

After 2 decades of monumental effort, physicists still cannot explain high-temperature superconductivity. But they may have identified the puzzles they have yet to solve

High *T*_C: The Mystery That Defies Solution

TWENTY YEARS AGO, A FIRESTORM OF discovery swept through the world of physics. German experimenter J. Georg Bednorz and his Swiss colleague Karl Alexander Müller kindled the flames in September 1986 when they reported that an odd ceramic called lanthanum barium copper oxide carried electricity without any resistance at a temperature of 35 kelvin—12 degrees above the previous record for a superconductor. The blaze ran wild a few months later when Paul Chu of the University of Houston, Texas, and colleagues synthesized yttrium barium copper oxide, a compound that lost resistance at an unthinkable 93 K—conveniently warmer than liquefied air.

A frenzy of slapdash experimenting and sensational claims ensued, says Neil Ashcroft, a theorist at Cornell University. He organized a session on the new high-temperature superconductors at the meeting of the American Physical Society in New York City the following March. The "Woodstock of physics" stretched until 4 a.m. and bubbled over with giddy enthusiasm. "We had prominent people saying it would all be explained quickly and that we would have superconducting power lines and levitating trains," Ashcroft says.

Ashcroft himself had doubts, however, as he told a class of graduate students a few months later. (I was a member of the class.) The materials comprised four and five elements and possessed elaborate layer-cake structures. They broke the rules about what should make a good superconductor. In short, Ashcroft predicted, high-temperature superconductivity would remain the outstanding problem in condensed matter physics for the next 25 years.

That prognostication is coming true. Two decades after high-temperature superconductors were discovered, physicists still do not agree on how electrons within them pair to glide through the materials effortlessly at temperatures as high as 138 K. Researchers haven't failed for lack of trying. According to some estimates, they have published more than 100,000 papers on the materials. Several theorists claim they have deciphered them although their explanations clash. Still, hightemperature superconductivity has refused to submit to some of the world's best minds.

"The theoretical problem is so hard that there isn't an obvious criterion for *right*," says Steven Kivelson, a theorist at Stanford University in Palo Alto, California. Experimenters are producing a flood of highly detailed data, but physicists struggle to piece the results together, says Joseph Orenstein, an experimenter at the University of California, Berkeley, and Lawrence Berkeley National Laboratory. "It must be close to unique to have so much information and so little consensus on what the questions should be," Orenstein says.

The problem is more than a sliver under the nail. High-temperature superconductivity has shown that physicists' conceptual tools can't handle materials in which electrons shove one another so intensely that it's impossible to disentangle the motion of one from that of the others. Such "strongly correlated" electrons pop up in nanodevices and novel magnets, organic conductors and other exotic superconductors. "Hightemperature superconductivity is the stumbling block of the whole discipline of condensed matter physics," says Peter Abbamonte, an experimenter at the University of Illinois, Urbana-Champaign.

In spite of the difficulty of the puzzle, many physicists say they are closing in on a solution. Most now agree on certain key properties of the materials. Precision experiments are

17 NOVEMBER 2006 VOL 314 SCIENCE www.sciencemag.org Published by AAAS Hot stuff. The structure of mercury barium calcium copper oxide, a superconductor at 138 K.

revealing surprising details of the compounds. And computer simulations—and perhaps even mockups fashioned of ultracold atoms and laser light—could soon show physicists whether their basic model of the problem is correct. "If I had to make a prediction," Kivelson says, "I would say that in 10 years time the problem will be solved."

The ultimate chess game

Even "conventional" superconductivity, which was discovered in 1911, is mind-bending. Electrons in a metal move in quantum waves of distinct energies. Quantum mechanics prohibits two electrons from occupying the same wave or "state," so they stack into the states from the lowest energy on up. But when metals such as lead and niobium are cooled to near absolute zero, the electrons in them can lower their total energy by pairing like ballroom dancers. That partnership produces superconductivity, as explained in 1957 by theorists John Bardeen, Leon Cooper, and John Robert Schrieffer.

The pairing alters the spacing of the rungs on the energy ladder, creating a gap near the top of the stack. To break from its partner, an electron must jump the gap to an empty state. There isn't enough energy around to allow that, so the pairs glide along unperturbed. Something must glue the pairs together, and according to the Bardeen-Cooper-Schrieffer (BCS) theory, the adhesive is quantized vibrations of the crys-

talline material, or "phonons." A passing electron attracts the slowermoving ions in the crystal lattice, which squeeze together to produce a knot of positive charge that attracts another electron (see diagram).

