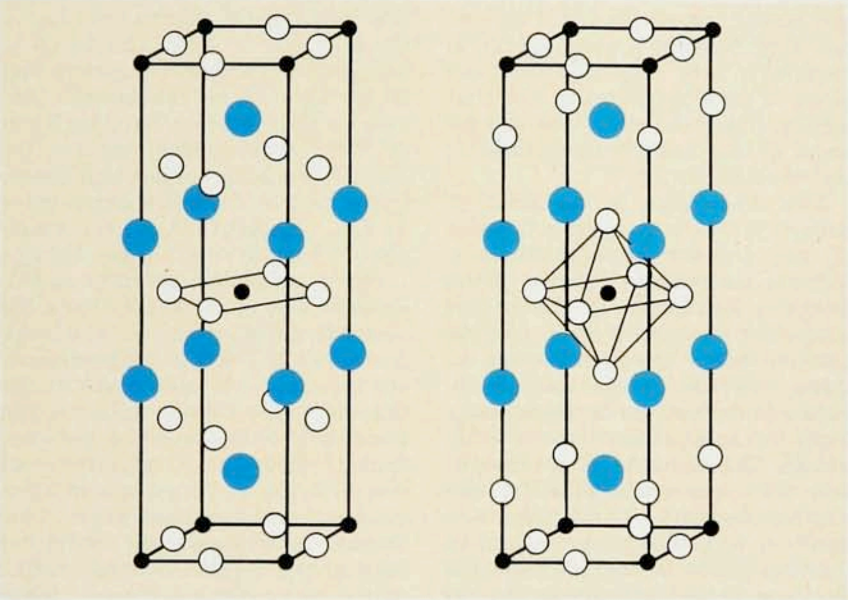
ELECTRON SUPERCONDUCTORS CHALLENGE THEORIES, START A NEW RACE

Just when discoveries of superconductors having critical temperatures up to 70–80 K had ceased to cause much commotion in the popular press, or to compel researchers to give up their ongoing projects and start studying the new materials, announcement of a new class of 20-K superconductors in January once again put the superconductivity community on a high alert. In all of the high-temperature, cuprate superconductors discovered in the past three years, the charge carriers are holes, or vacancies in the valence band. By contrast, in the superconductors announced in January the charge carriers are electrons. The discovery may provide the key to the correct theoretical model for the cuprate superconductors. It might also guide the search for new materials with critical temperatures even higher than the current record of 125 K.



Crystal structure of Nd_2CuO_4 (left), the parent material for electron superconductors. Unlike in La_2CuO_4, the parent material for hole superconductors (shown at right), the tetragonal unit cell for Nd_2CuO_4 has no apical oxygen atoms (the ones above and below the Cu atoms). Copper atoms are shown in black, oxygen atoms are shown in white and lanthanum or neodymium atoms are shown in blue.

Chemically, the new materials are similar to the first family of cuprate superconductors discovered in January 1986 by Georg Bednorz and Alex Müller of the IBM Zurich Research Laboratory. The Bednorz–Müller superconductor—$La_{2-x}(Ba,Sr)_x CuO_{4-y}$—was obtained by partially substituting divalent barium or strontium for the trivalent lanthanum in La_2CuO_4. In the first paper on electron superconductors, Y. Tokura, H. Takagi and Shin-ichi Uchida (University of Tokyo) reported observing superconductivity in $Ln_{2-x}Ce_x CuO_{4-y}$, where Ln was one of the light trivalent lanthanides praseodymium, neodymium or samarium.[1] Soon after the Tokyo report, Brian Maple's group at the University of California, San Diego, reported[2] superconductivity in $(Nd,Pr)_{2-x}Th_x CuO_{4-y}$ and in $Eu_{2-x}Ce_x CuO_{4-y}$. Thus electron superconductors are obtained when a tetravalent lanthanide is partially substituted for the trivalent lanthanide in compounds of the form Ln_2CuO_4. Anthony James, Donald Murphy and Susan Zahurak (AT&T Bell Labs) have reported[3] superconductivity when fluorine is partially substituted for oxygen in Nd_2CuO_4.

The crystal structure of the electron superconductors is also similar to that of the hole superconductor of Bednorz and Müller (see the figure above). The only difference between the two structures is that each copper atom is bonded to four oxygen atoms in the electron superconductor, whereas the copper is surrounded by an octahedron of oxygens in the hole superconductor.

