Closing In On Superconductivity

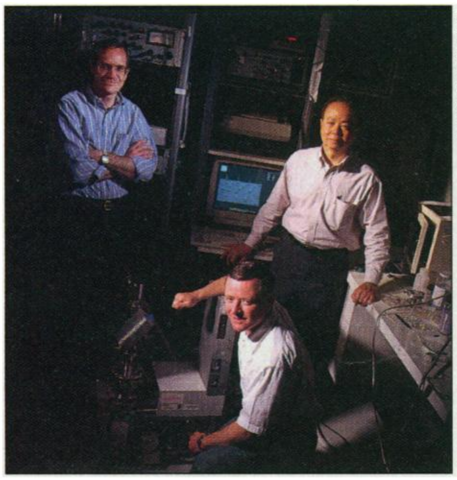
Two camps have been battling to explain how new crystals can conduct electricity at high temperatures without resistance. Now one camp says a new result eliminates many opposing theories

Nine years after the discovery of high-temperature superconductors, attempts to explain how electricity races through these complex crystals without resistance still meet a great deal of resistance themselves. Life was simpler when the only superconductors were metals cooled to below 25 Kelvin, more than 240 degrees below freezing. Theorists felt they had the mechanism down cold as well: Electrons surf through the metals on a wave of energy called a phonon. But when new copper oxide crystals pushed the superconductivity record up to more than 125 K, debate over the mechanism also heated up: Higher temperatures could give the surfing electrons too rough a ride.

Since then, those seeking to adjust the old theory to the new materials have been battling another camp, which is seeking an entirely new explanation. These reformers have lately had the upper hand, and many say a new result reported in this issue of *Science* will put many of the more traditional theories out of the running. On page 329, Chang-Chyi Tsuei and John Kirtley of IBM's Thomas J. Watson Research Laboratories in Yorktown Heights, New York, and their colleagues report evidence that the behavior of electrons racing through a superconductor is best described by a mathematical function called d-wave, behavior that favors the newer models in which the electrons ride, not on phonons, but magnetic fluctuations.

"It clears away a whole lot of dross," says theorist Tony Leggett of the University of Illinois, Urbana-Champaign. D-wave signatures have been seen before, but in materials with a more complex crystal structure that left room for non-d-wave explanations. The IBM team has now narrowed that loophole by studying a simpler material. "It's not a decisive breakthrough for one approach, but it certainly narrows the field" to theories compatible with d-wave, says theorist Maurice Rice of the Swiss Federal Institute of Technology in Zurich.

This effort is driven by more than academic curiosity. The push to find superconductors that operate at higher temperatures seems to have stalled at around 130 K. A comprehensive theory might just help researchers get around this impasse and even find materials that superconduct at room temperature. But not everyone is convinced the field has truly been narrowed: "It's certainly not settled," says theorist Richard Klemm of the Argonne National Laboratory, noting there are still other experiments that lend support to rival "s-wave" theories.



RANDY MASSER/IBM

Three for "d". (*Clockwise from top left*) Mark Ketchen, Chang-Chyi Tsuei, and John Kirtley have shown that superconducting electrons are consistent with a theory called "d-wave."

The starting point for both camps is the observation that in all superconductors, the conducting electrons travel around in pairs. Pairing implies that something forces the electrons to overcome the mutual repulsion produced by their negative charges. Where the theoretical camps part company is over the nature of that mechanism.

In the traditional theory, a phonon, acting like a ripple in the material's lattice structure, pulls the electron pair together. The ascendant new theory, however, says that electrons are held together by magnetic interactions. High-temperature superconducting crystals are characterized by atoms whose magnetic fields point in random directions, but occasionally patches develop where the fields briefly organize themselves into a regular up-down-up-down pattern. The new theories say that a pair of electrons can get locked into one such patch, known as a spin fluctuation, and can then move with it through the crystal meeting no resistance.

Each pairing mechanism has a corollary in the way the electron pairs move. In quantum mechanics, a mathematical equation known as a wave function describes the motion of groups of particles, specifying where they are most likely to be. Phonon-based theories predict that the electron pair will have an s-wave function, which has a spherical shape and implies the pair has an equal chance of moving in any direction. Models based on magnetic interactions normally have the d-wave function, which is shaped like a four-leafed clover aligned along the two axes of the crystal, implying that pairs cannot move along the 45° diagonals.

