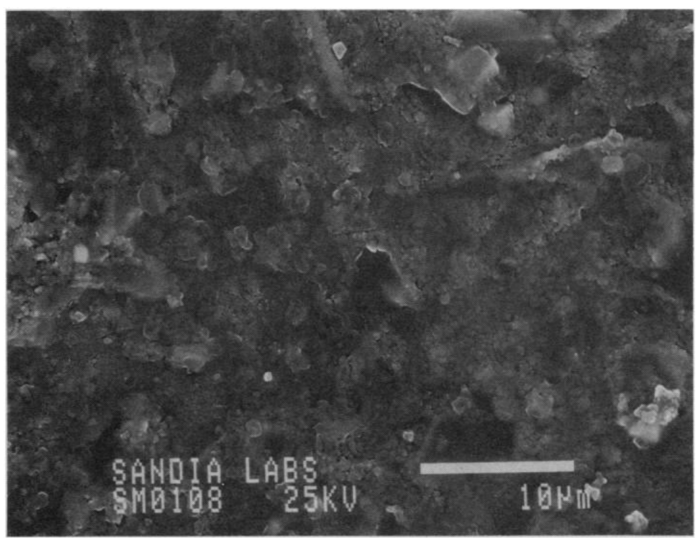
New Superconductors Come Through

High-temperature superconductors have proved difficult to put to practical use, but recent advances in thallium- and bismuth-based materials should bring applications closer to reality.

TWO NEW CLASSES of superconductors are beginning to live up to the hoopla that accompanied their discovery several months ago. The materials—one class containing bismuth and the other thallium—lose their resistance to electric current at higher temperatures than any other known substances, which raised hopes that the goal of practical high-temperature superconductivity would soon be within reach. Recent results have pushed those expectations even higher.

The latest phase in the search for practical high-temperature superconductors has gone on for nearly a year and a half, ever since the discovery by Paul Chu at the University of Houston of an yttrium-barium-copper-oxygen mixture that lost all electrical resistance at 90 K. This discovery meant it might be commercially feasible to use superconductors cooled by liquid nitrogen, which has a boiling point of 77 K and is relatively cheap and easy to work with. But researchers quickly discovered that the high-temperature superconductors had various materials problems that stood between them and their dreams of new electronic components and magnetically levitated trains.



Sandia's thallium thin film. *An electron micrograph shows the polycrystalline structure.*

Thus, when scientists at several universities announced the discovery of the bismuth and thallium compounds early this year, it was welcome news. Not only did these materials become superconducting at higher temperatures than the earlier substances, but there were signs that they would be easier to work with.

Several results announced in the past few weeks indicate that this may be the case. Sandia National Laboratories in Albuquerque, New Mexico, for example, has made a thin film from a thallium-based superconductor that carries much more electric current than similar films made from earlier superconductors. Thin films, which are used in electronics components, are likely to be the first practical application of high-temperature superconductors. And a group at Stanford University has succeeded in making an exceptionally high-quality fiber out of a bismuth-based superconductor. (See page 1642 of this issue.)

David S. Ginley of the Sandia team said it has created thin films of the thallium material that lose resistance to electric current at 97 K and carry as much as 110,000 amperes per square centimeter at 77 K. Although thin films made from other superconductors have carried as much a 1 million amperes per square centimeter, there is a crucial difference. The earlier thin films with high current densities were single crystals, while the Sandia thin films are unoriented polycrystalline.

"For practical applications of superconductivity in microelectronic devices, you're going to have to have polycrystalline films," Ginley said. "Our films are the first polycrystalline films reported that have critical currents approaching those of interest for applications in such devices."

Single-crystal thin films are tricky to use in electronics because a mismatch between crystalline structures makes it difficult to apply single crystals of superconductors to a silicon base. Although the mismatch is unimportant for polycrystalline thin films (because they do not need to match up exactly with the molecules of the base layer), so far polycrystalline films made from earlier superconductors have not been able to carry practical amounts of current. Most electronics applications need current densities between 100,000 and 1 million amperes per square centimeter.

