Superconductivity Turns 10

A decade after their discovery, compounds that superconduct electricity at high temperatures (HTS) are making it into real-world devices—but still, no one can prove how they work

HOUSTON—Alexander Müller and Georg Bednorz knew they'd meet resistance of the intellectual kind when they reported a material with little resistance of the electrical kind 10 years ago. The pair of IBM-Zurich physicists had found a copper-oxide compound showing this "superconductivity" at 35 kelvin, 12 degrees above the previous record. Such high-temperature superconductivity was bound to raise eyebrows among physicists used to superconductors that had to be cooled practically to absolute zero. So in September of 1986, the pair published a cautiously worded paper on "Possible High Tc Superconductivity" in an obscure German physics journal and continued their studies, hoping to confirm their results before others caught wind of their news.

They did, the results were soon replicated, and today any resistance to the existence of high-temperature superconductivity (HTS) has been swept aside. "It's amazing what has been accomplished in the last 10 years," says C. W. "Paul" Chu, a physicist at the University of Houston. Two weeks ago, here at the 10th Anniversary HTS Workshop on Physics, Materials, and Applications, those accomplishments—and some frustrations—took center stage.

Scientists noted they've pushed the maximum temperature of superconductors up to 134 K and discovered over 100 HTS compounds. And while early visions of trains levitating on HTS magnets have not come to pass, other developments have become reality. Thin HTS films are already used to boost the sensitivity of scientific instruments, and those films are now being tested for use in filtering signals from noise in cellular phone base stations, potentially a huge market. Improvements in HTS wires recently have led to the first HTS underground power transmission cable, made not as a lab experiment, but with a standard industrial process. The need to cool these materials with liquid nitrogen still hobbles their commercial prospects, but John Rowell, an industry consultant and former chief technical officer of Conductus, an HTS company based in Sunnyvale, California, predicts the coming years will be "the decade of markets."


IBM

Yet researchers did acknowledge that HTS has been impeded in one important area. "There's still no consensus about the mechanism" of superconductivity in these materials, says Chu. Although a cluster of recent experiments has supported the idea that HTS is borne on magnetically paired electrons, concurrent theoretical developments, discussed at the meeting, have thrown some cold water on that idea. Researchers have also been stymied on pushing operating temperatures closer to room temperature—a long-sought goal—although schemes abound to get it there.

Marching to market

The early pace of HTS discovery was dizzying indeed. By December 1986, 3 months after Bednorz and Müller's paper was published, new compounds had been found that pushed the critical temperature (Tc) for superconductivity up to 38 K. In early 1987, the record rose again, to 93 K, when Chu and some colleagues discovered another material, yttrium-barium-copper-oxide (YBCO). At that temperature, the superconductor could be cooled with cheap and plentiful liquid nitrogen.

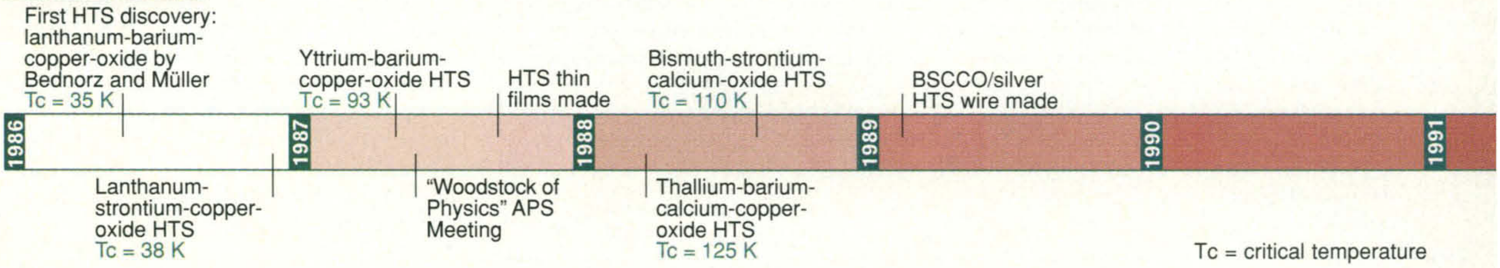
The flurry of events, and the prospect of saving millions of dollars wasted by ordinary conductors like copper when they lose electricity as heat, prompted a special session that March at the meeting of the American Physical Society in New York City. An estimated 3000 physicists jammed into the Hilton Hotel's largest ballroom, many staying up past 3 a.m. to discuss HTS possibilities in what was immediately dubbed the "Woodstock of physics."

