More Superconductivity Questions Than Answers

Although making liquid nitrogen–temperature superconductors is easy enough that high school science projects already feature them, researchers still have little idea how the new ceramic oxides work and therefore little guidance for improving them. At the International Workshop on Novel Mechanisms of Superconductivity, held from 22 to 26 June in Berkeley, California, theorists reviewed a host of competing explanations of how these materials come by their remarkable properties, but they could not get far in sifting through the candidates for the best one.

One cause of the unsettled situation is that theorists have not yet pushed their models far enough to make many specific predictions about physical properties and therefore to provide a reason to choose one theory over another. But experimental data for comparison with theory are lacking, too. For example, experimentalists are just now succeeding in being able to grow single crystals and thin films of the ceramic oxide superconductors, whose properties were shown at the workshop to be highly anisotropic. Measurements already made on the polycrystalline sintered material available up to now are difficult to interpret and therefore need to be repeated on good-quality crystals and films, where the variation of properties with crystallographic orientation can be mapped out.

Given the high level of Japanese activity in the field, it was surprising that no researchers from industrial laboratories in Japan presented their findings at the workshop. In the light of a budding international competition in commercializing superconductors, some American scientists interpreted the absence as an attempt to protect proprietary advances. A more pleasant surprise was the attendance of a delegation of six Soviet scientists, although one of the fathers of superconductivity theory, Vitaly Ginzburg of the P.N. Lebedev Institute of Physics in Moscow, who was expected, did not come.

Challenges Mounted to Accepted Structure

The most basic property of any material is its structure—where the atoms are. The ideal techniques for structural determinations are x-ray and neutron diffraction from single crystals. However, if single crystals are not available, with some intuition as to where the atoms might be and with refinement techniques that improve the initial guess, crystallographers can still deduce reliable structures from diffraction patterns obtained from powder samples. Several weeks ago, researchers using powder diffraction methods seemed to be converging toward an agreed upon structure for the rare earth–barium–copper–oxygen ceramics that remain superconducting up to 95 K or so. Now, some investigators are challenging that structure.

One radical proposal at the workshop came from Farrel Lytle and Robert Greegor of the Boeing Company and Armand Panson of the Westinghouse Research and Development Center, who used x-ray absorption techniques to probe the local environment around the absorbing atoms. Lytle, Greegor, and Panson concluded that a considerable fraction of the copper and rare earth atoms traded positions in the triple-layer perovskite unit cell, making the structure considerably less ordered than had been thought. An equally innovative suggestion was presented by K. Alex Müller of the IBM Zürich Research Laboratory on behalf of his colleagues A. Reller of the University of Zürich and J. Georg Bednorz of IBM. The proposed structure, which Müller claimed was consistent with existing diffraction data, was highly ordered but in quite a different way from the "conventional" structure.

One way to think about the conventional structure is to imagine a copper atom surrounded by six oxygen atoms at the vertices of an octahedron. The octahedra are then arrayed vertex to vertex in a three-dimensional cubic lattice. A rare earth or barium atom fits in each interstice between the octahedra in an ordered way, so that the rare earth and barium atoms are stacked in the repeated sequence barium–rare earth–barium. A crystalline compound having this structure would have the chemical formula $RBa_2Cu_3O_9$, where R is yttrium or one of the lanthanide rare earths.

Good superconducting material has seven rather than nine oxygen atoms per unit cell of the structure. This is achieved by removing all the oxygen atoms on the rare earth plane, so that the copper atoms nearest to the plane are each surrounded by five oxygen atoms at the vertices of a square pyramid. In addition, half the oxygen atoms on the copper planes between barium planes are missing, so that these copper atoms are each surrounded by four oxygen atoms at the vertices of a square (see left figure).

As compared to diffraction methods, x-ray absorption has the advantage of being element-specific; that is, the x-ray wavelength can be tuned to the absorption edge of the element whose local environment is to be probed. Other edges usually lie at different wavelengths. Absorption is thereby a powerful complement to diffraction. Lytle and his co-workers used the technique of x-ray absorption near-edge spectroscopy (XANES). As the name implies, it is the details of the absorption near the edge that provide the structural information.

