Superconductivity Seen Above the Boiling Point of Nitrogen

Anil Khurana

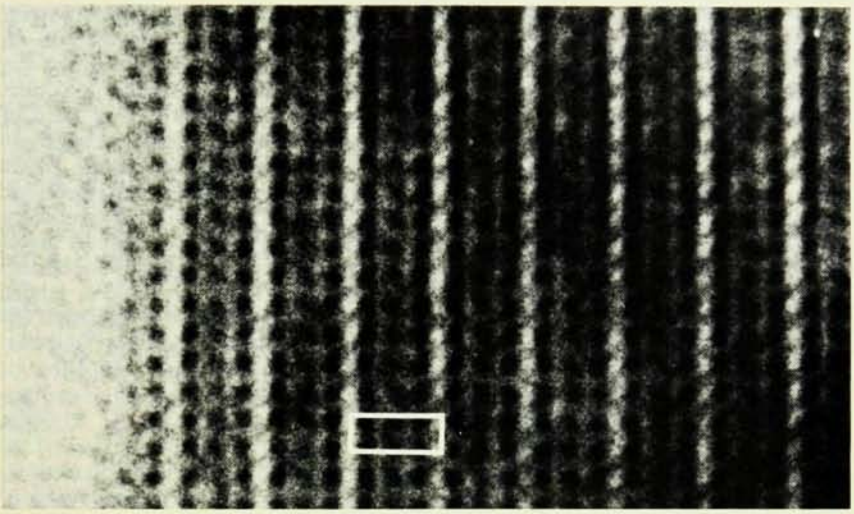
Citation: Phys. Today **40**(4), 17 (1987); doi: 10.1063/1.2819976
View online: http://dx.doi.org/10.1063/1.2819976
View Table of Contents: http://www.physicstoday.org/resource/1/PHTOAD/v40/i4
Published by the American Institute of Physics.

Superconductivity seen above the boiling point of nitrogen

Since the observation[1] by Karl Alex Müller and Johannes Georg Bednorz (IBM Zurich) in January 1986 that an oxide of barium, lanthanum and copper might be superconducting at temperatures up to 35 K, several groups around the world have reported seeing superconductivity above 90 K in a number of ternary oxides containing rare earth elements. Many laboratories are already exploring applications for these materials. Why they are superconducting at such high temperatures is one of many questions that theorists are trying to answer.

On 18 March, more than a thousand physicists jammed the outer lobbies of the ballrooms at the New York Hilton as they waited for more than an hour for the doors to open 45 minutes before the 7:30 pm panel discussion on high-T_c oxides. A brief, two-line announcement about the panel discussion had been made in the program for the annual March meeting of The American Physical Society, held in New York on 16–20 March. Of the 3080 contributed abstracts in the program for the meeting, there was only one—from IBM Yorktown Heights and Zurich—on superconductivity in Ba-La-Cu-O. But because of the growing interest in these oxides by the middle of December, Neil Ashcroft (Cornell University), then chairman of the Division of Condensed Matter Physics of the APS, told us, an effort was made to announce the panel discussion in the program even though it had already been closed.

There was a thunderous applause when Ashcroft, after introducing the members of the first panel—Müller, Shoji Tanaka (University of Tokyo), Paul C. W. Chu (University of Houston), Zhongxian Zhao (Institute of Physics, Academia Sinica, Beijing) and Bertram Batlogg (AT&T Bell Laboratories)—concluded his opening remarks with "These are some of the men, ladies and gentlemen, who set this engine running." The 1140 seats in the Rendezvous Trianon Ballroom had been filled in just a few minutes after the doors opened. Several hundred physicists stood patiently in the side aisles for several hours to listen to a series of five-minute presentations; many more watched the proceedings on monitors placed in the lobbies. According to Ashcroft, more than a hundred physicists were still present when he closed the session at a quarter after three. Many remained until 6 am, when the hotel staff reclaimed the rooms.



High-resolution transmission electron micrograph of $YBa_2Cu_3O_{9-y}$, looking along the (100) direction in the crystal. Assuming that the image can be interpreted as a projected charge density of the crystal, the three colinear black spots correspond to barium and yttrium atoms. The bright layers separating the darker (barium) layers suggest that oxygen vacancies are present on the copper planes between the barium planes. The white rectangle (dimensions approximately 0.4 × 1.2 nm) outlines the unit cell of the crystal. (Photo by Thomas Shaw, IBM Yorktown Heights.)

"A Woodstock for physics" is how Michael Schluter (AT&T Bell Laboratories) described the session at a press conference the following day. Indeed, the repeated requests that Ashcroft, APS vice-president James Krumhansl and APS headquarters staff had to make, requesting their colleagues to please clear the center aisle or the hotel security staff would not let the session begin, were easy reminders of the scene at a rock concert. But the analogy to Woodstock may apply at a deeper level as well: As leaders of research teams hurriedly discussed their evidence for superconductivity above 90 K—a phenomenon unheard of until a month earlier—one could have felt as if one were a part of a ceremonial gathering organized to affirm a new cult. Of course there were lively discussions—experimental details were asked about and questions raised—and theorists presented several, fundamentally different views on the mechanism for superconductivity at such high temperatures. A new cult may not have been born, but the few demonstrations by researchers from industrial laboratories that the new superconducting materials can be turned into useful devices left little doubt in anyone's mind that a new level of technological sophistication is within reach.

