then other "high temperature" superconductors have been engineered that are efficient at temperatures of 100 degrees K. or more. Exactly why the materials are superconducting remains a mystery, but several groups, including my colleagues and me at the Geophysical Laboratory of the Carnegie Institution of Washington, have shown that the new materials have this in common: they are structurally flawed members of a crystallographic family known as perovskites.

Perovskites, which derive that name from the specific mineral known as perovskite, are ceramics (solid materials combining metallic elements with nonmetals, usually oxygen) that have a particular atomic arrangement. They are the earth's most abundant minerals and have long been of interest to geologists for the clues they hold to the planet's history. They fascinate from a technological point of view as well because, as a group, natural and synthetic perovskites exhibit an array of electrical properties. Whereas a given crystal structure is usually associated with a specific electrical property,

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perovskites run the gamut from insulators (nonconductors) to semiconductors, superionic conductors (in which whole ions, rather than just electrons, flow through the crystal), metal-like conductors and now high-temperature superconductors. Perovskites currently form the basis of a $20-billion-per-year electroceramics industry, a figure that may soon be eclipsed by applications of the high-temperature superconductors.

What accounts for this remarkable range of properties? The flaws in the superconductors suggest the answer: slight modifications of the ideal perovskite architecture often result in new features. There is no one-to-one correlation; a given modification does not automatically produce a particular degree of electrical conductivity. Yet any time the ideal structure is altered, the possibility of new electrical—or other—properties arises.

The Perovskite Structure

In their ideal form perovskites, which are described by the generalized formula ABX_3, consist of cubes made up of three distinct chemical elements (A, B and X) that are present in a ratio of $1:1:3$. The A and B atoms are metallic cations (ions with a positive charge) and the X atoms are nonmetallic anions (ions with a negative charge). An A cation—the larger of the two kinds of metals—lies at the center of each cube, the B cations occupy all eight corners and the X anions lie at the midpoints of the cube's 12 edges [*see illustration on page 76*]. As one might expect, the mineral perovskite (the variety of calcium titanate, $CaTiO_3$, that forms at high temperatures) embodies the ideal structure. Its unit cell, or basic building block, consists of a single cube. The calcium in the A position is larger than the titanium in the B positions, and oxygen fills all 12 of the X sites. The crystal often grows into the shape of a

cube or an octahedron, reflecting the symmetry of the atomic structure.

Someone unfamiliar with crystals might well wonder why a crystal composed of units that have one A ion, eight B ions and 12 X ions is said to have the formula ABX_3 rather than AB_8X_{12}. The reason is that each cube is surrounded on all its sides by other cubes. These share corners and edges, and so any given cube is in full possession of only a fraction of the outlying atoms. When such sharing is taken into account, each cube is considered to have one A atom, one complete B atom and three complete X atoms.

A great many elements can combine to form the hundreds of ideal or modified perovskites now known. Barium, potassium and the rare-earth elements (those from cerium through lutetium, numbers 58 through 71 in the periodic table of the elements) are typical of the two dozen elements that can fill the A position. An astonishing total of almost 50 different elements—more than half of the stable entries in the periodic table—are known to adopt B sites. The X positions can be taken up not only by oxygen but also by members of the halogen family of nonmetals: fluorine, chlorine or bromine. Among the dozens of compounds that are known to conform to the ideal perovskite structure are such diverse chemicals as silver zinc fluoride ($AgZnF_3$), cesium cadmium bromide ($CsCdBr_3$), lithium barium fluoride ($LiBaF_3$), potassium iodate (KIO_3) and europium aluminate ($EuAlO_3$).

Like other ceramics, these ideal perovskites are electrical insulators: all atomic sites are filled, and strong ionic bonds—the attractive forces between the cations and the anions—hold the atoms and their electrons tightly in place. As a consequence electrons move through the crystal only with difficulty. The strong bonds in most ideal perovskites also make them rocklike, scratch-resistant, difficult to

deform and hard to melt. Moreover, the fact that the bonds along each of the three axes of the cube are alike leads to a three-dimensional uniformity of properties known as isotropy: the properties of the bulk material—such as compressibility or electrical conductivity—are the same along each of the axes.

Not all perovskites fit this model of the isotropic insulator, however. A number of them deviate slightly from the ideal in shape or composition and hence are less predictable.

Simple Alterations Abound

Many perovskites are somewhat distorted because the central A cation is too small in relation to the B cations at the corners of the cube. The disparity causes the X atoms, and sometimes the B's, to move out of position.

Crystallographers often visualize such movements by thinking of the ideal unit cell not as a simple cube but as a cluster of polyhedrons [see illustration on next page]. Each B cation, which defines the corner of adjoining cubes, is surrounded by and closely bonded to six anions, one from each of the six cube edges that converge at the corner. The anions define the points of an octahedron. The A cation, formerly viewed as being at the center of a cube, is now considered to be surrounded by eight corner-sharing octahedrons, each of which contains a B cation in the center. When A cations are too small in relation to the B cations, the octahedrons, whose axes are aligned in an ideal perovskite, tilt and twist; the framework collapses around the A cations, lowering the symmetry and potentially altering the perovskite's optical, elastic, electrical and other physical properties. Dozens of different perovskite tilt patterns have been identified.

