Ternary Compounds: A Promising Way to Make Superconductors

The announcement last month of a novel class of superconducting compounds is calling attention to a fresh approach to the search for new improved superconducting materials that can operate at higher temperatures and in higher magnetic fields than existing alloys and compounds. The new superconductors are called ternary compounds.

Superconductors are metallic materials that lose, when they are cooled to a sufficiently low temperature, all resistance to the passage of a direct electrical current, at least insofar as anyone has been able to measure it. The first superconductors were metallic elements. At present, the technologically most useful superconducting materials are either binary compounds or alloys. Comprising three elements, ternary compounds form superconductors with properties not possessed by any of the constituents or by binary compounds made from any two of them. The hope is that eventually researchers will find a ternary superconductor that can outperform the binaries.

So far, the importance of the ternary compound concept is more philosophical than practical. Because of the ternaries' complex crystal structures, researchers can substitute different elements into a given material without changing its structure drastically but with sometimes dramatic changes in its properties. One physicist characterized this ability to make numerous new compounds from one basic starting structure as doing organic chemistry with metals. And even if no practical superconductor ever resulted from the study, such elemental substitutions provide as nearly an ideal way as yet available to sort out the physical mechanisms responsible for superconducting behavior. This knowledge could, in principle, be applied to other systems of compounds to optimize their behavior for practical application.

In the back of everyone's mind, of course, are the practical applications of superconductors. Depending on the material, the transition from normal metallic behavior to superconducting takes place at temperatures ranging from less than 1° to about 23°K. These temperatures are so low, however, that superconductors require expensive cryogenic techniques to operate. The ultimate aim of researchers has been to discover a superconductor that can readily be used with liquid hydrogen, rather than the less abundant and more expensive liquid helium, as the coolant. A transition temperature of 30°K or more would satisfy this goal.

One of the most important uses of superconductors in an energy-conscious world may be as wires that can carry enormous electrical currents without loss of power. Applications that could make use of this ability include highly energy-efficient electrical power transmission lines, electric motors and generators, and magnets. In the latter category, large magnets for magnetic confinement fusion power generators and even larger ones for electrical energy storage are seen as future technologies. At present, however, small research magnets for laboratories constitute the biggest market for superconducting devices, although the next generation of accelerators for studying elementary particles could well require magnets that are built from superconducting wires.

It is as a material for magnet wires that a ternary compound may someday see use. One such compound formed from lead, molybdenum, and sulfur has, for example, been measured to have a critical magnetic field of about 60 tesla, about 50 percent higher than that obtainable in previous materials. The critical field is, for many applications, just as important a parameter as the more publicized superconducting transition temperature. Magnetism is a traditional foe of superconductivity in the sense that the presence of magnetic fields depresses the transition temperature, and, when in a field equal to or greater than the critical field, the material never becomes superconducting at any temperature. The critical field therefore limits the strength of the field that can be generated by a magnet made of superconducting wires.

Rhodium Boride Compounds

The discovery of the new class of ternary superconductors was made by Bernd Matthias of the University of California at San Diego (UCSD) and Bell Laboratories and his co-workers at Bell Labs. The compounds found by this group comprise any one of several rare earth elements, rhodium, and boron and have the general formula $RERh_4B_4$, where RE is the rare earth.

Although it is still too soon to know whether any of the rhodium boride compounds or new ones derived from them will lead to superconductors having higher transition temperatures or higher critical fields than those existing at present, the new ternaries already are exhibiting a variety of intriguing properties. Among these are (i) superconductivity occurs in compounds made from constituents that with only two exceptions are not superconductors themselves, nor are any of the binary compounds made from them superconducting; (ii) superconductivity takes place in a crystal structure not previously known to exhibit this behavior; (iii) superconducting transition temperatures are astonishingly high (ranging from 2.5°K for a ternary containing samarium to 11.9°K for one containing lutetium) in view of the usually destructive effect of rare earth impurities on superconductive compounds or alloys; and (iv) an $ErRh_4B_4$ compound turns out to be superconducting when cooled to 8.7°K but becomes magnetic and loses its superconductivity when cooled further to 0.9°K.

The new compounds are exciting in another way as well. Normally, superconductors are discovered after researchers have synthesized a new material and determined its crystal structure and basic properties and later test it for superconductivity. In the present case, Matthias, Ernest Corenzwit, and their colleagues at Bell Labs used superconductivity as a screening tool for detecting new solid phases. When new materials are prepared from mixtures of several elements, two or more phases, each with a different crystal structure and composition, can coexist. If one of these is superconducting and is extensive enough to provide a continuous path for electrical current through the sample, then a test for superconductivity becomes a sensitive probe for the new phase.

