New Clues to Superconductivity

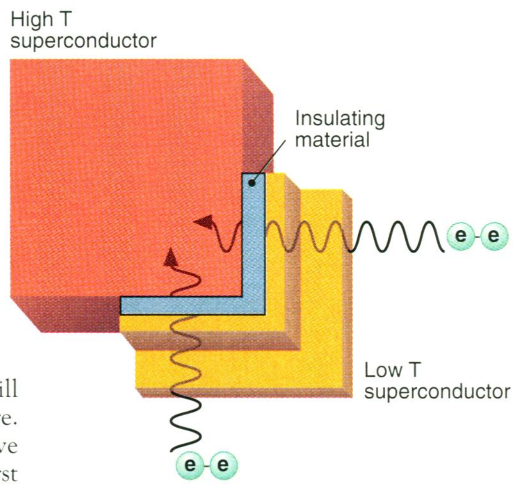
For the past 8 years, researchers have been struggling to understand high-temperature superconductors. Now some innovative new experiments are showing them the way

GRENOBLE, FRANCE—When solid-state physicists produced the first high-temperature superconductors in 1986, the accomplishment was hailed as one of the great scientific discoveries of the century. Until then, superconductivity—the flow of electrons through a material without any resistance—could be achieved only at temperatures close to absolute zero (0 kelvin or –273° Celsius). But the new materials discovered in 1986 could superconduct at 32 K. That triggered a cascade of results, as researchers rapidly improved on the record, raising the temperature to more than 125 K in just 2 years. Such progress raised hopes that they would soon have materials superconducting at room temperature, opening the way to resistance-free electric power lines and high-speed trains floating on a cushion of magnetism from superconducting electromagnets.

These dreams were soon chilled, however, as the temperature record stuck at 128 K until last year, when the generally accepted number edged up to 133 K—still more than 150°C below room temperature. You would think this impasse would have shrouded the field in gloom. But at the first major international conference on high-temperature superconductivity in 4 years, held here last month, the mood was far from somber. In fact, participants were buzzing about new results that may allow them to break through the temperature barrier.

Many researchers in the field are now optimistic that they are closing in on the mechanism that underlies superconductivity—which until now has been a complete mystery. Most advances in the field have come about through chemical "cookery," with researchers mixing compounds guided by experience and educated guesses. But they have long searched for a theory that would explain how electrons flow so effortlessly through superconductors, and, lately, two major types of theory have been competing for ascendancy: one based on the existing models of superconductivity, and the other on an entirely new mechanism. Both models have their staunch adherents, but researchers were unable to provide definitive evidence for either one. That picture may now be changing.

While as recently as 18 months ago there was little firm evidence supporting the newer theories, in a packed session at the Grenoble conference, researchers described a raft of new experimental results giving firmer and firmer support for these models. Although last rites have not yet been said for the old model, the proponents of the new theories express cautious optimism. "It's very nearly conclusive, but it's never over till it's over," says one of them, David Pines of the University of Illinois. Even people who do not advocate these theories are admitting that the situation has changed. "They have a little bit more experimental evidence on their side," says Philip Anderson of Princeton University.



Tunneling test. D-wave electron pairs should cancel each other out when entering a superconductor in perpendicular directions.

ILLUSTRATION: K. SUTLIFF

The work to settle the question is motivated by more than just academic curiosity. Researchers hope that once the answer is in, it will lead to an understanding of how the composition and structure of a specific material are linked to its ability to superconduct. Experimentalists may then be able to use the information to devise recipes for new superconductors that will work at ever higher temperatures—bursting through the current temperature barrier.

Superconductivity theorists have been puzzling long and hard over the new materials. Their discovery in 1986 came as a shock, as the existing superconductivity theory, put forward in 1957, predicted that the highest possible superconducting temperature was around 40 K. "[By 1986,] people had been banging their heads against the wall for more than 20 years just trying to get an incremental increase above 23 K." Achieving a sudden jump to 32 K "was totally unexpected," says Colin Gough of the University of Birmingham in the United Kingdom.