In tilted perovskites, as in the ideal forms, the B cations may remain at the center of their octahedrons. In some perovskites, however, the B cations are slightly shifted. Such "off-centering" of positively charged cations can give perovskite crystals electrical polarity: one end is positively charged and the
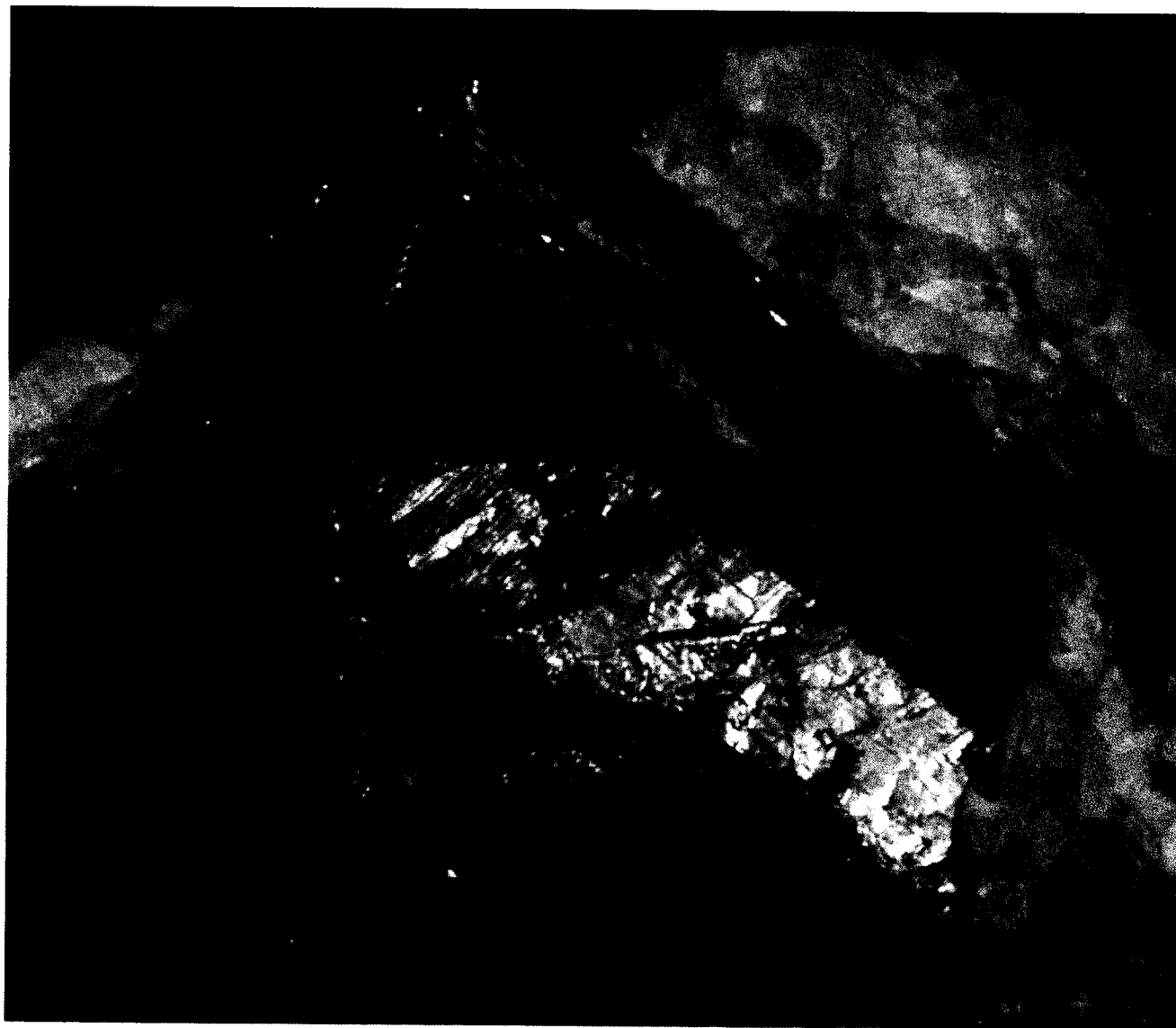
ARCHETYPAL PEROVSKITE (angular chunk) is a rare mineral formed from calcium titanate (CaTiO$_3$) at high temperatures. Other compounds in the perovskite family generally also conform to the formula ABX$_3$, in which A and B are metals and X is a nonmetal. The majority of natural perovskites are electrical insulators, but deviations from the standard formula or atomic arrangement can result in other electrical properties. Perovskite itself is an insulator. It was first described in the 1830's by the geologist Gustav Rose, who named it after the Russian mineralogist Count Lev Aleksevich von Perovski.

other end is negatively charged. Moreover, the direction of the off-centering can often be changed simply by subjecting the sample to an electric field. Materials that are both polarized and able to reverse polarity under the influence of an electric field are known as ferroelectrics and have many applications in electronic devices.

One ferroelectric perovskite—the synthetic compound barium titanate ($BaTiO_3$)—is perhaps the best-known electroceramic in commercial use. Its off-centered cations store and release electrical energy quite efficiently: the stronger the applied field is, the more the cations are energized and displaced and the more strongly polarized the crystal becomes. When the electric field is removed, the cations return slowly to their normal positions and release the stored energy.

Barium titanate is often incorporated in capacitors, the elements in electronic circuits that can smooth out an uneven flow of current. These capacitors can store charge from pulses of current and then release the stored charge between pulses, thereby producing a steady direct current. Barium titanate has also found wide application in voltage-surge protectors for computers: when a surge of electricity (from a lightning strike, for example) reaches the crystal, it absorbs the pulse and dissipates it slowly.

Barium titanate's off-centered cations also contribute to a commercially exploited property known as piezoelectricity. When an external electric field shifts the titanium atoms, the crystal as a whole changes shape: it elongates somewhat. Conversely, mechanical deformation of a barium titanate crystal generates an electric field. Piezoelectricity makes barium titanate valuable in the construction of transducers that convert mechanical energy into electrical energy or vice versa. In loudspeakers, for instance, barium titanate transducers vibrate against a membrane in response to electronic signals, generating sound waves. In microphones such transducers store and then release electrical energy in response to the pressure exerted by sound waves.

Mixed Cations

Perovskites that have off-centered cations or tilted octahedrons often conform to the simple ABX_3 formula. Yet these perovskites and others may also deviate from the ideal composition: their A or B sites can be filled with two or more types of cations. In calcium uranium oxide (Ca_2CaUO_6), for example, calcium atoms take up all the available A sites, but the octahedral B sites are equally divided between calcium and uranium ions. The B cations "order," or strictly alternate positions, throughout the structure, which is tilted because the calcium ions in the B positions are significantly larger than the uranium ions.

