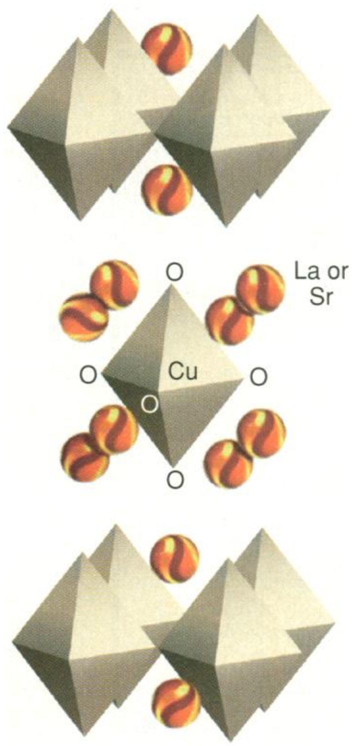
High-Temperature Mystery Heats Up

Take one of the new high-temperature superconductors, heat it up a bit, and the physics gets downright strange. The eventual theory of these materials will have to explain this strangeness

From the moment they were discovered 11 years ago, high-temperature superconductors have puzzled physicists by their weird behavior. But the more researchers learn about these strange materials, the odder they seem to get. These complex and brittle ceramics can conduct electrons without the least bit of electrical friction if they are chilled to temperatures about 175 degrees below freezing—positively balmy compared to the frigid conditions that metals require to perform this feat. But heat these copper-oxide–based materials, known as cuprates, up a bit to the point where they no longer superconduct, and their behavior becomes even more inexplicable. Their electrical and magnetic properties no longer resemble those of metals, other ceramics, or any other known materials. High-temperature superconductors enter a realm of physics all their own.

Today, it is at these higher temperatures—a regime that physicists refer to, apparently with no irony intended, as the "normal" state—where much of the focus of recent experiments on cuprates has shifted. "The normal state is one of the most bizarre animals we have come across in a long time," says Gregory Boebinger, an experimental physicist at Lucent Technologies Bell Laboratories in Murray Hill, New Jersey. In this state, cuprates behave like good metallic conductors in some ways, while in others like nonconducting insulators. "What's not clear is what gives rise to the strange behavior," he says.



Boxed set. Cuprates have a repeating structure, with layers of copper and oxygen atoms surrounded by others.

ILLUSTRATION: D. PUGH SOURCE: *PHYSICA C* 1994, ELSEVIER SCIENCE

Initial reports of these weird phenomena started trickling in years ago. But only recently have researchers amassed enough experimental results to identify behavior patterns that cut across the dozens of related species of cuprate superconductors. The hope is that these new behavior patterns will eventually help researchers understand why cuprates are superconductors at relatively high temperatures. They just don't seem to obey the theories that explain the properties of low-temperature metallic superconductors, and most physicists believe an entirely new mechanism must be at work. But theorists have yet to come up with a hypothesis that can make rigorous, testable predictions. "It's still heavy mystery time" for high-temperature superconductors, as Boebinger puts it.

Any theory that attempts to explain high-temperature superconductivity must also explain the many oddities of the normal state, says Bertram Batlogg, a physicist at Bell Labs. Adds Herb Mook, an experimental physicist at Oak Ridge National Laboratory in Tennessee: "I don't believe we can understand the mechanism of high-temperature superconductivity before we understand the normal state."

Early warnings

It didn't take long for physicists to realize that the cuprates were strange beasts. According to the standard superconductivity model, known as BCS theory, these materials shouldn't superconduct at all. American theorists figured out in 1957 that the necessary requirement for superconductors to conduct electricity without resistance is for electrons to overcome their natural repulsion for one another and surf through the material in pairs. Traditional metallic superconductors achieve this at very low temperatures, because as one electron moves through the metal, it creates what amounts to a vibrational wake that draws another electron along in its path. Raise the temperature, however, and the extra kinetic energy of atoms in the material kicks the second electron out of the wake of the first, and superconductivity is destroyed. Researchers soon discovered that electrons in the superconducting ceramics also traveled in pairs, but the much higher temperatures mean that something other than a vibrational wake has to be holding them together.

Soon after this realization, researchers around the world began seeing odd behaviors in the materials above their superconducting temperature. In all superconductors there is a critical temperature, or T_c, which marks the transition between their superconducting state and the normal state, where electrons glide about solo rather than in pairs. As the temperature of a standard metallic superconductor is raised above its T_c, it displays a characteristic pattern of conductivity changes: Its efficiency at conducting electrons steadily drops before finally leveling out as the added heat jostles the electrons, causing them to give up more and more energy to electrical resistance. Yet early experiments on the high-temperature superconducting (HTS) materials showed that as they are warmed above the T_c, their resistance first shoots up dramatically and then settles into a steady rise. Ceramics, it turns out, become very bad conductors in a hurry.

