Ultrasound measurements reveal a long-sought phase transition in superconducting cuprates

Vibrational resonances provide a sensitive probe into the materials' thermodynamic properties.

More than a quarter century has passed since the discovery of high-temperature superconductivity in a class of copper oxide compounds, and in many ways the materials remain as confounding as ever. The mechanism of their superconductivity is by no means their only mystery. Even far above the superconducting transition temperature T_c, the cuprates play host to a variety of perplexing phenomena that defy explanation by current theories of condensed matter.

Among the biggest puzzles is the origin of the pseudogap state, found in a large region of the cuprate phase diagram, in which the charge-carrier density of states resembles that of the superconducting state but the electrical resistivity remains far from zero. Two contending explanations have been advanced. In one, the pseudogap represents the gradual onset of a precursor to superconductivity. In the other, the pseudogap state is a distinct phase of matter, separate from superconductivity. Recent experiments have favored the latter theory, but the smoking gun—the thermodynamic signature of a phase transition at the pseudogap's upper boundary—remained elusive.

Now Arkady Shekhter, Albert Migliori, and their colleagues at the National High Magnetic Field Laboratory at Los Alamos National Laboratory have found that signature.[1] Using resonant ultrasound spectroscopy, they measured the temperature-dependent elastic stiffness, a fundamental thermodynamic parameter, of two cuprate crystals. The elastic stiffness exhibited a break in slope at a temperature near the onset of the pseudogap. The result may have implications for the understanding of not only the pseudogap but also the rest of the cuprate phase diagram.

Mind the pseudogap

The family of superconducting cuprates includes materials with a variety of crystal structures and compositions, including yttrium barium copper oxide, lanthanum strontium copper oxide, and many others. Common to all of them are the planar lattices of CuO_2 in which superconductivity occurs. But the so-called parent compounds—$YBa_2Cu_3O_6$, for example—are not just nonsuperconducting but insulating. That's because each Cu lattice site has exactly one unpaired electron, and those electrons repel each other strongly enough that they're effectively locked in place.

By changing the material composition slightly, to $YBa_2Cu_3O_{6+x}$, one can add or (more often) remove some electrons from the insulating CuO_2 layers. In the resulting electron- or hole-doped materials, charge carriers can easily hop from one Cu site to another. And at low enough temperatures, they can combine into Cooper pairs and condense into a superfluid.

As shown in the phase diagram in figure 1, there is an optimal doping level at which T_c reaches a maximum. The underdoped cuprates—those with doping levels less than the optimum—are the ones that host the pseudogap state.

In an ordinary metal, the charge-carrier states form a continuum: One can excite an electron with any amount of energy, no matter how small. In contrast, the superconducting state is a collective phenomenon: Changing the state of an electron means breaking a Cooper pair, which requires rearranging all the others. The rearrangement takes energy, and that energy is reflected in a gap in the energy spectrum of excited states. In the cuprates, because of their anisotropy, the gap is direction dependent: It's easier to give an electron a momentum boost in some directions than in others.

In the underdoped cuprates, the energy gap persists above T_c—but only in some directions—and it doesn't completely disappear until a much higher, doping-dependent temperature T^*. One explanation that emerged was that the pseudogap observed between T_c and T^* was a sign of the gradual appearance of a precursor to superconductivity: As a cuprate was cooled, Cooper pairs began to form at T^*, but they did not form a coherent superconducting condensate until T_c. Indeed, some experiments[2] showed hints of charge-carrier pairs well above T_c—but nowhere near T^*.

Alternatively, the pseudogap region could be its own phase of matter, distinguished from the adjacent phase by an abrupt change in the material's symmetry. Because many thousands of experiments have sought evidence of such a symmetry change and most have found nothing, theorists have wondered what form of "hidden order" might give rise to the pseudogap but remain otherwise invisible to experimental probes. In one prominent but controversial theory, proposed by Chandra Varma of the University of California, Riverside, a set of countercirculating electron currents