The Hall coefficient in the new superconductors is negative,[4] unlike in earlier cuprate superconductors, where it is positive.[5,6] For a system of free particles of charge e the Hall coefficient is given simply by $1/nec$ (in cgs units), where n is the particle density. Therefore in simple metals and semiconductors the sign of the Hall coefficient determines unambiguously whether the charge carriers are electrons or holes. The relationship between the nature of the charge carriers and the Hall coefficient is not so straightforward in solids with a complicated band structure (of electronic states), such as cuprate superconductors. But the sign of the Seebeck coefficient, which measures the voltage produced when a thermal gradient is applied across the sample, also is reversed in the new superconductors compared with that in the earlier cuprates.[4,6] The voltage produced in the Seebeck effect opposes the diffusion of mobile particles in response to the thermal gradient in

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the solid. So the sign of the Seebeck voltage, too, is evidence that the charge carriers in the new superconductors are electrons.

CuO_2 planes, again

The secret of the cuprate superconductors lies in their copper–oxygen planes. Both copper and oxygen are divalent in the parent compound—La_2CuO_4 or Nd_2CuO_4. With respect to the closed-shell configurations of $O^{2-}(2p^6)$ and Cu^{1+} $(3d^{10})$, the ground state of the parent compounds has electrons taken from—or holes added to—the copper sites. The holes are not mobile but are localized on copper sites, because it costs energy to remove a hole from one site and place it on a neighboring site that already has one hole. The ground state of the parent compounds is therefore insulating.

This description is the point of departure for the many-body theories of the cuprate superconductors. When a macroscopic fraction of the trivalent lanthanide in the parent compound is replaced by a divalent alkaline earth metal, according to these theories, charge balance requires that electrons be taken away from—or holes added to—the CuO_2 planes. The added holes are mobile, and they are responsible for the superconductivity. Conversely, substitution of a tetravalent cerium or thorium at the lanthanide site adds electrons to the CuO_2 planes. In the class of *magnetic* many-body theories proposed by Philip W. Anderson (Princeton University) and J. Robert Schrieffer (University of California, Santa Barbara), as well as in some theories in which pairing is induced by charge polarization or excitons, the physics of the cuprates is symmetric with respect to the interchange of electrons and holes. Therefore, for those who subscribe to the "symmetric" theories, discovery of electron superconductivity in Nd_2CuO_4 doped with tetravalent thorium or cerium is not a surprise but an occasion to ask why it took so long to confirm experimentally a feature inherent to these theories.

"I did try a few substitutions [in the hope of making electron superconductors] after the discovery of the 1-2-3 [90-K superconductor]," Robert Cava (AT&T Bell Labs) told us. Cava's substitutions did not work, and he gave up the idea of doping the CuO_2 planes with electrons because "the pace of research in those days was so fast that I could not for very long pursue a direction that did not seem very fruitful." The substitutions Cava tried, and perhaps many others that he did not try, were probably tried also by many an expert and amateur around the world. But the Japanese succcess story owes as much to systematic search as it does to interesting "accidents."

Now, 'reduce'

The University of Tokyo group turned its attention to cerium-substituted compounds after a group led by J. Akimitsu (Aoyama-Gakuin University, Tokyo) discovered, in February 1988, a superconducting phase with a critical temperature of about 20 K in Nd-Ce-Sr-Cu-O. Cerium substitution had been tried earlier in both $La_{2-x}(Ba,Sr)_xCuO_{4-y}$ and $YBa_2Cu_3O_{7-y}$ but was found to destroy superconductivity. This was not unexpected: The valence of cerium may be either three or four; so tetravalent cerium, because it would be an electron donor, might destroy the holes generated—in $La_{2-x}(Ba,Sr)_xCuO_{4-y}$, for example—by barium or strontium doping.

The superconducting phase in Nd-Ce-Sr-Cu-O was the puzzle that a big Japanese collaboration, in which the University of Tokyo group participated, last year set out to solve. By October 1988, Uchida told us, the University of Tokyo group had confirmed that the conductivity of $Nd_{2-x}Ce_xCuO_{4-y}$ increases with increasing cerium concentration. This finding underscored the suspicion that cerium in these materials might indeed be an electron donor. "Since that time," Uchida said, "we focused our effort on the possibility that $Nd_{2-x}Ce_xCuO_{4-y}$ might become an n-type [or electron] conductor. We did not expect the n-type conductor to show superconductivity. Instead, we expected to show that n-type cuprates, although they might exist and even though they might be metallic, were *not* superconductors." Uchida was merely echoing the experimenters' prejudice against n-type cuprates being superconductors, because no such superconductor had yet been found.