High-temperature materials literally take superconductivity to a new plane. The compounds contain planes of copper and oxygen ions that resemble chess boards, with a copper ion at every corner of a square and an oxygen ion along each side. Electrons hop from copper ion to copper ion. Between the planes lie elements such as lanthanum, strontium, yttrium, bismuth, and thalium. But it is along the copper-and-oxygen planes that the electrons pair and glide.

Just how that happens is anything but clear. The electrons in an ordinary metal hardly notice one another and interact mainly with phonons. In contrast, the electrons in high-temperature superconductors shove one another so mightily that they tend to jam up with one electron on each copper ion, like gridlocked commuters. That impasse can be broken only by tweaking the material's chemical composition to siphon away some of the electrons to create positively charged "holes," a process called doping.

The challenge then is to explain how electrons that fiercely repel each other manage to pair anyway. Some researchers argue that waves of magnetism play a similar role to the one phonons play in conventional superconductors. Others focus solely on how the electrons shuffle past one another in a quantummechanical game of chess. Still others say that patterns of charge or current, or even phonons, play a crucial role. Pairing might even require all of these things in combination, which would be many physicists' nightmare scenario.

Familiar solutions

Some of the theories being refined today emerged soon after Bednorz and Müller's discovery, and the dividing lines that run through the field were drawn in those heady days. For example, as early as 1987 some theorists argued that high-temperature superconductivity arose not from phonons but from the interaction of the electrons alone. But even those who agree on that principle often disagree on the details.

The idea that waves of magnetism drive the superconductivity is based on the fact that electrons act like little magnets. Those on adjacent copper ions point in opposite direc-

"The theoretical problem is so hard that **there isn't an obvious criterion for** *right*."

-Steven Kivelson, Stanford University







Shall we dance? Instead of the motion of ions, the subtle waltz of electrons along atomic planes may cause pairing in high-temperature materials.

tions, creating an up-down-up-down pattern known as antiferromagnetism. The electrons can tilt and flip, and waves of wobble coursing through this arrangement can provide the glue for pairing, says David Pines, a theorist at Los Alamos National Laboratory in New Mexico and the University of California, Davis.

But Philip Anderson, a theorist at Princeton University, says that no glue is necessary. Just months after the discovery of high-temperature superconductors, he proposed a scheme known as the resonating valence bond (RVB) theory, which focuses on subtle quantum connections between electrons on neighboring copper ions. In the theory, no waves of any kind pass between electrons, Anderson says.

Thanks to the weird rules of quantum mechanics, each electron can point both up and down simultaneously. Moreover, neighboring electrons can join in an odd quantum state called a singlet in which both electrons point both up and down at once, but the two electrons always point in opposite directions—either down-up or up-down. When enough holes open in the plane, singlets form and begin to slide freely past one another, eventually producing superconductivity.

Others contend that both the magnetic fluctuation and RVB theories leave out some essential piece of physics. Stanford's Kivelson believes stripes of electric charge on the planes, which have been seen in some materials, may be necessary to trigger the pairing. Chandra Varma, a theorist at the University of California,

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Riverside, proposes that loops of current flowing inside each copperand-oxygen square are key.

Still others argue that hightemperature superconductivity may not have one root cause. "There is no silver bullet that is going to explain everything," says Thomas Devereaux, a theorist at the University of Waterloo in Canada. The fact that materials with very similar structures have very different critical temperatures shows that the copper-andoxygen planes are not the whole story, he says. Phonons may still play an essential role, such as driving up the critical temperature, Devereaux says.

As in the beginning, the field is contentious. Recent experi-

ments have hinted at current loops. "If these are accepted, the theoretical game is over," Varma says. "That's why no one wants to accept it." Anderson is equally convinced that his RVB theory is correct-and underappreciated. "Eighty percent of the field is against anything-especially anything that might solve the problem," he says.