But many of these HTS hopes, like hopes from the Woodstock of 1969, haven't been realized yet. Yet there have been advances. "The improvement in the materials has been steady and very significant," says Rowell. And the strongest improvement may have come in the manufacture of long lengths of HTS wire that can carry high densities of current.

The wires are made from grains of superconducting ceramics, and if the boundaries of those grains are not smoothly aligned, they act as current barriers, preventing electrons from hopping from one grain to the next. At first, researchers tried to make wires from compounds such as YBCO, but its odd-shaped grains are difficult to orient uniformly. Today, however, the compound of choice is BSCCO, consisting of bismuth, strontium, calcium, copper, and oxygen, which has flat, regular-shaped grains that can be more easily aligned (*Science*, 15 January 1993, p. 306). By mechanically rolling, pressing, and heating a BSCCO powder in a tube, researchers have improved the alignment to the point where the wires carry up to 100 times more current than conventional copper wires (see chart). Wiremaking companies—including Sumitomo Electric Industries in Osaka, Japan, Intermagnetics General Corporation in Lantham, New York, and American Superconductor Corp. (ASC) in Westborough, Massachusetts—all say they can now spin out over a kilometer of such wire every week.

And 6 kilometers of BSCCO ribbon, researchers announced in Houston, has just been wound into a 50-meter underground transmission cable. Workers from an alliance between the European power cable giant Pirelli Cable, ASC, and the Electric Power Research Institute (EPRI) in San Francisco wrapped the wire around a hollow tube of liquid nitrogen, which keeps it at a superconducting temperature. While short lengths of

Superconductors Heat Up



such cable have previously been made by hand, "this was done on a production machine," says EPRI's Paul Grant. The transition from the lab bench to the factory floor means "we can make any length you want out of this process," says Grant. Testing of extended lengths should reveal how useful these cables will really be.

HTS thin films are already beyond the testing stage, for it's easier to align grains in films by growing them atop crystalline templates. Films are well-suited for applications such as filters for cellular phone base stations, which must screen out incoming microwave signals from background environmental noise and relay them via conventional phone lines to their destination. Signals run through conventional copper filters lose strength, making them harder to distinguish from background noise. But HTS-filtered signals retain their original strength, making it possible to detect signals from farther away. Conductus and several other companies are expected to introduce commercial HTS filters later this year, opening a market that Conductus Vice President Randy Simon expects to reach hundreds of millions of dollars. Other thin-film devices, including ultrasensitive magnetic detectors known as superconducting quantum interference devices, are already on the market.

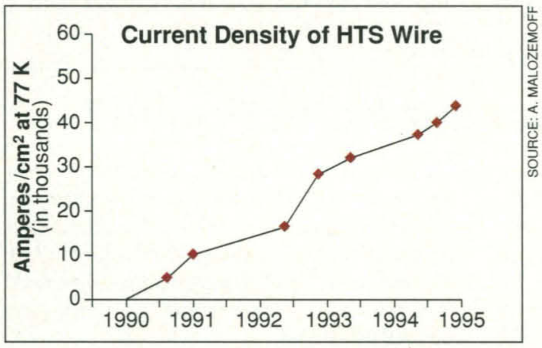
The stumbling block in the way of any widespread commercialization is the need for cooling systems, says Don Gubser, who heads materials science and technology research at the Naval Research Laboratory (NRL) in Washington, D.C. Cables, filters, and wires still need liquid-nitrogen cooling systems, which must be maintenance-free and therefore invisible to the end user to succeed in the marketplace, says Grant. "The goal now is getting systems engineers comfortable with cryogenic coolers," says Gubser. Right now, he admits, they're not. And there's no guarantee this will happen, says Grant, particularly in conservative industries such as power transmission, where companies must be convinced that a new technology is reliable before they are willing to adopt it.

Lots of theories, little proof

What's remarkable about the growth in applications, many researchers say, is that it's happened despite ignorance about how HTS really works. Observations have shown that superconducting electrons, at both high and low temperatures, always travel in pairs, a partnership that is key to their ability to avoid current loss (electrons in normal conductors travel alone). Electrons should resist this pairing, because their negative charges should push them apart. But while there is a theory to explain pairing in low-temperature superconductors, pairing in HTS materials remains a mystery.