Sandia's thallium thin films have reached the low end of this range, and it should be possible to push the film's current capacity up to at least 1 million amperes per square centimeter, Ginley said. One way will be to use a different thallium compound, the so-called 2223 phase ($Tl_2Ca_2Ba_2Cu_3O_{10}$) instead of the 2122 phase ($Tl_2CaBa_2Cu_2O_8$), from which the films are currently made. Since the 2223 phase has a critical temperature some 15 K higher than the 2122 phase, there should be a corresponding increase in critical current. Further, orienting the crystals in the thin film so that they point in a single direction instead of being aligned randomly could increase the current density by a factor of 10, Ginley said. The Sandia team has recently attained zero resistance at 107 K in films predominantly of the 2223 phase on substrates of strontium titanate, cubic zirconia, and sapphire, Ginley added.

At IBM's Almaden research center, Wen Lee and collaborators have made polycrystalline thallium thin films that show zero resistance to electric current up to 120 K, or 13 K higher than the best Sandia result. This high critical temperature seems to indicate the presence of the 2223 phase, but Alex Malozemoff, IBM's coordinator of high-temperature superconductivity research, said the films are complicated and the group has not completely characterized them. The films have critical current densities of 10,000 to 20,000 amperes per square centimeter, he said.

The reason that Sandia's maximum current densities are greater than IBM's even though the critical temperatures are lower seems to lie in the processing techniques. IBM's films "are not as clean as we would like them," Malozemoff said, and the intergrain structure seems to be holding down the maximum current capacity.

Ginley said the key to the high current-carrying capacity in the thallium films seems to be how well the current moves from one crystalline grain to the next inside the film. In 1-2-3 films, problems at the boundaries between the grains limit the amount of current that flows through a multicrystal sample, but Sandia's thallium compound seems to have much better current flow from grain to grain. "The present findings imply good (but not perfect) grain-to-grain coupling in these films," the Sandia group says in a preprint reporting its results.

What makes the thallium films even more impressive, Ginley said, is that the strength of the links between the grains can apparently be made weaker or stronger by changing the processing technique. "We may be able to tailor-make the materials [to have a desired critical current density]," he said. For instance, low critical currents and weak links are useful in infrared detectors, while interconnections on electronic chips need strong links and high currents.

Meanwhile at Stanford, a group of researchers led by Robert S. Feigelson reports success in making thin fibers of bismuth-based superconducting material. The fibers, created via a laser-heated crystal growth method, have shown critical current densities as high as 50,000 amperes per square centimeter at 68 K. With this technique, Feigelson said, researchers now have a simple, controlled method of producing high-quality fibers for use in testing various properties of the superconductor.

The Stanford group used a technique called laser-heated pedestal growth to make the superconducting fibers. They first formed pellets of superconducting $Bi_2CaSr_2Cu_2O_8$ by mixing together appropriate amounts of different ingredients, heating them, grinding them up, and reheating them. They then cut the pellets into rectangular rods 20 millimeters long (about 4/5 inch) and just over 1 millimeter wide. To form the fibers, they melted the top of one of the rods with a laser, then dipped a second rod into the melted material. As the melted material crystallized onto the seed rod, they pulled that rod back at a rate of from 1.5 to 50 millimeters per hour. The result was a fiber that was between 0.25 and 1 millimeter wide, depending on how fast the seed was pulled back, and whose length was between 10 and 40 millimeters.

By changing various conditions of the process—such as the composition of the source material, the speed of withdrawing

Copperless Superconductivity

In April, AT&T Bell Labs announced the fabrication of a high-temperature superconductor with a surprising property: it does not contain copper. Since the discovery 2½ years ago of a copper-oxide material that became superconducting at a record high 30 K, every high-temperature superconductor found has contained a set of copper-oxygen layers, and researchers wondered if the copper was essential. A Bell Labs research team headed by Robert Cava and Bertram Batlogg has shown that it is not.

The new material is a compound of barium, potassium, bismuth, and oxygen in the proportions $Ba_{0.6}K_{0.4}BiO_3$, and it showed an onset of superconductivity at 30 K. While this is a much lower critical temperature than the current crop of copper-oxygen superconductors have, it is about the same critical temperature as the first high-temperature superconductor found in 1986 by IBM's Georg Bednorz and Alex Müller. This leads some researchers to hope that copperless superconductors might follow in the footsteps of the copper-oxide compounds. "The new discovery may represent the first step toward the discovery of a new family of materials with high critical temperature," Cava said.