Raising the critical temperature for superconductivity to 30–40 K so that superconducting systems could be reliably run using, say, liquid hydrogen or neon has been one of the outstanding problems in physics ever since the discovery of superconductivity in 1911. Bernd Matthias and John Hulm (then at Bell Labs) in the 1950s carried out extensive searches for superconductivity in transition metal alloys and compounds. Their work led Eugene Kunzler to the discovery of materials that remain superconducting in the presence of high magnetic fields, and to the development of superconducting magnets based on NbTi and Nb_3Sn (see

0031-9228 / 87 / 0500 17- 07 / $01.00 © 1987 American Institute of Physics

the article by Hulm, Kunzler and Matthias, PHYSICS TODAY, January 1981, page 34). Such magnets are now used in the Tevatron at Fermilab and in magnetic resonance imaging devices. Further discoveries by Theodore Geballe (now at Stanford University) and Matthias in the sixties raised the transition temperature to above the boiling point of liquid hydrogen (20 K). These efforts culminated with the discovery in 1973 by John Gavaler (Westinghouse Research Laboratories) of the onset of superconductivity in thin films of Nb_3Ge at 23.2 K. "A few years after the discovery of Nb_3Ge in 1973, and especially after Nb_3Si could not be synthesized in a stable form with T_c higher than 18 K," Alex Braginsky of Westinghouse Research told us. "we were quite sure that the T_c can't be raised much higher in the A15 series." (A15 is a crystallographic symbol for structures like beta-tungsten; A15 superconductors, which are mostly compounds with composition Nb_3X or V_3X where X is a non-transition-metal element, also have this crystal structure.) Since the discovery by George Hardy and Hulm of superconductivity in V_3Si ($T_c = 17$ K) in 1952, A15 superconductors have provided the highest values of T_c.

The seeds of the recent revolution may have been sown more than ten years ago. In 1973, David Johnston (then at the University of California, San Diego) discovered superconductivity in $LiTi_2O_4$ at temperatures up to 13.7 K; in 1975, Arthur Sleight (DuPont Research) discovered superconductivity in $BaPb_{1-x}Bi_xO_3$ at temperatures up to 13 K. These discoveries did not raise the highest known value of T_c, nor did they cause among theorists the kind of excitement that discovery of superconductivity in heavy-electron materials later did (see the article by M. Brian Maple, PHYSICS TODAY, March 1986, page 72). But these oxides showed some anomalous features, the most notable being that their critical temperatures were much higher than what experts would have expected from their electron densities. Furthermore, detailed investigations showed[2] that the highest T_c in $BaPb_{1-x}Bi_xO_3$ is obtained for values of x for which the ground state is very close to a metal–insulator transition—a property that seems extremely puzzling when it is viewed in light of the empirical wisdom that T_c for superconductivity in semiconductors increases with the electron density. Because of these features, James Smith (Los Alamos) recalls, Matthias and Batlogg hoped that these oxides might provide an alternative route to high values of T_c. But as we now know, this hope was not to be realized for many years.

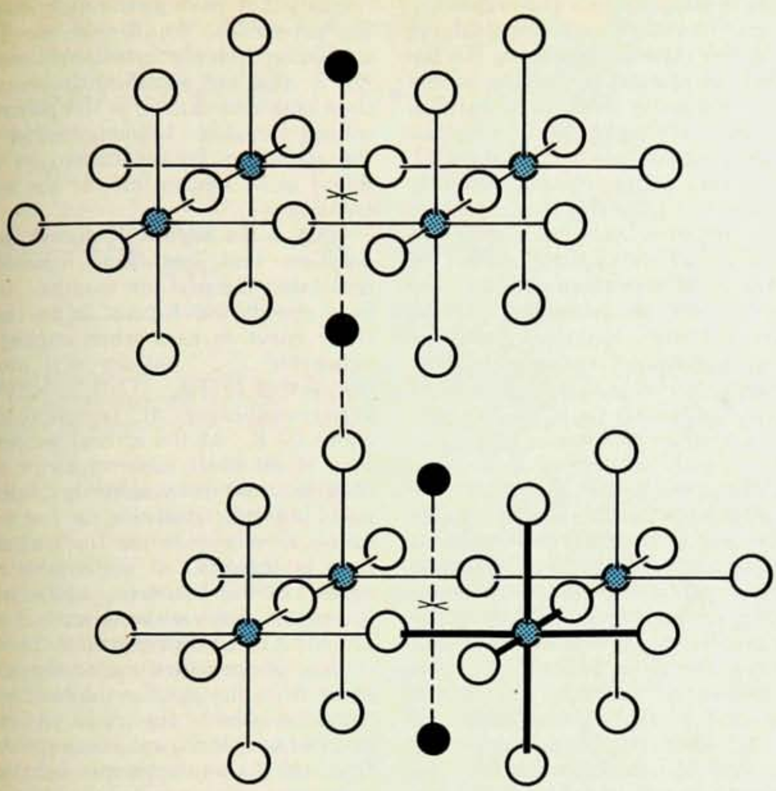
From Zurich to Boston. "When I became an IBM Fellow, I had time to do research again. I resumed my work on superconductors, but decided to move away from A15 intermetallics and search for high T_c's in metallic oxides," Müller told us. He regarded seriously the possibility, discussed by theorists a few years earlier, that the ground state of systems with very strong electron–phonon interactions may undergo a phase transition between superconducting and bipolaronic-insulating states. (Like a polaron, which is an electron that has trapped itself in the potential well of its interactions with the lattice, a bipolaron is a pair of electrons localized because of their interactions with the lattice.) Thus Müller, in collaboration with Bednorz, started studying oxides that were likely to have strong electron–phonon interactions but were also good candidates for polaron formation due to lattice deformations caused by the Jahn–Teller effect. In their first paper,[1] submitted in April 1986 and published in September, they discussed the synthesis of $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$, and its electrical resistivity for $x = 1$ and 0.75. Their conclusions: "In the concentration range investigated, compounds of the Ba-La-Cu-O system are metallic at high temperatures.... Samples annealed near 900 °C under reducing conditions show features associated with an onset of granular superconductivity near 30 K."

