Evidence Accumulates for Unusual Behavior in Underdoped High-T_c Superconductors

As you cool a conventional superconductor, it acts as a metal until it reaches the critical temperature T_c, below which it rapidly goes superconducting. But some of the high-temperature, copper oxide materials—in particular, the underdoped ones, whose densities of charge carriers are below that which gives the highest T_c—seem to be preparing for the transition to a superconducting state well before they reach T_c. Experiment after experiment on underdoped materials at temperatures above T_c has revealed some kind of crossover or change in behavior, which some feel is related to the eventual onset of superconductivity at lower temperatures. When the temperature does reach T_c, the material goes superconducting, but some of its properties exhibit relatively little additional discontinuity in behavior.

What's going on? There's no consensus yet among the many competing viewpoints. Nevertheless, some researchers have argued that the strange temperature dependence of such properties as electrical resistivity, specific heat, spin susceptibility and optical conductivity provides indirect evidence for the formation of some kind of gap in the excitation spectrum. Just such an energy gap has now been observed in photoemission studies of underdoped superconductors above T_c. Those results and other new data were intensely discussed at the 10th Anniversary HTS Workshop on Physics, Materials and Applications held in Houston in March.

Spin gaps?

Philip Anderson asserted in 1987 that the normal state of high-T_c superconductors do not behave like a Fermi-liquid, a model that successfully describes a normal metal.[1] The underdoped materials seem to manifest particularly large deviations from a Fermi liquid. Researchers began to discover the errant behavior over seven years ago. It showed up, for example, in nmr studies on underdoped samples of yttrium barium copper oxide (YBCO). Measurements of the temperature dependence of both the spin susceptibility and the nuclear spin-lattice relaxation rate indicated that those parameters were suppressed below some particular temperature, which was well above T_c. In

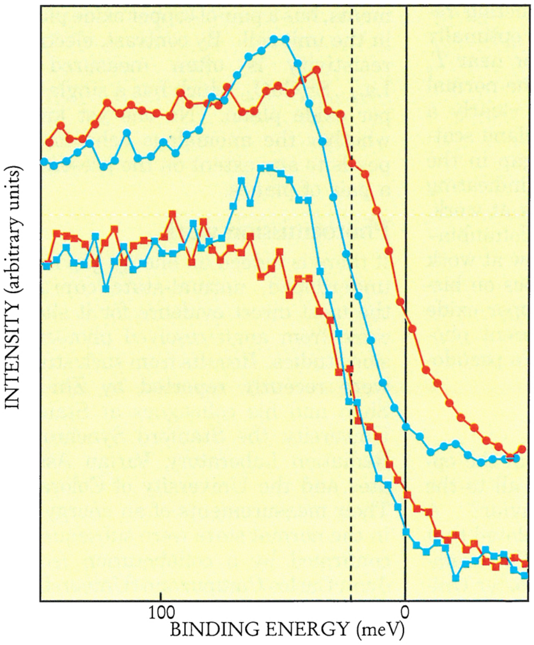
The energy gap that conventionally heralds the onset of a superconducting state has been seen in materials well above the temperatures at which they actually become superconducting.

the case of spin susceptibility, which is proportional to the difference between the number of electrons aligned with an applied field and those lined up opposite it, the suppression might result from electrons pairing up in singlet states because it takes more energy to flip a spin when it's paired. Similarly, the lowering of the relaxation rate implies the absence of spin excitations to which the nuclear spins can couple.

Researchers looking at the magnetic measurements started to talk about the opening of a gap in the spin excitation spectrum—that is, a spin gap. (A gap would denote a region of excitation energies where there is no density of states; particles could not be excited into that region.) More precisely the gap would be a spin pseudogap because certain responses are reduced but not all the way to zero. Robert Laughlin of Stanford University has quipped that what pseudogap really means is "a not-understood suppression of excited states."

The anomalous behavior of underdoped materials also manifests itself in the electrical resistivity. It is striking that the resistivity for $YBa_2Cu_3O_7$, an optimally doped compound, follows a linear curve over a very wide temperature range. But the resistivity of its underdoped stepsister, $YBa_2Cu_3O_{6.7}$, (with fewer oxygen atoms per unit cell), is more complicated. At some crossover temperature well above T_c, the resistivity changes slope, so that the decrease of resistivity with temperature is steeper below this crossover temperature than it is above it. Like the drop in spin susceptibility, this decrease in resistivity hints at a gap in the excitation spectrum. Even though resistivity determines the flow of charge, the gap could be consistent with the spin gap from magnetic measurements; for example, it could be affected by scattering off spin fluctuations.

