THERE'S STILL SOME RESISTANCE TO REPORTS OF EXTRA-HIGH T_C SUPERCONDUCTORS

Ever since the copper oxide superconductors were first discovered seven years ago, any number of experimenters have come across a sample or two that have exhibited traits suggesting superconductivity at temperatures over 200 K. Typically the behavior was fleeting or elusive, disappearing after the material was taken through several thermal cycles or stubbornly refusing to show up in other samples produced in the same way. In most cases the sample consisted of several phases, and the experimenters could not link the high-T_c behavior to a particular phase. Robert Dynes of the University of California, San Diego, refers to these teasers as "leprechauns." Paul Chu of the University of Houston has described them as "unidentified superconducting objects."

The USOs landed most recently in France, alighting in the data of groups from the Ecole Supérieure de Physique et de Chimie Industrielles de la Ville de Paris[1] and from two laboratories of the Centre Nationale de la Recherche Scientifique in Grenoble.[2] The new data are not strikingly different from earlier sightings, but they add to the sheer weight of evidence that is starting to convince a number of condensed matter researchers contacted by PHYSICS TODAY that there's something there.

Signs of superconductivity

Two key properties characterize a superconductor: a drop in the resistivity from some finite value to zero and, at the same critical temperature, the exclusion of an applied magnetic field by the Meissner effect. For the high-T_c materials, fluctuations make the transition more rounded rather than sharp. Many samples of the copper oxides have exhibited resistivity anomalies, sometimes just dips and other times complete drops to nearly zero. No samples have conclusively demonstrated the Meissner effect; often attempts to see it are hampered by the instability of the sample, by its small size or by the small volume fraction that is in the superconducting phase.

Some of the evidence for extra-high-T_c has come from groups that are growing copper oxide compounds epitaxially, atom layer by atom layer, to control precisely the structure and composition. Over a year ago a group from Osaka University led by Tomoji Kawai used laser molecular-beam epitaxy to grow a thin film of $Ca_{0.3}Sr_{0.7}CuO_2$ only about 30 nm thick. The group's film had a dip in the resistivity starting about 170 K (but not a full descent to zero) and a magnetization that went negative at about the same temperature.[3] Kawai and his colleagues speculated that one phase of their sample, making up perhaps a few percent of the whole, was superconducting.

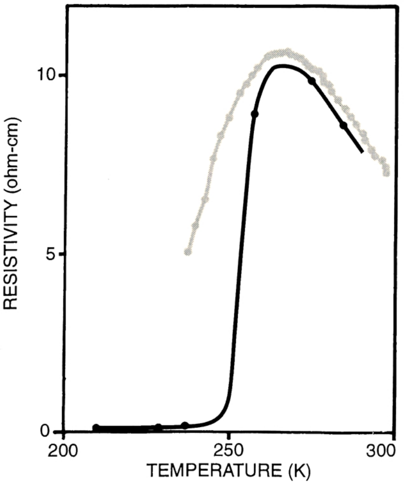
In the recent French work, the Paris researchers, led by Michel Laguës, were using a technique similar to that of the Osaka group to grow thin films of the BiSrCaCuO family with large numbers of copper oxide layers per unit cell. They wanted to see whether the critical temperature increases with the number of such layers per unit cell. (T_c is already known to increase with layer number, up to three layers, in some families of cuprate superconductors).

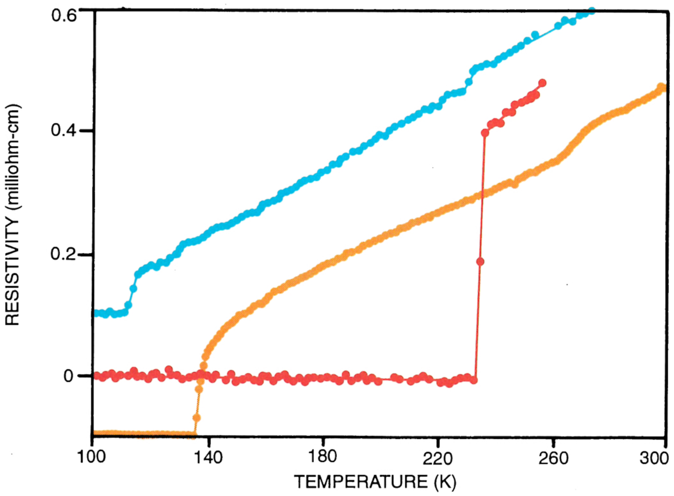
Several of the Paris samples manifested high-temperature anomalies in resistivity and magnetization, with the highest-temperature behavior coming from the sample with eight adjacent copper oxide layers in each unit cell—although it contained other phases as well. For that sample, the resistivity dropped sharply between 250 and 270 K from about 10 ohm-cm to less than 1 milliohm-cm. The accuracy of the measurements was limited by the high contact resistance, which lowered the signal-to-noise ratio, and by the small critical current. (See the left panel of the figure on page 18.) Some observers are uncomfortable with the sharpness of the drop; it starts from a high initial value more typical of an insulator than of a metal and might thus signal some strange kind of metal–insulator transition rather than a superconducting one. The Paris group is now working to lower the resistance of its samples and contacts and increase the sensitivity of its measurements.