Even more strange, their conductivity is worse in some directions than others; a normal metal conductor, in contrast, shuttles charge equally well in all directions. The explanation seems to lie in cuprates' crystal structure. They are complex crystalline compounds composed of four or more elements arrayed in repeating unit cells. Each cell is like a layer cake with copper-oxygen planes interleaved with planes of other atoms. In the late 1980s, a number of groups found that the cuprates conduct electrical charges up to 10,000 times more readily along the copper-oxygen planes than between them. "Within the plane, it conducts like a metal, but perpendicular [to it], it looks like an insulator," says Patrick Lee, a theoretical physicist at the Massachusetts Institute of Technology (MIT) in Cambridge. "It was very weird."

Odd magnetic behaviors also showed up above the T_c. For instance, when researchers measured how the motion of electric charges in the material is influenced by a magnetic field—a property known as the Hall effect—they also saw the magnitude of this effect steadily change as the temperature climbed above the T_c. Normal metals, by contrast, show no changes with temperature.

New experiments continue to expand the list of cuprate quirks. Last month, Mook, along with colleagues in Denmark, Canada, France, and the United Kingdom, reported that the degree of tiny magnetic fluctuations in cuprates also changes drastically as the materials are warmed above the T_c (*Science*, 21 November, p. 1432). In all of the cuprates, copper atoms act like tiny bar magnets that can point up or down. In the superconducting state, these magnets tend to align themselves alternately up, down, up, down. Above the T_c, this pattern breaks down. But when Mook and his colleagues slowly cooled a cuprate made from lanthanum, strontium, copper, and oxygen, they found signs that the amount of magnetic ordering in the material increased drastically just before it reached the T_c.

That's "very interesting," says University of California, Los Angeles, physicist Sudip Chakravarty. Researchers had suspected for some time that fluctuations in the magnetic orientation of copper atoms may be involved in pairing electrons when the material superconducts. If so, these fluctuations should be present above the T_c, but so weak that they are overwhelmed by thermal agitation. But previous studies had failed to find evidence of such magnetic fluctuations above the T_c. "[This] experiment is surprising because it does find a strong signal of magnetic excitation" above the T_c, says Chakravarty, although all involved acknowledge that this by no means settles the question about what causes electrons in the cuprates to pair up.

Into the gap

What has been perhaps the most striking oddity of all in the cuprate repertoire shows up when the materials are subjected to a little doctoring. All pure cuprates are electrical insulators, because their electrons are tied to atoms and are unable to roam about. To transform the cuprates into conductors, researchers add tiny quantities of substitutes—known as dopants—such as barium or strontium in place of a few lanthanum atoms. The overall crystalline structure of the material stays the same, but its electronic properties change dramatically. Barium can donate one less electron than lanthanum to the electron-hungry oxygen atoms. The result is that oxygen atoms end up with electron vacancies, known as holes. These holes act like positive charges that can hop from one oxygen to the next, and so conduct electrical charge. The level of doping is crucial: Replacing about 15% of the lanthanum atoms—or their equivalents in other recipes—results in the highest possible T_c for virtually all types of cuprates. Stuff in another 5%, and they do not superconduct at all. Go the other way and reduce the doping to 10%, and the physics gets very peculiar.

SUPERCONDUCTORS IN THE NORMAL STATE

Experiment	Cuprates	BCS Superconductors
Optical conductivity	Metallic in C-O plane	Metallic in all directions
Resistivity	Increases linearly with temperature	Linear increase with temp. at high temp. Faster at low temp.
Hall effect	Temperature-dependent	Non–temperature-dependent
Neutron scattering	Temperature-dependent magnetic signature	Non–temperature-dependent
NMR spin relaxation rate	Increases nonlinearly with temp. above T_c	Increases linearly with temp. above T_c
NMR spin susceptibility	Pseudogap	No pseudogap
Specific heat	Pseudogap	No pseudogap
Photoemission	D-wave pseudogap	No pseudogap
Electron tunneling	Pseudogap, superconducting gap same size	No pseudogap
Electronic Raman scattering	Pseudogap	No pseudogap
Phonon frequency shift	Pseudogap	No pseudogap

These "underdoped" cuprates are less effective as superconductors, yet they continue to display a unique electronic signature of superconductivity even when they are warmed above their T_c. Quantum mechanics dictates that electrons can exist only at certain well-defined energy levels. In a solid, these levels are bunched together in bands separated by gaps of "forbidden" energies. When conventional metallic superconductors are cooled below the T_c, a gap of forbidden energies opens up: A pair of electrons can only absorb an amount of energy larger than the binding energy of the pair—anything less is not absorbed. This gap is a signature that electrons are paired and are surfing through the material together. As the temperature is warmed up toward the T_c again, this gap begins to shrink, and at the T_c and above, it disappears altogether. At that point, the material stops superconducting and behaves like a normal metal.