Other researchers have determined the electronic specific heat of, initially, YBCO and subsequently of lanthanum strontium copper oxide (LaSrCuO) and thallium barium copper oxide. Such experiments have shown that there may be a pseudogap in the charge



PHOTOEMISSION SPECTRA near the Fermi surface reveal the presence of a superconducting energy gap even in the normal state of an underdoped sample. The top two curves (circular data points) are for an overdoped sample. At a temperature above T_c (red curve), the leading edge straddles the Fermi energy (solid black line); below T_c (blue curve), the edge moves back as a gap is formed. The bottom two curves (square points) are for an underdoped sample. In this case the energy gap has already formed above T_c. Dashed line runs close to the midpoint of the bottom two lines. (Figure courtesy of Anthony G. Loeser and Zhi-Xun Shen, Stanford University.)

excitations, not just in the magnetic ones. A measurement of the magnetoresistance along the c-axis—that is, perpendicular to the copper oxide planes—shows that a spin gap presents a barrier to c-axis conduction, but that the barrier is weakened when a magnetic field is applied.

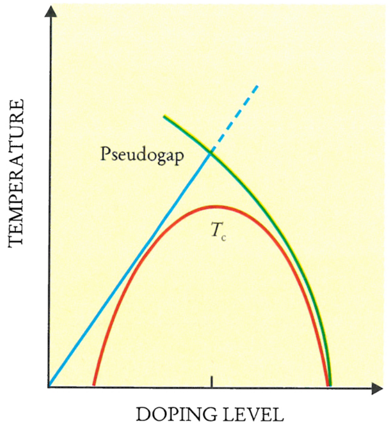
The strange behavior of the underdoped normal state manifests itself mildly in the copper-oxide planes but it showed up more dramatically in the optical conductivity along the c axis. In optical conductivity experiments, one excites the sample with far-infrared radiation, measures the reflectance and deduces both the electrical conductivity and the inelastic scattering rate at low frequencies. By taking such measurements on YBCO, researchers have found that the c-axis conductivity in underdoped samples is quite low and flat for frequencies ranging from near zero to about 200 cm^{-1}. The lower the doping level, the lower is this plateau in the conductivity. The conductivity rises at higher frequencies. Such a frequency dependence is indicative of a pseudogap.

A pseudogap is less evident in the optical conductivity measured in the copper oxide planes, although some features of the ab plane conductivity have been associated with a pseudogap. Recently, a team of experimenters from McMaster University, the University of British Columbia and Northern Illinois University reported in Houston that they have correlated the inelastic scattering rate in the ab plane with the pseudogap in the c-axis conductivity for several materials and at several temperatures. For underdoped materials, the behavior near T_c resembles that deep in the superconducting regime. By contrast, for an optimally doped material, the behavior near T_c more nearly tracks that in the normal state at 300 K. There is clearly a correlation between the in-plane scattering rate and the pseudogap in the c-axis optical conductivity, indicating that the same mechanism is at work. The McMaster–British Columbia–Northern Illinois group is now at work on optical conductivity studies on bismuth strontium calcium copper oxide (BSCCO) to compare with recent photoemission measurements of a pseudogap in these materials.

Universality

Are these pseudogaps seen in the optical conductivity related at all to the anomalous magnetic behavior? A number of analysts have explored that question in various ways. For example, Thomas Timusk of McMaster University, with his colleagues at McMaster and the University of British Columbia, showed that the temperature behavior of the c-axis conductivity tracked that of the Knight shift from magnetic measurements.[2] Bertram Batlogg and his colleagues from Bell Labs, Lucent Technologies, examined various types of measurements made on the underdoped normal state in both LaSrCuO and YBCO and plotted estimates of the temperatures at which there was some change of behavior as a function of doping level; the group found that the data points fell on the same curve.[3]

Measurement of a particular property of the high-T_c superconductors is likely to be done on just one type of compound, because certain materials may lend themselves more readily to that type of experiment. For example, photoemission studies are usually done on BSCCO because it has particularly well behaved surfaces. YBCO, which is typically the focus of spin measurements or optical conductivity measurements, has a pair of copper oxide planes in the unit cell. By contrast, electrical resistivity is often measured on $La_{(2-x)}Sr_xCuO_4$, which has a single copper oxide plane. No one yet knows whether the anomalous behavior depends to any extent on the presence of a pair of planes.