Mapping out the mysteries

In spite of the discord, researchers have made progress-especially the experimenters. For example, in 1994, John Kirtley and Chang Tsuei of IBM's T. J. Watson Research Center in Yorktown Heights, New York, probed the shape of the cloudlike quantum wave that describes the paired electrons. In a conventional superconductor, electrons can pair in any direction and can sit on top of each other, so the wave is a sphere. In high-temperature superconductors, Kirtley and Tsuei found, the cloud is shaped like a four-leaf clover. That "d-wave" shape means that paired electrons

sit on adjacent copper ions and never on the same ion.

D-wave pairing would be hard to explain with phonons, but it had been predicted by Anderson and others who favored purely electronic theories. As a result, even most of those who say phonons play a role do not believe that they alone cause pairing.

By dint of a variety of experiments, researchers have also agreed upon the properties common to all the materials, which change with the amount of doping. Cook up an



Doping (holes per copper ion)

Terra incognita. The mysterious and controversial pseudogap phase may hold the key to explaining superconductivity.

> undoped material, and it's an antiferromagnetic insulator. Dope it to draw between 6% and 22% of the electrons out of the planes, and it's a superconductor. Dope it more, and it becomes an ordinary metal.

> These properties can be plotted on a "phase diagram" that, like some medieval map, charts the mysteries physicists face (see figure, above). "To solve the whole problem, you're going to need to understand the whole phase diagram," says Séamus Davis, an experimenter at Cornell University. "It could be that focusing on the mechanism is the reason that the mechanism hasn't been found."

> Most intriguingly, at low doping a gap opens in the ladder of electron energy levels even at temperatures far above the superconducting transition. That "pseudogap" suggests that electrons pair at such toasty temperatures, and that superconductivity arises when the "preformed" pairs gather into a single quantum wave, some researchers say. "Everything we have seen goes in that direction," says Øys-

> > tein Fischer, an experimenter at the University of Geneva, Switzerland. And Tonica Valla of Brookhaven National Laboratory in Upton, New York, and col-

"Eighty percent of the field is against anything—especially anything that might solve the problem." -Philip W. Anderson, Princeton University

leagues present data online in Science this week (www.sciencemag.org/cgi/content/abstract/ 1134742) consistent with this interpretation.

Preformed pairs are too much to swallow for other researchers, who say the pseudogap is a sign of something else that clashes with superconductivity. For example, Zhi-Xun Shen of Stanford University and colleagues argue online in Science this week (www. sciencemag.org/cgi/content/abstract/1133411) that there may be two different gaps. Either way, the strange state might hold the key to explaining high-temperature superconductivity, says Michael Norman, a theorist at Argonne National Laboratory in Illinois. "The thing that explains the pseudogap may explain the superconductivity as well," he says.

Computers and cold atoms

Ultimately, the mystery of high-temperature superconductivity may be solved not in the lab or at the theorist's chalkboard but in the heart of a computer. Some theorists have turned to numerical simulations of the electrons hopping around the copper planes. If everything springs from the interactions between the electrons alone, then all the different phases and perhaps even the pairing mechanism should emerge from such simulations, much as the double helix, genes, and the mechanism of transcription arise from chemical interactions between the building blocks of DNA.

The mathematics can vary, but theorists generally study a scheme known as the Hubbard model, in which the only adjustable parameters are the ease with which the electrons hop and the strength with which they repel each other. Tracking electrons on a grid might sound easy, but the complexity of the quantum-mechanical calculations limits researchers to grids of a few dozen lattice sites. And still they must use approximation schemes to keep the calculation manageable.

Such simulations have begun to reproduce pairing, stripes, and features of the pseudogap, says André-Marie Tremblay, a theorist at the University of Sherbrooke in Canada. Unfortunately, different approximation methods can lead to different results for the same parameters, says Douglas Scalapino of the University of California, Santa Barbara. But that's not

> necessarily a bad thing, he says, because that very sensitivity suggests that the Hubbard model can produce a variety of effects with only a little tweaking, just as hightemperature superconductors do. "I interpret that to mean we have the right model," he says.

OM): BOB MATTHEWS

Meanwhile, a wild new kind of simulation could be gearing up to



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-Séamus Davis,

Cornell University

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leave computer simulations in the dust. Physicists have begun to construct artificial crystals by suspending ultracold atoms in corrugated patterns of laser light. In such an "optical lattice," the spots of light play the role of the ions, and the atoms play the role of the hopping electrons. The setup might be used to create an incarnation of the Hubbard model with hundreds of lattice sites and parameters that researchers can tune just by adjusting the spacing and the brightness of the spots.

