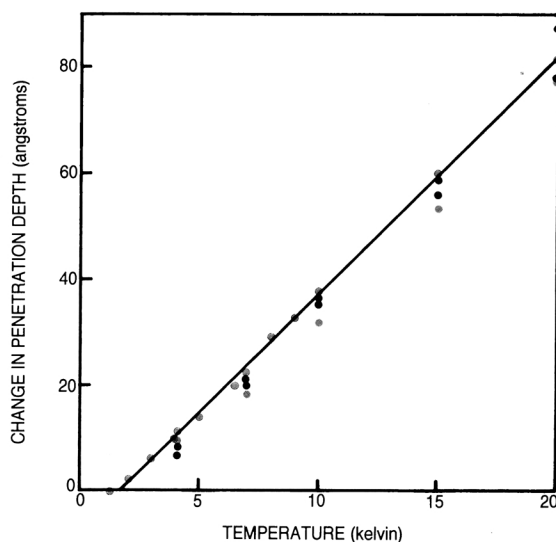


IN HIGH- T_c SUPERCONDUCTORS, IS d-WAVE THE NEW WAVE?

Theorists trying to explain the mechanism for superconductivity in the copper oxide materials may not agree on much, but they all do believe it involves the coupling of electrons of opposite spin. Paths quickly diverge when it comes to the angular momentum of the pair. Is it a BCS-like s-wave (with $l=0$)? A d-wave? Or something else? The answer is linked to the mechanism that couples the electrons. Although early experiments seemed consistent with an s-wave pairing, recent measurements suggest that the pairing state is at least not isotropic. If the experiments can further delineate the symmetry of the pairing state, they might help narrow the field of contending theories.

How does the angular momentum of the pairing state manifest itself? For one, it determines the wavevector dependence of the energy gap that develops at the Fermi surface when a substance goes superconducting: This gap is the energy needed to break the electron pairs in the superconducting state. If the electrons were paired in an ideal s wave, the energy gap would have the same value at all points on the Fermi surface. More realistically, s-wave pairing gives rise to an energy gap that has the same symmetry as the crystal. But if the electron pairs have a form of d-wave pairing called $d_{x^2-y^2}$, the shape of the gap in k space resembles a four-leaf clover, and is described by the function $\cos(k_x a) - \cos(k_y a)$ (or, in real space, by $x^2 - y^2$ for points (x, y) on a circle). For $d_{x^2-y^2}$ -wave pairing, the superconducting gap is positive in some directions in k space and negative in others, and it goes through zero in between. Because of these zeros, the hallmark of this type of pairing is the appearance of "nodes in the gap." There are other possible forms of anisotropic pairing states, but they do not necessarily have nodes.

Evidence of anisotropic pairing has surfaced in nuclear magnetic resonance measurements and, more re-



Penetration depth of microwaves in a high- T_c crystal, compared to some reference value, is predicted to vary linearly with temperature at low temperatures if the electrons in the superconductor are paired in a particular type of d-wave state. That theoretical prediction is compared here to recent measurements on four different crystals. (Adapted from ref. 6.)

cently, in studies of angle-resolved photoemission and measurements of the microwave penetration depth in a crystal. Hints of anisotropy have also been seen in nuclear quadrupole resonance studies, Raman scattering and neutron scattering. But, perhaps because the data come from different techniques applied to a variety of copper oxides, the details of the results are not all consistent with one another. Many researchers are now designing new experiments as well as going back to look more critically at old data.

Noting that lots of first-rate experiments are now focused on this fundamental question of the pairing symmetry, Malcolm Beasley (Stanford University) remarked, "It's great that the experiments once again have a lot to tell us."