The search for ternary superconductors had its origin in Matthias' conviction that present binary materials were unlikely to undergo more than incremental improvements in their properties, and that such dramatic advances as a superconductor that could operate in liquid hydrogen rather than in liquid helium coolant would require a new approach. Ternaries seemed to be that approach, if for no other reason than there was little other choice.

Early entrants in the ternary sweepstakes were the so-called Chevrel phases, named after a French graduate student at the University of Rennes named Roger Chevrel, who, along with Marcel Sergent and Jacques Prigent, synthesized these compounds and studied their structure. These molybdenum sulfide ternaries had the general formula $M_xMo_6S_8$, where M stands for a metal and x is a number near 1. The researchers found numerous metallic elements that could be incorporated into the structure but did not test for superconductivity.

Soon after, Matthias' group found that many of these compounds were also superconducting. The highest transition temperature found was 13.2°K (later raised to 15°K) in a compound with lead as the M constituent. The discovery of the superconductivity set off a period of intensive investigation of these compounds. Some rather startling properties were uncovered as a result.

The first surprise came when Øystein Fischer and his colleagues at the University of Geneva, in collaboration with the group at Rennes, learned that they could make superconducting ternary molybdenum sulfides with rare earths as the metal constituent. Having the same general formula as before, $RE_xMo_6S_8$, these compounds were radically new in that they were the first superconductors to have paramagnetic rare earths as essential constituents. In the past, researchers adding paramagnetic rare earth impurities to superconductors had found that these additions always increasingly depressed the transition temperature as more and more impurity was added. The highest transition temperatures were, however, observed in compounds containing rare earths that were not paramagnetic. One such compound containing ytterbium had a transition temperature of 8.6°K. More recently, Robert Shelton and his associates at UCSD made a series of rare earth molybdenum selenide superconductors, most of which had even higher transition temperatures than their sulfur analogs, the highest being 11.4°K for a compound containing lanthanum.

In a second surprise, two groups, one headed by Fischer at Geneva and the other by Simon Foner at the Massachusetts Institute of Technology's National Magnet Laboratory, reported obtaining critical fields for some of the molybdenum sulfide ternaries containing lead of the order of 60 tesla despite their moderate transition temperatures of between 14° and 15°K. This finding of a high critical field was surprising because, in previous superconductors, high critical fields had been associated with high transition temperatures.

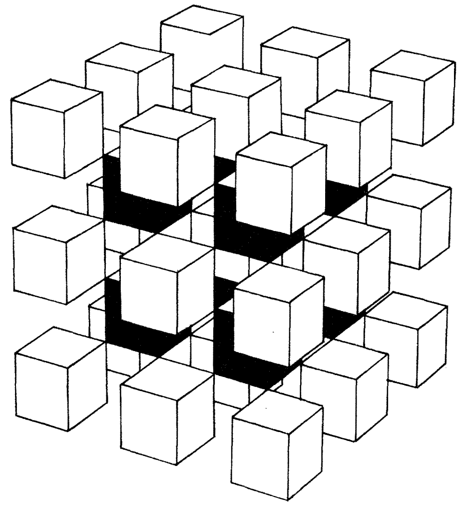

Fig. 1. Idealized cubic structure of $PbMo_6S_8$. The solid cubes represent cubes of eight sulfur atoms containing six molybdenum atoms in the form of tetrahedrons. The open spaces are sulfur cubes that are empty. The dark cubes in the center two planes contain lead atoms at their centers. In the molecular crystal model, it is the former cubes that form the Mo_6S_8 "molecules," which do not strongly interact with one another or with the lead atoms. [Source: M. Marezio and B. T. Matthias, Bell Laboratories]

Even more exciting was the report by the Swiss researchers that a lead-based molybdenum sulfide ternary containing the magnetic rare earths gadolinium and europium also had high critical fields and that a tin-based ternary exhibited a critical field that, while not so high, actually increased as europium was added. Both kinds of behavior were contrary to previous experience with superconductors.

The models devised by physicists to explain these results are based on the peculiar crystal structure of the molybdenum sulfide and selenide ternaries. A number of crystallographic studies of the various ternary compounds have been made. One study of the compound $PbMo_6S_8$, by Massimo Marezio, Matthias, and their colleagues at Bell Labs, provides a relatively simple way of looking at a complex crystal structure. In crystallographic terms, the compounds form with a triclinic lattice having rhombohedral symmetry. However, viewed from a certain direction, the structure takes on a slightly distorted cubic form.