At low temperatures, waves of energy, known as a phonons, propagate through the superconductor's crystalline lattice, pulling electrons together into pairs in their wake. But high temperatures should add a lot of energy to the lattice, causing it to shake and knock the electrons off. While some scientists think phonons could be responsible for HTS, many others doubt it.

The main alternative theory, advanced by researchers such as Douglas Scalapino at the University of California, Santa Barbara, and David Pines at the University of Illinois, Urbana-Champaign, suggests that pairing is prompted by an odd patch of the magnetic fields in the lattice. Normally these fields point in random directions, but sometimes the fields around atoms in a patch briefly adopt an alternating up-down orientation, known as a spin fluctuation, which creates a magnetic attraction that can pull a pair of electrons together.



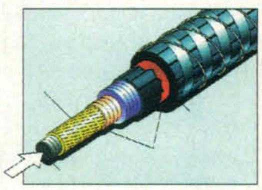
Hot-wired. Amount of electricity carried by an HTS wire (made of a compound called BSCCO) has increased.

It's hard to test these alternatives, however—to see electrons actually surfing behind a phonon or whirling in a spin fluctuation. But each event does leave unique, observable fingerprints—or so researchers have thought. The prints come in the form of a mathematical construct known as wave function symmetry, which describes, in part, how electrons are most likely to travel. Phonon theories predict electron pairs have an equal probability of traveling in any direction, giving them something called "s-wave" symmetry. Spin fluctuation theories, on the other hand, suggest that electron pairs move primarily in two perpendicular directions, producing a four-leaf clover–shaped "d-wave" symmetry.

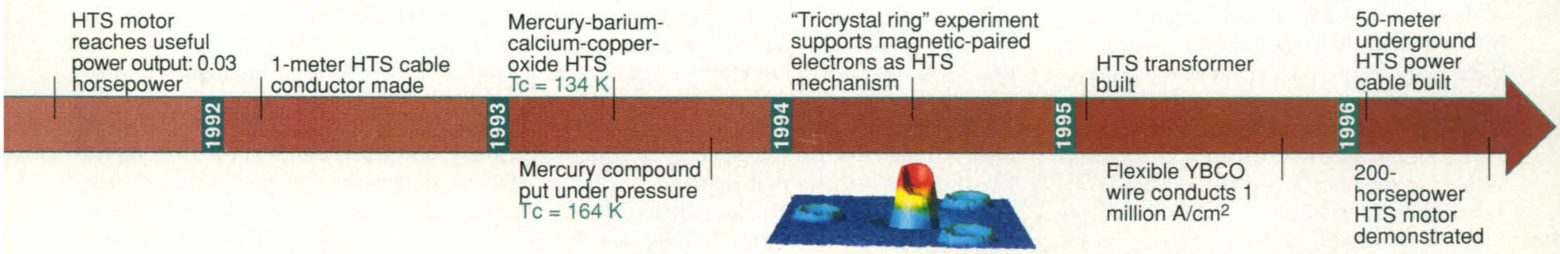
In recent years, most experiments designed to measure this symmetry have detected d-wave symmetry, and those results seemed to favor spin fluctuations as the pairing mechanism in HTS materials. But the theoretical sands beneath the spin fluctuation–d-wave connection have shifted, says Scalapino. "If you would have told me a few years ago that the experiments would be coming up d-wave, I would have thought we won," says Scalapino. "But we haven't."

Why? New pairing theories have cropped up that can also account for d-wave behavior, Scalapino explains. Thus while d-wave behavior is "a feather in the cap" of spin fluctuation theories, "it isn't unique to that mechanism," adds Anthony Leggett, a theoretical physicist at the University of Illinois, Urbana-Champaign. One new theory, for instance, is a fluctuation mechanism mediated not by magnetic spins but by a redistribution of electric charges and current in the crystalline lattice. This mechanism, published last summer by Chandra Varma of Lucent Technology's Bell Laboratories in Murray Hill, New Jersey, also restricts the direction of electron travel in a manner that produces d-wave symmetry (*Physical Review Letters*, 31 July 1995).