Evidence from nmr

Nuclear magnetic resonance studies probe the local magnetic field around an atom and hence reflect the susceptibility of the material. They have been of special interest for the high- T_c materials because many research-

ers have wondered whether spin correlations might play a role in the mechanism of superconductivity: When copper oxides are in their insulating state—that is, before they are doped—the electron spins associated with the copper atoms in the copper oxide have an antiferromagnetic ordering, with the spin of each copper atom opposite to those of all its nearest neighbors. In the metallic, or doped, state this order disappears, but the copper spins still exhibit short-range antiferromagnetic spin fluctuations, with the spins ordering themselves fleetingly over a fairly short distance. Those theories that postulate a role for the spin fluctuations in superconductivity predict d-wave pairing. But there are also predictions of $d_{x^2-y^2}$ -wave pairing that are not based on spin fluctuations.

Nmr measurements of the resonance frequency on $\text{YBa}_2\text{Cu}_3\text{O}_7$ indicated several years ago that electrons in the copper oxide superconductors are paired in spin-singlet states. This indication came from the behavior of the Knight shift, the frequency shift

that occurs when the internal field is different from the applied field: In a normal metal, the magnetic moments of the conduction electrons in the neighborhood of the ion being probed align with the applied field and create a larger internal field. As these metals go superconducting, electrons with oppositely directed spins couple to form singlet states, having zero spin. Thus the internal field decreases and the Knight shift it causes falls sharply to zero at temperatures below T_c . A similar drop in the Knight shift was seen in nmr measurements on high- T_c materials, suggesting that the pairing state in these oxides is also likely to be a spin singlet.¹

In the anisotropic high- T_c materials, perhaps not surprisingly, nmr measurements have found that the relaxation rate for copper depends on the direction of the applied static magnetic field, with the rate being higher when the static field is parallel to one of the axes in the copper oxide plane. More unexpected was the finding by Charles Slichter and his colleagues at the University of Illinois² that the ratio of these relaxation rates, which is fairly constant with temperature above T_c , varies as the sample is cooled below T_c . The Illinois group had some indication that these measurements might be affected by the anisotropic effects of the magnetic field, but when they, as well as an IBM-Los Alamos collaboration, repeated³ the measurements at very weak field, they found that the ratio still had anomalous behavior. By now the Illinois group has determined⁴ the relaxation rates for oxygen as well as copper and has found that the rates for both vary as T^3 below T_c . This behavior is consistent with the predictions of some $d_{x^2-y^2}$ -pairing models.

Inelastic neutron scattering can determine the susceptibility as a function of wavevector as well as frequency. It essentially probes the spin excitation processes. In ordinary BCS theory, when the gap opens, the spin excitations with energies less than the gap value are suppressed, but not necessarily if there is a node in the gap. When neutron measurements on both $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and YBCO probed the regions where $d_{x^2-y^2}$ -wave pairing would predict a node, the low-energy antiferromagnetic spin fluctuations were found to decline below T_c but never really to go to zero.⁵ That much would support d-wave pairing. But, complicating the picture, Gabriel Aeppli (Bell Labs) told us that in very recent neutron measurements, his group did not see the change in position or width of the spin-excita-

The Pairing State

Electrons once wanted to mate
In a superconducting s-state.
As they circled around
Was isotropy found
Or was d wave their ultimate fate?

—BARBARA GOSS LEVI

tion peaks that one would expect from any simple d-wave pairing.

Penetration depth

If electrons pair in a $d_{x^2-y^2}$ wave, theory predicts that the microwave penetration depth will vary linearly with temperature, but early measurements did not see such behavior. A group led by Walter Hardy and Douglas Bonn at the University of British Columbia, Vancouver, recently reported a linear variation⁶ in experiments they did on very clean YBCO crystals at temperatures extending lower than previous measurements. The results of this experiment must be reconciled with the previous penetration depth measurements, which gave evidence for anisotropic pairing of some other type in both single crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and thin films of YBCO, as well as other measurements in electron-doped copper oxides, that seem consistent with s-wave symmetry.