Several groups are already racing to produce such systems. "In very quick succession, we have

jumped over the first few hurdles, and maybe the number of hurdles ahead of us is not that much bigger than the number behind us," says Wolfgang Ketterle, an experimenter at the Massachusetts Institute of Technology in Cambridge. Using optical lattices, experimenters could map out the phase diagram of the Hubbard model within a few years, says Henk Stoof, a theorist at Utrecht University in the Netherlands. "They have all the things they need to do it," he says.



standing of the pairing, some researchers say. Others question the relevance of the simulations to high-temperature superconductors. "We don't know that the Hubbard model is what's going on in the [materials]," says Cornell's Davis. "That's a hypothesis."

A threshold

Even without a theory to explain the materials, physicists agree that the pursuit of high-

temperature superconductivity has already paid off handsomely. "It has led to the discovery of new materials, of new states of matter, of new concepts," says Aharon Kapitulnik, an experimenter at Stanford University. Shen says that in their quest to unravel the phenomenon, experimenters have honed their techniques to new levels of sensitivity, precision,

and speed. "High-temperature superconductivity has completely changed the landscape of experimental condensed matter physics," he says.

At the same time, condensed matter researchers have come to see high-temperature superconductivity as the gateway to a new area of study: strongly correlated electrons. "This problem of strongly correlated electrons is the new frontier," says Argonne's Norman, "and high-temperature superconductors have brought it to the fore." Two decades after their discovery, high-temperature superconductors are viewed less as a singular mystery and more as a threshold to new realms of physics. Physicists hope it won't take another 20 years to cross it. -ADRIAN CHO

APPLICATIONS The Next Big Hurdle: Economics

Researchers have solved most of the technical challenges. Now companies are struggling to make HTS devices competitive

Six months after J. Georg Bednorz and Karl Alexander Müller discovered that a family of ceramics could conduct electricity without the electrical equivalent of friction, the scientific buzz swelled into full-scale hype. News accounts gushed at the prospect of magnetically levitated trains, novel sensors, superfast superconducting computers, and of course, lossless electricity transmission cables. For a generation that grew up watching the technological utopia of the Jetsons, the future, it seemed, was just around the corner.

The trouble is, it's still there. Two decades into the revolution, the effort to commercialize high-temperature superconductors (HTS) is not for the fainthearted. Successful applications exist, although with names and roles that few people would recognize, such as current leads and cellular base station filters. And although those and other niche applications are turning a profit for their owners, the field is

nothing like its founders envisioned. "In my opinion, we oversold high-temperature superconductivity," says Lucio Rossi, who heads the magnets and superconductors group at CERN, the European particle physics laboratory near Geneva, Switzerland.

Today's outlook is decidedly less rosy. "It's very difficult to make money on HTS," says John Rowell, a physicist at Arizona State University in Tempe, who notes that no venture capital-funded HTS company in the United States has ever had a year of profitability. Still, hope springs eternal, and after 20 years of development, HTS equipment makers seem to be finding ground beneath their feet. "It's a slow process," says Al Zeller, a superconducting magnet expert at Michigan State University in East Lansing. "But the applications are taking off." "The materials science in HTS has been terrific," says Bruce Strauss, who helps run the superconductivity program at the U.S. Department

of Energy (DOE). "The engineering is just beginning. I've been seeing a lot more engineering than before of motors, coils, and so on. That's a good sign."

Slowing to a crawl

Part of what made the HTS revolution so exciting was that the novel superconductors looked and acted so differently from conventional low-temperature superconductors (LTS). The earlier materials were ductile metals, such as the alloy niobium-tin, that could be forged into wires for power cables or wound into spools for use in magnets, a key component for motors and generators.

HTS materials, by contrast, are brittle ceramics. In the early discoveries of HTS materials, researchers placed electrodes on opposite sides of a millimeter-sized ceramic fleck or perhaps a few-centimeters-long film of the material. That setup worked to show the drop in resistance characteristic of the onset of superconductivity. But nobody knew how to turn these hard, brittle flecks into kilometers of wire.

Part of the problem is that electrons passing through HTS materials, unlike those in conventional superconductors, prefer to travel in particular directions through the