Hall-effect measurements by the University of Tokyo group confirmed the presence of mobile electrons in $Nd_{2-x}Ce_xCuO_{4-y}$, but contrary to expectations, adjusting the cerium concentration did not produce a metal. The conductivity of $Nd_{2-x}Ce_xCuO_{4-y}$ for all values of x up to the solubility limit ($x = 0.2$) increased at low temperatures, an indication of semiconducting behavior. But something like a miracle happened when a student, H. Matsubara, *quenched* a sample in air from 900 °C to room temperature: That sample showed superconductivity below about 10 K. This outcome of the unpremeditated quench in a not-so-strongly oxidizing atmosphere suggested that reducing the oxygen content of $Nd_{2-x}Ce_xCuO_{4-y}$ might be necessary for obtaining superconductivity or even metallic conductivity. Further work on samples synthesized in *reducing* conditions finally established that $Nd_{2-x}Ce_xCuO_{4-y}$ with x near 0.15 is a superconductor with a critical temperature of about 20 K. The emphasis on the synthesis conditions is important because all of the earlier (hole) cuprate superconductors must be cooled in an oxidizing atmosphere after being sintered.

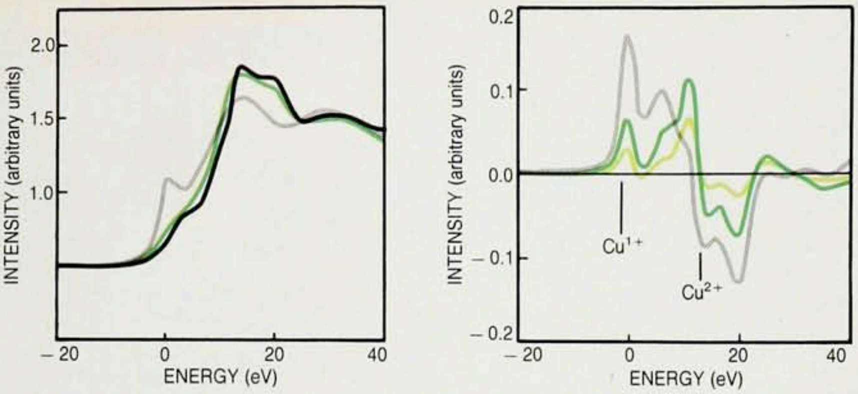
What about the University of Tokyo group's original attempt to fabricate electron metals among the cuprates? The resistivity of most superconducting samples decreases linearly with decreasing temperature over a large temperature range, in agreement with the expected metallic behavior as well as the behavior observed in hole superconductors. Unlike the behavior observed in the hole superconductors, however, the resistivity of even the best "metallic" samples of electron superconductors begins to increase just before the onset of superconductivity. This residual semiconducting tendency suggests to Zachary Fisk (Los Alamos National Laboratory) that "we have not yet mastered some subtle aspect of the oxygen processing of the electron superconductors."

XANES

The many-body theories of cuprates fall into two broad classes: the electron–hole symmetric theories; and those, such as the one discussed by Victor Emery (Brookhaven National Laboratory), that do not have this symmetry. In some theories the normal state of the cuprates is regarded as similar to a conventional metal, and, like almost all Fermi systems studied before the discovery of superconductivity in cuprates, this state is described by Lev Landau's Fermi-liquid theory. In the theory proposed by Anderson, however, the cuprates have a very unusual normal state, to which the Fermi-liquid theory does not apply.

On the issue of electron–hole symmetry, Emery thinks that the discovery of electron superconductors by itself does not imply that that symmetry holds among the cuprates. He points to the x-ray absorption studies, which show that the doped holes—in, for example, $La_{2-x}(Ba,Sr)_xCuO_{4-y}$—go to the oxygen sites, whereas the doped electrons in the new superconductors go to the copper sites. For a free atom the cross section or the intensity for x-ray absorption is a discontinuous function of the energy of the incident x rays. The positions of the discontinuities, also called absorption edges, or their appropriate linear combinations give the binding energies of the atomic orbitals. In a solid, however, the absorption spectrum shows structure, called x-ray absorption near-edge structure, or XANES (pronounced *exanes* or *zanes*), which gives a wealth of information about the electronic states. A variety of such studies have been carried out on the cuprates. The figure at right shows the absorption spectrum of $Nd_{2-x}Ce_xCuO_{4-y}$ for $x = 0.075$, 0.15 and 0.2. In the right-hand panel in the figure, which shows the spectrum after subtraction of the Nd_2CuO_4 spectrum, the feature due to Cu^{1+} grows and that due to Cu^{2+} diminishes as the doping level increases.[7] This trend is regarded as evidence that the added electrons go to copper sites and turn Cu^{2+} into Cu^{1+}. Similar studies on $La_{2-x}(Ba,Sr)_xCuO_{4-y}$ show no change in the valence of copper.[8] Thus in cuprates, according to Emery, the orbitals occupied by holes are different from those occupied by electrons, so the cuprates are not electron–hole symmetric at energies on the order of the binding energies of the atomic orbitals (1 eV, or 10^4 K). He thinks that more detailed experiments, such as ones probing the symmetry of the order parameter in the superconducting state, are needed before the issue of electron–hole symmetry in the temperature range of interest for magnetism and superconductivity can be definitively settled.

