Superconductors' Material Problems

The excitement over recent discoveries of new superconductors has tended to gloss over the serious material science problems that might hinder their practical application

MORE than a year after the heralded discovery of high-temperature superconductors, these potentially revolutionary materials remain a long way from practical use. Researchers across the country are experimenting with new processing techniques in an effort to overcome physical limitations such as the material's brittleness and its poor current-carrying capacity, but the problems are proving rather stubborn. Even with the discovery of an entirely new class of superconductors, there are no guarantees of when—or even if—these materials will live up to their promise.

That promise is nearly unlimited, some say. A workable high-temperature superconductor could make possible a number of applications, from superpowerful motors and superfast computers to zero-loss electric transmission and magnetically levitated trains. Many have compared the potential with that of the transistor 40 years ago.

Earlier types of superconductors are used now in high-field magnets and magnetic field detectors, but other applications have been limited by the need to cool them below 10 K with liquid helium. Since the superconductors discovered last year lose their electrical resistance at around 90 K, they can be chilled with liquid nitrogen, which is both cheaper and easier to handle than liquid helium.

The problem is that although the new materials are greatly superior to the old in terms of critical temperature, they are inferior in most other ways. For instance, where the older superconductors can carry plenty of current for practical applications, wires made of the new materials lose their superconductivity under relatively small loads. The earlier, metallic superconductors are easily formed into wires and coiled to make magnets, but the new, ceramic materials are brittle and inflexible. And while the older materials are easily integrated into electronic components, the new ones perform erratically when in contact with other materials.

The most recently discovered high-temperature superconductors—reported in February—are still too new for anyone to be able say what the materials' strengths and weaknesses are. Most researchers expect to come across the same types of problems that dog the earlier materials.

However, a recent success at AT&T Bell Labs that improved the current-carrying capacity of the superconductors is encouraging researchers that at least some of the limitations can be overcome. Research done at IBM last summer had first shown that single crystals of superconductors could carry as much as 100,000 amperes per square centimeter, but the current-carrying capacity of bulk quantities had been several orders of magnitude less. By using a special processing technique called melt-textured growth, a group of Bell Labs scientists led by Sungho Jin manufactured bulk quantities of superconductor that carry several hundred times as much current in magnetic fields of practical size as any that had been made up to that point.

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The researchers modified the standard heating process that turns yttrium–barium–copper oxide powder into a 1-2-3 superconductor (so called because the chemical formula is $YBa_2Cu_3O_7$). Instead of just heating the powder to the 700°C necessary to sinter it—cause the individual grains to fuse together—they took it up to 1300°C and melted it, then cooled it back to room temperature with a special, proprietary process. Electron micrographs show that the resulting material consists of needle-like crystals that are aligned roughly in the same direction, instead of the randomly oriented grains which the standard process produces.

The result is a superconducting sample that carries 17,000 amperes per square centimeter at zero magnetic field and 4,000 amperes per square centimeter in a field of 1 tesla when it is cooled to 77 K, the temperature of liquid nitrogen. This is only about 1 percent of the critical current density in single crystals of the superconductor, but it is several hundred times greater than any previously reported value for bulk samples, which consist of many individual crystals. And it is only a factor of 10 or so away from that needed for many practical applications, such as magnetic resonance imaging.

Melt-textured growth processing, said Robert Dynes, director of chemical physics research at Bell Labs, Murray Hill, New Jersey, seems to address both of the problems that researchers believe cause the low critical current density of bulk samples relative to single crystals, which can carry well over 1 million amperes per square centimeter.

The first problem is that the grains in bulk samples tend to line up randomly. Current in the 1-2-3 superconductors flows easily in two directions and flows poorly in the third direction. Putting current through a jumble of grains oriented in every which way means that sometimes the current will have easy going and other times it will flow poorly.

Fortunately, the melt-textured growth technique causes the crystals to grow in exactly the right direction to improve the material's current-carrying capacity, Dynes said. The crystals grow preferentially along the axes of good current flow and line up pointing in approximately the same directions, which removes some of the random crystal alignment in bulk samples. "Sometimes nature is a little good to you if you push a little," Dynes said.