The octahedral centers can be filled not only by two different elements but also by differently charged ions of the same element. Barium bismuth oxide, a lustrous bronze semiconductor that is sometimes described by the formula $BaBiO_3$, is such a "mixed valence" perovskite: it has two distinct varieties of bismuth cations, one that has surrendered three valence electrons (electrons in its outermost orbital shell) and one that has surrendered five. The usual designation is therefore $Ba_2Bi^{3+}Bi^{5+}O_6$. As is true for calcium uranium oxide, the octahedrons containing the two types of cations alternate throughout the crystal.

Barium lead oxide ($BaPbO_3$), a black, metal-like conductor, provides a dramatic demonstration of the changes in properties that can result from slight variations in the elements that fill the B positions. By replacing the lead with increasing amounts of bismuth, one can create a "continuous series" of compositional variants from barium lead oxide to barium bismuth oxide. As the composition approaches $BaPb_{.8}Bi_2O_3$ the compound becomes a semiconductor. In addition, unlike either barium lead oxide or barium bis-
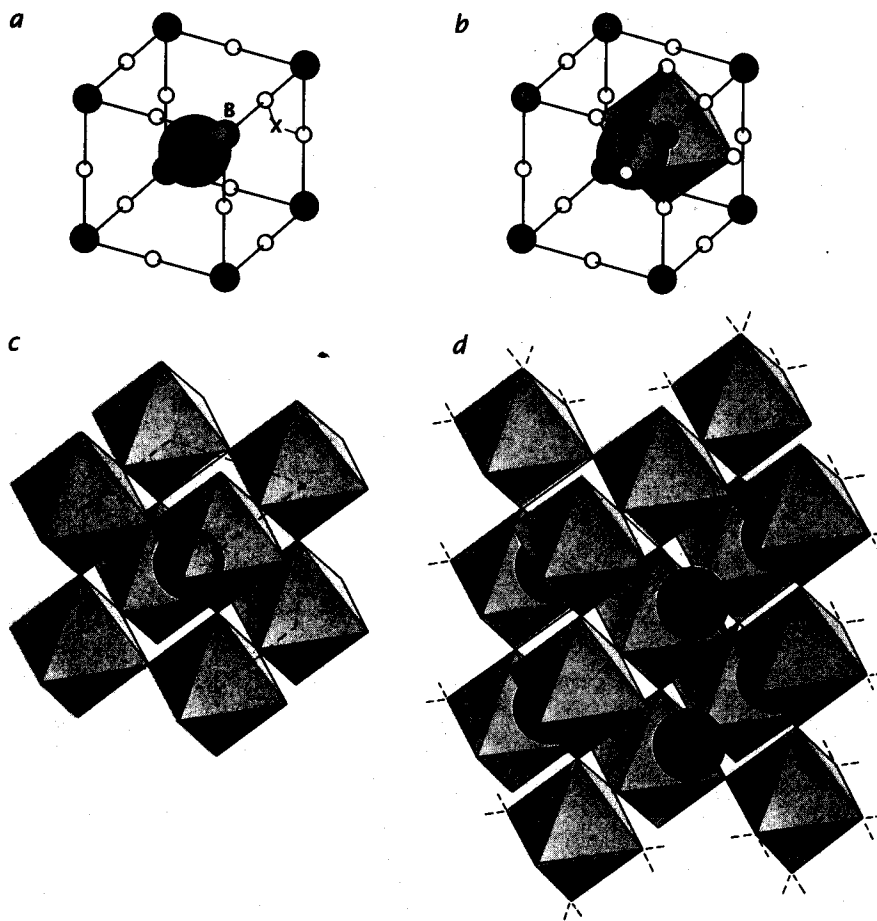
BASIC STRUCTURAL UNIT of perovskites is a cube (*a*). One metallic atom (*A*) lies at the center, eight smaller metallic atoms (*B*) occupy the corners and 12 nonmetallic atoms (*X*) are the midpoints of the edges. The A and B atoms are cations, or positively charged ions, and the X atoms are negatively charged anions. (Perovskites have the formula ABX_3 instead of AB_8X_{12} because each B cation is shared by eight neighboring cubes, and each X anion by four cubes.) Crystallographers often replace the cubic model with a polyhedral one (*b*). The six X anions that surround each B cation and are closely bound to it form the points of an octahedron (*yellow*). In such a model the basic structural unit becomes a group of eight corner-linked octahedrons around an A cation (*c*). The bulk crystal is a continuous network of such groupings (*d*). These polyhedral drawings and the ones that follow are based on computer-generated images made by Ross J. Angel of the Geophysical Laboratory of the Carnegie Institution of Washington, who used a modified version of the program STRUPLO.

muth oxide, some of the intermediate compounds become superconducting when they are cooled almost to absolute zero.

B-cation substitutions are put to work in the commercially important group of perovskites known collectively as *PZT*. The designation encompasses lead titanate ($PbTiO_3$) and the continuous series created when zirconium is substituted for titanium until lead zirconate is formed ($PbZrO_3$). All the *PZT* crystals exhibit a remarkably strong piezoelectric effect (a slight compression can result in the storage and release of 100 volts of electric potential); they are found in a wide assortment of devices, including loudspeaker buzzers, electrical relays, pressure gauges, and spark igniters for lawn mowers. *PZT* crystals of differing compositions vibrate at distinct frequencies in response to an electric field. Television designers have capitalized on this compositional effect and routinely employ several *PZT* perovskites as filters to reduce unwanted noise: the crystals intercept incoming electrical impulses and mask undesirable frequencies.

Multiple *A*'s

Another kind of compositional variation—multiple cations in the *A* positions—may control the properties of the earth's interior. At the Geophysical Laboratory my colleagues and I have intensively studied magnesium-iron silicate ($(Mg,Fe)SiO_3$, which adopts the perovskite structure at pressures of several hundred thousand atmospheres. The parentheses indicate that the proportions of the magnesium and iron filling the *A* sites can vary. Because both magnesium and iron are rather small, the octahedrons that enclose the silicon atoms at the corners cannot remain upright; instead they tilt.

