Bednorz and Müller Win Nobel Prize for New Superconducting Materials

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BEDNORZ AND MÜLLER WIN NOBEL PRIZE FOR NEW SUPERCONDUCTING MATERIALS

Georg Bednorz and Alex Müller (IBM Zurich Research Laboratory at Rüschlikon, Switzerland) share this year's Nobel Prize in Physics for "their discovery of new superconducting materials." The announcement of the prize, worth \$340 000 this year, caused little surprise among physicists. Few doubted that the discovery by Bednorz and Müller merited the Nobel Prize; speculations on what year the prize would be awarded have abounded since last January.

Alex Müller and Georg Bednorz (right) at the IBM Zurich Research Laboratory in Rüschlikon, Switzerland.

In the spring of 1986, Bednorz and Müller reported the onset of superconductivity in a mixed-phase oxide of lanthanum, barium and copper at temperatures about 10 K higher than any previously known for superconductivity. Since the early 1960s, the superconductors with the highest known critical temperatures had been found among intermetallic materials with the so-called A15 structure; the last increase in T_c had occurred in 1973 with successful synthesis of thin films of Nb_3Ge. The search for high-temperature superconductors then lost direction when efforts in the late 1970s to raise the T_c even higher in the A15 materials were abandoned because the maximum critical temperature in A15 niobium–silicon compounds could not be raised above 20 K.[1]

About three months after the discovery by Bednorz and Müller was confirmed in November 1986, Paul (C. W.) Chu (University of Houston) reported superconductivity above 90 K; Chu disclosed the composition of the 90-K material, an oxide of yttrium, barium and copper, two weeks later. Obtaining superconductivity above 77 K, the boiling point of liquid nitrogen, had been a psychological barrier that many experts felt had to be broken before large-scale applications of superconductivity would be economically viable. Many properties of the new oxide superconductors must be optimized before they can be turned into useful devices, but groups led by Praveen Chaudhari at IBM (Yorktown Heights, New York) and by Malcolm Beasley and Theodore Geballe at Stanford University demonstrated this summer that the critical current, an important parameter for many applications, is not inherently small in the new superconductors. Because of the allure of the new markets that applications of superconductivity might generate, the worlds of engineering and technology, business and finance, politics and science policy have all felt the impact of the developments in superconductivity since Bednorz and Müller made their discovery.

The Swedish Academy announcement says: "Bednorz and Müller stand out clearly as the discoverers of this specific superconductivity. They have inspired other researchers to synthesize substances which are superconducting at temperatures more than four times higher (reckoned from the absolute zero at $-273\,^{\circ}C$) than the earlier ones. The development is being followed with interest by workers in electrotechnology and microelectronics, and by physicists who envisage exciting new applications in measurement technology." The academy characterizes the breakthrough by Bednorz and Müller as a "result of systematic work, deep insight and experience of structural problems in the physics and chemistry of the solid state . . . [and] the audacity to concentrate on new paths in their research."

Bednorz and Müller carried out a

detailed and determined search for superconductors with high critical temperatures among oxides with metallic properties. They were motivated to undertake this search by the properties of the superconducting phase of $BaPb_{1-x}Bi_xO_3$ and $LiTi_2O_4$. The critical temperature of $BaPb_{1-x}Bi_xO_3$ varies with x. The highest T_c is only 13.7 K, but the electronic density of states is significantly smaller than in superconductors with comparable critical temperatures.[1] Bednorz and Müller argued that the lower density of states in oxide superconductors was probably compensated for by the enhanced electron–phonon interaction. In the theory of John Bardeen, Leon Cooper and Robert Schrieffer, electrons in the superconducting state are paired by their interaction with lattice vibrations, or phonons. The critical temperature in the BCS theory increases with the strength of the pairing interaction, which in turn increases with both the electron–phonon coupling and the electron density. But at none of the many laboratories around the world that studied $BaPb_{1-x}Bi_xO_3$ in great detail was the possibility of examining other oxides for superconductivity seriously considered. Bednorz and Müller, in contrast, regarded the unusual properties of $BaPb_{1-x}Bi_xO_3$ seriously and saw in them a possibility of finding superconductors with high critical temperatures. Increasing the electron density in oxides to values comparable to those in good metals, for example, might allow a way to realize this possibility, they reasoned. Based on their knowledge of the structure and properties of oxides, Bednorz and Müller concentrated on oxides containing copper or nickel in mixed-valence states, that is, oxides in which a fraction of the transition metal ions are in one valence state and another fraction are in a different valence state.