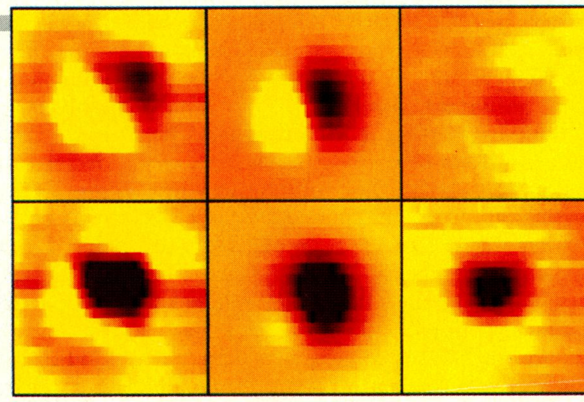
A common denominator of both conventional low-temperature superconductors and the new high-temperature materials is that the electrons travel in pairs, despite the fact that their negative charges should cause them to repel one another. This pairing is crucial to the theory that explains low-temperature superconductors.

In a normal conducting material, such as a metal, electrons do not get an easy ride: They are impeded by knocking into defects in the crystal and by colliding with atoms that jiggle about as a result of thermal energy. But in some metals at very low temperatures, the thermal energy drops to such a low level that electrons are able to avoid bumping into these obstacles by creating a distortion, or wave, in the crystal lattice, called a phonon, and riding through the crystal like a surfer. But this only works if the electron surfers travel in pairs.

While this account works fine for the old conventional superconductors, it was thought that above 40 K thermal agitation would break the pairs of electrons apart, destroying their affiliation with the phonon and hence their ability to move through the crystal without collisions. Yet soon after the discovery of the new superconductors, which are complex copper oxide crystals, researchers found that at temperatures above 40 K electrons still travel in pairs.

To explain this phenomenon, many theorists have tried to modify the phonon-based theory by looking for some new effect, specific to the structure of these new materials, that binds the pairs tightly enough together to withstand higher temperatures. The new superconductors have structures very different from the old. Rather than consisting of simple metals, for example, they are layered structures in which sheets of copper and oxygen atoms are separated by layers of other atoms. And this layered structure constrains the movements of the electron pairs: Rather than being able to move freely in three dimensions, they are largely stuck in the copper-oxygen plane.

Putting this information together with the phonon theory, Princeton's Anderson and Sudip Chakravarty of the University of California, Los Angeles, suggested last year



ANNA MATHAI *ET AL.*/UNIV. OF MARYLAND

Symmetry spotting. The images show what happens when electron pairs with d-wave symmetry circulate in a loop made partly of a high-temperature superconductor. When they turn through 90°, they undergo a phase change and so produce a magnetic flux *(in red-black in lower right)*. A 180° turn produces no phase change and no flux *(top right)*.

that electron pairs carried by phonons are able to hop from one copper-oxygen layer to another. This ability—denied to single electrons—makes staying in a pair advantageous for the electrons and adds sufficient strength to their pairing that they can stay aboard their phonons and superconduct at higher temperatures (*Science*, 16 July 1993, pp. 294 and 337). "It's a very strong empirical fact," says Anderson, that superconducting temperatures are highly dependent on the number of copper-oxygen planes and the types of atoms separating them. "You must get the relationship between the planes into any theory."

But other theorists, including Pines, believed there were clues that something different was going on. One finding buttressing this idea was the discovery that high-temperature superconductors will not work unless extra atoms are added to the crystal, disturbing its normal magnetic state.

In these new materials, a magnetic state called anti-ferromagnetic order normally prevails. Electrons spinning around each copper atom in the crystal produce a magnetic field for each atom, and normally, says Alexander Balatsky of the Los Alamos National Laboratory, the axes of the copper atoms' spins, and hence of their magnetic fields, alternate strictly up and down throughout the copper-oxygen plane. But in this anti-ferromagnetic state, materials will not superconduct. Superconductivity occurs only when extra atoms break down that magnetic regime, causing the spins of atoms to point in random directions.

The second theoretical camp in this field, beginning with Douglas Scalapino of the University of California, Santa Barbara, and including Pines and Balatsky, believes that this breakdown of anti-ferromagnetic order is at the heart of the phenomenon. The high-temperature materials superconduct, they say, because small groups of copper atoms keep their spins in anti-ferromagnetic order for short periods of time. This short-term reversal is called a spin fluctuation, and when one occurs, this camp argues, a pair of electrons can get locked into it. The magnetic attraction holds the electrons in pairs and allows them to move around following the spin fluctuation and superconduct at high temperatures.