So it seems that superconductivity above 30 K was discovered not by serendipity, but by carefully planned and motivated research. However, chance did play some role. Claude Michel and Bernard Raveau had studied the Ba-La-Cu-O system in 1984 at temperatures up to 77 K! Moreover, they prepared their samples by annealing in air at 1000 °C—a procedure that, according to Bednorz and Müller, gives no superconductivity because it does not produce the $Ba_xLa_{2-x}CuO_{4-y}$ phase with the K_2NiF_4-type tetragonal structure (see the figure on page 19) that later x-ray studies found to be the superconducting one in the multiphase $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$.

M. Takashige (University of Tokyo) joined Bednorz and Müller at IBM Zurich last summer; by the middle of October, they had determined by x-ray diffraction the chemical composition and crystal structure of the superconducting phase in the Ba-La-Cu-O system and also obtained further evidence for superconductivity in magnetic susceptibility measurements. But many at the forefront of research in superconductivity were getting ready to go to Bangalore in January, to attend the fifth International Conference on Valence Fluctuations, where superconductivity in heavy-electron materials would be the focus of interest.

On 4 December, in a session on low-carrier-density superconductors at the annual Materials Research Society Meeting in Boston, Chu presented a paper in which he emphasized some of the difficulties in obtaining homogeneous specimens of $BaPb_{1-x}Bi_xO_3$. Toward the end of this talk, he told us, he presented some resistivity data on the Ba-La-Cu-O system that supported the findings of the IBM Zurich group, as further evidence of the unusual superconducting properties of oxides. Koichi Kitazawa (University of Tokyo), who had presented a paper on the anomalous properties of $BaPb_{1-x}Bi_xO_3$ earlier in the same session, now told the audience about the evidence he and his collaborators at Tokyo had obtained for superconductivity in the Ba-La-Cu-O system from both magnetic susceptibility and resistivity measurements. Geballe invited Kitazawa to report on the work by the Tokyo group on the Ba-La-Cu-O system the next day in a session for which he was the chairman. Tanaka, leader of the group at Tokyo, told us that he informed Kitazawa during their phone conversation on the evening of 4 December that the group "had succeeded in obtaining single-phase specimens of $Ba_xLa_{2-x}CuO_{4-y}$ with K_2NiF_4-type structure" and that "a specimen with $x = 0.15$ had exhibited zero resistivity at temperatures as high as 23 K." The following week, Kitazawa received by facsimile from Japan a preprint of their work on superconductivity in the single phase $Ba_xLa_{2-x}CuO_{4-y}$ that was made available to major laboratories in this country. Tanaka also told us that Kitazawa discussed this work in seminars he gave that week at AT&T Bell Labs and Stanford University.

For decades in superconductivity research every little increase in the highest known value of T_c has been greeted with enthusiasm and has kept alive the hope that large-scale applications of superconductivity in technology may become possible someday. Everyone, therefore, would have been quite satisfied to see the highest T_c jump from 23.2 K to about 30 K in 1986. But before the year ended, there were three independent reports—from the University of Tokyo, AT&T Bell Labs and the Institute of Physics in Beijing—that by substituting strontium for barium in the class of oxides studied by Bednorz and Müller, the T_c can be raised up to 40 K. Also, in the last week of December, Chu's group at Houston reported seeing onset of superconductivity at temperatures up to 52 K in the



Tetragonal K_2NiF_4-type structure of $(Ba,Sr)_xLa_{2-x}CuO_{4-y}$ at room temperature consists of alternating layers along the *c*-axis of perovskite (CuO_3) and rock-salt (La–O) structures. Barium or strontium is substituted on lanthanum sites (black). The perovskite layers consist of corner-sharing CuO_6 octahedra. Each perovskite layer is shifted relative to the next so that the copper sites (blue) in one layer are aligned with the oxygens (white) in the next layer. In the CuO_6 octahedra, the Cu–O distance in the perovskite layer is smaller than the Cu–O normal to the layer. Because of the weak coupling between layers, the band structure and other electronic properties show features associated with two-dimensional behavior. (Based on a figure provided by IBM Yorktown Heights.)

Ba-La-Cu-O system under a pressure of 12 kbar. After these reports, everyone with experience in superconductivity research dropped everything and started working on the new oxide superconductors. "We have been working for almost a year to make thin films of other superconducting materials, but now we must start again and do the same for the oxides," Allen Goldman (University of Minnesota) told us.

On 16 February, the National Science Foundation announced formally that a team of experimenters from the University of Alabama in Huntsville and the University of Houston, led by Chu, had observed onset of superconductivity at temperatures as high as 92 K. The announcement left active researchers waiting for the 2 March issue of *Physical Review Letters* with the impatience of a runner waiting for the baton in a relay race.

The Alabama–Houston group did not reveal the chemical composition of their compound in the press releases issued on 16 February, nor did they send out to their colleagues preprints of the two papers that were received at the *Physical Review Letters* office on 6 February. They did this, Chu told us, on the recommendation of their patent attorney. For almost two weeks, the group deferred all inquiries about their work to 2 March, when the issue of *Physical Review Letters* containing their papers would come out. But because of the developments of the previous two months, the superconductivity community received the news about their 90-K superconductor less skeptically than it might normally have. For example, when we asked Philip Anderson (Princeton University) on 3 February about the highest possible T_c in the theory he had developed[3] a month earlier for superconductivity in Ba-La-Cu-O and Sr-La-Cu-O, he had said, "The antiferromagnetic transition temperature is the limit [for NiO this is about 600 K]. . . . Maybe it is realistic to expect a superconducting T_c as high as 100 K or some fraction of the antiferromagnetic exchange interaction. . . . How close to the maximum you can reach is very difficult to predict." And Geballe told us on 20 February, "We now know that there is *bulk* superconductivity at 40 K. . . . I think there really is superconductivity at 94 K, but I don't know how much there is, whether it is a minority phase in the sample that goes superconducting or the whole sample." After making some initial resistivity measurements that showed the possibility of superconductivity at about 90 K, the Alabama–Houston group sent their sample to Los Alamos for dc susceptibility measurements using a SQUID magnetometer, because a dc diamagnetic response (flux exclusion) is clearer evidence for superconductivity than a rapid decrease in electrical resistivity. Commenting on this, Smith told us on 23 February, "We are not an interested party; we consider ourselves neutral. [Chu] sent us something and it went superconducting at a high temprature. We believe it and I think it is an important confirmation."