PHASE DIAGRAM of copper oxide superconductors shows the curve (red) of critical temperature as a function of doping level. The green curve indicates temperatures below which there seems to be some kind of pairing, as evidenced by the energy gap there. The blue line indicates the upper limit on the temperature at which phase coherence sets in. The blue and green curves delimit the pseudogap region on the underdoped side. Only for optimally doped superconductors do the pairs form at the same temperature at which they condense into a coherent state. (Adapted from ref. 5.)

Photoemission work

If there is indeed an energy gap in the underdoped, normal-state cuprates, the most direct evidence for it should come from angle-resolved photoemission studies. Results from such studies were recently reported by Zhi-Xun Shen and his colleagues at Stanford University, the Stanford Synchrotron Radiation Laboratory, Varian Associates and the University of Colorado.[4] Their measurements of an energy gap in the normal state were subsequently confirmed by a collaboration led by Juan Carlos Campuzano (University of Illinois at Chicago and Argonne National Laboratory). This collaboration works at the Aladdin synchrotron radiation center at the University of Wisconsin—Madison.

The photoemission spectrum for an ideal metal at zero temperature would be constant as a function of energy up to the Fermi energy, where it would drop sharply to zero. In the Bardeen–Cooper–Schrieffer theory of superconductivity, when the temperature goes below T_c, a gap develops at the Fermi energy; the density of states drops to zero at some energy (the gap energy) below the Fermi surface. A peak develops just below that gap. To estimate the size of the energy gap in the underdoped samples, both the Aladdin and Stanford teams measured the midpoint of the leading edge of the spectrum relative to the Fermi energy.

The figure on page 17 shows the photoemission spectra near the Fermi energy (vertical black line) for both an overdoped sample (circular data points) and an underdoped sample (square data points). The red curves are above T_c; the blue curves below it. The overdoped sample shows the behavior one normally expects for a superconductor: As superconductivity sets in below T_c, the leading edge moves to the left (away from the Fermi surface), signalling the opening of an energy gap. In the underdoped sample, the leading edges of both curves lie below the Fermi energy, showing that an energy gap has already developed above T_c. The dashed line in that figure is drawn close to the midpoints of the three curves that have moved back from the Fermi energy.

As if it weren't surprising enough to find an energy gap, both the Stanford and Aladdin groups find that the gap as a function of wavevector seems to have the same anisotropy as that already observed for the optimally doped samples below T_c (see PHYSICS TODAY, January 1996, page 19 and May 1993, page 17). Even more striking, the magnitude of the gap stays constant as the doping level—and hence T_c—decreases, whereas in a conventional superconductor, T_c is directly proportional to the gap size. Finally, there is some indication that the gap either goes away at temperatures around 200-300 K or becomes much weaker there.

Theoretical explanations

There seems to be no dispute now that something strange and important is occurring in the underdoped cuprates above T_c. But what is the mechanism behind it all? There is no consensus on that question, although plenty of ideas have surfaced.

The figure on page 18 shows a model-independent phase diagram proposed by Victor Emery of Brookhaven National Laboratory and Steven Kivelson of the University of California, Los Angeles,[5] which is a useful visualization of the situation. (Similar phase diagrams have been drawn in conjunction with various models.) The figure shows, first of all, the curve (red) of critical temperature as a function of carrier concentration, with a maximum at the optimal doping level. The green curve, which extends from the lower right to the upper left, represents the temperatures below which a number of theorists think there is some type of pair formation, as suggested by the evidence of a pseudogap. The blue line from the origin represents an upper limit on the temperature at which phase coherence, or superconductivity, sets in. The blue and green curves form the borders of the pseudogap region.