High-pressure studies suggest that magnesium-iron silicate and calcium silicate ($CaSiO_3$), which also adopts the perovskite structure when it is under great pressure, are probably the predominant minerals in the earth's lower mantle, a region extending from a depth of about 670 kilometers to about 2,900 kilometers and constituting more than half of the earth's volume. Studies done on upper-mantle silicate minerals such as garnets, olivines, spinels and pyroxenes show that at the pressures and temperatures of the earth's deep interior these silicates become transformed, combining with other minerals to form rocks that are dominated by pe-

(Mg,Fe)SiO₃
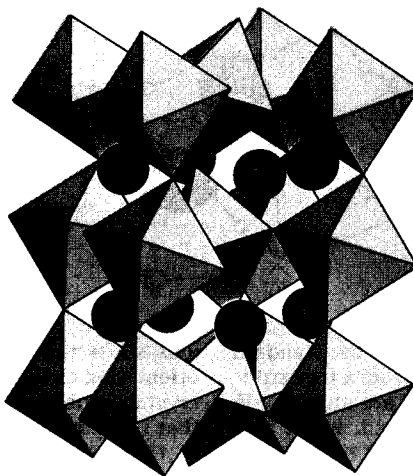
Ca₂CaUO₆
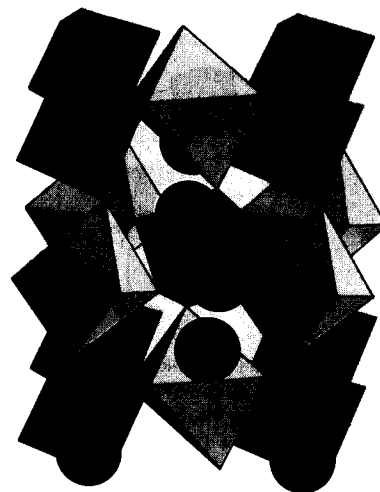
DEVIATIONS from the standard perovskite formula and structure are evident in magnesium-iron silicate and calcium uranium oxide. In the first compound (*left*) two distinct elements (magnesium and iron) can fill the *A* position (*blue*), resulting in the formula $(Mg,Fe)SiO_3$. In calcium uranium oxide (*right*) calcium alone fills the *A* position, but it also alternates with uranium in the *B* sites; the compound's formula is Ca_2CaUO_6. In magnesium-iron silicate the octahedral structural units tilt because both kinds of *A* cations are too small to support the silicon-centered octahedrons in a more upright position. In calcium uranium oxide it is the *B* cations that are mismatched: the octahedrons twist out of position because the calcium-centered octahedrons (*yellow*) are significantly larger than the uranium-centered ones (*red*).

Ca₂FeTiO₅.₅
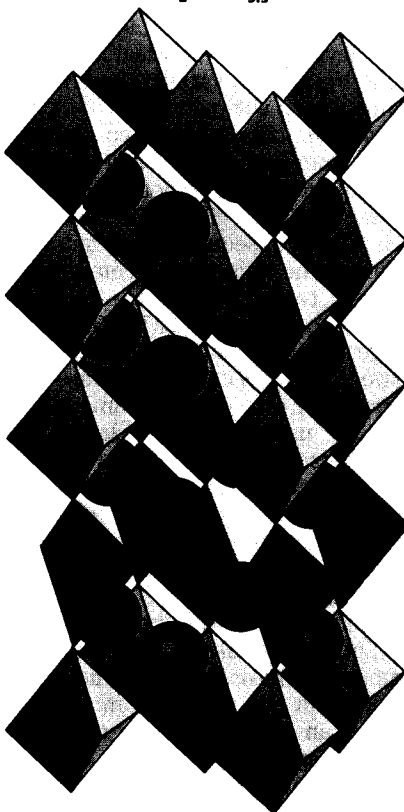
Ca₂Fe₁.₃₃Ti.₆₇O₅.₃₃
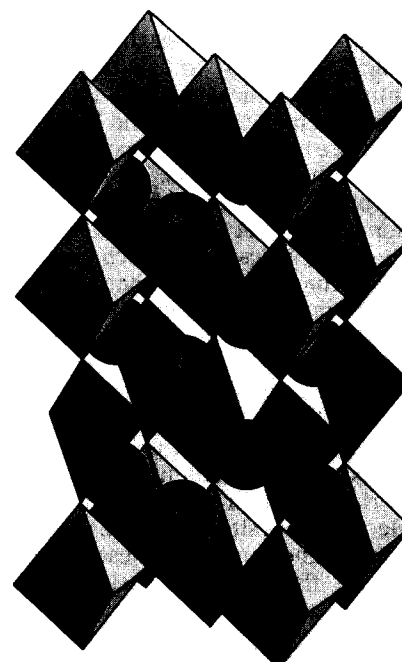
LAYERED STRUCTURE sometimes arises in perovskites that lack a full complement of oxygen atoms. Entire sheets of octahedrons are replaced by smaller polyhedrons. In two of the oxygen-poor compounds that result when iron replaces some of the titanium in calcium titanate—$Ca_2FeTiO_{5.5}$ (*left*) and $Ca_2Fe_{1.33}Ti_{.67}O_{5.33}$ (*right*)—every fourth and third layer respectively consists of iron-centered tetrahedrons (*red*).

a   *b*   *c*
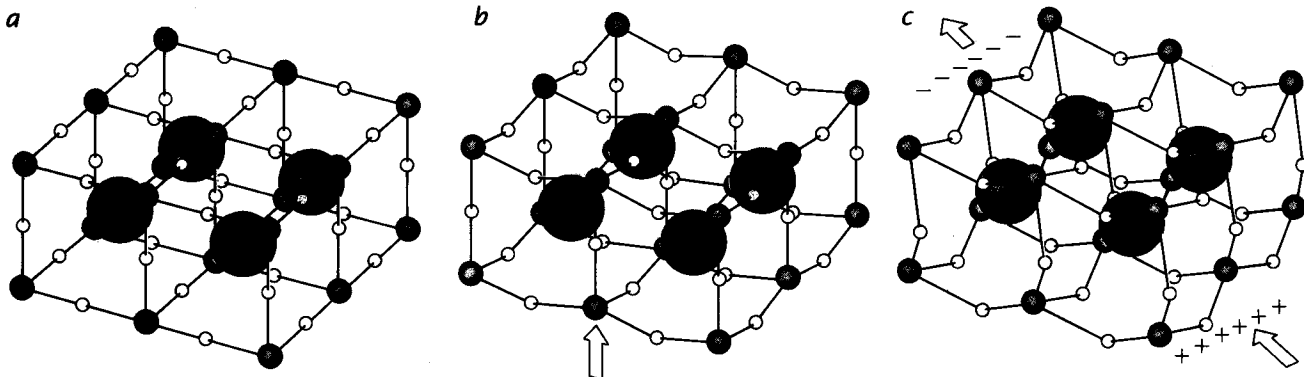
BARIUM TITANATE (BaTiO₃) conforms strictly to the standard ABX_3 formula of perovskites, but it deviates from a true cubic structure (*a*) in that its *B* (titanium) cations are slightly off-center (*b*). As a result the crystal is polarized. When it is subjected to an electric field (*c*), the orientation of the titanium ions shifts toward the negatively charged electrode. As the orientation changes, so does the shape of the barium titanate crystal—a phenomenon that is known as piezoelectricity and that is the basis for many electronic devices. Here the shifts of the titanium atoms are greatly exaggerated for clarity.