These two types of theory have been developing in parallel over the last few years and have split high-temperature superconductivity researchers into two opposing camps, but they have also raised hopes of resolving the difference, because the two theories make different—and experimentally testable—predictions about the symmetry of the electron pair. Spin-fluctuation theories predict that the pair has some angular momentum apart from the spin on each electron. In this theory, says Gough, "the electrons orbit around each other like a binary star system," a form of symmetry known, in quantum mechanics, as d-wave. In phonon-based theories, on the other hand, electron pairs would have no angular momentum, and so have s-wave symmetry.

Beginning about 3 years ago, several types of experiments began pointing to the possibility that electrons do indeed pair with d-wave symmetry. Among other things, researchers used nuclear magnetic resonance, microwaves, and photons to probe the symmetry state of the electron pairs. But even though they all suggested that the pairs had a symmetry at least similar to d-wave, they were not totally conclusive. By about a year ago, "all the standard experiments had been done," says Praveen Chaudhari of IBM's T. J. Watson Research Center in New York state. "We had to think of new ways to test."

And it is these new tests that so excited researchers at Grenoble, by adding further support to the theory of d-wave symmetry. The first of these new tests appeared through pioneering work by Anthony Leggett, Dale Van Harlingen, and their colleagues at the University of Illinois, Urbana-Champaign. It relies on a quantum mechanical quirk of d-wave symmetry that allows researchers to eliminate all types of s-wave symmetry.

In quantum mechanics, moving electron pairs can be treated as waves as well as particles. A requirement of d-wave symmetry is that any "pair wave" moving parallel to one line of copper atoms in the superconductor will always be half a wave out of phase with a pair moving in the perpendicular direction. In contrast, pair waves with s-wave symmetry will have the same phase in every direction. The new experiments aim to determine this difference by getting pair waves to travel into a piece of superconductor along two perpendicular directions at the same time. D-waves should be out of phase, so that the peaks of one wave meet the troughs of another, thus canceling each other out.

In the latest version of Van Harlingen's experiment, the results of which are not yet published, he uses a high-temperature superconductor crystal with a layer of insulator covering one corner, which is itself covered by a layer of lead (see diagram). A unique property of superconductors is that electron pairs can "tunnel" through such an insulator sandwich into the high-temperature superconductor crystal. The fact that the insulator is on the corner is crucial, because electron pairs will tunnel in two perpendicular directions simultaneously. And when the experiment is cooled to near absolute zero, the researchers found that charge did not flow into the superconductor crystal. The waves had canceled each other.

But when the team built an identical experiment except that the insulating layer was flat on one face of the crystal, there was no block to the current because all the pair waves were in phase. "It's really strong evidence of a phase shift. The interpretation must be d-wave," says Van Harlingen. Several other groups have conducted other variations of tunneling experiments, mostly yielding similar results. "I was not a great exponent of d-wave; I expected to find s-wave," says Frederick Wellstood of the University of Maryland, who also has results await-

EXPERIMENTS THAT DISTINGUISH BETWEEN S-WAVE AND D-WAVE SYMMETRY

Experiment	Consistent With: Isotropic s	Anisotropic s	d
NMR (Martindale *et al.*)			●
Microwave penetration depth (Hardy *et al.*)		●	●
Photoemission (Shen *et al.*, Yokoya *et al.*)		●	●
SQUIDS (Van Harlingen *et al.*, Brawner and Ott, Wellstood *et al.*)			●
Grain-boundary tunneling (Tsuei *et al.*, Iguchi and Wen)			●
Grain-boundary tunneling (Chaudhari *et al.*)	?	?	?
Corner tunneling (Van Harlingen *et al.*)			●
c-axis tunneling (Dynes *et al.*)	●	●	?

ing publication. "I was surprised when it only came up with d-wave."

But the issue is not yet cut-and-dried: The tunneling experiments have thrown up some contradictory results that are causing spin-fluctuation theorists to wait before claiming victory. IBM's Chaudhari carried out two different experiments: the first favored s-wave symmetry; the second gave ambiguous results. "I personally sit on the fence," says Chaudhari. "We haven't found evidence for d. It could be because of some reason we don't yet know, but we think our next experiment will be decisive."

In another experiment that gives d-wave proponents pause, Robert Dynes of the University of California, San Diego, forced electron pairs to tunnel into the superconductor in a direction perpendicular to the copper-oxygen plane. Spin-fluctuation theories do not normally allow conduction in this direction, but Dynes detected some. Results such as these give Anderson heart. He has reworked his theoretical calculations and says that his theory does not exclude spin fluctuations: They could be causing pairing in the copper-oxygen layer, and so creating d-wave symmetry, but alone they are not strong enough to hold pairs together at high temperature. Hopping between planes is still required. Evidence such as Dynes' "is about as definitive as you can get," he says.