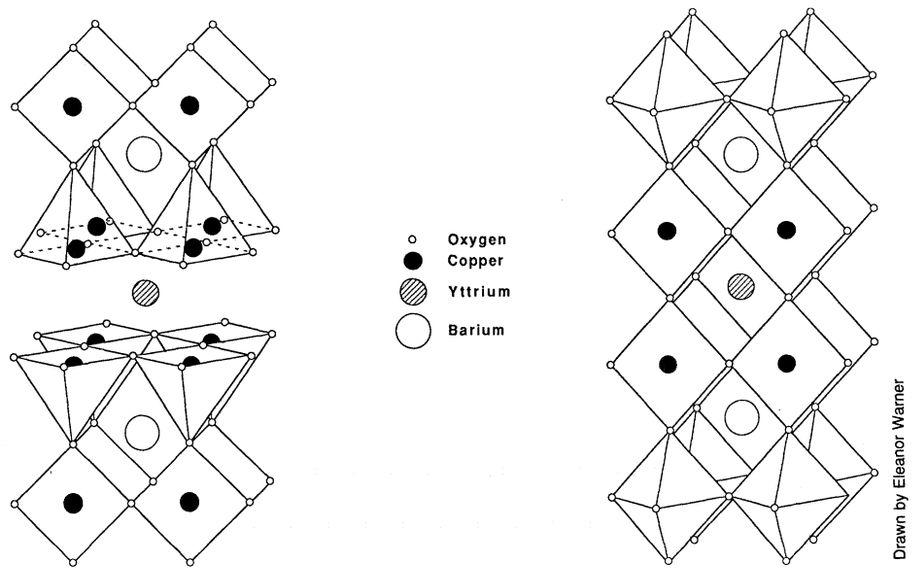
How to convert spectroscopic data into structural information is not so obvious. The principle is one that XANES shares with extended x-ray absorption fine structure (EXAFS). A peak or valley in the XANES spectrum occurs when a photoelectron ejected from an absorbing atom scatters from a neighbor atom and returns to its source, giving rise to an interference between the quantum mechanical wave functions of the outgoing and incoming electron waves. Constructive interference increases the absorption cross section, while destructive interference reduces it. In contrast to the older EXAFS technique, near the absorption edge of an element, the x-ray wavelength is about equal to the distance between neighboring atoms. The investigators showed that this feature translates into an approximately universal curve relating wavelength and bond length, which they could obtain empirically from a series of reference compounds in gaseous, liquid, and solid form.

Having established their molecular ruler, Lytle and his colleagues applied it to the superconducting compounds $YBa_2Cu_3O_7$ and $La_{1.8}Sr_{0.2}CuO_4$. As compared to the first, the second compound becomes superconducting at a lower temperature of about 40 K and has a distinctly different but related layered perovskite structure in which lanthanum and strontium atoms randomly occupy the same lattice sites. In both cases, the researchers found that the bond lengths obtained from copper *K*-edge XANES spectra could be fitted to the conventional structures from diffraction experiments with one major exception. In the high-temperature compound, an anomalous copper-oxygen bond length (about 2.5 angstroms) could only be explained by transferring some of the copper normally in the planes nearest the yttrium (black circles in pyramids) to the yttrium site and vice versa. Analysis of

EXAFS spectra gave the same conclusion. From the peak intensity, the researchers estimated that from 20 to 30% of the copper took this position. Furthermore, their analysis of oxygen *K*-edge XANES spectra in the literature reinforced this picture. A similar mixing that places copper on lanthanum/strontium lattice sites was inferred for the low-temperature compound, as well.

At Zürich, the motivation for proposing a new structure was a desire to lessen the structural dissimilarities between the low- and the high-temperature ceramic oxide superconductors and to make the structure of the high-temperature material more consistent with the extensive literature on copper oxide perovskites. The principal offending feature in the conventional structure is the absence of all oxygen atoms on the rare earth plane, which gives the nearest copper atoms their unusual square pyramidal environment of five oxygen atoms. The Zürich alternative is to place the oxygen vacancies in the copper planes nearest the rare earth, whereas the other copper atoms retain their octahedral coordination. Diffraction data clearly show the structural unit cell to be orthorhombic (three unequal but orthogonal lattice vectors), so the Swiss researchers postulate the ordered arrangement of oxygen vacancies shown with the copper atoms surrounded by four oxygen atoms at the vertices of a square (see right figure).

Given the central role of structure in determining the electronic properties of the ceramic oxide superconductors, getting the structure right is plainly important. In his conference summary, Theodore Geballe of Stanford University called the implications of the XANES experiment, in particular, "severe" and said it had to be looked at very carefully.