rovskite-type magnesium-iron silicate and calcium silicate. The studies also suggest that when the iron atoms in magnesium-iron silicate have a charge of +2, the resulting perovskite is an insulator; when the iron atoms have a charge of +3, however, the perovskite may become a more efficient conductor of heat and electricity.

If silicate perovskites rich in +3 iron are indeed abundant in the lower mantle, the earth might be a better conductor than has been thought. The finding of additional evidence supporting this possibility could make it necessary to reexamine prevailing ideas about the earth's initial temperature, the rate at which it has cooled over time and how quickly it is likely to lose heat in the future. My colleagues and I plan to carry out high-pressure and high-temperature studies in the near future to test such speculations.

Iron and magnesium appear randomly in the *A* positions of magnesium-iron silicate, but such disorder pales compared with what is found in several natural perovskites crystallized from volcanic magma. These rocks, which include latrappite, loparite, leushite and several other related perovskites, incorporate a plethora of exotic elements. As a group they are hosts to calcium, sodium, potassium, yttrium, thorium and all 14 rare-earth elements at *A* sites; titanium, niobium, iron, magnesium, manganese and zinc occupy their *B*-cation positions. The perovskite structure is so adaptable that these minerals act like sponges, soaking up various elements that do not fit readily into other mineral structures. The resulting perovskites are exceedingly disordered: a given sample may contain some 20 different *A* cations and a dozen *B* cations, all

apparently distributed at random in their respective sites.

Added Complexity

No matter how distorted or compositionally varied they are, all the perovskites described above are stoichiometric: they have a total of two cations for every three anions. A variety of other perovskites or perovskite-related structures are nonstoichiometric: they deviate from the ideal ABX_3 formula by having vacant sites where atoms would normally be.

The compounds in the continuous series from perovskite (CaTiO₃) to the oxygen-deficient compound calcium ferrite (CaFeO₂.₅) illustrate well the structural consequences of missing atoms. In the oxygen-poor compounds beyond calcium titanate—such as $Ca_2FeTiO_{5.5}$ and $Ca_2Fe_{1.33}Ti_{.67}O_{5.33}$—the oxygen deficit results in layers consisting of iron *B* cations that are surrounded by four oxygen atoms rather than the usual six. These layers are interspersed with ones featuring normal octahedrons [*see bottom illustration on preceding page*]. The bulk crystal is far from uniform: it grows in flat, platelike crystals, reflecting its layered atomic arrangement.

Such complexities as nonstoichiometry, octahedral tilting, cation off-centering and multiple cations can occur together in almost any combination. Indeed, an infinite number of perovskite variants seems possible, and yet even this picture is incomplete. In a uniform perovskite one can in theory predict the atomic arrangement of one section of a crystal by analyzing another section, even in a crystal that has tilted octahedrons or alternating cations. In reality most perovskites, like

other types of crystals, are nonuniform: they are loaded with defects, random faults that cannot be anticipated. Among the many small defects that can occur are a misplaced cube, an anomalously tilted polyhedron, a layer of one type where another type of layer would normally form, a break in an alternating sequence of cations and point defects, which arise when a single atom is missing or is replaced by an errant element.

Perovskite defects can also occur on a larger scale. For example, in a phenomenon known as twinning, large sections of a crystal may be identical with other parts but oriented in a different direction. (The boundaries of such twins often appear as striations on bulk crystals.) An almost ubiquitous feature of perovskites, twinning is likely to occur in any specimen that deviates from the ideal cubic form, and it can have dramatic effects—favorable and unfavorable—on electrical properties. For example, electric fields can cause twin boundaries to shift, a process that consumes energy and potentially reduces the polarization of ferroelectric perovskites. In order to ensure reliable performance for commercial applications, manufacturers sometimes introduce impurities that have the effect of "pinning" twin boundaries and preventing them from moving. For instance, manganese is routinely added to pin the boundaries in barium titanate, which invariably displays twinning.

Superconductors: Rich in Defects

In no perovskite are the electrical effects of structural variations or crystal defects more striking than they are in the newest perovskites: the high-

temperature superconductors. My intimate acquaintance with these materials began as a result of a request made in February, 1987, by Ching-Wu (Paul) Chu of the University of Houston. Chu and his co-workers at Houston and the University of Alabama at Huntsville had shown beyond a doubt that a substance they had developed was superconducting at a record-breaking temperature, 93 degrees K. They had formed the material by baking a finely ground mixture of yttrium and copper oxides along with barium carbonate, and they knew the ratios of elements in the starting mixture.

Yet they had a problem. The superconducting sample that emerged from the oven was a mixture of two phases, or distinct chemical compounds. A high-powered optical microscope revealed that the dominant phase, making up perhaps two-thirds of the material, was a deep emerald green, was transparent and appeared to crystallize with rounded edges. The other phase was black, opaque, more regular in shape and square-edged; it was suspected of being the superconductor, because all known conductors are opaque. The problem was that the two phases were so thoroughly intergrown that it was impossible to separate them and analyze their composition by routine techniques. Chu needed to know the composition of the superconducting phase before he could attempt to engineer a pure form or to produce chemical variants that might be superconducting at even higher temperatures.