Anderson, however, says that the character of orbitals at the atomic level is absolutely irrelevant to the many-body physics. He regards the symmetry of the bands as the important feature, not the atomic orbitals the holes or electrons occupy. "The mistake in the two-band theories [like the one proposed by Emery]," Anderson said, "is that they emphasize the character of the states at the atomic level." About the XANES data, Anderson pointed out that the degree of hybridization between orbitals does change as the ions' valence state changes but that the fundamental excitations continue to behave as if they belong to a single band because of severe limitations on their Hilbert space. "In my opinion the two-band theories never had any validity, and it is good to have that obvious fact confirmed by the discovery of the electron superconductors," Anderson said.



X-ray absorption spectra. Left: Spectra of $Nd_{2-x}Ce_xCuO_{4-y}$ for $x = 0$ (black) and 0.15 (dark green) and of Cu_2O (gray). The energy is measured with repect to the copper K edge (8.98 keV). Right: Spectra of $Nd_{2-x}Ce_xCuO_{4-y}$ for $x = 0.075$ (light green) and 0.15 (dark green) and of Cu_2O (gray), after subtracting the spectrum due to Nd_2CuO_4. The features in the spectrum due to Cu^{1+} and Cu^{2+} are indicated. The spectrum for Cu_2O has been scaled down by a factor of 0.4. (Adapted from reference 7.)

Elihu Abrahams (Rutgers University) also thinks that "the class of theories that do not ignore the copper–oxygen hybridization and allow superconductivity when the parent compounds are doped with electrons or holes are strengthened by the new discovery." As examples of such theories, Abrahams mentioned the ones based on Anderson's spin liquid, on Schrieffer's spin bag and on charge-polarization-induced pairing of electrons.

We asked Kathryn Levin (University of Chicago) whether the discovery of electron superconductors might indeed turn out to be the smoking gun that gave away the secrets of the cuprate superconductors. "We need two smoking guns," she said, "one for the normal state and one for the superconducting state." Levin expressed hope that the discovery might help sort out several outstanding questions about the cuprates, and concern that a negative Hall coefficient would be difficult to understand in the traditional (Fermi-liquid) theories for the normal state. "The band structure [of the electron-doped systems] just isn't that different" from that in the hole-doped systems, Levin said, referring to the electronic band structure obtained by Arthur Freeman (Northwestern University). Even before the discovery of electron superconductors, according to Nai Phuan Ong (Princeton University), there had been considerable concern about whether the Hall coefficient in the hole superconductors could be explained by band structure results.

While the theoretical debate continues, one may ask, What does the discovery mean to all those, be they physicists or chemists, crystal growers or thin-film specialists, who can endow ordinary materials with wondrous properties and turn ceramic insulators into superconductors? "I have been trying to find new ways to dope the copper–oxygen planes with holes for the past two years," Cava said. "I may have tried out as many as ten thousand samples. Now, it seems, there are ten thousand more out there that I have to try." A matter of immediate concern, Paul Chu (University of Houston) said, is synthesis of electron analogs of 90-K superconductors.

—ANIL KHURANA

References

1. Y. Tokura, H. Takagi, S. Uchida, Nature **337**, 345 (1989).
2. J. T. Markert, M. B. Maple, Solid State Commun., in press. J. T. Markert, E. A. Early, T. Bjornholm, S. Ghamaty, B. W. Lee, J. J. Neumeier, R. D. Price, C. L. Seaman, M. B. Maple, Physica C in press.
3. A. James, D. Murphy, S. Zahurak, Nature, in press.
4. H. Takagi, S. Uchida, Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).
5. N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, W. R. Mckinnon, Phys. Rev. B **35**, 8807 (1987).
6. S. Uchida, H. Takagi, H. Ishii, H. Eisaki, T. Yabe, S. Tajima, S. Tanaka, Jpn. J. Appl. Phys. **26**, L440 (1987).
7. J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang, M. Croft, Nature **337**, 720 (1989).
8. J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, Phys. Rev. B **36**, 5263 (1987). ■