In addition to the alignment problem, researchers believe that impurities lying between the grains in bulk samples make it harder for the current to pass from grain to grain, which lowers the critical current density. Here, too, melt-textured growth seems to help, Dynes said. "We suspect it cleans up the grain boundaries."

The real advantage of the melt-textured growth process, Dynes added, it that it points out a direction for further advances. "We haven't even got close to the limit yet. We don't really even know what the most important variable is." Asked whether he expects the critical current density can be pushed up by a factor of 10 or 100, he said he was hopeful but " 'expect' is too strong a word."

Even if the critical current density can be brought to an acceptable level, researchers point to several other problems that could limit practical applications. Perhaps the most acute of these is the brittleness and inflexibility of the superconductors. If, for instance, the new superconductors are to be practical for high-field magnets—which are the most important current use of superconductors—researchers must learn how to form them into wires and then coil the wires to make the magnets.

So far, they have had little luck. Merwin Brodsky, acting director of materials science at Argonne National Laboratory in Argonne, Illinois, said that when the lab first made superconducting wire, a 9-inch piece could be bent just 1/4 inch before it broke. Since then, Argonne has only managed to improve the flexibility of its superconducting wires to the point where a 9-inch piece will bend 3/4 inch. Other labs have had similar experiences.

Still, ceramists know a number of tricks to make ceramic materials more malleable, and various groups are trying to apply these techniques to the 1-2-3 superconductors.

At Argonne, for example, materials researchers are experimenting with controlling the distribution of flaws in a superconducting sample, said Roger Poeppel, head of ceramic processing. When a load is put on a ceramic, the stress concentrates at the flaws, which are imperfections in the crystalline structure. The largest flaws get the greatest stress, and cracks begin at these flaws and propagate outward. Poeppel said his group is trying to get a uniform distribution of small flaws so that the material will absorb stress evenly and not crack so easily.

The trick, Poeppel said, is to control the size of the particles in the original mixture and then to control the grain growth when the material is sintered. Unless the temperature regimen is carefully controlled, the larger particles tend to grow at the expense of the smaller ones, which creates an uneven distribution of flaws.

Such techniques may improve the mechanical properties of the 1-2-3 superconductors somewhat, but many researchers expect they will remain relatively inflexible. And it may prove especially difficult to improve strength and flexibility while at the same time attaining other desired properties, such as a high critical current density. For example, Dynes reported that melt-textured superconductors show the same brittleness as normally processed samples, although his group had originally hoped the technique might improve the mechanical properties as well as the current density.

It is even possible that the large grains produced by the Bell Labs process may work against improving strength and flexibility. Poeppel pointed out that larger grains tend to cause cracks during the final processing step, when oxygen is added at around 400 K and the material is cooled. In this step, $Ba_2Cu_3O_6$ changes into $YBa_2Cu_3O_7$, which has a slightly different crystalline structure. Larger grains cannot easily absorb the stress of the change from one structure to the other, Poeppel said, and this leads to cracking.

In addition to work on the critical current density and mechanical properties, a number of labs are studying how the complex 1-2-3 superconductors behave in contact with various materials. The contact question is particularly pressing in the case of thin film applications—where a thin layer of superconductor is applied atop a base layer and then much of it etched away—because in this case no part of the superconductor is very far from the other material. Scientists envision thin film superconductors playing a number of roles in electronic circuits, from resistanceless connections to superfast electronic switches.

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The base layer, or substrate, must be matched carefully with the superconductor if the thin layer of superconductor is to perform predictably. Ideally, the substrate's crystalline structure should be identical to that of the superconductor so that the thin film can be laid down with a minimum of flaws and dislocations. Strontium titanate, with a crystalline structure very close to $YBa_2Cu_3O_7$, is a common choice of substrate, for instance.