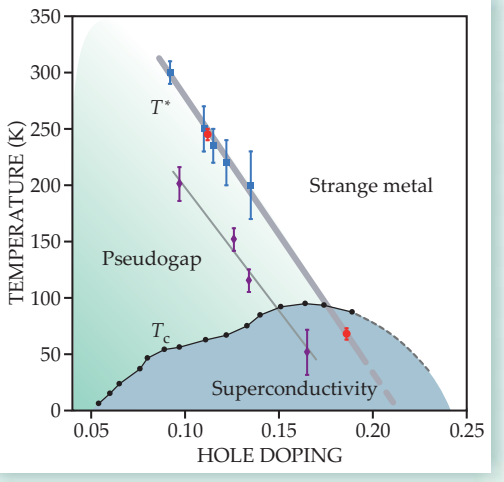


Figure 1. The phase diagram of a family of yttrium barium copper oxides of formula $YBa_2Cu_3O_{6+x}$. The parameter x determines (but does not equal) the level of hole doping. Below the temperature T_c lies the superconducting phase, and between T_c and T^* lies the pseudogap region. Results of several experiments are shown: neutron-scattering measurements of the onset of magnetic order[4] (blue); optical measurements of the polar Kerr effect, another indicator of order[5] (purple); and new resonant ultrasound spectroscopy measurements of a thermodynamic phase transition at the boundary of the pseudogap[1] (red). (Adapted from ref. 1.)

arise in each CuO_2 unit cell.[3] The currents would set up a pattern of ordered orbital magnetic moments, but with no net magnetization (on the whole, the currents would cancel each other out) and no change in the lattice translational symmetry (the currents in every unit cell are the same).

Experimental evidence for a magnetically ordered pseudogap came in 2006. Philippe Bourges and colleagues at the Léon Brillouin Laboratory in Saclay, France, scattered a spin-polarized beam of neutrons off cuprate crystals and measured the fraction of neutrons whose spins were flipped.[4] In every cuprate they studied, the spin-flip fraction increased abruptly—signaling the onset of magnetic order—below a temperature consistent with the pseudogap temperature T^*. Their data are shown in blue in figure 1.

Two years later came another experiment, by Aharon Kapitulnik and colleagues at Stanford University, who looked at the scattering of polarized light from cuprate surfaces.[5] In the pseudogap region, the polarization angle rotated by a tiny but noticeable amount—a phenomenon called the polar Kerr effect, interpreted at the time as another sign of magnetic order. But the onset of that rotation, shown in purple in figure 1, occurred at a much lower temperature for a given doping than the onset of the neutron spin flips.

The sound of science

If the pseudogap is really a distinct phase, its boundary must be marked not only by a change in symmetry but also by a thermodynamic signature such as a sharp anomaly in the specific heat. But the specific heat of a crystalline material is dominated by lattice vibrations. A phase transition brought about by the electrons' behavior alone is difficult to detect.

Resonant ultrasound spectroscopy (RUS) has the potential to be an extremely sensitive way of probing the thermodynamics of a solid. (See the article by Julian Maynard in PHYSICS TODAY, January 1996, page 26.) A crystal is held between two transducers, one to drive vibrations in the crystal and the other to measure the crystal's response. Sweeping the driving frequency gives a spectrum of the crystal's natural resonances. From the crystal's size, shape, and resonant frequencies, extracting its elastic constants is a nontrivial calculation, but any personal computer these days is up to the job. The elastic constants are derivatives of the material's free energy and thus are measures of its thermodynamic properties.

Migliori had pioneered the application of RUS to condensed-matter physics,

Figure 2. The apparatus for resonant ultrasound spectroscopy[1] contains two transducers 1.5 mm in diameter, which weakly couple to a crystal to probe its vibrational resonances. Balsa wood provides vibrational isolation over a broad temperature range.

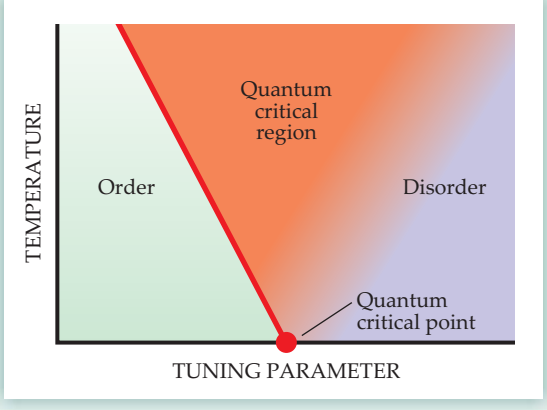


Figure 3. The phases of a generic quantum critical system. At zero temperature, quantum fluctuations drive a phase transition between the ordered and disordered states. The quantum critical region is typically bounded by a line of classical phase transitions on the left and by a smooth crossover on the right.

