

Image of magnetic fields associated with currents flowing in superconducting rings.

Electron Pairs and Waves

Tackling the puzzle of high-temperature superconductivity

By IVARS PETERSON

The detectives have been hard at work gathering clues, building theories, and sketching portraits of the perpetrator. Yet, after years of dogged effort, no satisfying resolution of the mystery appears in sight. The culprit continues to elude the supersleuths.

In the case of high-temperature superconductors, the missing factor—the elusive culprit—is the mechanism that allows certain copper oxide ceramic compounds to conduct electricity without resistance. How do electrons manage to flow effortlessly through the ceramic compounds at temperatures as high as 135 kelvins?

The discovery of these unusual superconductors in 1986 took researchers by surprise. No one had ever suspected that such ceramic compounds could become superconductors or, indeed, that any material could be a superconductor at a temperature higher than about 20 kelvins, the highest temperature at which certain metals can behave as superconductors.

Besides their high transition points, these ceramic compounds have several features that set them apart from previously known superconductors. At temperatures at which the ceramic materials are not superconductors, they exhibit behavior quite unlike ordinary metals. Made up of sheets of copper and oxygen atoms sandwiched between layers of other atoms, they conduct electric current better in some directions than in others, and minor chemical changes transform them into electrical insulators with striking magnetic characteristics.

For most metals, including aluminum, scientists can apply quantum theory to explain why mobile electrons act as if they were free. At least one electron from each atom moves about independently, collectively forming a so-called Fermi liquid. On this basis, the scientists can make predictions about the metals' characteristics and behavior.

"The new materials, however, seem to require new principles," says Sudip Chakravarty of the University of California, Los Angeles.

"In these materials, electron motions are so strongly modified by the repulsive forces exerted by their neighbors that we can no longer approximate their motions as being independent," says Piers Coleman of Rutgers University in Piscataway, N.J.

Writing in the December 1995 *PHYSICS WORLD*, he contends that high-temperature superconductivity is just one example of "the unexpected consequences of collective behavior in vast assemblies of interacting particles."

Hence, detailed investigations of electron activity within such compounds provide important clues that may ultimately lead to a theory that accounts for their distinctive character both as metals and as superconductors.

Pinpointing the mechanism of high-temperature superconductivity would also make it possible for researchers to tailor new materials to specific purposes. Conceivably, they could push superconducting transition temperatures significantly higher than those presently achievable—perhaps even to room temperature (about 300 kelvins).

"It's a fascinating puzzle," says M. Brian Maple of the University of California, San Diego. "These high-temperature superconductors were completely unexpected in the beginning, and they are now a rich reservoir of interesting phenomena to study."

The theoretical starting point is a model, proposed in 1957 by John Bardeen, Leon N. Cooper, and J. Robert Schrieffer to account for superconductivity in metals such as aluminum and zinc at temperatures close to absolute zero.

This theory, called BCS after its originators, is based on the notion that current-carrying electrons can overcome their mutual repulsion and pair up in ways that allow them to pass unhindered through the host material. In conventional, low-temperature superconductors, this pairing is facilitated by vibrations of

the crystal lattice through which the electrons travel.

A moving electron induces slight displacements in the positions of positively charged ions along its path, causing a ripple-like effect. A second electron can get caught in this ripple, and it can end up traveling as if its motion were coordinated with that of the first.

Because the electrons of a pair have opposite spin, as a unit they can move through material without resistance. Quantum mechanics describes the pair by means of a single wave function, which mathematically specifies a probability distribution showing where the two electrons are most likely to be.

In this case, the wave function is spherical, indicating that the electron pairs have an equal chance of moving in any direction. Such a pairing is said to display s-wave symmetry.

When the copper oxide superconductors were discovered, researchers tried to apply the same theory, beginning with the notion that the current-carrying electrons must move in pairs. They quickly realized that in these materials, lattice vibrations alone aren't strong enough to maintain such pairing at the high superconducting transition temperatures observed in the copper oxides.

Theorists have since proposed a number of different mechanisms that they believe could produce the necessary electron pairing and permit superconductivity at elevated temperatures. Some of these theories invoke magnetic spin interactions between electrons and copper ions in the copper oxide layers, while others rely on such effects as electron tunneling between sheets of copper and oxygen atoms in these compounds.

To shed some light on the mechanism responsible for electron pairing, researchers have performed a wide range of experiments on high-temperature superconductors. One particular series has focused on whether electron pairs in these compounds fit an s-

wave pattern or an alternative symmetry known as d-wave.

In the d-wave case, the wave function of the electron pair resembles a four-leaf clover, with lobes aligned along the crystal axes of the material (see illustration below). This shape means that the probability of electron travel is higher in some directions than in others. Moreover, electrons moving along one axis are out of step, or phase, with electrons moving along the axis at right angles to it.

One approach is to check whether the energy needed to break up an electron pair depends on its direction of travel. That can be done by bombarding a crystal's surface with high-energy photons. These photons knock electrons out of the material, and researchers can measure the energies of the ejected particles.

Last year, Zhi-Xun Shen of Stanford University and his collaborators used this technique, known as photoemission spectroscopy, to determine the binding force between paired electrons in six high-temperature superconductors, including yttrium barium copper oxide. They measured the energy and direction of electrons emitted by each material, and they

Thomas J. Watson Research Center in Yorktown Heights, N.Y., used an ingenious arrangement to probe these effects in yttrium barium copper oxide (SN: 4/2/94, p. 213). Their results were consistent with d-wave pairing.