Superconductor crystal structure. *(Left) The accepted crystal structure of the yttrium-barium-copper-oxygen superconductor is characterized by the absence of oxygen on the yttrium plane. Note that not all the copper atoms are visible. (Right) By moving the oxygen vacancies to the copper planes neighboring the yttrium, an alternative crystal structure with a more common mixture of octahedral and square planar coordinated copper atoms is generated.*

Chains May Not Be Needed for 90 K Superconductivity

A key ingredient of the highly ordered conventional structure of the rare earth–barium–copper–oxygen superconductors is the existence of linear chains of copper and oxygen atoms that seem to be associated with superconductivity at temperatures above 90 K. In brief, the missing oxygen atoms on the rare earth planes divide the structure into isolated layers with little or no electrical communication between them, which gives the material a two-dimensional character. Morever, the ordered arrangement of oxygen vacancies on the copper plane within each layer gives rise to the linear chains of copper and oxygen atoms (running horizontally through the squares in the left figure).

Electrons can flow through the chains or through the copper planes bounding the layers, but there is considerable evidence that the chains are necessary for high-temperature superconductivity. For example, several groups around the world have prepared material with a reduced oxygen content and found a reduction in the critical temperature for superconductivity. At the workshop, for example, Bertram Batlogg, representing a large group at AT&T Bell Laboratories, showed the results of a study of the critical temperature as a function of oxygen content. As the number of oxygen atoms per unit cell was reduced from 7 to 6.2, the critical temperature dropped suddenly in two stages, first from 90 to 55 K or so and then to 20 K.

The now standard interpretation of the first drop, which is supported by x-ray and neutron diffraction experiments, is that, when the oxygen decreases, the oxygen vacancies become disordered. With the disorder, the chains are disrupted and the high-temperature superconductivity goes with them. Most researchers also believe that a transition from an orthorhombic to a tetragonal crystal structure accompanies the disordering of the oxygen. This explanation is by no means proven, however. At the workshop, a wide variety of evidence questioning the role of chains in high-temperature superconductors, if not their existence, was presented by researchers from Hiroshima University in Japan, Stanford University, and the IBM Yorktown Heights Laboratory.

In a poster presentation, the Hiroshima researchers, represented at the workshop by Yoshiteru Maeno, described several experiments in which they substituted a small percentage of iron and other elements for copper to make the series of compounds $YBa_2(Cu_{1-x}M_x)_3O_7$, where M is the substituted element and x is the percentage. As the investigators increased the amount of iron, for example, x-ray diffraction data indicated an orthorhombic-to-tetragonal transition at 2% iron. But the critical temperature for superconductivity decreased only gradually, even at higher concentrations, and there was no sharp drop when the structure changed. The conclusion was that linear chains are not necessary for superconductivity above 90 K.

Malcolm Beasley, representing a large group at Stanford, reported that researchers there have synthesized a new lanthanum-based superconductor with the composition $La_{3-x}Ba_{3+x}Cu_6O_{14}$, where x is a number less than 1 whose value determines whether the material is superconducting or not. In particular, for x greater than 0.75, the onset critical temperature for superconductivity is consistently 90 K or so. For x equal to 1, the composition is the same as that of the lanthanum-containing member of the rare earth–barium–copper–oxygen series. However, the Stanford researchers found an extra x-ray diffraction line in their material that indicates the structure must be different.

Several years ago a group including Claude Michel and Bernard Raveau, of the

University of Caen in France, reported x-ray diffraction studies of the compound with x equal to 0. These investigators deduced a structure with a tetragonal unit cell and no linear copper-oxygen chains, although the lanthanum plane was devoid of oxygen atoms. The Stanford group argued that this may be the structure that they have seen. If so, once again, the conclusion was that linear chains are not necessary for high-temperature superconductivity.

The final piece of evidence from IBM is less direct but indicates how important it is to have good single crystals for sorting out the intricacies of these highly anisotropic superconductors. For example, Debra Kaiser and Frederick Holtzberg of IBM have recently been able to grow single crystals of $YBa_2Cu_3O_7$ with dimensions in the millimeter range. The presence of linear chains implies an approximately one-dimensional character for the superconductivity, and this would be reflected in a parameter called the coherence length, which is a measure of the distance over which the quantum mechanical wave functions of the superconducting electrons extend. The coherence length would be larger in the direction of the chains than in directions perpendicular to them. It is possible to deduce the coherence length from the critical magnetic field, the maximum field at which the material remains superconducting.