But underdoped cuprates, it turns out, obey their own laws. These materials cease superconducting when warmed above their T_c, just like conventional BCS superconductors, but the gap that's the signature of superconductivity and paired electrons in metals remains. There's an odd quirk, however: Some electrons can now reside in the previously forbidden zone. Like ledges on a cliff face, a few energy levels develop in the gap, allowing some electrons to sit there. Still, the number of electron energy states in this region—the ledges—remains well below that found in metallic superconductors warmed above the T_c. The ledge density—or in this case the density of electronic states—is all wrong.

Over the past few years, a number of experimental techniques have probed this partial gap, or "pseudogap," as it has come to be known. But these experiments had largely left open the question of whether the presence of the pseudogap above the T_c is directly related to the formation of the superconducting gap below it. But experiments over the past year have begun to provide an answer.

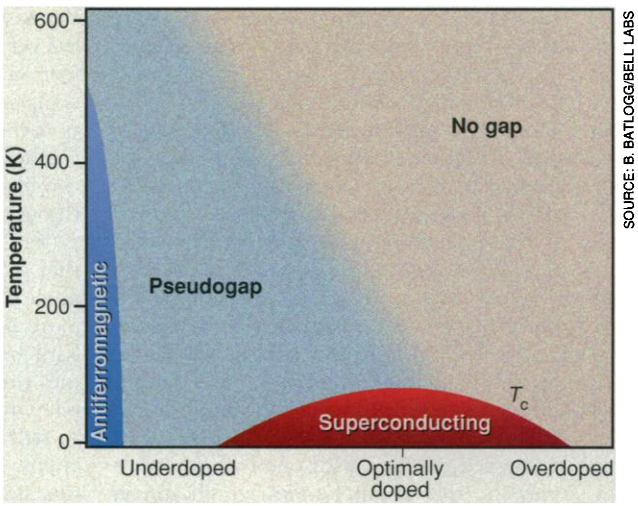
In 1996, a team of Stanford University researchers led by physicists Anthony Loeser and Zhi-Xun Shen first used a technique known as angle-resolved photoemission to show that the size of the energy gap in both the superconducting state and the normal state varied according to the direction in which charges are flowing within the copper-oxide planes (*Science*, 19 July 1996, p. 325). The gap was large in some directions and small in others; when mapped out, the variations resembled a cloverleaf, a pattern characteristic of what physicists call a d-wave superconductor. Numerous experiments have shown this cloverleaf pattern for the superconducting gap (*Science*, 19 January 1996, p. 288), but the Stanford team was the first to show that it applies to the pseudogap in the normal state as well. That was a "strong indication," that the physics underlying the pseudogap and the superconducting gap are the same, says Bell Labs' Batlogg.

In an upcoming issue of *Physical Review Letters*, a Swiss team reports an equally strong link. In this case the team, led by University of Geneva physicists Øystein Fischer and Christophe Renner, used a different technique known as electron tunneling to show that the superconducting gap and the pseudogap also have the same magnitude—the same amount of energy must be added to the materials to overcome the superconducting and pseudogap alike. "That means that the pseudogap is intimately related to the superconducting gap," says Fischer.

Start making sense

If the two gaps are related, and electron pairing causes the superconducting gap, what causes the pseudogap? "It's still not clear," says Tom Timusk, an experimental physicist at McMaster University in Hamilton, Ontario, Canada. But another recent experiment may offer some insight. This experiment, carried out by physicist Girsh Blumberg of the University of Illinois, Urbana-Champaign, and colleagues in the United States and Japan, uses a technique called electronic Raman scattering to show the characteristic pseudogap in the normal state. But that's not all they see. Raman scattering is a technique whereby researchers fire photons at a material and watch how the light scatters off. The difference in energy between the fired and scattered photons reveals the energy levels of the electrons in the material.

When Blumberg and his colleagues fired photons at a cuprate made from bismuth, strontium, calcium, copper, and oxygen above the T_c, instead of producing the sharp peaks of discrete energy levels, the scattered photons showed a flat, smeared-out spectrum from low to high energies. This, says Blumberg, suggests that electrons in the cuprates interact with each other strongly, so that when incoming photons scatter from the material they excite not just one electron, but a whole group of electrons collectively.



Persistent gap. The gap signature of superconductivity hangs around in underdoped cuprates as a pseudogap above T_c.