A "unit cell" of the distorted cubic structure comprises eight small cubes stacked to form a large cube. Each of the small cubes has a sulfur atom, which it shares with its neighbor cubes, at each of its corners. The small cube closest to the origin of the lattice contains six molybdenum atoms in the form of an octahedron. The molybdenum atoms sit at the centers of each of the six faces of the small cube. The lead atom sits in the center of the small cube farthest from the origin. The remaining six small cubes are empty. Finally, the entire crystal consists of a cubic array of the unit cells (Fig. 1).

The rest of the model for superconductivity follows from this structure. Fischer and his colleagues have postulated, on the basis of numerous experiments involving substitutions of metallic elements for lead, that the electrons taking part in the superconductivity come from the molybdenum atoms. A major role of lead and other metal atoms that can take its place seems to be to fix the distance between the sulfur cubes containing molybdenum octahedrons. Apparently there is a most favorable separation distance that gives the optimum transition temperature and critical field. When rare earth atoms are substituted for the lead, they are largely shielded by the sulfur from the molybdenum and thus have little effect on the superconductivity, according to the model. And the higher transition temperatures of the molybdenum selenide compounds can be attributed to the larger size of selenium cubes, as compared to sulfur cubes. The resulting larger distance between rare earth atoms and the molybdenums further reduces interactions that are destructive of superconductivity.

Support for this picture has come more recently from neutron scattering and heat capacity experiments by Samuel Bader, Gordon Knapp, and their coworkers at the Argonne National Laboratory and by B. P. Schweiss, W. Reichardt, and their associates at the Institute for Applied Nuclear Physics in Karlsruhe, and from nuclear magnetic resonance and Mössbauer effect studies by Frank Fradin of Argonne, Clyde Kimball of Northern Illinois University, and their colleagues.

Neutron scattering and the heat capacity were used to probe the spectrum of lattice vibrations of lead and tin molybdenum sulfide ternaries. In crystals, lattice vibrations are divided into groups called normal modes, but in contrast to molecules in which each mode has a discrete characteristic vibrational frequency, each normal mode has a spectrum of frequencies. The details of this spectrum prompted Bader and his Argonne colleagues to propose what they call a molecular crystal model in which clusters of molybdenum and sulfur atoms consisting of a sulfur cube filled with the molybdenum octahedron (Mo_6S_8) would constitute the molecule.

Interactions between molybdenum atoms in one cluster were proposed to be strong, whereas interactions between molybdenum atoms in neighboring clusters would be weaker (although still strong enough for metallic and superconductive behavior), and interactions between molybdenum atoms and lead or tin atoms, which are outside the clusters, would be weakest of all.

This spring Fradin, Kimball, and their colleagues showed how the tin molybdenum sulfide could have its critical field enhanced by additions of gadolinium and europium. Their argument depends on the details of the interactions between the electrons from the molybdenum atoms, which are said to be the source of the superconductivity, and those on the rare earth atoms, which are responsible for magnetic behavior in these elements. Again, the key seems to be that the rare earths are shielded from the molybdenums inside the sulfur cubes. The shielding permits the two types of electrons to interact in such a way that an effective internal magnetic field is created which opposes the external applied magnetic field. Thus, the superconductor "thinks" that the applied field is lower than it actually is, and it will continue to be superconducting at applied fields higher than the critical field of the compound which has no rare earth additions.

Matthias, who is well known in the superconductivity community as a skeptic about the usefulness of theoretical models in guiding researchers to new materials, says that he and his co-workers completely disregarded the theoretical models generated in the study of the molybdenum sulfide ternaries in their search for new superconductors that led to the rhodium boride compounds reported on last month. The discovery was the simple result of a selective screening program guided by intuition and past experience.

Joanne Vandenburg of Bell Labs and Matthias have studied the crystal structure of the new ternaries, and they found a tetragonal lattice. This structure is quite unlike that of the molybdenum sulfides, and it is therefore not clear to physicists whether models derived to explain properties of the latter will also explain those of the rhodium borides. As shown in Fig. 2, rhodium atoms are grouped in tetrahedrons containing four rhodiums. The tetrahedrons, in turn, are bound together in sheets or layers. The role of the rare earth atoms seems to be to hold the tetrahedrons within a sheet together. The distance between rhodium atoms in neighboring sheets is larger than that between rhodiums in neighboring tetrahedra in the same sheet. The latter distance is, in turn, larger than that between rhodiums in a given tetrahedron. Some physicists have speculated that rhodium is analogous to molybdenum in that its electrons give rise to the superconductivity, but the compounds are so new that no model exists for their behavior. Indeed, many of their properties are yet to be measured.