"A stable and reproducible superconductivity transition between 80 K and 93 K has been unambiguously observed both resistively and magnetically in a new Y-Ba-Cu-O compound system at ambient pressure," reads the first sentence of the abstract to the first of a series of two papers in the 2 March 1987 issue of *Physical Review Letters* by M. K. Wu, J. R. Ashburn and C. J. Torng (University of Alabama in Huntsville), P. R. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang and Chu (University of Houston). With words like "stable and reproducible" and "unambiguously observed," Chu told us, "we wanted to assure the readers that we have seen genuine superconductivity and to dispel any skepticism our colleagues in superconductivity research might have." There have been several cases in the past when fortuitous anomalous decreases in electrical resistivity were mistaken for superconductivity, the reports on TTF-TCNQ (see PHYSICS TODAY, May 1973, page 17) being the best known example of such "irreproducible" high-T_c superconductors.

News about superconductivity at temperatures up to 100 K in an oxide of yttrium, barium and copper also appeared in the *People's Daily* (China, 25 February)[4] and, John Rowell of Bell Communications Research told us, prompted researchers at Bellcore to measure the resistivity of an oxide of yttrium that their magnetic measurements had earlier suggested was very likely not superconducting. "A set of five samples containing different ratios of yttrium and barium were prepared on 3 January, but x-ray measurements showed these to have multiple phases," Rowell said. However, their resistivity measurement of 25 February showed a superconducting transition at 91 K in two of the samples. *Physical Review Letters* received a paper[4] "Superconductivity at 90 K in multi-phase oxide of Y-Ba-Cu" by researchers at Bellcore on 27 February.

According to Tanaka, on 21 February Kagoshima (University of Tokyo, but in a different department from Tanaka) announced finding a new superconductor with T_c around 90 K. However, Kagoshima also did not disclose the composition of the material, and Tanaka's group obtained superconductivity above 90 K only after they heard about the work in China on Y-La-Cu-O.

No sooner had the race ended to find out what the Alabama–Houston group's 90-K superconductor was than another one started: What was the composition and the structure of the superconducting phase in the multiphase Y-La-Cu-O? Since the 16 February announcement there had been a rumor that the sample the Alabama–Houston group had sent to Los Alamos for dc susceptibility measurements "looked green." However, within a few days after they started working with Y-La-Cu-O, researchers at a number of laboratories had determined that the superconducting phase in the multiphase green sample was in fact black, an oxygen-deficient perovskite, $YBa_2Cu_3O_{9-y}$ (see the figure on page 21). Different research groups arrived at this answer using a variety of different analytical instruments and techniques—the Bell Labs group carried out a detailed study of the phase equilibria of the ternary oxide system BaO, CuO and Y_2O_3, the Bellcore–National Research Council of Canada group studied x-ray diffraction from a $40\times30\times15$-micron single crystal of $YBa_2Cu_3O_{9-y}$, and the IBM Almaden group used a combination of analytical transmission electron microscopy, microprobe and x-ray diffraction.

Suddenly superconductivity above 90 K seems like a very common phenomenon. At the marathon APS session on 18 March, groups from Ames and Brookhaven; Los Alamos; AT&T Bell Labs; Tokyo; and Alabama, Houston and the Carnegie Institution's Geophysical Laboratory reported superconductivity above 90 K in a whole class of compounds with chemical composition $RBa_2Cu_3O_{9-y}$, where R stands for a transition metal or a rare earth ion. Scandium, lanthanum, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, ytterbium and lutetium have been successfully substituted to obtain superconductivity above 90 K.

'Every third world country can make them," Smith observed about how easy it is to synthesize the oxide superconductors. In their first paper, Bednorz and Müller reported preparing the Ba-La-Cu-O compound by mixing in the appropriate ratio nitrates of barium, lanthanum and copper, and precipitating the solid mixture with oxalic acid. The solid precipitate was subsequently heated at 900 °C for five hours, pressed into pellets at 4 kbar and sintered at 900 °C. X-ray diffraction studies by Takashige, Bednorz and Müller, and independently by Shin-ichi Uchida, Hidenori Takagi, Kitazawa and Tanaka (University of Tokyo) revealed that samples prepared in this way consisted of three phases: $La_{1-x}Ba_xCuO_{3-y}$ with perovskite structure, $La_{2-x}Ba_xCuO_{4-y}$ with a layered perovskite structure of the K_2NiF_4 type and CuO.[5] The relative proportion of these phases in a sample depends on the heat treatment. The fraction of a sample that is superconducting can be determined from the magnetic susceptibility measurements: A superconductor in low magnetic fields behaves as a perfect diamagnet and has a magnetic susceptibility (in Gaussian units) of $-1/(4\pi)$; comparing the measured moment against this value for an ideal superconductor gives a good estimate of how much of the sample is superconducting. The two groups determined the composition and structure of the superconducting phase by relating the intensities of lines in x-ray diffractograms to the fraction of the sample that was superconducting.

Most laboratories now prepare samples of $La_{2-x}Ba_xCuO_{4-y}$ and $La_{2-x}Sr_xCuO_{4-y}$ from La_2O_3, CuO and $BaCO_3$ (or $SrCO_3$) rather than aqueous solutions of nitrates. (But Robert Cava, of AT&T Bell Labs, told us that they "prefer to use lanthanum hydroxide because commercially available lanthanum oxide usually has some hydroxide in it.") The powders are mixed in the appropriate cation ratio and heated in air for several hours. The reacted mixture is cooled, ground, pressed into pellets and sintered again at 900 °C to 1100 °C. This procedure gives single-phase material with the K_2NiF_4-type structure for x less than 0.3. Additional annealing of the sample is sometimes necessary for larger values of x and to improve the superconducting properties of the sample.

