New Superconductors Answer Some Questions

"Triple-digit" materials raise critical temperatures for superconductivity, may also yield important clues to understanding it

New Orleans

It may have lacked the frenzied excitement of last year's "Woodstock of physics," but "Woodstock II" at the 1988 meeting of the American Physical Society in New Orleans had its own drama. In a hastily arranged evening session on 22 March, 30 researchers presented their results on the recently discovered "triple-digit" superconductors—two classes of materials that become superconducting at temperatures higher than 100 K. By the time session organizer Timir Datta of the University of South Carolina ended the meeting around midnight, it was clear that another milestone on the road to high-temperature superconductivity has been reached.

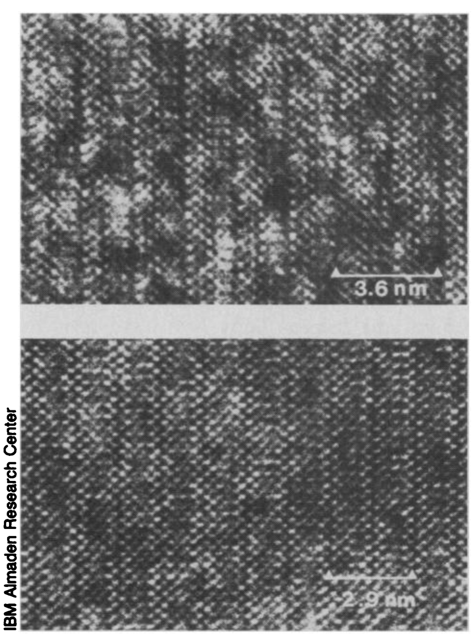
The most obvious significance of the triple-digit materials is that they take the critical temperature for superconductivity up another few notches to 125 K, from a previous best of around 95 K. However, workers in the field say these materials are important more because of the clues they provide to understanding superconductivity at these temperatures and finding superconductors at even higher temperatures. Although the mechanism that causes these materials to lose their resistance to electrical currents remains cloudy, the recent discoveries have cleared up some of the fog.

The discovery of triple-digit superconductors came at a time when some researchers were openly wondering if the limit had already been reached. January marked the 1-year anniversary of the discovery of 95 K yttrium-barium-copper-oxygen superconductors by Paul Chu and co-workers at the University of Houston, and during those 12 months no materials with a higher critical temperature had been found.

Then on 22 January, Japanese researchers headed by Hiroshi Maeda at the National Research Institute for Metals in Tsukuba, Japan, announced a bismuth-strontium-calcium-copper-oxygen material that showed an onset of superconductivity (the first sharp drop in resistance) at 120 K. The material has since shown signs of full superconductivity around 110 K. (The precise critical temperature is still in doubt because of problems with obtaining a pure sample of the 110 K phase.) Three days later, Chu announced his group had been working with the same material.

On 15 February, a group at the University of Arkansas headed by Allen Hermann unveiled a thallium-barium-calcium-copper-oxygen compound that showed onset at 123 K and zero resistance at 103 K. The group had actually discovered the material in October and had sent samples to other labs for testing and verification, holding off an announcement for nearly 4 months. Datta, whose laboratory was among the first to get samples from Hermann, commended the group, noting that some superconductivity researchers have seemed unwilling to wait even 4 days to announce results. This has led to claims of superconducting materials of 300 K or more that later could not be verified.

Two weeks after the Arkansas announcement, researchers at IBM Almaden Research Center perfected a processing compound with a 125 K critical temperature. This currently is the record high temperature.



IBM Almaden Research Center

Close-up. *Thallium atoms make dark vertical lines in these transmission electron micrographs. They are separated by trilayers of copper oxide in the 125 K phase (top), and by bilayers in the 108 K phase (bottom).*