"Alex reminded me recently that he did not have to use very strong arguments to convince me to look for superconductors among metallic oxides," Bednorz told us at an interview we had with the two laureates on 28 October in Yorktown Heights. The search started in the summer of 1983; the breakthrough occured in January 1986. Bednorz told us that he searched the literature for known oxides of copper and nickel and studied carefully whatever was known about their high-temperature properties. Metallic behavior for electrical conductivity, he said, was an important criterion in selecting the compounds they tried for superconductivity. The search started with $LaNiO_3$, a metal in which nickel is in valence state +3. According to Bednorz, they tried to change the electronic bandwidth of the materials internally, by substituting aluminum for nickel, for example. But the substitution was not successful: La-Ni-Al-O became insulating by cooling. "We then tried substitution on the lanthanum sites," Bednorz said. "We tried yttrium; at that time we easily missed discovering the 90-K superconductor. But we got insulating material. We had the wrong combination—yttrium with nickel instead of copper. But that's life! Our breakthrough came much later." The focus of the search shifted to copper because partial substitution of copper for nickel in $LaNiO_3$ improved the metallic properties. In the course of a literature search, Bednorz learned about the work of Claude Michel, L. Er-Rakho and Bernard Raveau (Université de Caen) on Ba-La-Cu-O, soon after it was published in 1985. "Having worked already with a few copper substitutions, when I saw this material, I realized one could do something with copper alone and with replacement of lanthanum by two-valent barium," Bednorz said. And he and Müller did something quite wonderful with it. In their first paper, they reported resistivity measurements on samples of $La_{5-x}Ba_xCu_5O_{5(3-y)}$ for $x = 1$ and 0.75, and y positive, that showed onset of superconductivity above 30 K.

One might feel tempted to regard as serendipitous the events that led Bednorz and Müller to the discovery of superconductivity in Ba-La-Cu-O. But as experts around the world found out last winter, ternary oxides are very complicated materials. Several stable chemical compositions are possible for a given set of elements, and among oxides with the same set of elements but different compositions some are insulators and some good conductors. Moreover, the ones that are superconducting at low temperatures are extremely fragile chemically and lose oxygen readily. But their conductivity in the normal state as well as the transition to the superconducting phase depends sensitively on the oxygen content. For example, in the measurements Bednorz and Müller reported in their first paper, the resistivity of the superconducting sample began to rise at temperatures below about 100 K. Because the resistivity of good metals continues to decrease with decreasing temperature, we asked Bednorz and Müller why, in view of their search for superconductors among metallic oxides, they even bothered to measure the resistivity to very low temperatures. "We did a systematic and careful study, and even if the resistivity went up to extremely high values at low temeperatures, we always went down to liquid helium temperature [4.2 K] in order to have a complete set of data," Bednorz replied. Furthermore, both Bednorz and Müller said they were aware that the resistivity of thin films of $BaPb_{1-x}Bi_xO_3$ also increases before the onset of superconductivity, especially if the films do not have the right amount of oxygen.

The discovery by Bednorz and Müller has engendered unprecedented, worldwide research activity in superconductivity. The story of some of the major developments their work has spawned and the rapid pace at which these occurred has become somewhat of a legend. Their first paper was received at the editorial office of *Zeitschrift für Physik* on 17 April 1986; it was published in the September issue of the journal. The paper received little attention. But Shoji Tanaka's group at the University of Tokyo (see the article on page 53) and Chu's at the University of Houston independently confirmed superconductivity in Ba-La-Cu-O after they saw the paper by Bednorz and Müller in *Zeitschrift für Physik*. The groups presented their evidence at an impromptu session of the Materials Research Society meeting in Boston on 5 December 1986. The Tokyo group had by this time independently determined $La_{2-x}Ba_xCuO_{4-y}$ to be the superconducting phase, as had Bednorz, Müller and their collaborator M. Takashige, and both groups had obtained further evidence of superconductivity by measuring the Meissner effect, or magnetic flux exclusion. But Bednorz, Müller and Takashige did not circulate any preprints reporting their work on the Meissner effect, although they had completed the work in the beginning of October.

"When in October I saw the results from Zurich on the Meissner effect," Richard Greene (IBM Yorktown Heights) said, "I believed that Bednorz and Müller had indeed discovered a new, higher-temperature superconductor." Chaudhari told us that he brought back a few superconducting samples from Zurich, and Greene started in late October experiments on specific heat and on determining the strengths of the critical magnetic fields that destroy superconductivity. "During 1986, we at IBM proceeded cautiously," Chaudhari said. "Even though we were convinced that Bednorz and Müller had discovered a new high-temperature superconductor, Alex and I discussed studying time-dependent properties such as persistent currents to make sure we understood why the Meissner effect was so small." But the news from Boston spread fast. In the last week of December, several groups from around the world reported that the critical temperature for superconductivity in the oxide studied by Bednorz and Müller could be raised to about 40 K by replacing barium with strontium. And Chu stunned the world of physical sciences with his announcement on 16 February that he and his collaborators had obtained superconductivity above 90 K in an oxide material. Chu's paper reporting the discovery was received at the editorial office of *Physical Review Letters* on 6 February; he announced the discovery, he told us, only after the paper was accepted for publication. Chinese and Japanese physicists announced in the last week of February that they had independently discovered superconductivity above 90 K. As a result of these developments, a hastily arranged special session on the new superconductors at the annual March meeting of The American Physical Society in New York turned into a historic occasion and was dubbed the "Woodstock of physics." The theme song at this Woodstock was one–two–three, after the chemical composition $RBa_2Cu_3O_{7-y}$, where R is a rare earth element, of the materials with T_c above 90 K. (See PHYSICS TODAY, April 1987, page 17.)