Researcher are not, however, completely satisfied with strontium titanate. Besides being very expensive, the substance tends to interdiffuse with the superconductor during the annealing phase of the cooking process. This isn't surprising—at the 700°C that 1-2-3 superconductors must be cooked at, most materials will exchange some of their atoms with atoms in an adjacent layer. This causes a problem with the superconductors because they are extremely sensitive to the proportions of individual atoms in the sample, and atoms leaking over from the substrate can degrade the superconductivity. If the substrate contains silicon, for example, researchers have found interdiffusion completely destroys the superconductivity.

Unfortunately, silicon is the basis of much of semiconductor technology and thus scientists would like to be able to combine silicon with superconductors in electronic circuits. Researchers are looking for a barrier between silicon and superconductor during processing, so as to prevent interdiffusion.

The most straightforward thin application of superconductors—short of using them as connections between electronic components—is the Josephson junction, a two-terminal electron device that switches a voltage on and off depending on an applied current or an external magnetic field. "The obvious first thing to try to make is Josephson tunneling junction," said John Talvacchio of Westinghouse.

Not only is a Josephson tunneling junction a useful electronic component in its own right, but two of them connected in series compose a SQUID (superconducting quantum interference device), a very sensitive detector of magnetic fields. SQUIDs made with liquid-helium superconductors are used now in medical diagnostics and geological surveying.

So far, no one has built a practical Josephson junction, although several labs are working on it. The tunneling junction consists basically of two superconducting layers sandwiched around a thin insulating layer; current flows through the insulator from one superconducting layer to the other via quantum tunneling. At Westinghouse, Talvacchio said his group is stuck at laying down the first layer of superconductor.

The problem, Talvacchio said, is that the superconducting layer must have a near-perfect composition right up to its edge with the insulating layer. The electrical characteristics of the Josephson junction depend on the portion of the superconducting layer that lies within one coherence length of the insulating layer. Since the coherence length—the physical separation of the electron pairs that carry a superconductor's current—is much smaller for 1-2-3 superconductors than for the older materials, Josephson junctions made with the new materials are much more sensitive to variations next to the boundary.

Talvacchio said his group has been unable to manufacture a layer of superconductor that is superconducting in the top 10 angstroms—that is, within one coherence length of the surface. When the superconductor is annealed in oxygen, the process tends to bring too much barium to the surface. When his group tried ion milling to trim off the top 50 angstroms, the remaining layer had too much yttrium near the surface.

The most promising technique, Talvaccio said, seems to be to cook the superconductor very quickly during the oxygen treatment. If done fast enough, the barium does not have time to move to the surface.

Another possible materials problem with the 1-2-3 superconductors that has gotten little attention but could prove important for commercial applications is their questionable stability. There are reports that the materials react readily with water and carbon dioxide. Several researchers said, however, that the stability problems seemed to disappear as they learned to make purer samples, and they speculated that the reactions with water and carbon dioxide depended on impurities in the samples.

With the different problems facing the 1-2-3 superconductors, perhaps the simplest solution would be to find high-temperature superconductors that are easier to work with. That may have happened.

Last month, two groups—one in Japan and one at the University of Houston—announced the discovery of a material that becomes superconducting at 110 K. The increase in critical temperature is important, but equally important is the fact that initial reports indicate that the new bismuth-strontium-calcium-copper-oxygen superconductors are not as balky as the 1-2-3 superconductors.

For one, their flaky structure—much like mica—seems to be more flexible than the 1-2-3 superconductors. The new material also seems to be more stable, it does not have to be processed at quite as high a temperature, and it does not need the final annealing step to add oxygen that the 1-2-3 superconductors demand. Researchers have not yet announced the new material's critical current density.

More recently, yet another high-temperature superconductor has been discovered, this one with a critical temperature of about 125 K. This substance, which consists of thallium, barium, calcium, copper, and oxygen, is too new for investigators to predict its physical and mechanical properties.