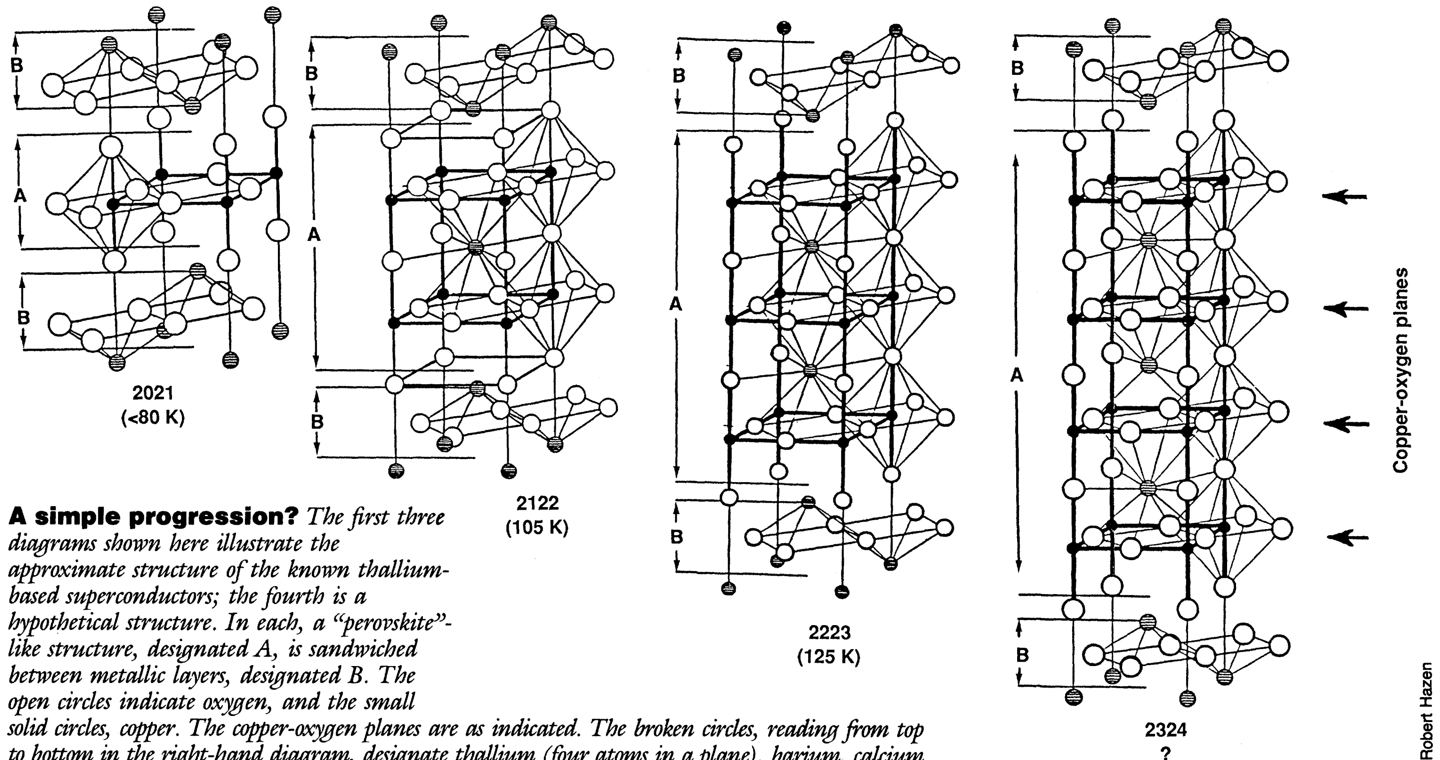
One of the results that emerged from the "Woodstock II" session was that the structures of these two classes of triple-digit superconductors are very closely related. By coincidence, both Chu and Hermann had sent samples of their materials to Robert Hazen at the Geophysical Laboratory of the Carnegie Institution of Washington for analysis. Hazen said at the session that both the bismuth-based and thallium-based materials have layered structures, with planes of copper and oxygen atoms separated by pairs of planes of bismuth-oxygen or thallium-oxygen. In general, he said, the thallium material is almost identical to the bismuth-based material, with thallium replacing the bismuth and barium replacing the strontium.

More importantly, Hazen and other researchers pointed to a direct correlation between the copper-oxygen layers and the materials' superconductivity. The number of copper-oxygen layers between the bismuth (or thallium) layers varies according to how the sample is prepared, and the critical temperature of the material depends on the number of layers in a very simple way: The more copper-oxygen layers, the higher the critical temperature. For example, crystals with a chemical composition $Tl_2Ca_1Ba_2Cu_2O_8$—the so-called 2122 phase—have two copper-oxygen layers and become superconducting at 110 K. The 2223 phase has three copper-oxygen layers and loses resistance at 125 K. In the other direction, the 2021 phase—$Tl_2Ba_2Cu_1O_6$—has one copper-oxygen layer and a critical temperature of about 80 K.

The bismuth materials have the same crystalline pattern, but have smaller critical temperatures. The 2021 phase becomes superconducting somewhere below 23 K; the 2122 phase at 80 K; and the 2223 phase somewhere around 110 K.

