radicals, although for the most part these are not oxygen free radicals, that can also inactivate the protease inhibitor.

Charles Cochran of the Scripps Clinic and Research Foundation described another way in which the superoxide radicals and other oxidants released in inflamed tissue can injure the lungs. The agents inhibit the production of adenosine triphosphate (ATP), which provides much of the energy for cellular activities. The oxidants block ATP synthesis both directly and indirectly by causing strand breaks in the DNA. One of the consequences of the DNA damage is activation of the enzyme poly-ADP ribose polymerase, which consumes a cofactor needed for ATP production.

Activation of this enzyme might also contribute to cancer development, according to Peter Cerutti of the Swiss Insitute for Experimental Cancer Research in Lausanne. Tumor promoters are chemicals that are not carcinogenic by themselves but enhance the formation of malignant tumors in cells that have been previously exposed to true carcinogens. A few years ago, Cerutti, among others, proposed that tumor promoters work by generating oxygen free radicals that produce DNA strand breaks.

This may alter gene expression, he notes, possibly because of the ensuing stimulation of poly-ADP ribose, which can modify DNA-binding proteins that may be involved in gene control. Decreased expression of the superoxide dismutase and catalase genes, for example, might enhance the damage caused by oxygen free radicals.

Further circumstantial evidence that oxygen free radicals might contribute to carcinogenesis comes from Bruce Ames of the University of California at Berkeley. He and his colleagues have found that the concentrations of the oxidation products of DNA constituents increase with age in the urines of men and rats. The incidence of cancer also increases with age. Moreover, cell lipids are targets for oxidation by oxygen free radicals. The Ames group finds that rat tissues contain high concentrations of lipid peroxides, many of which are carcinogens. "Clearly, there is an enormous amount of oxidation going on all the time," Ames says.

Finally, oxygen free radicals may convert exogenous chemicals to active carcinogens, in addition to acting on normal cell constituents, notes Sigmund Weitzman of Northwestern University Medical School.

Not all the effects of the oxygen free radicals are deleterious. Phagocytes are, after all, an important part of the body's defenses against foreign invaders. Nevertheless, the oxygen free radicals produced by phagocytes and other types of cells can cause damage in many ways. ■ JEAN L. MARX

Record High-Temperature Superconductors Claimed

Several groups have reported evidence for superconductivity at temperatures up to 70 K in samples containing lanthanum, copper, oxygen, and either barium or another group IIA metal

LAST April, the European physics journal *Zeitschrift für Physik* received a manuscript from the IBM Zürich Research Laboratory titled "Possible high T_c superconductivity in the Ba-La-Cu-O system," which it duly published several months later. Although the paper reported evidence for the onset of superconductivity at temperatures as high as 35 K, well above the previous record of 23 K that had been set 13 years earlier, what little attention it initially attracted was mainly skeptical. That has now changed.

John Bardeen of the University of Illinois, who shared a Nobel Prize for his work on and is the "B" in the BCS theory of how superconductors work, says the new materials open a new era in superconductivity. "It's likely to be the biggest advance in superconducting materials since World War II," concurs experimentalist Theodore Geballe of Stanford University. Geballe adds that one of the most important features of the new materials for possible technological applications is that they are simple and inexpensive to make, once one learns how. Adds Douglas Finnemore of the Ames Laboratory at Iowa State University, "a hundred laboratories around the world are trying to make the material, including ours."

The source of this new enthusiasm is confirming evidence submitted in October by the Zürich researchers J. Georg Bednorz and K. Alexander Müller, and independently shortly thereafter by groups at the University of Tokyo and the University of Houston. A late news presentation in December at the annual fall meeting in Boston of the Materials Research Society by Koichi Kitazawa of Tokyo was particularly effective in turning the tide.

Still unknown is the maximum temperature at which these materials become fully superconducting. Researchers want to find the answer to the question for both fundamental scientific and technological reasons. Theorists had argued that the conventional explanation for superconductivity probably limited the phenomenon to temperatures less than about 35 K, and experimentalists have been unable to get above 23 K.

The highest temperature now reported is 36 K, achieved in a strontium-lanthanum-copper-oxygen compound by Robert Cava, R. Bruce van Dover, Bertram Batlogg, and Edward Rietman of AT&T Bell Laboratories. Kohji Kishio, Kitazawa, Kazuo Fueki, Shoji Tanaka, and five co-workers at Tokyo have nearly equaled this, reaching 35 K in a similar material.