A year's intense work on the 1-2-3 superconductors has prepared the ground for a much more rapid development of the new materials. "Within 1 or 2 weeks, we'll know enough about these materials [to know if they are promising]," said Argonne's Brodsky. "If the properties look that much better, I think people will rush off in that direction." If this proves to be the case, the 1-2-3 superconductors may slowly sink out of sight, but the time spent studying them will not have been wasted. "We can use the information we've already got together to study the new materials," he said, "and they look much more complicated." ■

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Diet and Health in China

Chinese food can tell us a lot about the relationship of diet and disease, a relationship that, in countless studies, has proved slippery to pin down. So says T. Colin Campbell of Cornell University, who, with three colleagues from China and England, is now completing a 6-year study of Chinese dietary patterns. He provided glimpses into the study, which will be published later this year, at a recent Senate hearing on nutrition and health.

What drew the investigators to China is that country's enormous variation in cancer incidence, which became apparent with the 1981 publication of the *Cancer Atlas of China* by the Chinese Cancer Institute. The atlas revealed that in China cancer is very much a local disease, with mortality rates varying from several dozenfold to 300-fold among regions. And in most regions, diet and life-style also vary tremendously: people usually live their entire lives in the county where they were born, eating locally grown foods.

These characteristics afford an opportunity to look at the effects of specific—and constant—diets on health, an opportunity that does not exist in the United States and other Western nations. With coinvestigators Chen Junshi of the Chinese Academy of Preventive Medicine, Li Junyao of the Chinese Academy of Medical Sciences, and Richard Peto of Oxford University, Campbell set out to do so, with funding from the National Cancer Institute (NCI) and the Chinese government.

They selected 65 counties across the country, reflecting the nation's wide variation in cancer incidence, and two villages or communes within each, for a total of 130 sites. The heart of the study was a 3-day survey of some 12,000 people, which recorded what they actually consumed over those 3 days.

The dietary survey was supplemented with laboratory analysis of food samples that provided a precise breakdown on the proportion of various fiber fractions, trace metals, pesticide residues, and other components. For about 6500 men and women between the ages of 35 and 64, blood and urine samples were analyzed to assess nutritional status. In all, they collected 350 items of information, which they are using to examine the role of diet in 12 cancers and 35 other diseases.

Details on the relation of diet to disease incidence in China will not be released until later this year, but at the hearing Campbell described a few key findings, focusing on what the Chinese data might reveal about U.S. dietary policy.

■ **Cholesterol**. Plasma cholesterol levels range from 90 to 175 milligrams per deciliter, which puts the Chinese high near the U.S. low. Cardiovascular disease continues to decrease as cholesterol levels drop below 180, Campbell reported. Moreover, the incidence of colon cancer also decreases along with cholesterol levels, in contrast to a few studies that have suggested the reverse.

■ **Fiber**. Chinese eat three times more fiber than do Americans, consuming anywhere from 8 to 77 grams of fiber a day, with an average of 34 grams a day. The U.S. average is 10 grams; NCI has set a target of 20 to 30 grams a day. However, because some evidence has suggested that a high-fiber diet may interfere with mineral absorption, NCI recommends an upper limit of 35 grams a day. The Chinese study does not bear that out, says Campbell. In fact, he says, hemoglobin levels are positively correlated with fiber intake.

■ **Fat**. Fat intake ranges from a low of 6% of total calories to a high of 25%, with an average of 15%, compared with a U.S. average of 40%. There is no evidence, Campbell says, that health is compromised by such low-fat diets, but further investigation is necessary.

■ **Total calories**. Although Chinese consume 20% more calories, per body weight, than do Americans, there is very little obesity. The Chinese are considerably more active than Americans, on average, says Campbell, "but I think that is only part of the story." He suspects it may be related to the type of calories consumed and how they are utilized. What this finding does imply, according to Campbell, is that caloric intake is not necessarily a determinant of obesity, nor is it necessarily a determinant of chronic disease risk, though obesity itself certainly is.

The opportunity for such studies may soon disappear. Diet has remained constant in rural areas, where the study was mostly conducted. But in urban areas, says Campbell, dietary patterns are already changing as the country opens its doors to the Western world. ■ LESLIE ROBERTS