About 3 years ago, experimentalists came up with a new breed of tests to distinguish between s-wave and d-wave pairing (*Science*, 12 August 1994, p. 860). With d-wave, an electron pair moving along one axis of the superconducting crystal will always be half a wave out of step, or "phase," from a pair moving along the perpendicular axis. Making an electron pair cross the 45° diagonal also forces it to change phase. This phase shift does not happen with s-wave.

Detecting such a phase shift is not easy. Although many of the dozen or so results so far have favored d-wave, contradictory reports have clouded the picture. But many consider the most persuasive series of experiments to have come from Tsuei and Kirtley's team begin-

KEY ELECTRON PAIRING EXPERIMENTS

	Experiment	Investigators	Reference
1993			
●/✣	Microwave penetration depths	Walter Hardy *et al.*	*PRL* **70**, 3999
●/✣	Photoemission	Zhi-Xun Shen *et al.*	
✣	SQUID Interferometry	Dale van Harlingen *et al.*	*PRL* **71**, 2134
1994			
✣	SQUID Interferometry	David Brawner and H.R. Ott	*Phys Rev B* **50**, 6580
✣	Tricrystal ring magnetometry	Chang-Chyi Tsuei *et al.*	*PRL* **72**, 593
●	Grain boundary tunneling	Praveen Chaudhari and Shawn-Yu Lin	*PRL* **72**, 1084
●	C-axis tunneling	Robert Dynes *et al.*	*PRL* **72**, 2267
1996			
✣	Tricrystal ring magnetometry	Chang-Chyi Tsuei *et al.*	*Science* **271**, 329

✣ D-Wave ● S-Wave *PRL = Physical Review Letters* ning in 1994 (*Science*, 30 September 1994, p. 2014).

The IBM team manufactured a ring from three separate crystal grains of a high-temperature superconductor known as yttrium-barium-copper-oxide (YBCO). The three grains were arranged so there were three boundaries in the ring at which the direction of the crystal lattice changed. These direction changes meant that, if paired electrons racing around the ring were d-wave, their phase should change one or three times, producing a net phase change around the ring. Researchers can detect this change as a small amount of magnetic current, or flux, spontaneously generated through the center of the ring. There would be no such flux if the pairing was s-wave.

The IBM team duly detected the flux using a scanning magnetic probe. But s-wave proponents were quick to note that complexities in YBCO's structure complicate the picture. YBCO conducts current in two closely stacked copper oxide layers, and some theorists suggested that two s-wave pairs, one in each layer, traveling in perpendicular directions and out of phase, could mimic phase changes similar to a d-wave pair. YBCO also has "chains" of copper and oxygen atoms near the copper oxide layer, which make movement in one lattice direction easier than in the perpendicular direction; this means that the observed flux in the ring could be explained by more complex pairing wave functions, known as s+d or s+g. "The question is, 'is the [phase] change really due to the superconductivity, and not the crystal structure?'" says theorist James Annett of the University of Bristol in the United Kingdom.

So last year, with the help of colleagues from the State University of New York, Buffalo, the IBM team manufactured a ring made from a different high-temperature superconductor, thallium-barium-copper-oxide. Although harder to coax into the required three-grain shape, its crystal structure within each grain is much simpler: only a single copper oxide layer and no copper chains. "It kills two birds with one stone," says Tsuei.

And sure enough, the researchers again found flux in the ring. "It is an important result. It's the first time any of these experiments have been done on a material other than YBCO," says Leggett. "The simplest phonon theories really are dead," says Philip Anderson of Princeton University in New Jersey, a veteran of the field.

There are still some experimental results keeping s-wave alive, however. In particular, there is work from a group led by Robert Dynes of the University of California (UC), San Diego, in which they observed current perpendicular to the copper oxide planes—which is forbidden by d-wave—in YBCO. And according to results yet to be published, researchers at UC Berkeley—working with the San Diego team—have duplicated their results. "These provide strong evidence of s-wave pairing in YBCO," says Klemm.

Similarly, Praveen Chaudhari, also of IBM Yorktown Heights, has been looking for a d-wave phase change for several years using a different method than Tsuei and Kirtley. "We're trying hard to look for d-wave, but not succeeding," he says, adding "I'm still sitting on the fence myself."

