

Although Susman is happy to see continuity of an overall primitive apelike skeleton between *A. afarensis* and *H. habilis*, he does see signs of modification of the foot in the human direction between the two species. "There is a tremendous difference between *afarensis* and *habilis*," he notes. "Lucy's foot is more primitive, more mobile, whereas the [*habilis*] foot is more human-like." In the overall anatomy Susman therefore sees a mosaic of stability and change, which incorporates a gradual transition from ape to human.

White and his colleagues disagree. "There's no substantial functional difference between the foot of *afarensis* and *habilis*," says White. "Their interpretation is influenced by the fact that they continually compare fossils against modern humans and modern apes. This leads them to overemphasize the 'apeness' of the *afarensis* foot and the 'humanness' of the *habilis* foot." As a counter, Susman argues that White and his colleagues overemphasize the "humanness" in the fossils from the beginning, starting with Lucy. Having done that, the lack of significant change in the *H. habilis* foot is an inevitable component of the Berkeley argument, says Susman.

The evolutionary transition between *H. habilis* and *H. erectus* appears to have occurred in the narrow window of time between 1.8 and 1.6 million years ago. "Given the primitiveness we see in *habilis* and the advanced characteristics in *erectus*, it's clear that the transition was much more abrupt than has been appreciated," says White. Brain size increased further during that event, and the anatomical adaptation to upright walking became enhanced. Although the degrees of change in these two features across the *habilis/erectus* transition were substantial, they can be seen as the continuation of trends already established. The dramatic diminution of sexual dimorphism in body size was, however, something new in human history.

Exactly what is implied by the shift from a situation in which males were twice as big as females to one in which the ratio was about the same as in modern chimpanzees and humans is difficult to determine. For instance, a large sexual dimorphism in modern large primates is associated with a "harem" structure in one case (gorillas) and with a very loose, almost solitary social system in another (orangutans). In both cases, however, there is a sharp element of competition between males for access to females, which is responsible for the exaggerated size of the males compared with the females. The dramatic reduction in sexual dimorphism in *H. erectus* might therefore have been associated with an equal reduction in competition and

an increase in cooperation between males.

It may be no coincidence that in addition to the apparent adoption of a new social structure for hominids, the origin of *H. erectus* was also accompanied by the inclusion of meat as an important component of the diet, and by a dramatic extension of the hominid range, which expanded out of Africa about a million years ago.

Louis and Mary Leakey worked for more

than three decades at Olduvai Gorge, and many people assumed that when Mary Leakey folded up her camp there in 1984, little new remained to be recovered. Johanson, who led the first IHO expedition there in 1985, says that the discovery of OH 62, and its impact on the interpretation of human history, "justifies the continued exploration at Olduvai Gorge." ■

ROGER LEWIN

## An Oxygen Key to the New Superconductors

*First it was the physicists, then the chemists, and most recently the materials scientists and ceramists who have hastily included in their annual meetings symposia on the new high-temperature, ceramic superconductors. Below are briefings from the 1987 Spring Meeting of the Materials Research Society (MRS) that was held in Anaheim, California, from 21 to 24 April, 1 week before the American Ceramics Society's conclave in Pittsburgh.*

*With the initial wave of euphoria now past, the atmosphere in Anaheim was decidedly more professional than that of the now fabled "Woodstock of Physics" that was part of the American Physical Society's March Meeting in New York City only 5 weeks before. Nonetheless, perhaps 1500 materials researchers listened to 69 scheduled papers and several late walk-ons that were crammed into a 2-day symposium. With a martial strictness, cochair Michael Schlüter of AT&T Bell Laboratories and Donald Gubser of the Naval Research Laboratory kept the talks to the allotted 10 minutes each.*

*Except for an impassioned presentation by Juei-Teng Chen of Wayne State University, who sought to convince listeners that a group there had seen clear signs of superconductivity at 240 K, which is ambient temperature during a cold night on the northern plains, no significant indications of room-temperature superconductivity were reported. The most skeptical view was that of Theodore Geballe of Stanford University, who suggested that some of the unreproducible signs seen in several laboratories could be due to something other than superconductivity, as similar effects disappeared in Stanford samples with repeated cycling between room and liquid-nitrogen temperature.*

*If there was one theme at the symposium, it was that oxygen is the key to the family of rare-earth-based ceramic materials now in hand that remain superconducting up to about 100 K.*