A Chinese group at the Institute of Physics of the Academia Sinica in Beijing may have a claim to even higher temperatures. In a report accepted by the Chinese journal *Ke Xue Tongbao*, Zhongxian Zhao, Shanling Li and seven co-workers discuss materials containing either strontium or barium that seems to become fully superconducting at about 39 K. Unfortunately, the performance degrades markedly when the samples are exposed to air for a few days.

The highest temperature being mentioned anywhere is 70 K, which was also reported by the Chinese physicists. However, this temperature refers to the onset of the transition from normal metallic to superconducting behavior, rather than to the completion of the transition. Moreover, in their report to be published, the researchers say this performance is not repeatable and suggest only that "possible superconductivity might exist around 70 K."

In this issue of *Science* (p. 567), Ching-Wu (Paul) Chu, Pei-Heng Hor, Ru-Ling Meng, Li Gao, and Zhi-Jung Huang of Houston discuss the attainment of an onset temperature of 52 K in a lanthanum-barium-copper-oxygen compound under hydrostatic pressure, but it became fully superconducting at 25 K.

In theory, the switch from metal to superconductor, which is a second-order phase transition, should occur at a well-defined temperature. But, in inhomogeneous material, the transition may occur gradually over a wide range of temperatures. The justification for quoting the onset temperature is the hope that it represents the transition temperature of good quality material.

Applications of superconductors range from large-scale systems, including high-field magnets, electric motors and generators, and electric power transmission lines, to small-scale systems, such as high-speed digital electronics and ultrasensitive electromagnetic radiation detectors. For large-scale applications the transition to superconductor should be complete well above the boiling point of the cryogenic fluid used to cool the material. For small-scale applications, a transition temperature only a few degrees above the boiling point suffices. Because the technology of liquid nitrogen (boiling point 77 K) is so much more convenient and so much less expensive than that of liquid helium, which is needed for all present superconductors, raising the transition temperature sufficiently to allow its use would be a revolutionary advance.

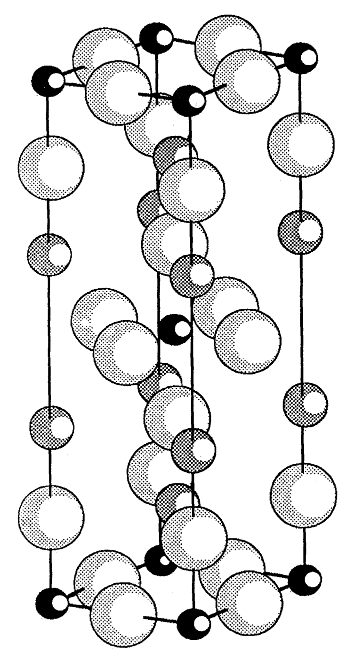
Making new superconductors is as much the province of solid-state chemists and metallurgists as of physicists, and the new class of metallic oxide materials is no exception. According to the standard BCS theory, superconductivity occurs because an attractive interaction between free electrons in the metal and lattice vibrations lowers the energy of the superconductive state relative to that of the normal metal. The transition temperature is proportional to $\omega_D \exp[-1/n(E_F)V^*]$, where ω_D is the highest lattice vibrational (Debye) frequency, $n(E_F)$ is the density of electronic quantum states per unit energy at the chemical potential or Fermi energy, and V^* is a measure of the interaction between the electrons and the lattice vibrations. For a high transition temperature, all of these parameters should be as large as possible.

Apart from empirical rules developed by the late Bernd Matthias, however, there is little to guide researchers in using this formula in finding new materials. In the past, for example, most superconductors with high transition temperatures, such as the niobium-germanium that held the previous high-temperature record, contained a transition metal, which can boost the electron density of states when the *d* electrons are clustered in a narrow range of energies near the Fermi energy. But in the mid-1970s, physicists were surprised to find that certain oxide compounds with comparatively low electron densities of states nonetheless had quite high transition temperatures up to about 13 K. However, it never proved possible to improve on this performance, and oxides moved back out of the limelight.

Encouraged by some speculative theoretical work on the possibility of increasing the strength of the interaction between the free electrons and the lattice vibrations and thereby raising the superconductive transition temperature, Bednorz and Müller of IBM bucked the conventional wisdom and began a new series of investigations into metallic oxides about 3 years ago. In the course of their studies, which were initially unsuccessful, they became aware of 1984 and 1985 reports by the French chemists Claude Michel and Bernard Raveau of the University of Caen, who synthesized metallic lanthanum-copper-oxygen material containing barium, strontium, or calcium. The IBM researchers modified the method of synthesizing similar material and found for barium fractions equal to 0.15 and 0.2 the behavior suggestive of superconductivity that was published last September.