The microwave penetration depth λ is determined by the superfluid density responsible for screening the external field. In the s-wave BCS theory, because pairs can be thermally excited across the gap Δ , the change in the superfluid density per unit change in temperature goes as $\exp(-\Delta/k_B T)$. In that case $\Delta\lambda$ also varies exponentially with temperature T . But if there are nodes in the energy gap, electron pairs can more easily be broken, the superfluid density should have a stronger temperature dependence, and $\Delta\lambda$ is expected to increase as a power of T at low temperatures. If the symmetry is specifically $d_{x^2-y^2}$ then $\Delta\lambda$ should vary linearly with T at low temperatures.

One way to measure λ is to place the sample in a microwave cavity, whose resonant frequency depends on its volume. With a sample in the cavity, the effective volume includes only that part of the sample penetrated by microwaves. As the sample cools, λ shrinks and so does the effective cavity volume, shifting the measured resonant frequency. While this method has high sensitivity, it can determine only the changes in λ relative to its zero-temperature value,

not its absolute value.

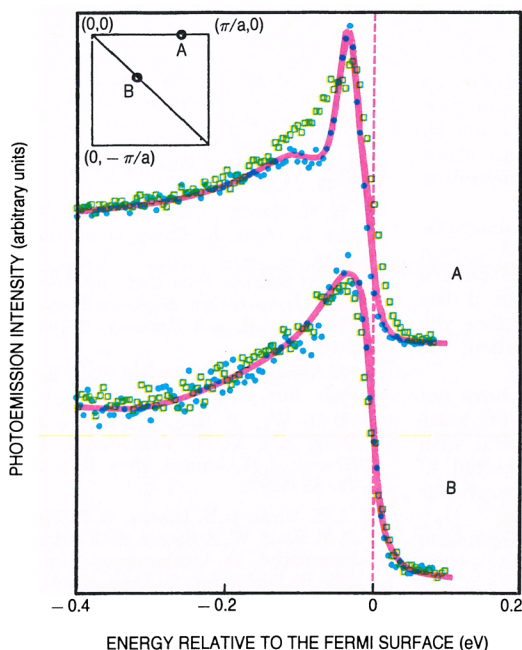
A collaboration of researchers from Stanford University and Hewlett-Packard Research Labs have developed parallel plate microwave resonators with very thin dielectric separators to gain high sensitivity in measurements of $\Delta\lambda$ in thin films. The values measured⁷ by this collaboration for both YBCO thin films and BSCCO single crystals are consistent with a T^2 dependence, rolling over to a weaker temperature dependence at the lowest temperatures.

Before these recent results some experiments had reported that the penetration depth varied exponentially with temperature, consistent with s-wave pairing, but a trio of theorists⁸ reexamined the data and found a power-law dependence on temperature.

Hardy, Bonn and their colleagues built an especially small cavity to gain sensitivity for a measurement on a single crystal comparable to that of the thin film work. They had to be sure that the sample did not move as the temperature changed, because the field is not perfectly homogeneous, and that the cavity temperature remained constant as the sample within it was cooled. Hardy feels that he and his colleagues have carefully checked for systematic errors.

When the Vancouver group plotted the changes in penetration depth for four YBCO samples as a function of temperature from 1.3 to 20 K, the points fit a straight line (see the figure on page 17), the dependence expected for a $d_{x^2-y^2}$ -wave gap. How can one explain the discrepancy between the Vancouver results on crystals with earlier measurements on thin films? Hardy points out that thin films are inherently dirtier than crystals and speculates that therein may lie the answer. But others point out that the amount of impurities needed to change the temperature dependence would degrade the critical temperature as well, although this theoretical argument has not been empirically tested. Furthermore, asks Beasley, a member of the Stanford-HP collaboration, what about the discrepancy with their single-crystal BSCCO data? Both Beasley and Philip Anderson (Princeton) urge caution in interpreting measurements on YBCO because of such structural complexities as its chains of copper atoms.