Several chapters in standard textbooks in solid-state physics may have to be rewritten when the properties of the new superconducting oxides and the mechanism of superconductivity in them are properly understood. Many theorists have proposed novel mechanisms for superconductivity in the oxides because they believe that phonon-mediated pairing of electrons cannot give critical temperatures as high as 90 K. The critical temperature of the 90-K materials changes negligibly with the isotopic mass of the various elements. (See PHYSICS TODAY, July, page 17.) Theorists regard this lack of the isotope effect as evidence that pairing of electrons in the oxide superconductors is mediated by an electronic or magnetic excitation and not by phonons. We asked Bednorz and Müller how high they thought they could raise the critical temperature when they set out on their search and whether any of the limits that theorists have discussed on how high the T_c can be in the phonon mechanism in any way discouraged them in their research. Müller related an anecdote in reply. During his sabbatical at IBM Yorktown Heights (1978–80), he said, he collaborated with Melvin Pomerantz on an experiment on microwave absorption in thin films of granular aluminum. The critical temperature of the films, composed of small, oxide-coated grains of aluminum, was about two times that of pure aluminum which has a T_c of 1.1 K. Müller found that very interesting and wondered whether a similar enhancement in T_c could be obtained in metallic superconductors whose critical temperatures were already in the 10–15-K range. But the theorists told him that because of its low T_c, aluminum is described by the weak-coupling BCS theory, but that the enhancement was not possible in superconductors with T_c of 10–15 K, which are better described by the so-called strong-coupling theory. "After I heard this," Müller said, "I decided not to listen to theorists anymore."

How much longer would Bednorz and Müller have continued their search if they had not discovered superconductivity in January 1986? "We were quite persistent," both the laureates smiled and said. What was the next combination on their list? Did they have a list? "We had a list, and we still have one in the lab. Maybe we will meet each other again in a few years and I will then tell you more about our list," Bednorz said. Details of the three-year search at IBM Zurich, it seems, will provide grist for the mill of historians and sociologists of science for many years.

Müller got his master's and doctoral degrees in physics at the Swiss Federal Institute of Technology (ETH) in Zurich in 1952 and 1958. He was a staff member at the physics department of ETH from 1952 to 1958. He was next a project manager at the Batelle Institute, Geneva, from 1959 to 1963. Müller was appointed as a lecturer at the University of Zurich in 1962 and was made Titular Professor in 1970. He joined the IBM Zurich Research Laboratory as a research staff member in 1963, managed its physics department from 1972 to 1985, and has been an IBM Fellow since 1982. "It is very satisfying that our work has generated so much interest and has been recognized by the Swedish committee," Müller said about winning the Nobel Prize less than a year after his work with Bednorz was accepted by their colleagues. "We never thought about the prize," he added. "We only wanted to go beyond the intermetallic A15 compounds."

Bednorz got his undergraduate degree at the University of Münster in 1976 and his doctorate at ETH in 1982. He did research for his PhD thesis at IBM Zurich under Müller's supervision. He has been a research staff member at IBM Zurich since 1982. "It is hard to describe," he said when we asked him about what it feels like to win the Nobel Prize. "I have to look at myself.... I have to learn," he added.

—ANIL KHURANA

Reference

1. For a summary of major developments in superconducting materials in the past two decades, see, for example, M. R. Beasley, T. H. Geballe, PHYSICS TODAY, October 1984, p. 60.

TWO-NEUTRINO DOUBLE β-DECAY SEEN; NEUTRINOLESS DECAY SOUGHT

Many nuclei with even numbers of protons and neutrons can undergo double beta decay, emitting two electrons and two neutrinos, but the halflife for this process is so long that it had been deduced until recently only by measuring the abundance of daughter nuclei from double beta decay of elements in geologic materials. Now Steven Elliott, Alan Hahn and Michael Moe of the University of California at Irvine have observed the double beta decay of selenium-82 in their laboratory and determined its halflife to be $1.1^{+0.8}_{-0.3} \times 10^{20}$ years,[1] a time interval that is orders of magnitude longer than any previously detected in a laboratory. Besides being a feat in its own right, the Irvine measurement is a milestone en route to a more elusive goal—observation of a double beta decay in which two electrons but *no* neutrinos emerge. This neutrinoless decay, which proceeds by the exchange of a virtual neutrino between the two neutrons, can occur only if neutrinos have mass. It is strictly forbidden by the standard theory of electroweak interactions but is predicted as a manifestation of the small symmetry breaking that arises in some grand unified field theories.

The Irvine measurement of a two neutrino double beta decay rate gives hope that future experiments may be sensitive even to very low rates for the neutrinoless double beta decay. It