While most researchers believe that it is only a matter of months before they will be able to say, without reservation, that the electron pairs have d-wave symmetry, a comprehensive theory that everyone agrees to may still be years away. But after years of stumbling around in the dark, deciding the issue of pair symmetry is for theorists a glimpse of light at the end of the tunnel. "It's an exciting time," says Scalapino. "We may yet learn what is really happening."

–Daniel Clery

HEALTH-CARE REFORM

Support Grows for NIH Trust Fund

All but overlooked in the current congressional debate over health-care reform is the growing prospect of a sizable boost in funding for biomedical research. The essence of a proposal to increase support for the National Institutes of Health (NIH)—first offered last summer by Senators Tom Harkin (D–IA) and Mark Hatfield (R–OR)—has survived the skirmishes over health care and appears in both leadership reform bills now before Congress. If passed, it could yield a bonus of up to several billion dollars to a cash-strapped NIH.

Proposing trust. Hatfield *(left)* and Harkin.

Harkin and Hatfield would like to increase NIH funding in two ways: by giving NIH 1% of every dollar paid in health-insurance premiums, and by inviting taxpayers to donate an amount of their choice to NIH by filling in a blank on their federal tax-return forms. Representative William Coyne (D–PA) introduced companion legislation in the House, where the proposal was incorporated into a bill approved by the Ways and Means Committee at the end of June. An element of the proposal was then adopted as part of the House Democratic leadership bill. The set-aside legislation has 25 sponsors in the Senate and 62 in the House, the majority of whom are Democrats.

Harkin, chair of the Senate Appropriations subcommittee on Labor, Health and Human Services, and related agencies, has pushed long and hard for an increased federal commitment to biomedical research. Writing more than a year ago in *The New York Times*, he argued that Congress is barely able to give NIH enough money for its research programs and that finding additional money to refurbish the nation's biomedical research infrastructure is beyond its means. This year, for example, the House and Senate have each trimmed by about $150 million the president's request for $11.47 billion—a rare act for a body that historically added money to what the president sought for NIH.

Harkin and Hatfield see an additional threat to research from the sweeping changes taking place in the medical marketplace. Those changes are forcing academic medical centers, many of which are in the inner cities, to compete on cost and efficiency with community hospitals, which do not typically shoulder the burdens of teaching or providing care for indigents. By increasing the pot of money for extramural grants, the trust fund would provide additional funds for research, an activity that might otherwise get squeezed by hospital administrators who are looking to hold down costs.

If the Harkin-Hatfield measure were to be adopted exactly as written by its sponsors, it would increase NIH's annual $11-billion budget by almost 50% after being phased in over 4 years. The scaled-down versions now under consideration would raise amounts ranging from $1 billion to $2.5 billion a year, depending on the specific bill.

At this point the odds that some version of the trust fund will emerge in the final bill appear good—assuming, of course, that any health-care reform measure is passed and sent to the president. Elements of the Harkin-Hatfield proposal appear in the plans crafted by Senator George Mitchell (D–ME) and Representative Richard Gephardt (D–MO), virtually guaranteeing that the idea will reach the floors of both chambers. The concept also has bipartisan support: It's part of legislation introduced by Senate Minority Leader Bob Dole (R–KS) and Senator John Chafee (R–RI). An aide to Harkin says, "It's going to happen. The only question is how much there will be."

The answer hinges on which proposal is adopted. Although both Gephardt and Mitchell have chosen versions of the proposed 1% set-aside, they have trimmed the amount to be deposited in a fund for NIH. The precise level is open to debate; it could be as little as one-third to one-half of the original proposal. But half would be fine, says Roy Silverstein, chief of hematology and medical oncology at Cornell Medical College in New York and president of the American Federation for Clinical Research. "Two and a half billion [dollars] is a lot," he says. "The scientific community would be happy with that."

The voluntary taxpayer contribution would probably raise less than one-tenth of that amount, according to congressional estimates. But Republicans might be more willing to support the tax checkoff than to support what they view as a "tax" on insurance premiums.

Given the amount of money involved, the days of relative anonymity for the trust fund are probably numbered. At the same time, its presence gives the biomedical research community a bigger stake in the minutiae of the debate over health care.

–Steve Sternberg

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