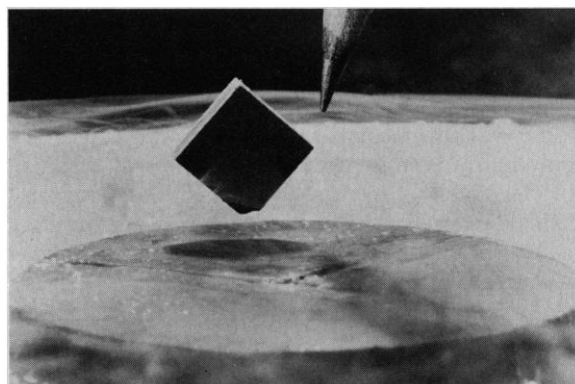
### Where the Oxygen Vacancies Are

It was already apparent at the American Physical Society's March Meeting in New York that the new superconductors are members of a family of compounds having the generic composition  $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ . R stands for yttrium or one of the lanthanide rare earths, and  $x$  is a number less than 1 whose value depends on the method used to prepare the material. Researchers also agreed that the structure of the compounds is something called a triple-layer perovskite with some oxygen sites vacant, but they disagreed on which sites.

Now, with the aid of neutron and x-ray diffraction and high-resolution electron microscopy, investigators are converging on a common interpretation that indicates the simultaneous presence of two- and one-dimensional characters in the electrical properties. The figures (page 1065) show the triple-layer structure derived from neutron diffraction studies at Argonne National Laboratory by researchers from Argonne, the Illinois Institute of Technology, and Western Michigan University. At least five other groups in Canada, France, Japan, the United Kingdom, and the United States have reached the same conclusions from independent neutron experiments. Neutrons are

## Floating on air.

*Because of the Meissner effect, a superconductor excludes from its volume all magnetic flux lines. The small permanent magnet (above) therefore floats above the superconductor (below) that is chilled in liquid nitrogen.*



raised simply by, for example, first removing from and then reinserting oxygen atoms into the linear chains by means of high-temperature heat treatments (annealing) in vacuum and in air. The number of oxygen atoms strongly influences the critical temperature for superconductivity of these compounds, as well as their crystal structure.

Begin the story with the by now well-known insensitivity of the critical temperature to the specific rare earth. Researchers have succeeded in making superconductors with every lanthanide rare earth except cerium and praseodymium and uniformly have obtained critical temperatures around 90 K. The Bellcore group reported lattice constant measurements on a series of compounds with different rare-earth atoms and found in every case that the structure was orthorhombic. Tomoaki Yamada of the Nippon Telegraph and Telephone (NTT) Corporation in Tokyo presented very similar findings.

When the Bellcore investigators then vacuum-annealed their series of compounds, they found that all had become tetragonal. The tetragonal structure was associated with a decrease in the number of oxygen atoms and a decrease in the critical temperature. In the case of a compound containing yttrium, the critical temperature for superconductivity dropped from 91 K when the number of oxygen atoms per unit cell was 6.8 to 55 K when the vacuum annealing reduced the number to 6.6. Interestingly, the NTT researchers could only make their lanthanum-based compound with a tetragonal structure and found a similarly reduced critical temperature near 50 K.

The question of the role of structure has been on everyone's mind from the beginning. Donald Capone of Argonne National Laboratory, speaking for an Argonne, Catholic University of Leuven (Belgium), Illinois Institute of Technology group, and Robert Beyers, representing the IBM Almaden and Yorktown Heights Laboratories, reported high-temperature x-ray diffraction studies that showed a transition to a tetragonal structure at about 750 K. Tetragonal material that was then cooled slowly regained the orthorhombic structure and retained a high critical temperature for superconductivity of better than 90 K. However, material that was rapidly cooled (quenched) did not have time to complete the structural transformation. Apparently because of the presence of the tetragonal phase, the transition temperature dropped to 50 K or so.

Similarly, Y. Kubo of the NEC Corporation in Kanagawa, Japan, reported that NEC researchers had found a correlation between the structure, the superconductivity, and the number of oxygen atoms per unit cell from x-ray diffraction measure-

more sensitive to oxygen than x-rays and therefore provide a comparatively unambiguous picture of where the oxygen atoms are.

To understand the structure, first consider a perovskite cube with a copper atom at each corner and oxygen atoms on each of the cube edges. Leave the center unoccupied for the moment. Then join three cubes together, placing a barium atom at the center of the top and bottom cubes and a rare earth atom at the center of the middle cube. The unit cell of such a structure is tetragonal with three orthogonal axes and one lattice constant considerably larger than the other two, which are equal. The ideal compound has nine oxygen atoms per unit cell, but the missing oxygen atoms lower the number. The vacancies also distort the structure slightly so that it just barely becomes orthorhombic with the two once equal lattice constants now slightly different.