In brief, the investigators found that the electrical resistivity dropped precipitously as the temperature decreased. For example, in a sample with barium fraction equal to 0.15, the resistivity dropped by a factor of 1000 to a value below the sensitivity of the measuring apparatus over the temperature range from 35 to 13 K.

Traditionally, there are two tests for superconductivity, the first being the disappearance of the electrical resistivity. The second is the Meissner effect or flux expulsion in which a magnetic field in a metal is pushed completely out when the metal becomes superconducting. Because drops in resistivity can occur for reasons other than the onset of superconductivity, physicists require the measurement of a significant flux expulsion to verify the superconductivity. Flux expulsion shows up as a large negative susceptibility in a specific type of magnetic susceptibility measurement.



Layered perovskite *body-centered tetragonal structure. A copper atom sits at each lattice point surrounded by six oxygen atoms and eight lanthanum/barium atoms. [Courtesy A. J. Freeman, Northwestern University].*

In addition to the IBM researchers, apparently only the Tokyo and Houston groups followed up the initial report by making magnetic susceptibility measurements. In a report submitted for publication in October, Bednorz, Masake Takashige (a visitor from Tokyo), and Müller described tests on samples that showed large resistivity drops and negative susceptibilities. However, the magnitude of the negative susceptibility was small, indicating that only a part of the samples were superconducting.

In the first of two reports submitted for publication in November and December, Shin-ichi Uchida, Hidenori Takagi, Kitazawa, and Tanaka of Tokyo found a modest negative susceptibility in a sample with a barium fraction of 0.15. But it was their December report, some of which was presented at the Materials Research Society meeting, that elicted so much interest.

X-ray diffraction studies at IBM, Tokyo, and Houston were showing that the original material consisted of three phases. One had a cubic perovskite structure with barium and lanthanum randomly sharing the same lattice sites and a 1:1 concentration ratio of barium and lanthanum to copper. The second phase had a tetragonal layered perovskite structure in which alternating layers of perovskite cubes are displaced diagonally (see figure). This phase also had a 2:1 concentration ratio of barium and lanthanum to copper. The third phase was cupric oxide.

Apparently material synthesized with a nominal 1:1 ratio naturally ended up as a three-phase mixture. But careful preparation with a nominal 2:1 ratio and not too high a barium fraction could yield a nearly single phase material of the composition $(Ba_xLa_{1-x})_2CuO_4$, where x is the barium fraction. In their December report, the Tokyo researchers showed that this single-phase material with x equal to 0.075 exhibited a much sharper resistivity drop than had been reported before, extending only over a few degrees, and a large negative magnetic susceptibility, indicating that a substantial fraction of the sample was superconducting. From this result, the Tokyo group concluded that the layered perovskite phase was the source of the superconductivity, in concurrence with the findings of the IBM researchers, who also studied samples with the 2:1 concentration ratio.

At Houston, Chu and his co-workers

took a somewhat different tack. In the experiments reported in this issue of *Science*, they discuss resistivity and susceptibility measurements on a sample with a concentration ratio of 2:1 and x equal to 0.1. After verifying a high onset temperature of 39 K and a modest negative susceptibility, the investigators then repeated their measurements under hydrostatic pressure.

In the past, pressure has been known to increase the prospects for superconductivity in materials that otherwise are not good candidates for exhibiting the phenomenon. Moreover, although the technological usefulness of a superconductor that requires high pressure is not obvious, some materials scientists believe that, once the material is found, it is possible to "engineer" a material showing a high superconducting transition temperature only under high pressure so that it performs just as well under ambient pressure.

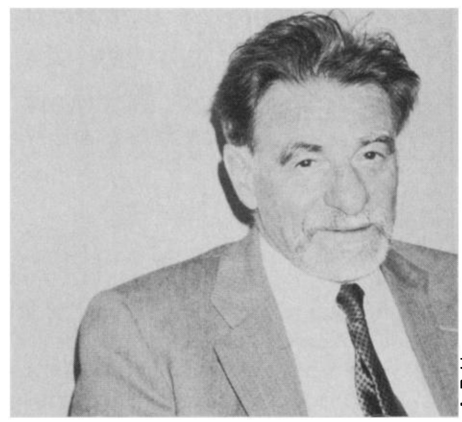
In any case, the Houston researchers found a steady increase in the temperature for the onset of the resistivity drop from about 39 K at ambient pressure to 52 K at 12 kilobars, a much larger effect than ever observed before. The temperature at which the resistivity became too small to measure also rose from 20 K to 25 K over this pressure range. In earlier experiments with sample having a 1:1 concentration ratio, the group also found a dramatic enhancement of the onset temperature from 32 K at ambient pressure to 40 K at 14 kilobars.