Several experiments are planned to address the muddy situation. The Stanford-HP collaborators will ship some of their thin films to Vancouver to be measured in the resonant cavity there. At the same time Hardy and his collaborators hope to further



Photoemission probes the Fermi surface at two different locations in k space, marked as points A and B in the Brillouin zone diagram in the upper left. Above T_c (squares) the data show a peak whose leading edge crosses the Fermi surface at its midpoint. Below T_c (dots) this edge is pulled back at A, indicating an energy gap, while at B it appears unchanged. In some d-wave pairing the gap is expected to have a node along the diagonal line. Curves are theoretical normal-state Fermi surfaces, considering only the copper oxide planes. (Adapted from ref. 10.)

check for possible systematic errors and to improve the frequency resolution by a factor of five.

Further complicating the penetration depth story are the measurements by a group at the University of Maryland.⁹ The group has studied $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, a material that exhibits a high T_c when doped with electrons rather than with holes, as in YBCO or BSCCO. The temperature dependence of λ for this material is just what one would expect for an s-wave BCS superconductor.

Photoemission

A Stanford-Los Alamos collaboration led by Zhi-xun Shen has probed the energy gap at different directions on the Fermi surface using angle-resolved photoemission.¹⁰ This group uses BSCCO crystals, grown by Aharon Kapitulnik's group at Stanford, that are identical to those on which the Stanford-HP group measured the penetration depth. By scattering photons off electrons in the crystal, one can sample the energy spectra of the electrons. Because the technique is sensitive to the angle of the emitted electrons one can determine the spectrum for different wavevectors on the Fermi surface.

The spectra shown in the figure above were measured at two different temperatures and at two different locations in phase space in a crystal of BSCCO. The inset in that figure is a sketch of the Brillouin zone, which represents the domain of the electron wavevectors in momentum space.

The points labeled A and B on the diagram mark the k vectors corresponding to the two sets of curves. If the pairing is isotropic s-wave, one should see a gap of the same size at both sites. But if the pairing is $d_{x^2-y^2}$, there would be nearly a full gap at A and a node at B and, indeed, everywhere along the diagonal line.

For both locations, the spectra measured above the critical temperature—specifically, at 85 K—follow roughly the same pattern: There is a peak whose leading edge crosses the Fermi level at its midpoint. In the superconducting state (at 20 K), the spectrum at B is not changed, but a gap has clearly developed at the Fermi surface at point A. The leading edge is pulled back to a higher binding energy, reflecting the opening of a superconducting energy gap. Shen and his coworkers measured the magnitude of such a shift at various points in k space and found a considerable anisotropy. In some samples, they report, the shift varies from 20 ± 4 meV in some directions to within the experimental detection limit of about 4 meV in other directions.

Within the resolution of their experiment, the Stanford-Los Alamos group cannot tell whether the gap ever goes to zero or just gets very small. Their measurements are sensitive only to the magnitude and not to the sign of the gap, so they cannot tell if the gap goes negative at some point. They conclude that their results are certainly consistent with $d_{x^2-y^2}$ pairing but could fit other

forms of anisotropy as well.

This anisotropy in the gap was *not* seen in another high-resolution experiment done three years ago by Clifford Olson (Iowa State University) and his colleagues from Iowa State and from Argonne and Los Alamos National Laboratories. Both Olson and Shen are puzzled. Perhaps, suggests Shen, the difference lies in the higher quality samples available today; both agree that more experiments are needed.