and to phase transitions in high-T_c superconductors in particular, more than 20 years ago.[6] But he and his group still found the search for the pseudogap transition to be a technical challenge. Cuprate crystals of the necessary ultrahigh quality are available, thanks to Ruixing Liang, Walter Hardy, and Douglas Bonn of the University of British Columbia (UBC), but at less than a cubic millimeter, they're much smaller than the crystals for which typical RUS systems are designed. A new, more delicate apparatus was required, shown in figure 2, with better vibration isolation, lower acoustic power, and smaller contact forces between the crystal and the transducers.

The Los Alamos researchers obtained two cuprate samples from the UBC group. One sample was of the underdoped cuprate $YBa_2Cu_3O_{6.60}$; the other was of the overdoped material $YBa_2Cu_3O_{6.98}$. For each sample, a RUS scan revealed the well-known superconducting phase transition at T_c, characterized by a discontinuity in the resonant frequencies of a few parts in 10^4, and a previously unknown feature, in which the frequencies remained continuous but their slopes abruptly changed. The temperatures of the latter transition are shown in red in figure 1.

In the underdoped sample, the transition temperature coincided with the onset of the pseudogap and with the neutron-scattering data (but not with the Kerr-effect measurements); from that agreement, the researchers concluded that they had observed the phase boundary of the pseudogap region. Crucially, for the overdoped sample, the transition temperature was less than T_c. Such a phase transition can't mark the onset of a precursor to superconductivity, because the phases on both sides of it are already superconducting. Migliori and colleagues concluded that the pseudogap is a distinct phase, bounded by a phase transition line T^* that intersects the superconducting boundary T_c. Extrapolating to even higher doping, at which $T^* = 0$, should yield a so-called quantum critical point.

Letters and commentary are encouraged and should be sent by email to ptletters@aip.org (using your surname as the Subject line), or by standard mail to Letters, PHYSICS TODAY, American Center for Physics, One Physics Ellipse, College Park, MD 20740-3842. Please include your name, work affiliation, mailing address, email address, and daytime phone number on your letter and attachments. You can also contact us online at http://contact.physicstoday.org. We reserve the right to edit submissions.

Mission critical

Quantum criticality is one of the most complicated phenomena of condensed-matter physics. (See the article by Subir Sachdev and Bernhard Keimer in PHYSICS TODAY, February 2011, page 29.) It stems from a phase transition in the system's ground state—that is, at zero temperature—as a function of some parameter other than temperature. Unlike more familiar phase transitions, in which thermal fluctuations drive a material from order into disorder, quantum phase transitions are driven by zero-point fluctuations, which create patches of entanglement in the material. At the transition point itself, those patches pervade the entire system, entanglement acts over arbitrarily long distances, and the system's wavefunction has no simple form.

But the effect of quantum criticality extends beyond zero temperature, as shown in the generic phase diagram in figure 3. Quantum fluctuations continue to dominate the system whenever the characteristic length scale of entanglement exceeds the de Broglie wavelength of thermal excitations. Because the de Broglie wavelength decreases as the thermal energy increases, the quantum critical phase grows wider at higher temperatures.

Comparing figures 1 and 3 shows that in the cuprate system, charge-carrier doping is the tuning parameter and the pseudogap region is the ordered phase. The adjacent "strange-metal" phase makes up most of the quantum critical region. (Among other anomalous properties, a strange metal's electrical resistivity has a linear dependence on temperature rather than the expected quadratic dependence; see the Quick Study by Hong Liu in PHYSICS TODAY, June 2012, page 68.) But the quantum critical region also includes a slice of the superconducting phase, which raises the intriguing possibility that quantum criticality may be central to the mechanism of high-T_c superconductivity.