Even the phonon theories haven't been altogether eliminated. Theorists including Roland Zeyher of the Max-Planck Institut für Festkörperforschung in Stuttgart, Germany, have produced variants of phonon theories that limit electron-pair wanderings, giving rise to d-wavelike behavior. As a result, says Brookhaven National Laboratory theoretical physicist Victory Emory, "there is absolutely no consensus about the mechanism." D-wave symmetry, agrees NRL physicist Stuart Wolf, "can help eliminate some of the [theoretical] contenders, but it can't give you a definitive answer."



That doesn't mean that symmetry experiments are being



tossed aside, say Chang Tsuei and John Kirtley, physicists at IBM's T. J. Watson Research Center in Yorktown Heights, New York. The two lead a team that's produced some of the most convincing evidence that d-wave symmetry is present in YBCO and a thallium-based compound (*Science*, 19 January, p. 288). Although symmetry experiments can't rule out pairing mechanisms, they may be able to do the opposite and rule in some possible mechanisms. Tsuei and Kirtley say they are currently extending their experiment to other HTS materials to see if they also show a d-wave. If not, it would suggest that different HTS materials use different mechanisms to hold electrons together as they travel, says Kirtley.

Turning up the heat

The pairing issue isn't entirely an academic question. Researchers hope that insights into the superconducting mechanism may help experimentalists devise new recipes that could break the 134 K barrier. Of course, experimentalists have pushed up temperatures in the past without theoretical guidance. And many experimentalists at the meeting were optimistic that they will do so again. "There's no fundamental reason why we shouldn't be able to get the Tc even higher," says Chu.

In fact, there are good reasons to expect that they should. For one, when crunched in a diamond anvil, a copper-oxide compound made with mercury superconducts at 164 K, 30 degrees higher than it does at ambient pressure. So researchers are trying to alter the chemical composition of the materials to simulate the effect of pressure on the crystal lattice—but without the anvil. For instance, by replacing mercury atoms with smaller gold and silver atoms, researchers might shrink the spacing between atoms, simulating the pressure effect and driving up the superconducting temperature.

Not everyone is optimistic, at least as far as the copper-oxide-based superconductors are concerned. Oregon State University physicist Arthur Sleight says that "people have been trying these strategies for years" with these compounds, to little avail. That sentiment has convinced other researchers, such as physicist Robert Cava of Bell Laboratories, to continue their search in noncopper-oxide materials, such as boron-carbides.

The next breakthrough could come from just about anywhere, says Grant. If this field has demonstrated anything, he says, it's that "there are no signposts" for superconductivity: "If you find a new metal, you better cool it down and find out what happens. You may be surprised."

–Robert F. Service

EXTINCTIONS

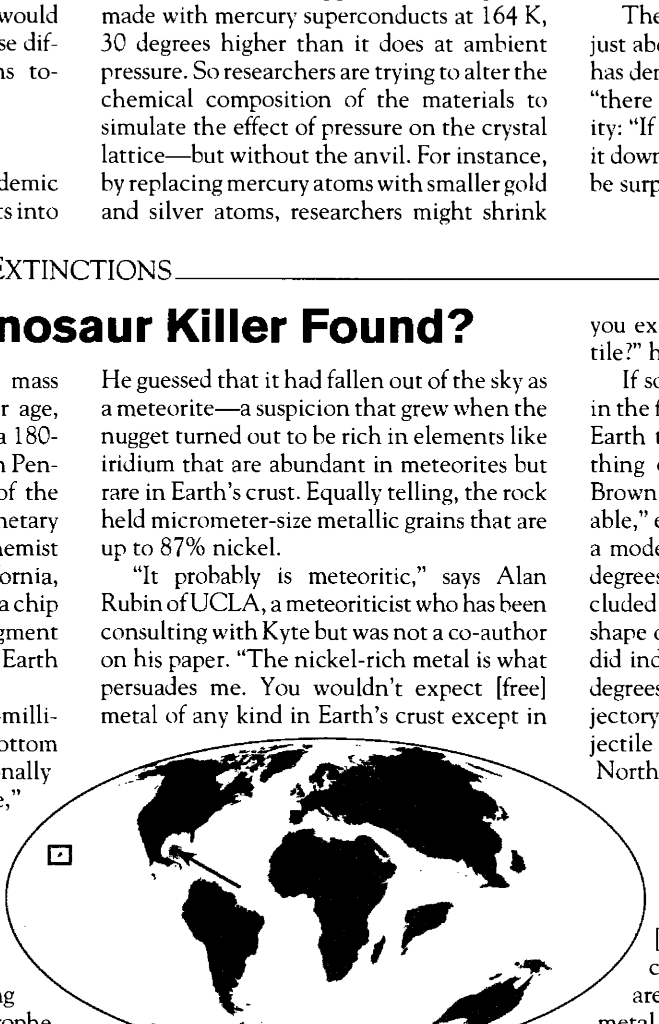
A Piece of the Dinosaur Killer Found?