Even if it does not, it should give physicists additional insights in their struggle to explain high-temperature superconductivity. "The missing magnetic copper ion will stimulate some theorists to rethink their models for the underlying mechanism of high critical temperature superconductivity," Batlogg said.

Not only does the new superconductor not contain copper, it does not have the layered molecular structure that seems to be at the heart of copper-oxygen superconductors. Until now, all high-temperature superconductors have contained planes of copper and oxygen atoms which apparently play a major role in the materials' superconductivity, although the exact mechanism is still being debated. Because of this structure, current flows through the copper oxide superconductors easily in the two directions along the layers, but poorly in the direction perpendicular to the layers.

The new material, however, is a three-dimensional structure of bismuth and oxygen interspersed with atoms of barium and potassium, and its current-carrying properties are much less sensitive to direction. The layers that are so prominent in other high-temperature superconductors are nowhere to be seen.

Since Bell Labs' discovery of the copperless superconductor, researchers at Argonne National Laboratory in Argonne, Illinois, have re-created the compound by a different, much simpler method and measured its chemical composition with a technique called neutron diffraction. The researchers, headed by David Hinks, found they could create a range of superconducting materials that had varying proportions of barium, potassium, and oxygen.

Changing these proportions changed the critical temperature, the researchers found. The compound with the highest critical temperature—27 K—had a chemical composition of about $Ba_{0.7}K_{0.3}BiO_3$, and increasing the proportion of potassium past that point lowered the critical temperature. On the other side, when the percentage of potassium fell below the proportions $Ba_{0.75}K_{0.25}BiO_3$, the molecular structure of the crystal shifted into another phase, and this phase was not superconducting.

Neither Argonne nor Bell Labs has succeeded in measuring how much current the copperless superconductors can carry. However, a group at Bell Labs led by Sungho Jin has measured the effect of a magnetic field on the material's critical temperature. Jin said that a 0.2-tesla magnetic field caused a 4 K drop in the temperature at which the material lost resistance to an electric current. This implies that the barium-potassium-bismuth-oxygen superconductors may be too sensitive to magnetic fields for practical applications, he said.

As for the question of whether researchers will discover a whole family of copperless superconductors, Jin said it is too early to tell. "This is basically a new game," he said. "The fact that the synthesis of the material is so complicated means that there are a lot of aspects that can be explored in looking for higher critical temperatures."

If researchers do find copperless superconductors at temperatures significantly higher than 30 K, they might be much easier to develop for practical applications than existing superconductors. The three-dimensional structure of the copperless materials might allow workers to sidestep some of the problems created by the two-dimensional structures now present in high-temperature superconductors. ■ **R.P.**

the seed, or the atmosphere in the growth chamber—the group was able to control the composition of the resulting fiber. One of the impressive things about the process, Feigelson said, is that the fiber is superconducting as it crystallizes, and needs no further processing. Other techniques for making superconducting wires require an extra step to change the material into a superconducting form.

The Stanford tea[illegible] the laser-heated pedestal growth process on more than 50 different types of materials, Feigelson said, and this process produces closer-to-perfect crystals than any other. He said he expects therefore that the superconducting bismuth fibers will prove to be very high quality crystals, which will make them quite valuable to researchers investigating the properties of the bismuth superconductors. So far these superconductors have proved quite difficult to grow in pure form.

The Stanford group has also grown fibers of the 1-2-3 superconductors, Feigelson said, but they required an extra annealing step (heating in the presence of oxygen, then cooling) after the wires were formed. Still to come are attempts to grow useful fibers from the 2223 phase of the bismuth superconductor as well as from the thallium compounds.

Whether the growth process will ever be commercially feasible for making superconducting wires depends partly on how much it can be speeded up, since it is very slow now. "In principle, there is no limit to the length of the wire," Feigelson said, but "right now it's more of an experimental tool for studying high-quality fibers."

■ **Robert Pool**

A Landmark in Speech Recognition

A computer science graduate student at Carnegie Mellon University, Kai-Fu Lee, appears to have toppled some of the largest barriers to building a genuinely useful computer system for speech recognition—a goal that has tantalized and frustrated the likes of IBM and the Defense Department for decades.