The eight-layer sample exhibits a very small diamagnetic susceptibility and magnetization around 250 K. However, the sample volume is very small ($5 \times 10^{-8} cm^3$), and the Paris group admits in its paper that "the observed value of the diamagnetic transition . . . is very close to the sensitivity limit of the equipment, and it should be interpreted with caution."

Other evidence for extra-high-temperature anomalies has come from experiments on samples prepared by solid-state reactions rather than epitaxial techniques. One such group is the Grenoble collaboration, whose members come from the CNRS Center for Research on Very Low Temperatures and the CNRS Laboratory of Crystallography. The Grenoble researchers encountered anomalous behavior as they were trying to optimize the preparation of mercury barium calcium copper oxides. In one sample, $HgBa_2Ca_2Cu_3O_{8+\delta}$, the resistivity dropped rather suddenly at 235 K from a little over 0.4 milliohm-cm to zero. The resistivity curves in another sample of $HgBa_2Ca_2Cu_3O_{8+\delta}$ and in one of $HgBa_2Ca_4Cu_5O_{12+\delta}$ had partial but smooth drops in resisitivity at around 260–270 K and at 230 K, respectively. These two samples also had dips at 130 K, near the known T_c for $HgBa_2Ca_2Cu_3O_{8+\delta}$. (See the right panel of the figure on page 18.) The resistive behavior was not stable, disappearing after the first measurement.

Since the Grenoble researchers published their paper, they have measured extra-high-temperature transitions in the diamagnetic susceptibility of some of their samples. Massimo Marezio of the Grenoble team told us that they are finding that the magnetic behavior is repeatable even when the resistive behavior is not present; he is inclined to lay more stock in the magnetic measurements because, for one thing, they do not require physical contacts. The ac susceptibilities measured at Grenoble indicate that for most of the samples only a few tenths of a percent is superconducting. Part of the group took the samples to Brookhaven Na-





Evidence for extra-high T_c? Left: The resistivity of a thin film of bismuth strontium calcium copper oxide measured at a very low current (black curve) shows a sharp drop around 250 K. The drop suggests a superconducting transition, but the high initial value of resistivity might signal a type of metal–insulator transition instead. (Adapted from ref. 1.) Right: For one sample of $HgBa_2Ca_2Cu_3O_{8+\delta}$ (red), the resistivity went to zero at about 235 K. The drop was not seen when the resistivity was later measured at a higher current. For another sample of $HgBa_2Ca_2Cu_3O_{8+\delta}$ (orange) and one of $HgBa_2Ca_4Cu_5O_{12+\delta}$ (blue), the resistivity shifted only slightly downward at temperatures above 220 K. (Adapted from ref. 2.)

tional Laboratory to determine by x-ray powder diffraction the exact phases present.

Stability

Laguës notes that the samples produced by his group are especially stable, unlike many of the earlier materials that exhibited extra-high-T_c behavior. The transition persisted even after several days although the critical temperature was shifted slightly downward.

Instability has indeed plagued many of the samples that have hinted at extra high critical temperatures. It seems as if the superconducting behavior is destroyed as the sample is taken up and down the temperature scale or simply by the passage of time. J. T. Chen and his colleagues at Wayne State University have managed to produce single crystals and ceramic samples of yttrium barium copper oxide that showed resistive transitions near 265 K; the transitions were reproducible over a period as long as one month when the samples were kept in an oxygen gas environment.[4]

But stability is not the same thing as reproducibility. While some researchers are getting stable samples that repeat their behavior after several thermal cycles, they are less successful in producing *new* samples with the same behavior. Following the same prescription sometimes they produce material with extra-high-temperature anomalies; sometimes they don't.

In many of the experiments that have found some extra-high-temperature anomalies, the data suggest that only part of a given sample—often less than a few percent—is in a superconducting phase. Some researchers have thus speculated that these samples may have a filamentary superconducting path, threading its way through the sample. If the path is connected, resistive anomalies will appear; if not, they won't. In either case, diamagnetism might show up.

Theory

There is no known theoretical upper limit on T_c, so no one can rule out the validity of the USOs. In fact, Philip Anderson (Princeton University), whose theory of high-temperature superconductors is based on a coupling between the copper oxide planes, has a formula for predicting T_c, with the number of copper oxide planes as one parameter. The new results do not present any problem for his theory, claims Anderson, although the T_c is a little higher than he would have predicted based on the assumption that the superconductivity is coming from the phase with eight adjacent copper oxide layers. His formula also predicts that T_c increases with pressure, as Chu and his coworkers in Houston have demonstrated for the mercury-based copper oxides.[5]

The very high critical temperatures may pose more of a challenge to one of the competing theories, which postulates that magnetic spin fluctuations play a role in high-T_c superconductivity. Nevertheless, one proponent of that theory, Douglas Scalapino (University of California, Santa Barbara), told us that he finds the prospect of extra-high T_c's very interesting.

James Smith of Los Alamos National Laboratory points out that the signature for superconductivity may be different for the high-temperature materials; he is inclined to believe the evidence for extra-high T_c's. Smith wonders if having a critical temperature above 200 K is any more amazing than having a Curie temperature well above the ambient, as in permanent magnets; electrons are no happier in a ferromagnetic state than they are in a superconducting state.

—Barbara Goss Levi

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