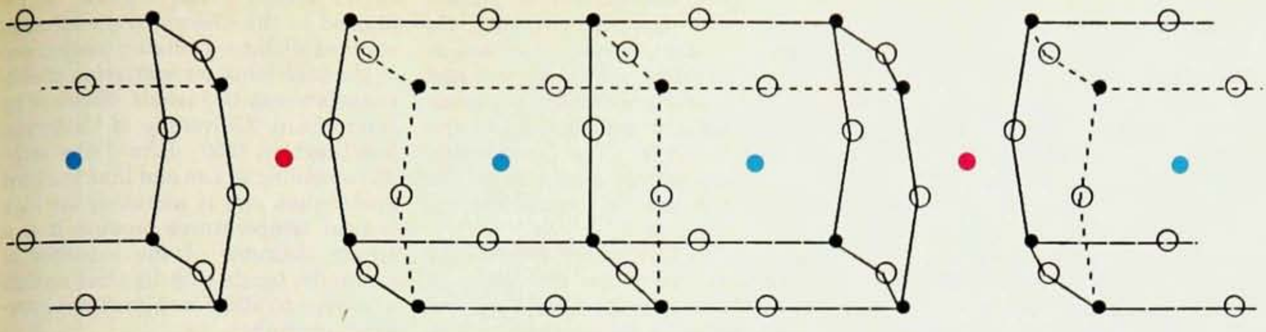
The Houston–Alabama group also prepared their sample through a solid-state reaction of appropriate amounts of Y_2O_3, $BaCO_3$ and CuO, producing $Y_{1.2}Ba_{0.8}CuO_{4-y}$.

Several laboratories have grown single crystals of $La_{2-x}Ba_xCuO_{4-y}$ and $(La_{1-x}Sr_x)_2CuO_{4-y}$. Having the right concentration of oxygen is one of the difficulties encountered in growing crystals that have good superconducting properties, Smith told us. The transition in single crystals obtained so far is also not significantly sharper than obtained earlier in the polycrystalline samples. Inhomogeneities in the strontium concentration are believed to be responsible for the wide transition.

'What is the highest T_c today?' is a question that has been repeatedly asked over the past few months. "One must specify which point in the resistivity curve is used when quoting a value for T_c," Batlogg said about claims that $Sr_xLa_{2-x}CuO_{4-y}$ may be superconducting at temperatures above 50 K. At the critical temperature of an ideal superconductor the electrical resistivity suddenly drops to zero, but the transition in the new oxides is very wide—as the temperature is lowered, an appreciable decrease in the resistivity starts well before the zero-resistance state is obtained. A conservative estimate for the critical temperature, called the midpoint T_c, is the point in the resistivity curve at which the resistivity has dropped to half the value extrapolated from the high-temperature behavior. It is also useful to know the temperatures at which the resistivity has dropped by 10% and 90%, respectively, for these give an estimate of how wide the transition is and whether it is symmetric about the midpoint. The midpoint T_c is usually much lower than the onset T_c, the temperature at which the resistivity first begins to deviate from its behavior at high temperatures.

When discussing the new oxides it is also important to remember that the critical temperatures of $Ba_xLa_{2-x}CuO_{4-y}$ and $Sr_xLa_{2-x}CuO_{4-y}$ depend sensitively on the barium or strontium concentration. Moreover, two samples with the same chemical composition may have different critical temperatures if they have been given different heat treatments. The oxygen deficiency, the factor y in $Ba_xLa_{2-x}CuO_{4-y}$, $Sr_xLa_{2-x}CuO_{4-y}$ and $RBa_2Cu_3O_{9-y}$, depends both on the temperature and the atmosphere in which the powders are sintered. It is extremely hard to control and must be optimized for each material and composition. Detailed studies of $Sr_xLa_{2-x}CuO_{4-y}$ provide a good illustration of some of the remarkable properties of these oxides.

Jean-Marie Tarascon, Laura H. Greene, Ross McKinnon, George Hull (Bell Communications Research) and Geballe have studied[6] in detail the superconducting properties of $La_{2-x}Sr_xCuO_{4-y}$ as a function of the strontium concentration x. They find



Crystal structure of $YBa_2Cu_3O_{9-y}$, an orthorhombically distorted perovskite, also consists of layers of Cu (black) and O (white) normal to the c-axis, here along the horizontal. Every third layer is yttrium (red) rich. The CuO_2-Ba-CuO_2-Ba-CuO_2 sandwich shown in the middle is important for superconductivity; Ba sites shown in blue. (Adapted from a figure provided by the Bellcore group.)

that T_c is highest and the transition sharpest for $x = 0.15$. Robert Bruce van Dover, Cava, Batlogg and Edward Rietman (AT&T Bell Labs) have independently determined $x = 0.15$ to be the best composition for superconductivity.[6] The Bell Labs group also reports that the fraction of the sample that is superconducting is also maximum for this value of strontium concentration. The two groups agree that the transition width is 1.5–2 K. No group has reported genuine superconductivity for x below 0.05 or above 0.4. The critical temperature in $BaPb_{1-x}Bi_xO_3$ also depends sensitively on the bismuth concentration and is maximum when x is 0.25, but the transition width in single crystals is only 0.25 K.

Concerning the oxygen concentration y, the Bellcore group reports[6] that annealing $La_{2-x}Sr_xCuO_{4-y}$ in vacuum, instead of in air or oxygen, reduces the diamagnetic signal and smears out the transition. But this loss of superconductivity can be restored by annealing the sample once again in oxygen, Greene told us. The Bellcore group claims that by optimizing the oxygen treatment they have obtained the highest T_c (41 K at midpoint) for this compound.