The journey continues

The Los Alamos group's RUS measurements have identified the existence of a thermodynamic phase transition bounding the pseudogap, but so far they offer no new insight into the nature of the accompanying change in symmetry. Varma's countercirculating current theory is a candidate, but the experimental evidence for it is mixed. Nuclear mag-

netic resonance measurements that were designed to look for such a magnetic signature failed to find it.[7] A more thorough analysis of the Kerr effect in several families of cuprates suggests that it's evidence of a type of chiral charge order, not magnetic order at all.[8] And other recent experiments point to the importance of a charge-stripe order that emerges in $YBa_2Cu_3O_{6+x}$ under strong magnetic fields.[9] Migliori and colleagues' next step is to repeat their RUS measurements under a magnetic field: Whether the pseudogap phase is magnetically ordered or not, its response to an external field will yield important clues.

Johanna Miller

References

1. A. Shekhter et al., *Nature* **498**, 75 (2013).
2. Y. Wang et al., *Phys. Rev. Lett.* **95**, 247002 (2005).
3. C. M. Varma, *Phys. Rev. B* **55**, 14554 (1997).
4. B. Fauqué et al., *Phys. Rev. Lett.* **96**, 197001 (2006); H. A. Mook et al., *Phys. Rev. B* **78**, 020506 (2008).
5. J. Xia et al., *Phys. Rev. Lett.* **100**, 127002 (2008).
6. A. Migliori et al., *Phys. Rev. B* **41**, 2098 (1990); A. Migliori et al., *Phys. Rev. Lett.* **64**, 2458 (1990).
7. A. M. Mounce et al., http://arxiv.org/abs/1304.6415.
8. P. Hosur et al., *Phys. Rev. B* **87**, 115116 (2013).
9. T. Wu et al., *Nature* **477**, 191 (2011); D. LeBoeuf et al., *Nat. Phys.* **9**, 79 (2013).

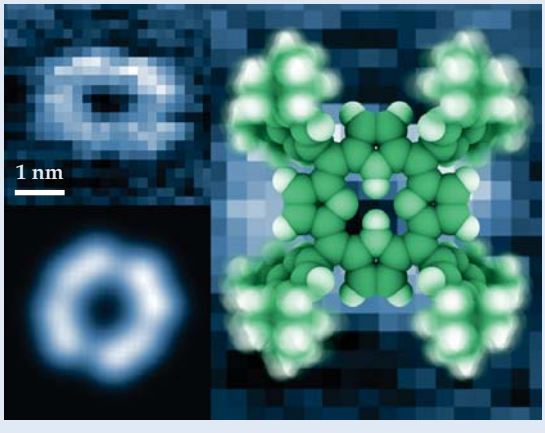
Optical spectroscopy goes subnanometer

A scanning probe technique simultaneously maps the topographic structure and vibrational spectra inside a single molecule.

When photons interact with matter, they can scatter inelastically and gain or lose energy. Their frequency accordingly shifts by an amount that corresponds to a vibrational excitation. That Raman effect is the basis for a decades-old spectroscopic tool that identifies molecules by their unique vibrational fingerprints. Because the scattering cross section is low, the Raman signal is feeble. But it can be amplified more than a millionfold by, for example, placing the molecules in the tight space between a surface and the sharp metal tip of a scanning tunneling microscope (STM).

The simple act of shining light on the tip excites surface plasmons, collective electron-density oscillations in the metal. Those plasmons enhance the optical fields and localize them to a scale—typically tens of nanometers—far below the light's diffraction limit. The sharper the tip, the greater the localization (see the article on near-field imaging by Lukas Novotny, PHYSICS TODAY, July 2011, page 47). Using the technique, known as tip-enhanced Raman spectroscopy (TERS), researchers can map the topographic structure and vibrational spectra of molecules as a function of position (see the article by Katrin Kneipp, PHYSICS TODAY, November 2007, page 40).

Zhenchao Dong and Jianguo Hou, both at the University of Science and Technology of China, and their colleagues have now implemented the first cryogenic (80 K) version of TERS in ultrahigh vacuum and improved the technique's spatial resolution to less than 1 nm.[1] That's nearly four times better



A single porphyrin molecule is illustrated (right) with its four lobes blurred to emphasize the molecule's three dimensionality. A tip-enhanced Raman scattering image (top left) of a single molecule adsorbed on a silver surface produces the same ring structure that shows up in the simulated signal (bottom left).