At the Geophysical Laboratory we often analyze "dirty," or mixed-phase, natural and synthetic rocks. Furthermore, we were not engaged in our own hunt for a superconductor and hence posed no threat to Chu's proprietary interests. Our laboratory was therefore a logical place for Chu to turn for assistance. In addition to me, our team included crystallographers Ross J. Angel, Larry W. Finger, Charles T. Prewitt and Nancy L. Ross, geophysicist Ho-Kwang (David) Mao (Chu's initial contact) and chemical analyst Chris G. Hadidiacos.

We proceeded as we would for any fine-grained rock. We attempted to determine the nature of the elements in each phase by means of an electron microprobe, a device that focuses an intense beam of electrons onto a tiny sample. The energetic electrons excite the atoms in the sample and cause each element to emit X rays of a characteristic frequency. We determined the ratios of the separate elements by measuring the proportion of X rays
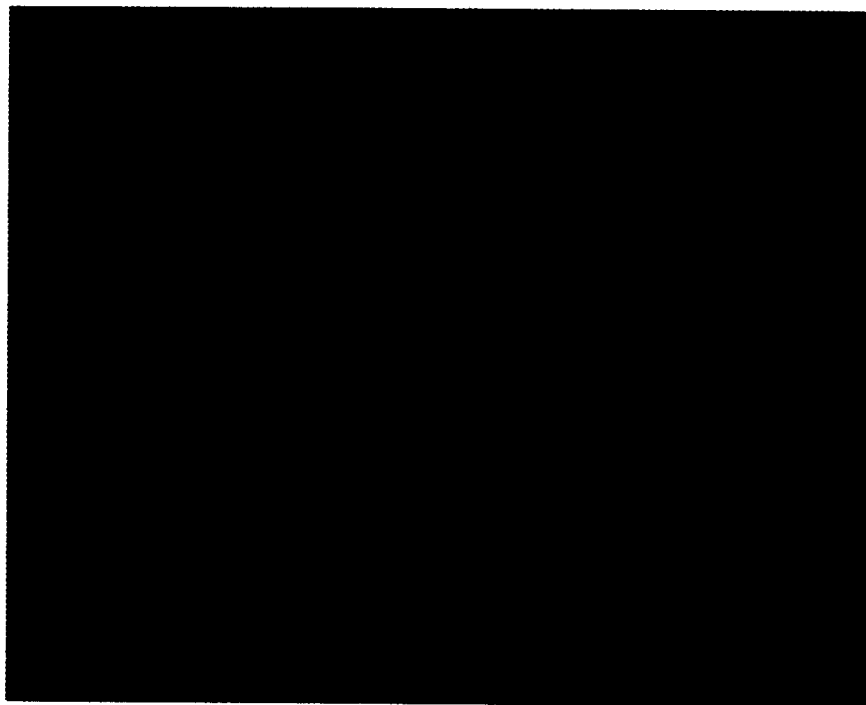
CROSS SECTION of a barium titanate crystal reveals a common defect in perovskites: twinning, or the formation of essentially identical domains that are oriented differently. Here the differing stripe patterns in the two large domains reflect differences in the titanium off-centering that is characteristic of barium titanate. The titanium atoms in adjacent light and dark bands are shifted in opposite directions. The sample, which was provided by Robert D. Shannon of E. I. du Pont de Nemours & Company, Inc., appears purple because it was photographed under polarized light.
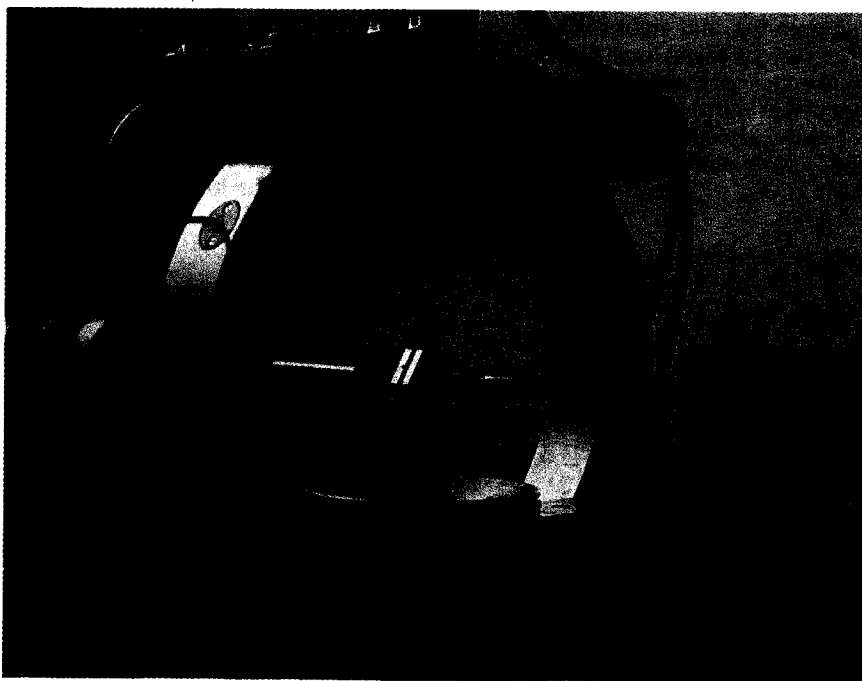
FOUR-CIRCLE DIFFRACTOMETER can provide information about the structure of a microscopically small crystal. The specimen is maneuvered into the desired orientation by two motorized "arcs" that move in a complete circle (inner part of large silver "doughnut" and the central pivot) and by a third arc that rotates the entire doughnut assembly. A fourth arc (arm extending to the left) cradles an X-ray detector to measure the positions and intensities of diffracted X rays. This device helped the author and his colleagues to demonstrate that one of the new high-temperature superconductors—yttrium barium copper oxide, or "1-2-3"—is a modified perovskite.

that were emitted at each frequency.