In their search for the cause of the mass extinction at the end of the dinosaur age, geologists already had a smoking gun: a 180-kilometer impact crater on the Yucatán Peninsula. Now they may have a piece of the bullet. At last week's Lunar and Planetary Science meeting in Houston, geochemist Frank Kyte of the University of California, Los Angeles (UCLA), flashed slides of a chip of rock that he thinks may be a tiny fragment of the 10-kilometer object that blasted Earth 65 million years ago.

From the age and makeup of the 3-millimeter chip, found in the ooze at the bottom of the North Pacific, Kyte is "personally convinced that it is a piece of the bolide," a conclusion other researchers say is at least plausible. "What all the implications are, I'm still trying to figure out," he adds. "The unfortunate thing is that it's mainly mud and rust" after sitting in Pacific sea-floor sediments for 65 million years. But it is already offering some clues to the nature of the catastrophe. A first look at the rock chip's makeup implies the fatal object was an asteroid, not a comet, as some researchers have speculated, and its survival supports an earlier suggestion that the parent body struck Earth at a shallow angle—which may have been the cruelest possible blow.

Kyte hadn't been looking specifically for bits of the bolide. He was methodically sampling a sediment core drilled years ago from the floor of the northwest North Pacific in search of the far-flung debris of the impact. As he sampled he noticed a bit of rock embedded in the mud, an odd find indeed considering nothing bigger than a microscopic piece of clay could wash that far out to sea. He guessed that it had fallen out of the sky as a meteorite—a suspicion that grew when the nugget turned out to be rich in elements like iridium that are abundant in meteorites but rare in Earth's crust. Equally telling, the rock held micrometer-size metallic grains that are up to 87% nickel.

"It probably is meteoritic," says Alan Rubin of UCLA, a meteoriticist who has been consulting with Kyte but was not a co-author on his paper. "The nickel-rich metal is what persuades me. You wouldn't expect [free] metal of any kind in Earth's crust except in bizarre places." But is it really a chip off the dinosaur killer? Chemical and mineralogical signs in the sediments surrounding it, says Kyte, put the rock fragment at the base of a 10-centimeter-thick layer rich in debris particles thrown from the impact crater. This would be only the second time a recognizable meteorite had been found in ocean sediment, so the odds against its being an unrelated small meteorite that happened to fall into the debris at exactly the right moment are just too great, Kyte feels. "Where else do you expect it to be from except the projectile?" he asks.



Long shot. Asteroid that struck the Yucatán may have flung a piece into the Pacific.

SOURCE: C. R. SCOTESE/PALEOMAP PROJECT

If so, it had to have escaped obliteration in the fireball at the crater and fallen back to Earth thousands of kilometers away, something cratering specialist Peter Schultz of Brown University says is "physically reasonable," especially if the impacter "comes in at a modestly low angle—probably around 30 degrees or so." Schultz had already concluded from his study of asymmetries in the shape of the buried crater that the impacter did indeed come in at an angle of about 30 degrees from the southeast. Given that trajectory, "I wouldn't be surprised to see [projectile debris] in the Pacific, especially the North Pacific," says Schultz.

Kyte is studying the rock chip in search of evidence that would clinch its identity as a meteorite and strengthen the case that it is a piece of the impacter. If it is, "my guess is [the original body] wouldn't be a comet," says Rubin, because comets are not thought to be sources of free metal. That could point to a milder catastrophe. Because asteroids are richer in iridium than comets are, a killer asteroid could have had a smaller mass and still account for the total mass of iridium deposited worldwide at the time of the impact. Asteroids also have slower impact velocities than those of comets, on average.

But if Schultz is right about the angle of impact, things get ugly again. By splashing material thousands of kilometers downrange, a shallow approach would have created a far larger fireball than a more vertical one would, visiting particularly severe devastation on the interior of North America. In that case, Kyte's rock may not be mitigating evidence.

–Richard A. Kerr