Now, the IBM team reports in the Jan. 19 *SCIENCE* that a new experiment involving thin films of another superconductor, thallium barium copper oxide, produces the same result.

These and several other key experiments over the last few years all strongly indicate that d-wave rather than s-wave interactions predominate in high-temperature superconductors.

"So the question in my mind is no longer whether it's d-wave," says Douglas J. Scalapino of the University of California, Santa Barbara. "Instead, the question becomes: If it's d-wave, what does that tell us?"

The trouble is that a variety of quantum mechanical effects can lead to d-wave symmetry. No single answer automatically emerges to pin down what causes the pairing.

Nonetheless, these results are encouraging for theorists, like Scalapino, who have proposed that pairing results from the way electrons interact with fluctuations in the spins of neighboring copper ions in the crystal lattice. The presence of such interactions favors electron pairs with d-wave symmetry, they argue, and the experimental results bolster this argument.

At the same time, detailed theoretical calculations have so far failed to demonstrate that spin fluctuations are sufficient to initiate superconductivity at the temperatures observed in the copper oxides—unless the calculations are based on unrealistic assumptions about the characteristics of the materials.

"My sense is that we are on the right track," Scalapino says. "But there may be a piece of this puzzle that we don't understand yet, something missing that would provide the necessary [interaction] strength.

"On the other hand, these ideas could be incorrect, as some people believe, and we need something else," he concedes.

In addition to problems with the calculations, there's one other discordant note.

Experiments by San Diego's Robert C. Dynes and his colleagues have consistently provided evidence of an s-wave contribution, at least in yttrium barium copper oxide. The researchers observe electron tunneling between the material's layers, a direction that s-wave, but not d-wave, symmetry would allow.

"It's possible that we have a situation in which there is both s-wave and d-wave character in the superconducting state of yttrium barium copper oxide," Maple says.

Alternatively, "there may be some subtle features that none of us fully appreciate which could lead to one conclusion or the other," he adds. "One simply needs to do more experiments on more materials, doing a variety of measurements."

It's even possible that no single mechanism applies to all the different high-temperature superconductors now identified. At least one, neodymium cerium copper oxide, is already known to have electrical properties that distinguish it from the others.

"I don't think the story is over yet," says Victor J. Emery of the Brookhaven National Laboratory in Upton, N.Y. "These are complicated materials, and one should try to take into account *all* the experiments.

"This whole business of [high-temperature] superconductivity has focused attention on a lot of scientific issues that are too interesting to be brushed away," he adds.

How to deal with the complexities has divided the physics community.

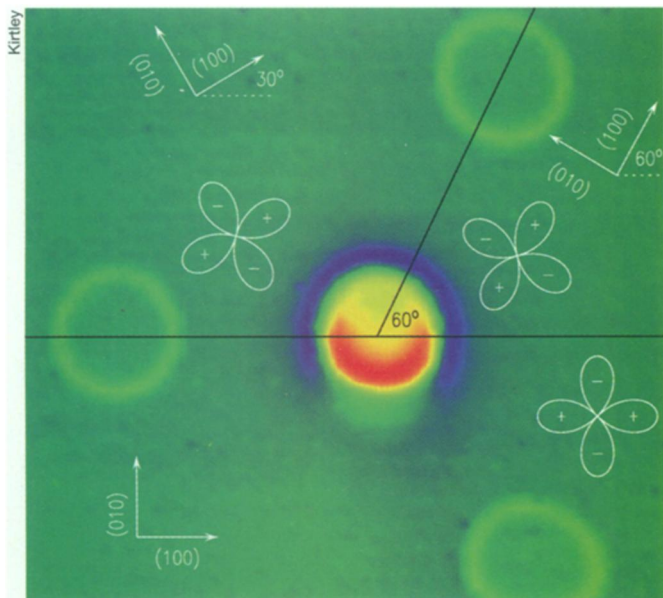
"One group believes that BCS theory can be extended to understand these systems without any major revision of the way we think about metals," Coleman comments. "An opposing school identifies many of the unusual properties of the normal [metal] state as evidence for new physics that is intimately related to high-temperature superconductivity."

Philip W. Anderson of Princeton University is among those in the latter category. He insists that it's time to rethink not only superconductivity theory but also the standard theory of electron behavior in metals.

In Anderson's view, high-temperature superconductivity is just one example of a phenomenon for which this picture may be misleading. Mechanisms such as pairing are too simple to account for this behavior, and repulsive interactions between electrons must also be included.

"What is clear is that the 2 decades or more of efforts to fit all these phenomena into a Fermi liquid description are a catalog of failure," Anderson argues in the December 1995 *PHYSICS WORLD*, "and it is time we opened our minds to new ways of thinking."

At this stage, the detectives can't even be sure they're on the trail of the culprit. It may be heavily disguised or an as-yet-unsuspected party. □



Four superconducting rings sit atop three adjoining crystal lattices having different orientations (arrows). If the wave functions for the paired electrons circulating in the rings have a d-wave symmetry (four-lobed shapes), the lobes will be aligned with the crystal axes. Each ring crosses a different number of lattice boundaries, and the electrons' d-wave alignment changes as they cross each boundary.

found that the binding force did vary, falling to nearly zero along certain directions relative to the material's crystal lattice (SN: 2/11/95, p. 88).

These results support the idea that electron pairing is characterized by d-wave symmetry.

Other groups have focused on detecting the changes in phase of the electron pair motion that should occur with d-wave pairing. In 1994, John R. Kirtley, Chang C. Tsuei, and their coworkers at the IBM