CC/NUMBER 14
APRIL 5, 1993

This Week's Citation Classic

Cava R J, Batlogg B, van Dover R B, Murphy D W, Sunshine S, Siegrist T, Remeika J P, Rietman E A. Zahurak S & Espinosa G P. Bulk superconductivity at 91 K in single-phase oxygen-deficient perovskite $Ba_2YCu_3O_{9-6}$ *Phys. Rev. Lett.* **58**:1676-9, 1987. [AT&T Bell Laboratories. Murray Hills. NJ|

We identified and prepared in pure form the high-temperature superconducting compound in the chemical system Y-Ba-Cu-O, an orthorhombic, oxygen-deficient perovskite of stoichiometry $Ba_2YCu_3O_7$. Basic physical parameters were estimated. The critical current density in a bath of liquid N_2 at 77 K exceeded 1,100 A/cm^2. [The *SCI*® indicates that this paper has been cited in more than 1,260 publications.]

The Identification of the First 90 K Superconductor

Robert J. Cava
AT&T Bell Laboratories
Murray Hill, NJ 07974

Superconductivity is the uncanny ability of some elements, metal alloys, or chemical compounds to carry electrical current without the loss of any energy; their resistivity is theoretically (and often practically) zero. Unfortunately this property generally occurs at temperatures close to absolute zero, restricting significantly its application in real-world technologies: The most familiar application is in modern magnetic resonance imaging machines, which employ superconducting magnets. Late in 1986 Georg Bednorz and Alex Muller, at IBM Research in Zurich, published a paper in *Zeitschrift fur Physik** showing a transition to a superconducting state near 28 Kelvin in a ceramic sample made by firing La_2O_3, CuO, and BaO together at high temperatures. The previous record high temperature, 23 K, established in the mid -1970s, was for the metal alloy Nb_3Ge. The Bednorz-Muller superconductor ignited a scientific revolution for which they received the 1987 Nobel Prize in physics.

The Bednorz-Muller ceramic sample contained a mixture of tiny crystallites of several different chemical compounds. S-i. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka at the University of Tokyo soon found that the superconductivity was occurring in one particular compound in the mixture, of stoichiometry $La_{,a}Ba_{0.2}CuO_4$.[2] Kitazawa visited Bell Labs for one day in mid-December of 1986, and, having just gotten the information about the identity of the superconducting compound by telephone from his collaborators, gave an informal seminar on their results, advertised only through word of mouth in the hallways. I went to the seminar on a whim, not knowing anything about superconductivity, and sat quietly in the back row. During his talk, however, I realized that my background, in solid-state chemistry, was perfect for working on this potentially exciting new material. Bruce van Dover and Bertram Batlogg, experts in superconductivity, were also at the talk.

That night my technician Ed Reitman and I had our first ceramic superconductor sample in the furnace. We quickly formed a collaboration with Bruce and Bertram, and during the Bell Labs Christmas Party on December 24, 1986, sent a paper by express mail to *Physical Review Letters* showing that by substitution of Sr for Ba in the University of Tokyo formula, the superconducting transition could be raised to a surprising 36 K.[3] We later learned that the Tokyo group had found the same result and had submitted a paper to a different journal a day or two earlier than ours.[4] Meanwhile a group led by M.K. Wu and C.W. Chu at the Universities of Alabama and Houston was investigating the properties of the original Bednorz-Muller mixed compound formulation.[3] Apparently, only a handful of groups were working on the new materials; most physicists and materials scientists were probably enjoying the relaxation of the holiday season, not aware of the brew that was beginning to cook up.

Then, some time around February 1987 rumors began circulating that the Wu-Chu group had seen the impossible: superconductivity at 90 K, above the temperature of liquid nitrogen (77 K), a convenient, inexpensive liquid coolant. The chemical ingredients were a closely held secret. (Although there apparently was a rumor going around that the samples contained Yb, we never heard it.) The world of physics was stood on its head. The superconductors were rumored to be *green,* with a color photograph of Chu holding a green ceramic disk even appearing in *Time* magazine.[6] Conventional thinking would say that a ceramic superconductor could not possibly be green, as the metallic conductivity would have to make the material black, or at least bronze, in color; but this was clearly no conventional phenomenon.

Finally, more details of the Wu-Chu results were announced just before the publication of their paper in *Physical Review Letters.*[7] The 90 K superconductivity had been observed in a ceramic sample with a seemingly innocent variation of the original Bednorz-Muller formulation, made by mixing Y_2O_3, CuO and BaO and firing. (Y is in the same chemical family as La.) In their publication the Wu-Chu team suggested that a mixture of crystallites of different compounds might be necessary for the ceramic to display 90 K superconductivity. Superconductivity was suggested to be an interfacial effect due to complex physics at the interface between an insulating dielectric (which is what made their samples green) and a metallic conductor. We, on the other hand, believed that the superconductivity m ust be associated with only one of the compounds mixed up in the Wu-Chu ceramic, and began feverishly to try to identify the compound responsible.