It has occurred to nearly everyone working in the field that other group IIA metals might work as well as or better than barium. Strontium in particular was high on the agenda because its ionic radius is close to that of lanthanum, whereas barium is larger, possibly causing some distortion in the lattice and a degradation in the superconducting properties. Müller told *Science* that lattice strains rather than inhomogeneities in the composition might be a cause of the rather wide range of temperatures over which the superconducting transition occurs in barium-lanthanum-copper-oxygen.

Only 3 days apart on 22 and 25 December, respectively, the Tokyo and Bell Labs groups submitted for publication reports on the efficacy of strontium with similar findings. (Researchers at several laboratories also have unpublished data for material containing strontium, including Toshiyuki Sato of the Institute of Molecular Science in Okazaki, Japan, who claims to have single crystals.) Both groups prepared $(Sr_xLa_{1-x})_2CuO_4$ with several values of x and found the best superconducting properties in samples with x near 0.075.

In a sample with this composition, for example, the Bell Labs investigators found a superconducting transition beginning at 40 K and ending at 36 K. For x a little higher at 0.1, the transition region was narrowed to only 1.4 K wide, but the midpoint temperature also decreased slightly to 36.2 K. The large negative magnetic susceptibility value for this composition suggested that the majority of the sample was superconducting. The Tokyo group also reported results for material containing calcium in place of barium. They found that calcium depressed the onset temperation to 18 K or lower.

Over the years there has been considerable speculation that some mechanism other than the accepted interaction between free electrons and lattice vibrations might also be found to drive the transition to superconductivity. Many physicists interested in superconductivity have believed that some new mechanism would be necessary if materials to work in liquid nitrogen were ever to exist.


A. Robinson

K. Alexander Müller. *"We decided to try the material of Michel and Raveau."*

Nonetheless there are some indications that a new mechanism may not be necessary to explain the findings so far. For one thing, according to Müller, as the materials quality gets better and better, the odd features of the first results that suggested something new may be happening are tending to go away. For another, there are already rather conventional models being proposed, although they emphasize different parameters in the equation for the transition temperature. J. Robert Schrieffer of the University of California at Santa Barbara, who is the *S* in the BCS theory, says he would be quite surprised if a new mechanism were needed.

The most conventional model, suggested by Arthur Freeman and Jae Jun Yu of Northwestern University on the basis of just completed electronic structure calculations, is similar to that thought to operate in high-transition temperature superconductors containing transition metals. In many of these materials, the superconductivity is associated with a lattice vibrations of a low frequency (soft phonons), which raise the parameter V^* and hence the transition temperature. Freeman and Yu calculated that such a soft phonon is present in the layered perovskite material and that the details of the electronic structure lead to an enhanced electron-lattice vibration interaction.

The thinking at Bell Labs does not make use of soft modes, but proceeds by analogy with another class of metallic oxide superconductors, barium-bismuth-lead oxide. Although there is still some debate on these materials, Bell Labs theorist Leonard Mattheis attributes both the comparatively high transition temperature of 13 K in these materials and the very high transition temperature in the new materials partly to the high Debye frequency rather than to an enhanced V^* parameter. The high Debye frequency is a consequence of the light oxygen atoms. Often a high Debye frequency is associated with a small V^*, so it is also important that the metal-oxygen, bond-stretching lattice vibrations involved interact with the free electrons sufficiently to give at least a modest V^*. On the basis of his electronic structure calculations, Mattheis suggests that this in fact occurs because the free electron quantum states derive to a considerable extent from oxygen orbitals, a feature also found by Freeman and Yu.

In the end, these and other questions will be answered when better quality, preferably single-crystal, samples become available, although preliminary results of specific heat measurements on sintered samples by Richard Greene of the IBM Yorktown Heights Laboratory already support the Bell Labs model with its high Debye frequency. In the meantime, researchers around the world are also giving the new superconducting materials a complete physical, as it were, in the form of a battery of structural, thermodynamic, and electronic measurements, in the hope not only of understanding what makes them tick but of appraising their technological promise.

Large-scale applications, for example, require that materials remain superconducting in the presence of high magnetic fields and while carrying large electrical currents. There are already preliminary indications that the critical magnetic field above which the new superconducting materials revert to normal metallic behavior exceeds the highest known. One test by Simon Foner of the National Magnet Laboratory of strontium-lanthanum-copper-oxygen material made by Jean-Marie Tarascon of Bell Communications Research and several co-workers indicated the critical field was at least 60 tesla. A similar test in Tokyo of barium-lanthanum-copper-oxygen suggested the critical field could be as high as 80 tesla. ■

ARTHUR L. ROBINSON