A poster presentation by Thomas Worthington, William Gallagher, and Timothy Dinger of IBM reported the outcome of measurements parallel and normal to the linear chains and at several angles in between on single crystals with average dimensions of about 0.2 millimeter on a side. The coherence lengths extracted for the parallel and normal orientations were 34 and 7 angstroms, respectively, both very short as compared to conventional superconductors. It is of particular interest that 7 angstroms is almost a factor of 2 larger than the spacing between the nominally isolated layers separated by rare earth planes. According to this finding, whether or not chains are necessary for high-temperature superconductivity, the macroscopic superconductivity properties are three-dimensional in character rather than two- or one-dimensional.

Good-quality single crystals and thin films could also help sort out several important questions that were hotly debated at the workshop. For example, a fundamental feature of superconductors is an energy gap between the superconducting and normal electronic states. But, as one physicist noted, "At the workshop we had one Nobel laureate saying there is no gap and another Nobel prizewinner arguing that there is." ■

ARTHUR L. ROBINSON

No Satellites of Asteroids

If the object of the search were a person, he would surely by now have been given up as lost for good. But it is companions to asteroids that astronomers have been searching the heavens for and, despite the steadily accumulating negative results, satellites of asteroids may still be out there. It is just that the available ground-based methods seem incapable of finding them, which suggests that the reported sightings that prompted recent efforts were in error.

The latest discouraging word comes from Tom Gehrels, Jack Drummond, and Nancy Levenson of the University of Arizona. While preparations were under way for other work with the Spacewatch Telescope and its charge-coupled device (CCD) detector on Arizona's Kitt Peak, these astronomers searched around the three largest asteroids—Ceres, Vesta, and Pallas—and another seven of the larger asteroids. They found nothing orbiting these asteroids larger than 3 kilometers in diameter as far as tens of thousands or hundreds of thousands of kilometers from the asteroid (depending on the asteroid), where the sun's gravity would wrest away any satellite, to as close as a few thousand or tens of thousands of kilometers. Closer than that, the asteroid's halo of scattered light obscured any close companions.

The Arizona group also reviewed the results of two survey projects completed in the 1950s and 1960s. The Yerkes-McDonald Asteroid Survey included most of the asteroid belt, and the Palomar-Leiden Survey covered a small section of it but photographed objects ten times as faint. Because no objects associated with asteroids were noted, Gehrels and his colleagues reason, there were no satellites recorded that were 17 kilometers or larger in the case of the complete survey and 3 kilometers or larger in the case of the small-area survey.

Relatively small, distant satellites would thus seem to be scarce or nonexistent; a recent search using the technique of speckle interferometry suggests that close-in companions are difficult to find as well. Otto Franz of Lowell Observatory and Harold McAlister of Georgia State University searched within a few thousand kilometers of about 50 asteroids, including about a dozen of those proposed as possible asteroid pairs. The speckle technique allowed a resolution of 75 kilometers because in it a series of brief exposures captures as points of light the "twinkling" of the asteroid that blurs long-exposure photographs . Mathematical processing restores the image to its undistorted form. This search revealed no companion larger than half the size of its accompanying asteroid.

Gehrels and his colleagues reason that these searches have covered most of the possibilities. Any widely separated companions should have been seen because they would probably not be undetectably small. An asteroid is not likely to hold onto newly created objects of any size recently knocked off it by the collisions that are inevitable in the asteroid belt. On the other hand, any old objects smaller than about 30 kilometers that formed along with the planets are thought to have since been ground up by collisions or knocked out of orbit by an impact.

Small, close-in satellites are not likely either. Under the influence of the tidal forces acting between two bodies, they would crash into the primary asteroid or be pushed well beyond the halo of obscuring light. Large companions can take up stable orbits close to the other member of the pair, but the speckle search would have turned up most of those. These companions would be so large that they would more accurately be said to form a double or binary asteroid.

There are some asteroids that may be such close binaries, perhaps almost touching, that they have escaped telescopic detection. Steven Ostro of the Jet Propulsion Laboratory, Donald Campbell of Arecibo Observatory, and Irwin Shapiro of the Harvard-Smithsonian Center for Astrophysics recently reported that radar observations had revealed some "exotically shaped objects" among the asteroids. Ivar appears to be one object from some angles but possibly two separate bodies when viewed from other angles. Asteroid 1986DA also reflects radar signals the way an extreme dumbbell or two objects nearly touching would. The resolution of the question of binary asteroids will probably only come with the launch of the Space Telescope. ■ RICHARD A. KERR

ADDITIONAL READING

T. Gehrels *et al.*, "The absence of satellites of asteroids," *Icarus* **70**, 257 (1987).