Working around the clock for several incredible days we found that the superconductivity was occurring in a never before isolated compound, $Ba_2YCu_30_7$. A patent was filed for the new material, and a day later this paper was submitted to *Physical Review Letters* and sent in preprint form by express courier around the world. The information it presented became the foundation for thousands of groups initiating work on the new material. The paper not only gave the exact chemical formula for the superconducting compound and presented a recipe for how to make it in pure form, it also presented a table with the first estimates for some important physical parameters, highlighting the uniqueness of the electronic state of the new materials. These first samples could carry electrical currents in excess of 1,000 amperes per square centimeter in a bath of liquid nitrogen at 77 K, suggesting great promise for future applications.

These were just the first months in a revolution which is still in progress. We have stayed in the thick of the battle, finding many of the new high temperature superconductors that were to follow.[8,11] Nothing that came after could compare with the intensity of those wonderful early days. For our part, it was a great pleasure to be able to get the information in this publication outto our colleagues in atimely manner. It will always serve for me as a reminder of those exhilarating times when we thought that anything could happen: when any day we had the chance of discovering a new extraordinary superconductor that might change the way people live.

1. **Bednorz J G & Müller K A**. Possible high f. superconductivity in the Ba-La-Cu-0 system. *Z Phys. B—Condens. Matter* **54**:189-93! 1986. (Cited 4.355 times.)
2. **Lchida S-i, Takagi H, Kitazawa K & Tanaka** S. High T. superconductivity of La-Ba-Cu oxides. *Jpn. J. Appl. Phys. Pi. 2* **26**:1.1-2. 1987. (Cited 305 times.)
3. **Cava R J, van Dover R B. Batlogg B & Rielman E A.** Bulk superconductivity at 36 K in $La_{1.8}Sr_{0.2}CuO_4$ *Phys. Rev. Lett.* **58**:408-10. 1987. (Cited 740 times.)
4. **Takagi H, Uchida S-i, Kitazawa K & Tanaka** S. High-r superconductivity of La-Ba-Cu oxides. II.—Specification of the superconducting phase. *Jpn. J. Appl. Phys. Pi. 2* **26**:L123-1. 1987. (Cited 195 times.)
5. **Chu** C W, **Hor P H, Meng R L. Gao L, Huang Z J & Wang Y Q.** Evidence for superconductivity above 40 K in the La-Ba-Cu-O compound system. *Phys. Rev. Lett.* **58**:405-7. 1987. (Cited 1.020 times.)
6. **Lemonick M D.** Superconductivity heats up: breakthroughs in transmitting electricity without energy loss. *Time* 2 March 1987. p. 62.
7. Wu **M K. Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L. Huang Z J, Wang Y Q & Chu** C **W.** Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-0 compound system at ambient pressure. *Phys. Rev. Lett.* **58**:908-10. 1987. (Cited 3,430 times.)
8. **Cava R J, Batlogg B. Krajewski J J, Farrow R, Rupp L W. Jr.. White A E, Short K, Peck W F, Jr. & Kometani T.** Superconductivity near 30 K without copper: the $Ba_{0.6}K_{0.4}BiO_3$ perovskite. *Nature* **332**:814-6. 1988. (Cited 380 times.)
9. **Cava R J, Batlogg B, Krajewski J J, Rupp L W, Jr., Schneemeyer L F, Siegrist T, van Dover R B, Marsh P. Peck W F, Jr., Gallagher P K, Glarum S H, Marshall J H, Farrow R C, Waszczak J V, Hull R & Trevor P.** Superconductivity near 70 K in a new family of layered copper oxides. *Nature* **336**:211-4. 1988. (Cited 235 times.)
10. **Cava R J, Batlogg B. van Dover R B, Krajewski J J, Waszczak J V. Fleming R M, Peck W F, Jr., Rupp L W. Jr., Marsh P. James A C W P & Schneemeyer L F.** Superconductivity at 60 K in $La_{2-X}Sr_XCaCu_2O_6$: the simplest double-layer cuprate. *Nature* **345**:602-4. 1990.
11. **Cava R J, Krajewski J J, Takagi H, Zandbergen H W, Van Dover R B, Peck W F, Jr. & Hessen B.** Superconductivity at 28 K in a cuprate with a niobium oxide intermediary layer. *Physica C* **191**:237-42. 1992.

Received February 5. 1993