To resolve more specifically whether there are nodes in the gap requires a measurement that is sensitive to the *sign* of the gap. Dale Van Harlingen, Anthony Leggett and their colleagues at the University of Illinois have designed such an experiment, based on the ideas of V. B. Geshkenbein, A. I. Larkin (both of the Landau Institute, Moscow) and A. Barone (University of Naples, Italy) and similar to a proposal of Manfred Sigrist and T. Maurice Rice (ETH, Zurich). Their design consists of a SQUID in which half of the loop is a single, untwinned crystal of YBCO. Recall that a SQUID consists of a loop of superconducting material broken at two points by superconductor-insulator-superconductor junctions. In the Illinois scheme, the superconductor on one half of the loop is lead, and on the other half it is the crystal. The leads are arranged so that one of the junctions is on a face of the crystal perpendicular to the a axis and the other is on a face perpendicular to the b axis. Thus the current in the loop enters in one face and must turn through 90° to exit through the other face. If the order parameter is negative in one direction and positive in another, this path introduces an additional phase shift of π that is reflected in a plot of the critical current versus flux.

At the March meeting of the American Physical Society in Seattle Van Harlingen presented the group's preliminary results: They observe a significant phase shift between the phases of the order parameter in the a and b directions, with several samples giving the phase shift of π predicted for the $d_{x^2-y^2}$ state.

Theoretical picture

Theoretically, the big question is what mechanism creates the attractive interaction between electrons. In the BCS theory that mechanism is the electron-phonon interaction. Some recent models postulate that it involves the antiferromagnetic spin fluctuations: An electron scattering off these fluctuations can cause a perturbation that in turn might scat-

ter a second electron. In this way the spin fluctuations might pair the electrons.

Spin fluctuations are believed to play a role in heavy-fermion superconductors, materials in which the pairs are formed from quasiparticles with especially large effective masses. These materials manifest more evidence for anisotropic superconductivity than do the high- T_c oxides.

Among those postulating a role for spin fluctuations are Douglas Scalapino and his colleagues at the University of California, Santa Barbara. They used¹¹ a Hubbard model to describe these spin fluctuations, finding that the pairing occurred in the $d_{x^2-y^2}$ state when the doping moves the material slightly away from the antiferromagnetic ordering it has in the insulating state. They then carried out strong coupling and Monte Carlo calculations, which further supported the $d_{x^2-y^2}$ pairing.¹¹ Their work was followed by weak coupling calculations by Toru Moriya, Yoshinori Takahashi and Kazuo Ueda (then at the University of Tokyo) and by Philippe Monthoux and David Pines (both of the University of Illinois, Urbana-Champaign) and Alex Balatsky (now at Los Alamos).¹² Monthoux and Pines have since undertaken strong coupling calculations for YBCO.¹³ Using nmr data to parametrize some of the interactions, they get good agreement with the observed T_c and some other measured properties.

Both Scalapino and Pines and their colleagues have calculated¹⁴ nmr relaxation rates, finding better agreement with the measured data than s-wave pairing provides.

One of the theories that does *not* postulate d-wave pairing is that proposed by Anderson. His picture features BCS-type pairing of the electrons in each copper oxide layer and Josephson-pair tunneling between the layers. Stimulated by the recent experiments Anderson, together with Sudip Chakravarty and Asle Sudbø of the University of California, Los Angeles, and Steven Strong of Princeton, calculated that the superconducting energy gap in this model is highly anisotropic: It does not change sign but has a finite s-wave component.¹⁵ They refer to its shape as anisotropic s-wave. Chakravarty told us that their calculations are consistent with the photoemission experiments.

Anderson pointed out that exotic pairing states like the d-wave state are highly sensitive to impurity scattering but that the behavior of copper oxides did not seem to depend very strongly on impurity levels: To him

this insensitivity to scattering suggests the absence of sign changes in the gap. Pines reports that calculations he has done with Monthoux indicate that the changes in quasiparticle energies caused by impurity scattering are smaller than those attributed to the spin-fluctuation scattering.

Regarding the antiferromagnetic spin fluctuation models, Anderson feels that you first need to have a theory that contains within it the origin of the fluctuations before you can trust them to tell you about the interactions.

Clearly the experiments have not converged on an answer to the question of the pairing states. But with more experiments now directed at this central question, more precise answers may be forthcoming.

—BARBARA GOSS LEVI

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