Locations that researchers now favor for missing oxygen atoms include the sites in the central rare-earth plane and half the sites in the top and bottom copper planes (left figure). These vacancies shift the composition to  $\text{RBa}_2\text{Cu}_3\text{O}_7$ . Donald Capone, who presented Argonne's structure at the MRS meeting, noted that a so-called Rietveld refinement of the neutron diffraction data for an yttrium-containing compound whose composition was optimized for superconductivity yielded a value of 6.81 oxygen atoms per unit cell of the triple-layer structure; that is, 81 of every 100 unit cells contained 7 oxygen atoms, whereas 19 contained only 6. Capone said the extra 0.19 vacancy per unit cell was also on the top and bottom copper planes. Moreover, the two copper planes adjacent to the rare-earth plane are "dimpled" because the oxygen atoms relax toward the now mostly empty rare-earth plane.

The oxygen vacancies in the rare-earth plane give the structure an electronically two-dimensional character. Theorists calculate that electrons flow mainly in copper and oxygen orbitals, and these orbitals are only continuous horizontally as a result of the

missing oxygen atoms in the rare-earth plane. If the oxygen vacancies in the top and bottom copper planes are ordered, so that they lie on opposite sides of the unit cell, an additional one-dimensional aspect to the electronic structure emerges because the copper-oxygen orbitals can form continuous chains in these planes in only one direction. However, in the dimpled copper planes, the orbitals remain continuous in two dimensions (right figure).

Although neutron diffraction directly shows the ordering of the oxygen vacancies, supporting evidence also comes from electron microscopy. Abbas Ourmazd of Bell Labs showed high-resolution electron micrographs at the symposium taken by him and colleagues at Bell Labs and at Arizona State University. As compared to the heavier metal atoms, the light oxygen atoms do not scatter electrons strongly enough to be directly visible, but ordered oxygen vacancies could be inferred from a series of micrographs on samples of different thickness.

## Vacancy Ordering and Superconductivity

There is strong evidence that the crucial effect of oxygen vacancies on both the superconductivity and the structure of  $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$  is their ordering, which gives rise to linear chains of copper and oxygen atoms (see previous briefing). As Jean-Marie Tarascon of Bell Communications Research (Bellcore) summarized it at the MRS symposium, what is important for superconductivity is not only how much oxygen there is but where it is.

X-ray and neutron diffraction experiments in conjunction with other studies at Bellcore and elsewhere indicate that the number of oxygen atoms per unit cell can be easily varied over a wide range from about 6.1 to 6.9, according to the oxygen pressure in the high-temperature furnace during preparation of the compound. Moreover, the concentration can be reversibly lowered and

ments on material quenched from several temperatures above and below the orthorhombic-to-tetragonal transition.

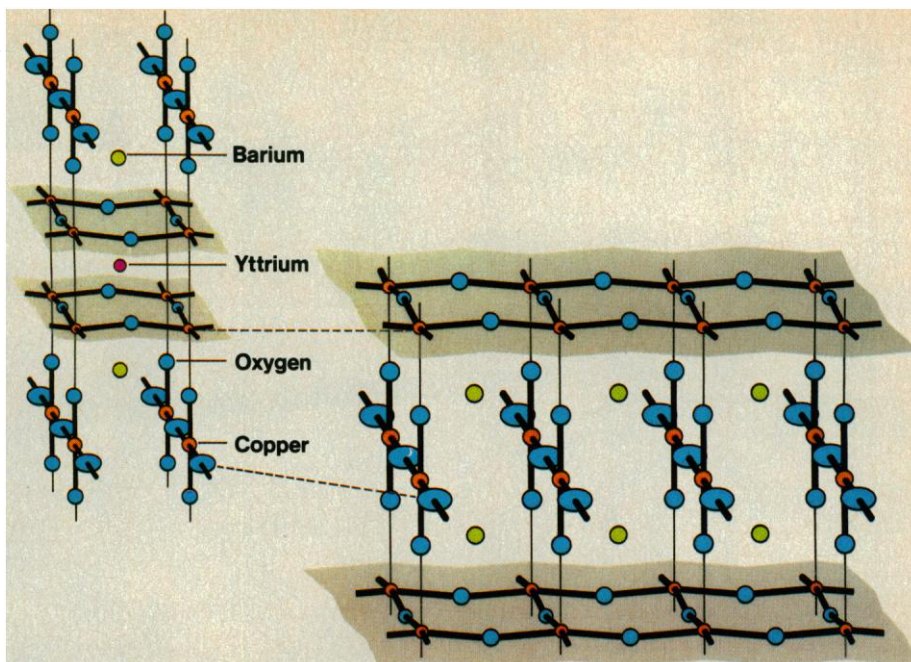
From these results and others, researchers have reached the conclusion that there may be two mechanisms for superconductivity. Critical temperatures of 90 to 100 K are associated with electrons flowing in the linear chains that only exist in the orthorhombic structure, whereas critical temperatures of 50 K or so are due to planar electron flow that is possible in both orthorhombic and tetragonal structures. A particularly direct piece of evidence supporting this idea comes from the Argonne group.