In the BCS theory of superconductivity, pair formation and phase coherence occur simultaneously but in the underdoped region, as the diagram illustrates, the two steps may be at different temperatures. Philip Anderson of Princeton University remarks that "what's going on here is not just BCS; we still have Cooper pairs but the physics of the phase transition is so far from conventional behavior that I wouldn't call it BCS any more."

Those theorists who agree with the basic picture represented by the diagram differ strongly about the microscopic mechanisms governing the behavior in the pseudogap region and even above it. For example, some think that electron pairs are being formed but that the pairs don't develop a long-range coherence until a lower temperature; they behave a bit like square dancers who are assigned partners but don't dance in formation until the music starts.

Others believe that the electrons separate into spinons and holons; spinons have spin but no charge, and holons have charge but no spin. According to some mean-field theory calculations,[6] the spinons are predicted to form singlet pairs well above the superconducting T_c, with superconductivity setting in only when the holons become phase coherent at T_c.

Some theorists agree that there is something unusual about the underdoped behavior above T_c but argue that it is not related to any particular crossover temperature. Still others say that there may be several crossover temperatures. All these theories have plenty of mysteries to solve not only about the underdoped region but about all the normal state properties.

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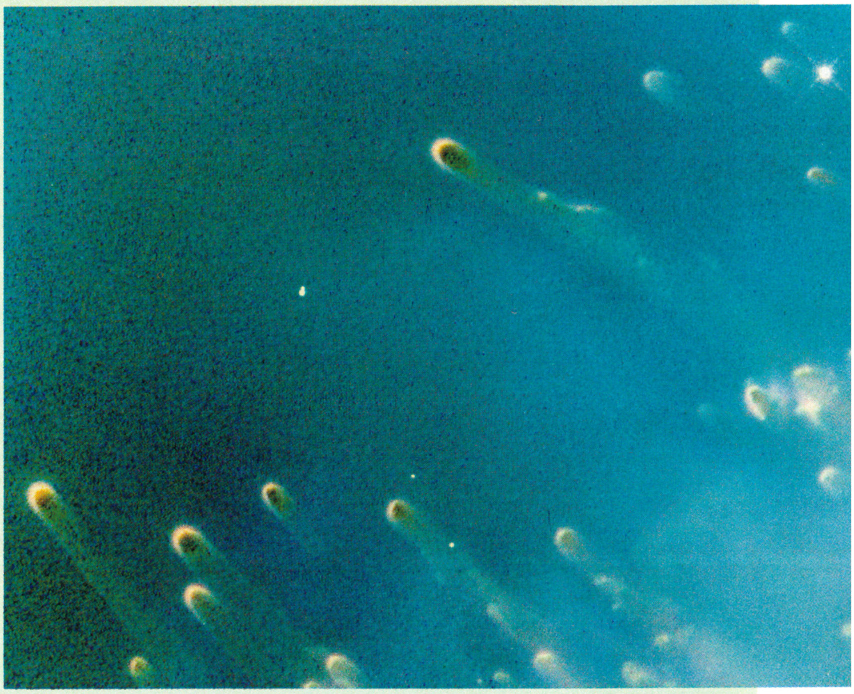
Helix Nebula Displays Hundreds of Gaseous Knots



These tadpole-like structures have been found in the Helix nebula, the closest planetary nebula to Earth—450 light-years away. With the aid of Wide Field Planetary Camera 2 on the Hubble Space Telescope, C. Robert O'Dell and Kerry P. Handron of Rice University observed 313 of the well-resolved structures, which they call cometary knots; their glowing heads and wispy tails resemble comets. O'Dell and Handron estimate that the entire nebula has 3500 of them.

A planetary nebula consists of a series of rings of gas thrown off a star as it enters the white dwarf stage. The tails of the cometary knots point away from the central star, which ultimately provides the energy for the light we see. Although previous ground-based observations showed some spokelike structure in the Helix nebula, the spokes were neither well resolved nor numerous. In their paper published in the *Astronomical Journal* (volume 111, page 1630, 1996), the Rice astronomers say the most likely explanation for the cometary knots is Rayleigh–Taylor instabilities, arising from either the earliest stages of the planetary nebula development at the ionization boundary between the ionized and neutral components or later when the stellar wind was shocking and shaping the inner part of the nebula.

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