Not only is superconductivity in $RBa_2Cu_3O_{9-y}$ even more sensitive to the heat treatment and oxygen content, it also is sensitive to the rate at which the samples are cooled after sintering. "The reaction time, the reaction temperature, the quenching rate, the reaction atmosphere and the composition are all interrelated," Chu told us. How then does one find superconductivity in a new material? "It cannot be all that difficult if several groups could verify existence of superconductivity above 90 K in just a few days," Chu joked.

A BCS superconductor? John Bardeen, Leon Cooper and Robert Schrieffer proposed in 1957 that superconductivity arises when electrons in solids are so correlated that they form bound pairs. Their theory also explained that the attractive interaction that binds members of a pair arises due to the electrons' interaction with the lattice vibrations, or in other words, due to exchange of virtual phonons between electrons. The theory assumed, successfully, that the pairing in metals is such that an electron with spin up and momentum **k** is paired with one with spin down and momentum $-\mathbf{k}$ and that the angular momentum of the pair is zero.

Every time a new superconductor is discovered, one of the questions foremost on everyone's mind is: Is it a BCS superconductor? The question does not challenge the explanation that superconductivity arises due to pairing of electrons; it merely asks what mediates the attractive interaction between the electrons and what configuration the pairs are in. Pair states more general than the singlet used in the BCS theory of 1957 are also possible—in the superfluid phases of He^3, for example, the pairs are in spin-triplet states.

One of the questions raised by the new discoveries in fact dates back to the 1960s, when theorists began to ask whether there is an upper bound on T_c in phonon-mediated superconductivity. Theorists seem to disagree on what the upper bound is or whether one exists, but Anderson and Marvin Cohen (University of California, Berkeley) argued in 1972 that T_c cannot be raised indefinitely in the phonon mechanism. The critical temperature in the BCS formula depends, among other factors, linearly on some "characteristic" phonon frequency, which, for the purpose of obtaining a bound on T_c, may be taken to be the Debye frequency, the highest phonon frequency in the lattice. But "if you raise the Debye frequency," Anderson told us, "then the attractive pairing interaction decreases [because it varies inversely as the square of the phonon frequency]." Anderson also said that for the large values of the electron–phonon coupling needed to explain critical temperatures as high as 90 K, the electrons would become so "heavy" that they would be localized in polaron-like states.

Most theorists agree that the same mechanism is operating in all the new oxide superconductors, but there is no agreement yet on what this mechanism is. All the ideas that have been proposed emphasize the importance of two-dimensional layers of copper and oxygen; their detailed implications have so far been discussed mostly in the context of superconductivity in La_2CuO_4 doped with barium or strontium. Pure La_2CuO_4 and $La_{2-x}(Sr,Ba)_xCuO_{4-y}$ for values of x for which there is no superconductivity are semiconductors. But views differ at present even about this semiconducting behavior.

According to Anderson, La_2CuO_4 behaves as a semiconductor because its ground state is that of a Mott insulator, in which each electron is localized on a lattice site due to strong electron–electron interactions. Pairs of nearest neighbor electrons in this insulating state are always in a spin-singlet state, but there is no long-range antiferromagnetism. The bonds that bind pairs of electrons in a singlet configuration fluctuate: The spin of an electron may point up at one instant because that of its neighbor to the right is down; the next instant it may be down because that of its neighbor to the left is now up. Anderson calls this a "resonating valence bond" state; the word "resonance" here is borrowed from the theory of the chemical bond, where, Linus Pauling first showed, delocalized or resonating bonds enhance the stability of molecules such as benzene. It is these "pre-existing" pairs of elecrons that cause the superconductivity as soon as they become delocalized, Anderson told us. Doping La_2CuO_4 with strontium or barium shifts it away from the insulating state and delocalizes the electron pairs.

Leonard Mattheiss (AT&T Bell Labs) and Arthur Freeman, Jaejun Yu and Jian-hua Xu (Northwestern) claim that La_2CuO_4 is a semiconductor because of a structural transformation of the crystal that opens a gap at the Fermi surface.[7] However, they differ on the type of distortion that is responsible for this transition. They have done detailed calculations of the band structure of La_2CuO_4. They both find, independently, that the band structure has two-dimensional character—there is very little dispersion perpendicular to the plane of the Cu–O octahedra—and that the Fermi surface lies in the states due to the hybridized 2p (oxygen) and $3d_{(x^2-y^2)}$ (copper) levels. The Fermi surface has the property of "nesting"—one part of the Fermi surface when translated along a symmetry direction will nicely fit into another. This property of the Fermi surface, combined with the strong electron–phonon interaction, makes the system susceptible to a structural phase transformation that doubles the unit cell and opens a gap at the Fermi surface.

A crystallographic transformation between tetragonal and orthorhombic structures has been observed in La_2CuO_4 when its temperature is lowered,[7] but the significance of this transformation for the electronic properties is still unclear. Schluter told us that electrons near the Fermi surface couple only to the so-called breathing mode, in which the four oxygen atoms around a copper atom vibrate in phase, and that no one has yet seen the structural transformation expected when the frequency of this breathing mode vanishes. Werner Weber (AT&T Bell Labs) finds, in his detailed calculations of the phonon spectrum, that the frequency of the breathing mode indeed becomes negligibly small due to the strong electron–phonon interaction. Both Matheiss and Freeman say that doping La_2CuO_4 with a divalent atom such as barium or strontium destroys the nesting of the Fermi surface and suppresses the structural instability. But a system close to such an instability will have phonon modes of very low frequency that, according to Matheiss and Freeman, will generate the strong pairing interaction needed to explain the high critical temperatures. Unlike Freeman, however, Weber and Mattheiss think that the observation of the lattice distortion corresponding to the breathing mode is crucial to the success of the phonon mechanism.

Vladmir Kresin (Lawrence Berkeley Laboratory) says that the pairing interaction in the oxides is mediated not only by low-frequency phonons but also by plasmons, the quanta of plasma oscillations of the electron gas. He argues that the plasma dispersion is that of a two-dimensional system and that these two-dimensional plasmons give a significant contribution to the pairing interaction. The contribution of three-dimensional plasmons to the pairing interaction is usually negligible, he told us.