With this evidence and from calculations based on the structure of the new materials, several theorists said the copper-oxygen planes are responsible for the superconductivity. "Electrons move in the copper-oxygen plane and there's essentially nothing [in the way of conduction electrons] in between," said Arthur Freeman of Northwestern University.

This appears to settle a dispute concerning which part of the earlier yttrium-barium-copper-oxygen materials was responsible for the superconductivity—the copper-oxygen planes or interlying rows of copper-oxygen chains. Since the new compounds have no copper-oxygen chains, it is apparent that the chains per se are not essential. On the other hand, they may not be superfluous, either. P. A. Sterne of the University of Maryland suggested that the superconduc-



A simple progression? *The first three diagrams shown here illustrate the approximate structure of the known thallium-based superconductors; the fourth is a hypothetical structure. In each, a "perovskite"-like structure, designated A, is sandwiched between metallic layers, designated B. The open circles indicate oxygen, and the small solid circles, copper. The copper-oxygen planes are as indicated. The broken circles, reading from top to bottom in the right-hand diagram, designate thallium (four atoms in a plane), barium, calcium, calcium, calcium, barium, and thallium (four atoms). The other diagrams are analogous.*

tivity may be enhanced by metallic layers lying between the copper-oxygen planes. If so, the chains may be what provides that layer in the yttrium-barium-copper-oxygen material. Freeman and others likewise speculated that bismuth or thallium may be what provides the metallic layers in those materials.

The correlation between the number of copper-oxygen layers and the critical temperature raises the natural question: Can compounds with still higher critical temperatures be fabricated by adding more layers? Paul Grant of IBM Almaden said the answer appears to be yes, but only up to a point. He predicted that a four-layer thallium compound—the 2324 phase—would be superconducting at 150 to 160 K, but ten layers would give only about 200 K, and extra layers would not take it much higher.

Grant based his prediction on the assumption that the critical temperature depends on the density of particle states that are available to electrons in the material, as is the case in low-temperature superconductors. Although this density does increase with the number of copper-oxygen layers, he said, adding more layers eventually gives diminishing returns: the density no longer increases appreciably when one more layer is added. On the other hand, some researchers point out that the critical temperature of the high-temperature superconductors does not seem to depend on the density of states in any simple way.

In any case, whether workers in the field can fabricate such multilayer materials is another question. Researchers reportedly have seen four-layer phases in both bismuth and thallium preparations, but no one has isolated them. The amounts of various phases in a sample depend closely upon the processing steps, and no one has learned to process for four-layer compounds.

Besides the scientific lessons the bismuth and thallium superconductors teach, they may also prove to be valuable as easier-to-work-with alternatives to the yttrium-based compounds. For instance, they are relatively insensitive to the amount of oxygen in them, while the earlier materials lose their superconductivity if a certain percentage of oxygen seeps out. And it looks as if the new materials will carry at least as much current as the yttrium compound—bulk samples of the thallium material reportedly carry 1000 amperes per square centimeter at 77 K in zero magnetic field, much more than the yttrium compound at a corresponding stage of development.

Session organizer Datta said the discovery of the thallium compounds at the University of Arkansas my have an important psychological effect as well. Although Chu's group at the University of Houston made the initial breakthrough in high-temperature superconductors, Datta said he thinks some American researchers have been "demoralized" by the strong efforts of the Japanese to commercialize the materials. "This work puts us back in the leadership position," he said.

On the negative side, the thallium and bismuth materials suffer some of the same handicaps as the yttrium superconductors. Laura Greene of Bell Communications Research said the new materials, like the earlier ones, are ceramics and so will probably have the same mechanical problems of brittleness and inflexibility.

And the thallium materials have a definite shortcoming for the researchers working with them—thallium is extremely toxic. Although the finished products may prove to be safe, lab workers fabricating the thallium superconductors need to follow careful procedures. "I personally do not want to enter the research with thallium compounds," said Georg Bednorz of IBM-Zurich. Bednorz, who won the 1987 Nobel Prize for physics with Alex Müller for their discovery of 30 K superconductors which started the whole high-temperature revolution, said he expects that the thallium will eventually be replaced by better, safer elements. "I have the feeling that it's a transient period."

Both Chu and Hermann predicted superconductivity will go much higher. Chu is still hopeful for room-temperature superconductivity (around 300 K), while Hermann said his "gut feeling" is that it will go to 230 to 240 K. ■ ROBERT POOL

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