So while d-wave proponents seem to be winning most of the battles, they have not yet won the war. Klemm is philosophical: "Now more people do favor d-wave, but science has its own truth; it's not a democracy."

–Daniel Clery

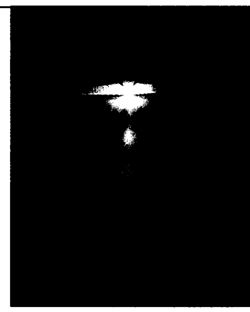
MATERIALS SCIENCE

Blue Laser Race Turns Red-Hot

In the race to make the first blue-light semiconductor lasers, the lead horse has come up slightly lame. Chip-based lasers that emit blue beams of light are expected to be an instant commercial hit, because the short blue wavelengths can be used to pack a lot of data in a very small space. But experimental lasers based on zinc-selenide (ZnSe), the one semiconductor material that's been capable of emitting a blue laser beam, have been hobbled by quick burnout. Now, however, a highly touted entry has finally stepped onto the track, ready to give the leader a run for the money.

In the 15 January issue of the Japanese *Journal of Applied Physics*, a team from Nichia Chemical Industries in Tokushima, Japan, reports making the first electrically powered laser—in this case violet in color—from a robust semiconductor alloy known as gallium nitride (GaN). The report has sent a ripple of excitement through the laser research community. "It's a very significant milestone," says J. J. Song, a physicist who heads the laser center at Oklahoma State University in Stillwater. "The whole world has been trying to make a GaN laser diode. This shows it can be done."

Although the performance of the new GaN lasers still lags behind that of those made from ZnSe—indeed, they also suffer from burnout problems—this gap could narrow rapidly, because GaN is inherently more durable, says Cammy Abernathy, a gallium nitride expert at the University of Florida, Gainesville. What's more, GaN is already used to produce other light emitters, known as light-emitting diodes (LEDs). This pre-existing research infrastructure is likely to push a GaN laser to the head of the field, where it could quadruple the storage capacity of devices that currently use longer wavelength red lasers, such as optical computer discs and audio compact discs.



NICHIA CHEMICAL INDUSTRIES

New blues. A semiconductor laser made from gallium nitride shines a blue light bright with promise.

The Nichia team was, in fact, the first to make commercial nitride-based blue LEDs (*Science*, 22 April 1994, p. 510), and—led by materials scientist Shuji Nakamura—they built on this technique to make lasers. Both semiconductor LEDs and lasers generate light when electrons and holes are injected into the device from electrodes placed on opposite sides. A series of sandwichlike layers of different semiconductor alloys then funnels these charges to one or more "quantum wells" in the center of the device, where the charges combine to give off photons of light. In LEDs, these photons fly out in random directions, but lasers incorporate a pair of mirrors that reflect and amplify the photons, turning them into a coherent beam.

The Nichia group's initial success at making blue LEDs stemmed from the ability to lay down these sandwichlike semiconductor layers, a hard task because they tend to develop a lot of defects. Nichia's GaN layers were also riddled with tiny cracks—but to the researchers' surprise the cracks didn't prevent the LEDs from functioning. GaN is very tolerant of defects.

Cracks, however, are bad for lasers, as photons ricochet off them in all directions. To prevent the cracks from forming, Nakamura and his colleagues added an extra semiconductor layer near the bottom of their sandwichlike devices. Unlike the hard and brittle layers that sit on top, the new layer, made from an alloy of indium-gallium-nitride, is relatively soft. This layer acts as a kind of expansion joint, relieving the strain between the atomic lattices of adjoining semiconductor layers that would otherwise lead to cracking.

The device still has one drawback: It can only handle short electrical pulses; continuous streams overheat it, causing it to burn out. ZnSe lasers, in fact, last longer, yet because GaN can handle thousands of times more defects than ZnSe without trouble, researchers expect that the growing research effort on GaN will quickly close the performance gap. "There's still a window of opportunity for [ZnSe] lasers," says Anis Husain, who directs research funding for semiconductor optics at the U.S. Defense Department's Advanced Research Projects Agency. "But that window is closing very rapidly."

–Robert F. Service