Although the grain size of Chu's superconductor was almost too small for our instrument, we were eventually able to deduce the elemental ratios of the two phases. Most of the finest grains—presumably the green stuff—included yttrium, barium and copper ions in proportions of 2:1:1 respectively. The important black phase was richer in copper: the metals were present in a ratio of 1:2:3, which accounts for the superconductor's nickname "1-2-3." (It is also called YBCO, pronounced "yibco," for its constituent elements.)

Our principal uncertainty regarding the composition of the black phase was the exact number of oxygen atoms, because the electron microprobe cannot tell us anything about that element. Yet we could make an educated guess on the basis of a well-accepted natural law holding that positive and negative charges in a crystal have to balance. We knew that the charges of yttrium and barium ions are +3 and +2 respectively, that copper ions can have a charge of +1, +2 or +3 and that all three types of copper ion can be present in a compound. Simple arithmetic then indicated that the black material had a total positive charge of from 10 to 16. The charge of an oxygen ion is −2, and so we knew there had to be between five and eight oxygen atoms for every six metal ions. We settled on an oxygen content of 6.5 because the copper in most compounds is in the +2 state. The black phase, then, had the approximate chemical formula $YBa_2Cu_3O_{6.5}$.

X-ray-diffraction analysis soon enabled us to learn something about the three-dimensional arrangement of the atoms. When X rays strike a crystal, they scatter in characteristic directions at distinctive intensities, providing information about the arrangement of the crystal's constituent atoms. Finding a single crystal large enough for study was difficult because the sample was so fine-grained, but we did in the end obtain a few black specks that were between 30 and 40 micrometers (millionths of a meter) in diameter. Counting ourselves fortunate, we glued a single black bit, too small to see with the unaided eye, to the end of a slender glass fiber and irradiated it with an X-ray beam.

We were thwarted at first because every "single" black speck we tried was actually a combination of two or more minute intergrown crystals, which made diffraction analysis difficult. After several false leads we did nonetheless manage to determine that the material in question had a cube-shaped arrangement of atoms, which were spaced at intervals of about 3.9 angstrom units (3.9×10^{-8} centimeter) along each edge. The arrangement was that of a perovskite.

We were delighted and puzzled: delighted because perovskites are one of the structures we most enjoy studying and puzzled because we had never encountered a perovskite with such a low ratio of oxygen atoms to cations. A normal perovskite would have had nine oxygens for every six cations ($A_3B_3O_9$, or three times ABO_3) and not 6.5 oxygens. The lowest ratio known,

in fact, was 7.5 oxygens for every six cations. We realized that this superconducting perovskite was going to have an unusual structure with several missing oxygens.

Our next clue to the arrangement of the atoms came from a search for "superstructure" diffraction effects: diffraction patterns that can indicate whether the unit cell is composed of one cube or more. (Although all perovskites are built from individual cube-shaped units, many have unit cells that consist of two or more cubes, each of which has a different composition or arrangement of atoms.) The pattern we discerned indicated that the basic repeating unit of Chu's black superconductor consisted of three cubes. For convenience I shall speak of the cubes in the unit cell as if they are stacked one above another; they could, however, be arranged in a horizontal manner.

Not as Simple as 1-2-3

The details of the structure began to take shape in our minds [see illustration on opposite page]. We assumed that the relatively large barium and yttrium atoms would fill the A sites, whereas the small copper atoms would occupy the B sites. The superstructure diffraction effects suggested that barium, which is larger than yttrium, was at the center of the upper and lower cubes and that the yttrium was in the middle cube; such Ba-Y-Ba three-cube units would then be stacked one on top of another throughout the crystal. But where did the 6.5 oxygens belong, and which normally filled oxygen sites were empty?

Additional X-ray-diffraction studies revealed part of the answer, albeit grudgingly. For one thing, the scattering of X rays by oxygen, which is a light atom, is difficult to discern in the context of the much stronger diffraction patterns produced by the heavier barium and yttrium atoms. Our task was also complicated by the intergrown nature of our crystals and by the presence of twinning even in the smallest specimens. Nevertheless, after several days of painstaking measurements a pattern began to emerge.

We found evidence for the presence of oxygen atoms in all available sites on the horizontal planes immediately above and below the yttrium atom (at the boundaries shared with the barium-centered cubes). In contrast, oxygen was clearly absent from the vertical edges of the yttrium cube. That settled, we assigned the remaining oxygens to anion positions that were
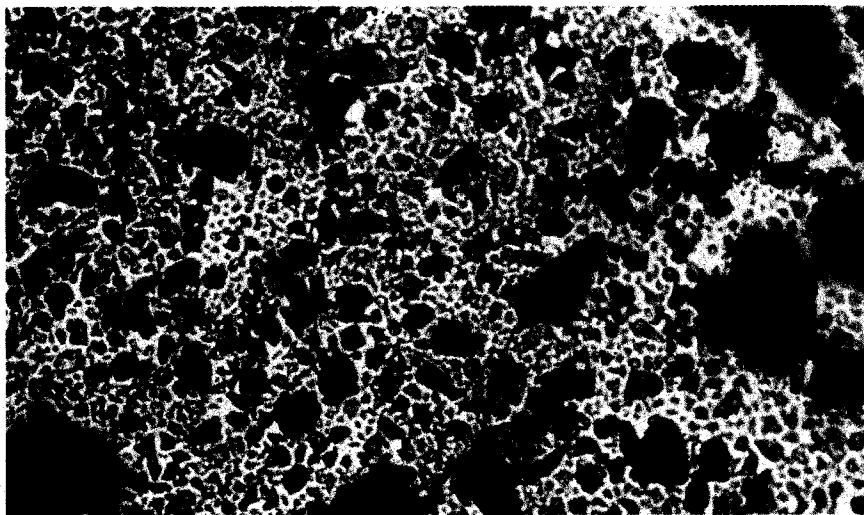
HIGH-TEMPERATURE SUPERCONDUCTOR known as 1-2-3 (*black crystals*) was originally produced together with an extraneous substance (*green crystals*). In 1987 at the request of the material's developer, Ching-Wu (Paul) Chu of the University of Houston, the author and his colleagues began the laborious process of separating the two substances and deciphering their chemical compositions and structures.