From measurements of the lattice constants just above and below the orthorhombic-to-tetragonal transition, the Argonne investigators concluded that the number of oxygen atoms per unit cell did not change during the transition from one structure to the other. One possibility is that the oxygen atoms simply move. In the tetragonal phase at high temperature, the oxygen atoms in the top and bottom copper planes of the unit cell randomly occupy the available sites. There are twice as many sites as atoms. On cooling, the atoms order in the manner previously described, converting a disordered, two-dimensional planar situation to an ordered, one-dimensional linear one in these copper planes.

## Oxygen Isotopes Spell Trouble for Phonons

The ease of moving oxygen atoms into and out of  $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$  provides a convenient way of testing the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity. At the MRS symposium, Robert Cava, representing a group from AT&T Bell Laboratories, and Donald Morris, speaking for a Lawrence Berkeley Laboratory team, reported similar findings in independent experiments that make it unlikely that the BCS theory in its entirety applies to the 90 K superconductivity in these compounds, which seems to be associated with linear chains of copper and oxygen atoms (see previous briefing).

In the BCS theory, superconductivity results from a second-order phase transition that occurs when certain electrons in a metal find it energetically advantageous to form pairs, known as Cooper pairs. No one disputes that pairing is essential for superconductivity. The specific mechanism by which electrons can lower their energy by pairing is what is at issue. The BCS theory posits an interaction between the electrons and lattice vibrations as being responsible. A negatively charged electron moving through the lattice



**High-temperature superconductor:** (Left) The triple-layer perovskite unit cell; (right) expanded view of linear chains of copper and oxygen atoms and dimpled copper-oxygen planes. The oxygen atoms immediately above and below the chains form a "picket fence" that weakly links the dimpled planes separated by barium atoms, but there is no communication between planes separated by yttrium atoms.

slightly drags the positive ions in the process, making it easier for the second electron to follow and thereby generating an attractive force between the two.

In applying this general picture to the high-temperature superconductors, theorists have focused on lattice vibrations involving oxygen atoms because they are thought to interact particularly strongly with the electrons that flow through copper and oxygen orbitals. The strong interaction makes the Cooper pairs more tightly bound and therefore translates to a high critical temperature, the temperature at which thermal effects break up the pairs. Werner Weber of Bell Labs and the Karlsruhe Nuclear Research Center in West Germany has worked out the details for the ceramic oxide superconductors  $\text{La}_{2-x}\text{A}_x\text{CuO}_4$ , whose discovery last year launched the current superconductor frenzy. In these compounds, which have critical temperatures up to 40 K, A is an alkaline earth.

Oxygen isotopes are an important consideration because, according to the BCS theory, the critical temperature increases with the frequency of the relevant lattice vibration. The frequency decreases with the masses of the vibrating atoms, however. Hence, replacing the oxygen-16 that is normally present with heavier oxygen-18 should have an observable effect on both the frequency and the critical temperature.

According to Cava, the Bell Labs group was able to incorporate about 75% oxygen-

18 in an yttrium-containing compound by means of a cycle of repeated heat treatments at 500°C in vacuum, which removes some of the oxygen from the lattice, and in oxygen-18, which inserts it. The researchers verified the incorporation of the oxygen-18 by observing the expected 4% decrease in the frequency of the oxygen vibration by means of Raman spectroscopy. However, they found no effect on the critical temperature, as measured by the Meissner effect. In a less detailed report, Morris estimated that the Berkeley group had managed to incorporate an even higher oxygen-18 content of 90% by means of a somewhat different technique, but still saw no effect on the critical temperature.

As it happens, the idea of one-dimensional superconductivity in linear chains dates back over two decades. At that time, William Little of Stanford University proposed a specific version of it in organic polymers as a possible route to a room-temperature superconductor. Little's theory is built around an attractive pairing force of an electronic nature, so that no isotope effect on the critical temperature would be expected. Although there is no evidence as yet linking electrons flowing through linear chains in the triple-layer perovskite compounds with Little's mechanism or any of the others that theorists have proposed, the absence of an isotope effect means that alternative models must be seriously considered. ■

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