SPHINX, as Lee's experimental program is known, has demonstrated up to 96% accuracy in identifying spoken words, while simultaneously meeting some of the field's most stringent performance criteria: continuous speech (no pauses between words); speaker independence (no restrictions on who is talking, and no requirement that each user spend time training the system); a natural task (questions about naval ship movements); and a large vocabulary (997 words.)

While running on special-purpose hardware, moreover, SPHINX can produce its output at roughly one-third the speaker's rate of input, with every indication that further improvements will enable the system to keep up with the speaker word for word.

Individually, any one of these achievements would put SPHINX close to the state of the art in speech recognition; taken together they are unprecedented. "I think we're entering a phase when [speech recognition research] will show some real payoffs," says Lee's adviser Raj Reddy, a former president of the American Association for Artificial Intelligence and an active contributor to this field for more than 15 years. SPHINX is hardly perfect, he says—"The Holy Grail of totally spontaneous, unrestricted speech is still 10, 20, 30 years away." Yet it does point the way toward some genuinely useful applications in the near term, with the possibilities ranging from office dictation systems to the voice command of robots on the factory floor. In fact, says Reddy, "It begins to be possible to imagine speech hardware and software as standard on every personal computer."

From a theoretical point of view, moreover, it is significant that SPHINX owes its power not to any one conceptual breakthrough, but to a series of incremental improvements within a thoughtfully planned framework. "Kai-Fu's thesis shows that there is no substitute for having a careful understanding of the phenomenon—speech—and then representing it in the very foundations of your program," says Reddy.

As Lee himself explains it, those foundations consist of four principles:

■ **A good model of speech.** One of the many things that makes speech recognition so hard is that the same word can vary wildly in sound depending on where it is in a sentence, what words come immediately before and after, how much stress it receives, how rapidly the speaker is talking, *who* is talking, and a host of other variables. At least 50 distinct pronunciations have been recorded for the word "the"—when it is not smothered or swallowed entirely—and at least half a dozen are typically found even for such formal words as "Atlantic."

Thus, says Lee, the first priority in a computer system is to encode all these possible variations in a form that is simple enough and compact enough for the computer to handle. In SPHINX this is done by a technique known as Hidden Markov modeling, which has become very popular in the field since it was introduced about 15 years ago. In effect, this method treats every distinct sound in English as a little computer that can generate a whole array of pronunciations; thus it can be viewed as a speech generator. Given a vocal input, conversely, the Hidden Markov method picks out the sound most likely to have produced it; thus it can function as a speech recognizer.

By adding in some restrictions derived from the "grammar" of the 997-word vocabulary—that is, a statistical measure of which sounds are likely to follow after one another—Lee was able to use this method to achieve accuracies of up to 75%. Adding more words to the vocabulary does tend to slow the system down. However, one of his top priorities for future research is to improve the modeling algorithms so that they can handle many thousands of words.

■ **Use of human knowledge about speech.** When we humans listen to an utterance we decipher it not just by sound alone, as the standard Hidden Markov method does, but by factors such as stress, duration, and the rise and fall of pitch, all of which have to do with the way the sounds are changing in a given context. Lee accordingly integrated such factors into SPHINX, along with some simple phonological rules, and found that its accuracy improved to some 90%. Another item on the agenda for future research is to add higher level knowledge about grammar and the meaning of words, using a variety of artificial intelligence techniques.

■ **Choosing a good unit of speech.** The way we pronounce a given sound is strongly influenced by what comes before and after it: listen carefully to the initial sounds in *tea* and *tree*. Lee therefore used his Hidden Markov models to encode not single sounds, but sequences of three sounds—"triphones." He also used separate models for function words such as *the* and *by*. This boosted the accuracy of SPHINX to almost 96%.

■ **Adaptation to individual speakers.** In much the same way that a human listener can adapt his or her ear to a strange accent, a speech recognition system ought to be able to improve its performance by adapting itself to the vagaries of the individual speaker—although it has to do so automatically and unobtrusively, says Lee, lest it degenerate into a speaker-dependent system. For SPHINX he investigated several algorithms for doing this, and found that they made only a marginal difference. However, he believes there is still a good deal of progress to be made in this area.

■ **M. Mitchell Waldrop**