a   b   c

Cu

OXYGEN

OXYGEN

OXYGEN
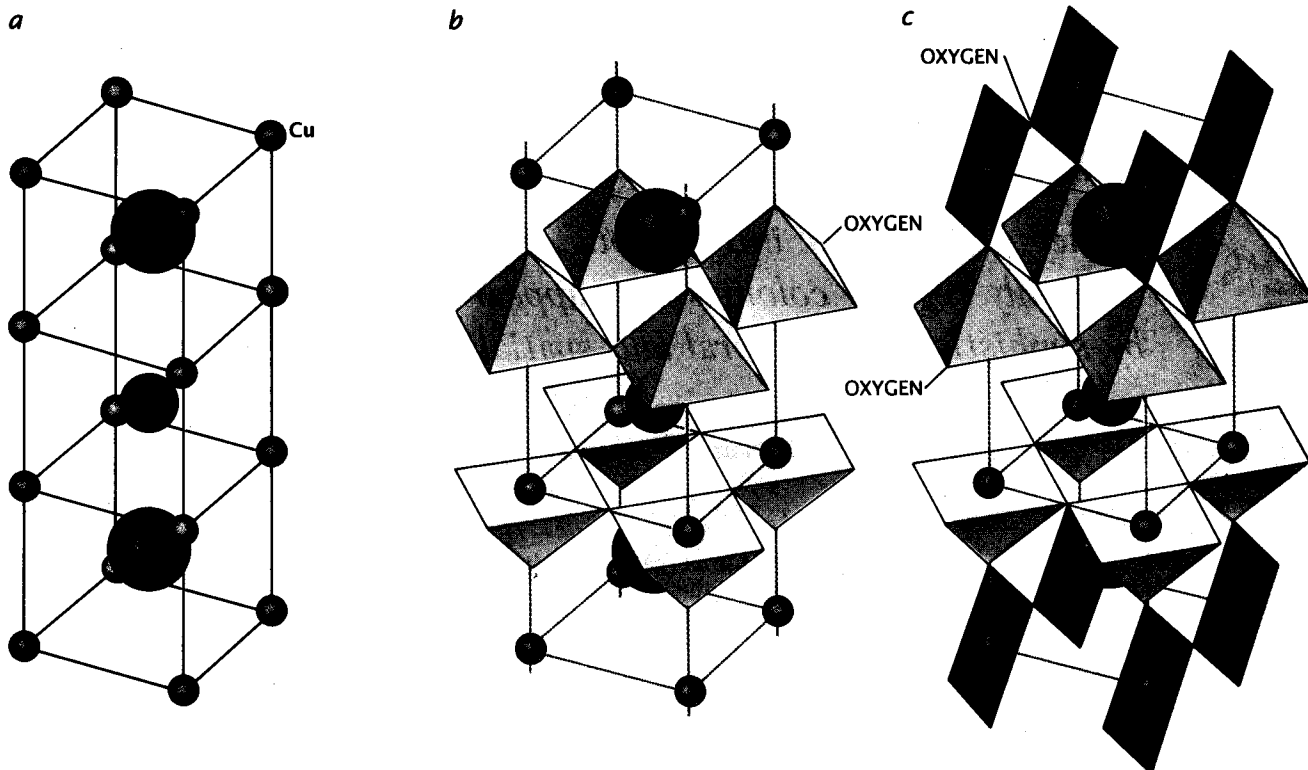
STRUCTURE OF 1-2-3 was determined in stages. Early studies showed that the unit cell, or smallest repeating unit, of the superconductor consists of three cubes (a). Copper (Cu) fills the B sites; barium (Ba) occupies the A sites in the outer cubes and yttrium (Y) occupies the A site of the central cube. But where were the oxygens? Later work showed that 1-2-3 has two main variants. Both lack oxygen on the vertical edges of the yttrium cube, but the variety that is poorer in oxygen, $YBa_2Cu_3O_6$ (b), also lacks oxygen in the horizontal planes at the top and bottom of the unit cell. The copper atoms in those planes are in linear coordination: each is tightly bound to one oxygen above it and one below. The other type, $YBa_2Cu_3O_7$ (c), is a better superconductor. Two oxygen atoms lie in both the top and bottom plane, and so the copper atoms in those planes fall at the center of squares formed by four oxygen atoms. Another model of $YBa_2Cu_3O_7$ appears on the cover of this issue.

still "open" in the two barium cubes, leaving about half of those positions unfilled so that on the average each unit cell had a total of 6.5 complete oxygen ions.

Several weeks later workers at the Argonne National Laboratory, employing a technique known as neutron-powder diffraction, determined the specific positions of the remaining oxygens. They also showed that 1-2-3 could have as many as seven oxygen atoms. Indeed, it is now known that yttrium barium copper oxide sometimes includes six oxygens, sometimes seven and sometimes a fraction in between. Apparently it is the more oxygen-rich varieties that are superconductors.

In addition to being highly deficient in oxygen, 1-2-3 is also an unusual perovskite in that the oxygen atoms near the barium cations can, with time, hop back and forth between anion sites in the same plane, altering the crystal structure. Moreover, the presence of many empty anion sites allows the material to take in extra oxygen atoms when the oxygen content of the environment increases.

Of particular interest is the finding that the copper atoms are not surrounded by the usual octahedral cages. Instead they are mostly in fourfold square-planar or fivefold square-pyramid coordination: they are closely bonded to the four or five surrounding oxygen atoms, which form a square and a square-based pyramid respectively. In both arrangements the copper atoms lie in the same plane as the square. Since 1-2-3 and other high-temperature superconductors are superconducting in directions parallel to the copper planes, many theorists now believe this unusual planar arrangement contributes to the remarkable electronic properties of the materials. Exactly how it does so remains to be clarified, however.

In spite of its unique features, 1-2-3 has many of the characteristics of other nonideal perovskites, such as ordered cations, missing oxygen atoms, layering, twinning, numerous point defects and errors in the order of stacked layers. Such deviations underscore the formidable challenges perovskites present to anyone who attempts to analyze them or engineer custom-made varieties. Yet, as the superconductor story strikingly demonstrates, the deviations that challenge also provide tremendous opportunity for the development of revolutionary electronic materials.

FURTHER READING

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