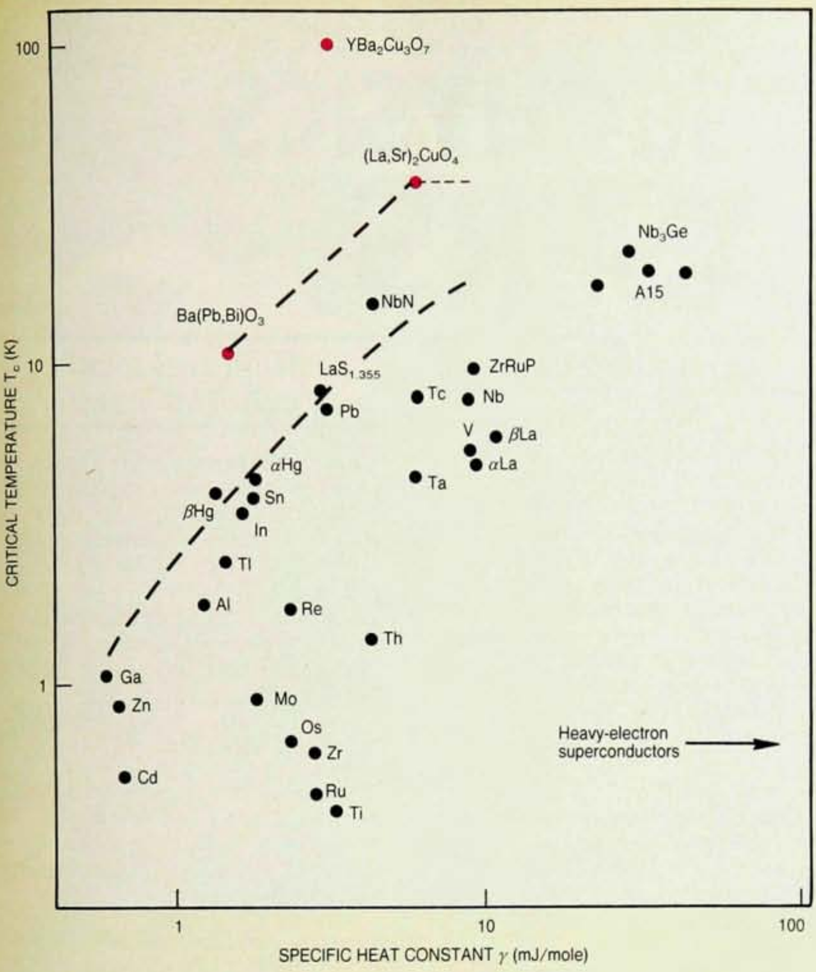
In 1973, David Allender, James Bray and Bardeen (all at the University of Illinois, Urbana, at the time) proposed a new mechanism for superconductivity, based on ideas earlier discussed by Vitaly Ginzburg and, independently, by William Little (Stanford University), to guide experimental searches for high-T_c superconductors. They proposed that in metal–semiconductor sandwiches, pairing between electrons in the metal may be mediated by electron–hole pairs, loosely called excitons, in the semiconductor. This mechanism could lead to high critical temperatures, they argued, if the gap between the conduction and valence bands in the semiconductor is small and extends over a large part of the Fermi surface. According to Bardeen, this same mechanism could, "with some help from phonons," explain a T_c as high as 90–100 K in the oxides. In an extension of the excitonic mechanism that is specific to the electronic properties of the oxides, Chandra Varma, S. Schmitt-Rink (AT&T Bell Labs) and Elihu Abrahams (Rutgers University) argue that the pairing is mediated by a localized excitation that transfers an electron from an oxygen to a nearby copper. The possibility of such an excitation arises, Abrahams told us, because the copper d levels are very close in energy to the oxygen p levels. The instantaneous charge configuration of copper and oxygen may be viewed as a tightly bound electron–hole pair and, therefore, as an exciton. The binding is strong because the copper–oxygen distance is small, and because the electron density is low, so that the Coulomb interaction is not screened. This charge-transfer excitation may be observable, the authors suggest, in optical absorption studies of the normal state of La_2CuO_4.

What about Müller's hunch for finding high critical temperatures in oxides with Jahn–Teller active transition metal ions? The Jahn–Teller distortion in $(Ba,Sr)_xLa_{2-x}CuO_{4-y}$ lowers the d_{z^2}–p band below the Fermi energy, but D. H. Lee (IBM Yorktown Heights) and J. Ihm (Bellcore) argue that this effect may be partially neutralized by electron–electron interactions. They assume that the d_{z^2}–p band is in fact lifted up in energy so that both the $d_{x^2-y^2}$–d and d_{z^2}–p bands straddle the Fermi surface. The high T_c is explained in this theory by an enhancement of phonon-mediated pairing due to the possibility for scattering of electrons between two bands, discussed by Harry Suhl (University of California, San Diego) in 1959. Jahn–Teller activity, according to Lee and Ihm, is a good guide when one is searching for high critical temperatures because it is a strong indicator of the existence of electronic bands that lie close enough in energy to allow for significant interband scattering.

Which one of these many theoretical ideas ultimately wins will be determined by careful analysis of data from experiments that probe the superconducting state. The BCS theory makes detailed predictions about the properties of a superconductor. Measurement of the lower critical field at which the magnetic response of a superconductor differs from ideal diamagnetism, of the upper critical field at which superconductivity is destroyed, and of ultrasonic attenuation and electromagnetic absorption all provide important tests of the BCS theory and mechanism. Many of these experiments, ultrasonic attenuation, for example, require single crystals and have not been performed yet. There have been measurements of critical fields, infrared absorption and tunneling on polycrystalline Sr-La-Cu-O. The data so far, especially from infrared absorption and tunneling, neither agree with the predictions of the BCS theory nor show conclusively what other mechanism might be operating.