The researchers found a different picture when they jacked the photons' energy up to 75 milli–electron volts: A large single scattering peak now appeared. "There are different interpretations of what this means," says Blumberg. "But my favorite is that superconducting [electron pairs] get established well above T_c, and their binding energy is 75 milli–electron volts." Hence, the higher energy photons are absorbed as they split the pairs apart.

If so, this suggests that somehow electrons in the cuprates manage to pair up at temperatures well above the superconducting temperature, maybe even as high as room temperature. Pairing is essential, but not enough, for electrons to superconduct. For this they also need "coherence," whereby they all travel together in step. But the extra heat present in the normal state probably causes the pairs to break apart almost as soon as they form. Thus, the pairs never get a chance to travel long distances, and superconductivity never arises.

That explanation agrees well with theoretical ideas advanced by Vic Emory of Brookhaven National Laboratory in Upton, New York, and Steven Kivelson of the University of California, Los Angeles, who argue that the pseudogap in HTS ceramics arises because the holes in doped cuprates are not distributed uniformly through the material. Neutron scattering experiments suggest cuprates have alternating striped regions with and without holes. And Emory and Kivelson suggest that interactions between these regions cause electrons to pair up. But at temperatures above the T_c, energy from heat prevents these pairs from becoming coherent. And although the notion is still by no means proven, "it is the simplest idea out there," says Timusk.

It's certainly not the only one. Another theoretical camp, led by Philip Anderson of Princeton University and MIT's Lee, argues that the architecture of the cuprates forces the two fundamental properties of electrons—their charge and spin—to separate. Spins on neighboring electrons then pair up, even as charges go their own way. The pseudogap, says Lee, is essentially a signature of this spin pairing, which takes energy to split apart.

Others propose that the behavior of the cuprates is tied to atomic-level magnetic fluctuations in the materials or a mixing of electronic excitations between oxygen and copper atoms. "The problem is not that there's no theory of high-temperature superconductivity," says Boebinger. "There's too damn many of them." And at this point, none of the theories is sophisticated enough to predict falsifiable properties of the materials. But Lee, Mook, and others believe that the host of new experiments on the normal-state properties of the cuprates is already beginning to put welcome constraints on theorists. "The challenge is to fit all those results together," says Mook. "We're not there yet. But I think we'll make it eventually."

–**Robert F. Service**

QUANTUM MECHANICS

Teleportation Beams Up a Photon's State

For "trekkies," being teleported from the bridge of the Starship Enterprise onto the surface of an alien world is still a dream. But at least in the quirky world of quantum mechanics, teleporting is now a reality. Anton Zeilinger and his team at the University of Innsbruck in Austria have shown that part of the spin orientation of a photon of light can be transferred instantaneously to another photon, irrespective of distance.

Zeilinger says his team's work is "the first experimental demonstration of quantum teleportation"—the transfer of a quantum state from one particle to another, first proposed by IBM's Charles Bennett and his collaborators in 1993 (*Science*, 25 October 1996, p. 504). "The real interest of this is [that] it represents a new kind of information transfer," says Bennett, of the Thomas J. Watson Research Center in Yorktown Heights, New York. Quantum teleportation could have applications in quantum computing, says Tony Sudbery of Britain's University of York: "constructing stable memories, protecting delicate quantum states, [and] communicating between quantum computers."

In today's computers, it is a simple matter to read off the digital 1s and 0s that are the two possible states of a computer circuit. In the quantum world, however, where 1 and 0 are labels for, say, the two spin states of a photon, taking the reading is a more interventionist act: It forces the system to adopt one of the two quantum states. Until then, it is some mixture of the two. If Alice—in quantum-speak, the person or circuit at one end of a quantum communication channel—wants to tell Bob (at the other end) about her photon, she has to take a measurement of it. The measurement forces it to be either a 1 or a 0, when what she really wants to tell Bob is about the mixed quantum state. But if computers based on quantum principles are ever to become a reality, they must be capable of moving quantum information around without ruining it by either having to read it before sending it or by sending photons through noisy, disruptive circuits.

Enter quantum teleportation. The key to the Austrian experiment, reported in this week's issue of *Nature*, is to create a pair of photon twins that are intimately related to each other. When photons from a laser are fired into certain crystals, a single photon can split into two identical twins. The quantum state of the parent photon must be conserved, so the sum of the two offspring photons must make up that original quantum state. In the language of modern quantum mechanics, the pair are "entangled," linked through some invisible quantum web. If a measurement on one indicates, say, that its spin is up, the entangled twin is forced into the opposite state—spin down.

Bennett and his collaborators realized that an entangled pair can serve as a vehicle for teleporting the state of a third photon, the "message" photon. In their scheme, Alice makes a combined measurement on one mem-