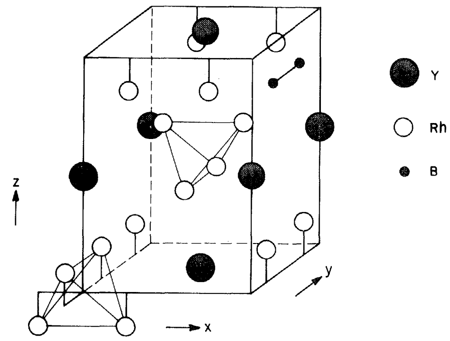

Fig. 2. Proposed structure of the rhodium boride ternaries based on x-ray diffraction studies of YRh_4B_4. In the tetragonal structure, the rhodium atoms form tetrahedrons in planes parallel to the *x-y* plane. The ytterbium atoms serve to hold the planes containing the tetrahedrons together. Interactions between planes are strong enough, however, that there is no question of considering the structure to be a two-dimensional layered structure with little or no interaction between layers. The boron atoms seem to occur in pairs, but their exact positions in the lattice are still under investigation. [Source: J. M. Vandenberg, Bell Laboratories]

The molybdenum ternaries and the rhodium borides differ in one additional aspect, and both behaviors are exciting to physicists. One group at UCSD headed by Brian Maple and David Johnston has recently found evidence for two phase transitions, one at 3.5° and one at 0.8°K, in a rare earth molybdenum selenide compound containing gadolinium. Neither phase change destroys the superconductivity, which begins at 5.8°K. The second transition at 0.8°K is to a phase in which superconductivity and magnetism appear to coexist.

A second group at San Diego, led by William Fertig and Matthias, observed the disappearance of superconductivity with the appearance of magnetism in the $ErRh_4B_4$ ternary when cooled to 0.9°K. A somewhat similar behavior, termed reentrant superconductivity, has been observed previously in several alloys by many investigators, including Maple of UCSD and Paul Chaikin of the University of California at Los Angeles. In one of these cases, a binary superconductor such as $LaAl_2$ that contained a small proportion of a rare earth such as cerium would show a disappearance of superconductivity when the compound was cooled to well below its superconducting transition temperature, but the compound did not become magnetic.

Although some observers disagree, Matthias thinks that the behavior of the ternary is, in principle, quite different from reentrant superconductivity. The difference, in fact, is central to the whole concept of ternary compounds. The $LaAl_2$ alloy containing cerium is really a ternary material in that it has three components. However, it is classified as a pseudobinary compound, which is a combination of the two binaries $LaAl_2$ and $CeAl_2$. In the pseudobinary, the lanthanum and the cerium share the same sites in a crystal structure that is common to both binaries and the pseudobinary. The pseudobinary is in essence a mixture whose properties are averages of those of the binaries. In a true ternary, there is a new crystal structure with three distinguishable types of lattice sites, each of which is occupied by only one of the three components, and altogether new properties are the result.

There is a further difference between the two cases in that rhodium and boron do not form a superconducting compound. It is essential that erbium, which is the source of the magnetic interaction that is assumed to cause the disappearance of the superconductivity, be present. As Matthias says, "The erbium does it all." In the pseudobinary case, far from being necessary or even beneficial, adding the rare earth is destructive of superconductivity in that it lowers the critical temperature and the critical field.

Numerous theorists are at work trying to construct models for this phenomenon. But, interesting as the transition from superconducting to magnetic behavior is, most observers think that the excitement over the new compounds should be reserved mainly for the prospect of new superconductors with more useful properties for technological application. There are, in fact, rumors that more ternary compounds with higher transition temperatures are on the way.

In the meantime, a few groups are said to be investigating ways to make the lead molybdenum sulfide ternaries in the form of solid wires—the first materials were powders. Once wires can be made, various sorts of metallurgical tricks, such as mechanical working and adding impurities to the superconductor, are needed to make the wires carry usefully high electrical currents. Ways to overcome the brittle nature of these compounds, so that they can withstand the huge forces occurring in large magnets, must also be found.

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