The insensitivity of $RBa_2Cu_3O_{9-y}$ to the presence of rare earth ions such as gadolinium that are magnetic and normally suppress superconductivity, Chu and Smith think, puts severe constraints on theoretical models. Schrieffer (now at the Institute of Theoretical Physics, Santa Barbara) told us that the data presented at the panel discussion by a group from Exxon Research and Engineering strongly suggest that antiferromagnetic fluctuations might be important for superconductivity. A good understanding of this mechanism will certainly help the search now under way for even higher critical temperatures.

"We will be living in a different world ten years from now," Batlogg said on 6 March, his optimism buoyed by the properties of single-phase $YBa_2Cu_3O_{9-y}$. For many applications, such as generating high magnetic fields and making power transmission lines, it is very important that both the critical current density and the critical magnetic field, at which superconductivity is destroyed, be high. All of the new oxides are type-II superconductors,



Critical temperature for superconductivity versus the density of states at the Fermi energy, measured by the electronic specific heat constant γ. Values of γ are obtained by fitting measured values of thermodynamic functions in the superconducting phase to the behavior predicted by the BCS theory. The oxide superconductors are well separated from all the others. Unlike other superconductors, the pairing interaction in the oxides is probably mediated not by phonons but by a different mechanism. (Based on a graph provided by AT&T Bell Labs.)

in which the critical current density is not necessarily an intrinsic property of the material but depends on, among other things, the method of preparation and the grain size. The Bell Labs group has determined that superconductivity in $YBa_2Cu_3O_{9-y}$ at 77 K, the boiling point of liquid nitrogen, is not destroyed in zero external fields by currents as high as 1100 amps/cm^2. This news about the critical current density in $YBa_2Cu_3O_{9-y}$ was extremely welcome: It came at a time when some experts were beginning to wonder whether, because of the unexpectedly small critical current densities (a few hundred milliamps/cm^2) in $Sr_xLa_{2-x}CuO_{4-y}$, these new superconducting materials may not be useful for the high-current applications producing high magnetic fields or for making power transmission lines. However, a group from the Westinghouse Research Laboratory has now obtained critical current densities as high as 10^5 amps/cm^2 in $Sr_xLa_{2-x}CuO_{4-y}$. As Müller pointed out, "The critical current density in Nb_3Sn was also not very high when it was first discovered."

Not all applications require the same properties of a superconductor. In high-energy accelerators, where superconducting magnets are now used extensively, superconducting properties of the material used for magnets must include very high average current density in regions of high fields, and stability when there are heat inputs such as beam loss and intense synchrotron radiation, Gene Fisk of Fermilab told us. Indeed, the magnets at Fermilab were developed to run at 4.6 K and not at a temperature closer to 23 K, the highest T_c then known.

The Stanford group has obtained thin films of $La_{2-x}Ba_xCuO_{4-y}$ by electron evaporation, sputtering and codeposition of cations in a beam of oxygen. At the panel discussion on 18 March, Müller reported that researchers at IBM Yorktown Heights have obtained thin films, about 400 nm, of $Y_{0.87}Ba_{1.53}Cu_3O_y$ that show onset of superconductivity near 97 K and zero resistance below 87 K. Several experts think that these films may provide the first technological applications of the new superconductors in fabricating electronic devices and in wiring electronic components in computers. "Because of our interest in developing faster communications systems, high current densities are not really important to us [at Bellcore]," according to Rowell.

While the theorists and experimenters are busy trying to understand the physics of the new superconductors and thinking of ways to turn these materials into useful products for society, everyone wonders whether the critical temperature can be raised even higher. Certainly, inquiries about superconductivity at room temperature no longer seem unreasonable. Several groups have observed sharp decreases in resistivity by two to three orders of magnitude in mixed-phase samples at temperatures near 240 K. The decrease in resistivity is reproducible and, many groups say, similar to the behavior that finally led to the discovery of superconductivity above 90 K. "If the same luck holds," Chu said, "superconductivity at 240 K may be obtained in the near future."

—Anil Khurana

References

1. J. G. Bednorz, K. A. Müller, Z. Phys. B **64**, 189 (1986).
2. B. Batlogg, Physica (Utrecht) **126B**, 275 (1984). K. Kitazawa, S. Uchida, S. Tanaka, Physica (Utrecht) **135B**, 505 (1985).
3. P. W. Anderson, Science **235**, 1196 (1987).
4. Z. Zhao, L. Chen, Q. Yang, Y. Huang, G. Chen, R. Tang, G. Liu, C. Cui, L. Chen, L. Wang, S. Guo, S. Li, J. Bi, to be published in Kexue Tongbao, March 1987. J. M. Tarascon, L. H. Greene, W. R. McKinnon, G. W. Hull, Phys. Rev. B1, to be published 1 May.
5. J. G. Bednorz, M. Takashige, K. A. Müller, Europhys. Lett. **3**, 379 (1987). H. Takagi, S. Uchida, K. Kitazawa, S. Tanaka, Jpn. J. Appl. Phys. Lett., in press.
6. J. M. Tarascon, L. H. Greene, W. R. McKinnon, G. W. Hull, T. H. Geballe, Science, **235**, 1373 (1987). R. B. van Dover, R. Cava, B. Batlogg, E. Rietman, Phys. Rev. B **35**, 5337 (1987).
7. Jaejun Yu, A. J. Freeman, J.-H. Xu, Phys. Rev. Lett. **58**, 1035 (1987). L. F. Mattheis, Phys. Rev. Lett. **58**, 1028 (1987). J. D. Jorgensen, H. B. Schüttler, D. G. Hinks, D. W. Capone II, K. Zhang, M. B. Brodsky, D. J. Scalapino, Phys. Rev. Lett. **58**, 1024 (1987). ☐