IBM Wins a Patent for Thallium Superconductor

But the materials were discovered by Allen Hermann of the University of Arkansas, whose own patent claim is still pending

IBM HAS BEEN AWARDED PATENT RIGHTS to the highest temperature superconductor now known—a thallium-based material that loses electrical resistance at 125 K. The announcement came as a surprise to many observers because the material was first discovered by Allen Hermann at the University of Arkansas. The U.S. Patent Office gave IBM priority apparently because the company's scientists were the first to discover how to process the material to produce a critical temperature of 125 K.

The ruling may do more than irritate Arkansas's Hermann—it could have implications for other pending patent disputes, including one between the University of Houston and three other claimants for the rights to $YBa_2Cu_3O_{7-x}$, the first superconductor discovered that works at liquid nitrogen temperature and still the best candidate for various applications (*Science*, 1 September, p. 931). These awards can be worth a great deal—the University of Houston sold its patent rights to $YBa_2Cu_3O_{7-x}$ to Du Pont for as much as $5.5 million, even though it has not yet received a patent (*Science*, 2 September 1988, p. 1156).

In late February 1988, Hermann and co-workers announced they had found superconductivity in a thallium-based compound. The materials had onset—the initial drop in resistance that precedes full superconductivity—at 120 K and zero resistance at 100 K. Hermann's group identified two compounds in the samples, $Tl_2Ca_1Ba_2Cu_2O_{8+x}$ and $Tl_2Ca_2Ba_2Cu_3O_{10+x}$, and gave details of their crystalline structure. Within a few days, researchers at IBM's Almaden Research Center had not only reproduced these results but had come up with a greatly improved processing technique. "What we were able to do was to develop a set of processing conditions and beginning compositions that allowed us to achieve a record critical temperature," said Edward Engler, a member of the IBM team.

"I don't think that what we did was obvious," Engler said. "If you don't process it right, you don't get a material that is superconducting at 120 K." At the time, researchers knew that $YBa_2Cu_3O_{7-x}$ was best prepared with a starting composition that matched its 1-2-3 ratio of yttrium, barium, and copper. This didn't work with the thallium material, however. Starting with a 2-2-2-3 ratio of thallium, calcium, barium, and copper gave a blend of the 2-2-2-3 phase and the 2-1-2-2 phase, plus other compounds, and the composite had zero resistance at just over 100 K.

IBM found that the ideal starting ratio was 1–3-1–3 for thallium, calcium, barium, and copper. This gave the greatest proportion of $Tl_2Ca_2Ba_2Cu_3O_{10+x}$ in the end product, yielding superconductivity at 125 K. For this discovery, the Patent Office awarded IBM a composition of matter patent.

What it will award Hermann is still unclear. Bob Barrett, a patent attorney representing the University of Arkansas, said the Patent Office can still give the university a general patent on the entire thallium system. In that case, the IBM patent would be subordinate to the Arkansas claim. Barrett pointed out that specific patents are often granted first and the broader, dominating patents come out sometime later.

Hermann, on the other hand, is concerned that the Patent Office might not recognize his broad claim to the thallium system. "The inventors of the system don't seem to be able to get patent coverage, and I don't know what to do about that," he said.

Bob Hazen, a geophysicist at the Carnegie Institution of Washington who worked with Hermann on the thallium material, said the IBM patent underscores the conflict between scientific openness and patent considerations. If Hermann had kept quiet until he found the right processing technique to reach 125 K, he would have had a much stronger claim. Instead, as soon as he had determined the structure of the material, he sent copies of his work to a number of laboratories, including IBM. "There's no question that Hermann is being penalized tremendously for being open with IBM," Hazen said. ■ ROBERT POOL

Zero Resistance at 250 K?

J. T. Chen, a physicist at Wayne State University in Detroit, says he has produced a material that loses its resistance to electricity at temperatures up to 250 K. That's almost double the critical temperature of today's best high-temperature superconductors. He warns, however, that the effect may not be due to superconductivity—or at least not to the same type of superconductivity that has been the object of so much research over the past 3 years.

The superconductivity, if that is what it is, has been hard to pin down. Many researchers, including Chen, have reported seeing hints of superconductivity in various materials at temperatures over 200 K, but they have always vanished as the sample was heated and cooled. Chen says he and co-workers from Wayne State and Ford Motor Company finally figured out how to stabilize the phenomenon.

Chen made the samples from a starting composition of $Y_5Ba_6Cu_{11}O_y$, using standard processing steps for a ceramic superconductor. The key modification, Chen says, was to keep the samples in an oxygen atmosphere throughout the testing cycle. Analysis of the samples shows they consist of a number of different compounds, he says. The predominant ones are $YBa_2Cu_3O_{7-x}$, Y_2BaCuO_5, and CuO, but there are signs that other compounds exist inside the complicated concoction.

Four samples have displayed electrical resistance so low that it is undetectable at temperatures up to 250 K. This behavior is reproducible, Chen says. Indeed, one sample was heated and cooled 29 times before the effect went away. However, he has not seen the Meissner effect, a magnetic behavior that all superconductors exhibit. Since the only samples that show zero resistance at 250 K are those with several phases, or different compounds, Chen surmises he may be seeing an interface phenomenon—an effect that depends on interactions between the different phases. In this case, the zero resistance would not be superconductivity, but a new phenomenon.

The results will appear in *Modern Physics Letters B* in November, Chen says. Other superconductivity researchers were generally unwilling to comment on Chen's claims, since few of them had seen the preprint. But some said the results were believable, given the number of different scientists who have seen resistance drops in the neighborhood of 250 K. ■ ROBERT POOL