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High-temperature superconductivity

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Superconductivity

Upon cooling metallic conductors, in general their resistance becomes smaller. In 1911, the Dutch physicist H. Kamerlingh Onnes observed that the resistance of mercury disappeared entirely below a temperature of −269°C (1). He had discovered the first superconductor. In the absolute temperature scale, −269°C corresponds to +4.3 degrees K. Shortly afterwards, the disappearance of the resistivity of lead at 11 K was observed. Since then, higher and higher superconducting transition temperatures (T_cs) have been found in various metals over the years, until in 1973 a temperature of 23.3 K was attained in Nb_3Ge by Gavaler *et al.* and Testardi *et al.* as cited in ref. 2. Until 1986, all attempts to find metals with higher T_cs had failed. Fig. 1 shows the time evolution of the T_cs reached with the various compounds. Extrapolating linearly from 1911 to 1973, one could expect to reach 30 K in 1990. One sees that by the end of last year, when about 40 K had been reached, this expectation had been exceeded by far.

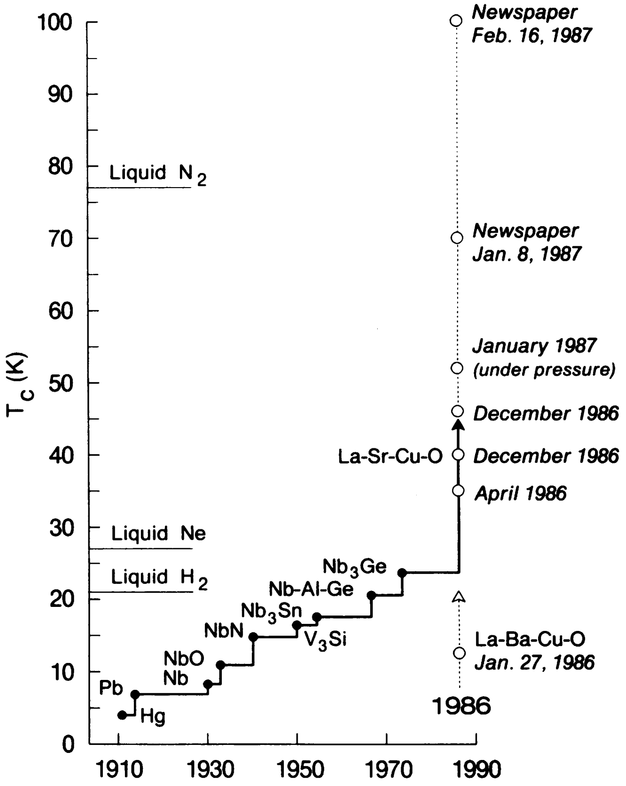

FIG. 1. Evolution of the superconductive transition temperature since the discovery of the phenomenon.

Applications

After the discovery of superconductivity, the lossless transmission of electrical energy and the generation of high magnetic fields were considered. However, in the so-called type I superconductors of which lead is a prototype, the phenomenon disappeared abruptly at a low critical current density j_c and a critical magnetic field H_{c_1} of the order of only 1000 Gauss (0.1 Tesla). The latter is the result of the magnetic field penetrating the superconductor entirely at H_{c_1}, as its supraenergy is smaller than the magnetic-field energy. In the intermetallic compounds NbN or Nb_3Sn (Fig. 1) discovered in the early 1950s, the superconductivity disappears gradually in a magnetic field because in these compounds the fields can partially penetrate the superconductor. These are so-called type II superconductors with H_{c_2} exceeding 200,000 Gauss (20 Tesla). Wires of such compounds can carry large currents with densities up to 5000 A/mm^2. Consequently, it was possible to construct magnets to generate very high fields. They are used in high-energy physics to deflect charged particles, such as electrons and protons, traveling at near relativistic speeds in accelerators. Magnets using such superconductors recently also made possible the nuclear magnetic resonance (NMR) tomography in medicine with resolutions of organs of 1 mm (for a review, see ref. 3).

Important applications became possible with the observation of the Josephson effect named after the theoretical physicist who predicted it (4): a superconductor–insulator–superconductor element can carry a supercurrent I_s in the absence of an applied voltage V, and its current–voltage (I–V) characteristic is highly nonlinear because of the energy gap present in the superconductor as understood by the famous Bardeen–Cooper–Schrieffer theory (5). The I–V nonlinearity allows the use of Josephson elements in microwave receivers and signal processors down to submillimeter wavelength. Two Josephson elements connected electrically in parallel form a superconducting quantum interferometer called a "squid." With such squids, it is possible to measure very tiny magnetic fluxes that are quantized in the loop formed by the two junctions. Therefore, they can be used to detect extremely low magnetic fields such as those that result from currents in the brain. Nowadays, squids are also used in detectors for gravitational quantum waves. At present, Josephson elements are not so much in the limelight as

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Abbreviations: T_c, superconducting transition temperature; H_{c_1} and H_{c_2}, critical magnetic fields for type I and II superconductors, respectively.

computer-switching elements because they are of a passive nature (no amplification like in a transistor) and, therefore, require very low tolerances in their fabrication.

The Discovery at the IBM Zurich Research Laboratory Rüschlikon

All superconductors discovered up to 1973 had to be cooled by liquid helium under practical conditions. This rare gas has a very small latent heat. Therefore, large quantities of this expensive coolant are required and render it impractical for transport of electrical energy. Hence, it was of great importance to find new high-T_c compounds that could be cooled with liquid hydrogen, neon, or nitrogen with boiling points at 22, 27, and 77 K, respectively, as compared with He at 4.2 K. These much cheaper coolants have a latent heat up to 100 times larger than He.

In Rüschlikon, on studying summaries and reviews on high-temperature superconductivity research, we were guided to the conviction that no further progress could be achieved with intermetallic compounds. This evolved into the *concept* of abandoning intermetallic compounds in *favor of metallic oxides*. In fact, in Rüschlikon, a tradition of two decades of research in structural and ferroelectric phase transitions in oxides existed, and high electron–phonon interaction was known. For instance, in metallic $SrTiO_3$ with only $n \simeq 2 \times 10^{20}/\mathrm{cm}^3$ carriers, a superconducting T_c of 0.7 K (6, 7) owing to the highest optical phonon present had been observed. Furthermore, the $Li_{1+x}Ti_{2-x}O_4$ spinel (8) and the $BaPb_xBi_{1-x}O_3$ perovskite exhibit T_cs of 13 K (9). These oxides have carrier concentrations of $\simeq 4 \times 10^{21}/\mathrm{cm}^3$, an order of magnitude smaller than that of a typical metal (10).

A large electron–phonon interaction V^* multiplied by the density of electrons n is necessary for the occurrence of high T_cs. This should be the case specifically in oxides containing Ni and Cu ions, as they may form so-called Jahn–Teller polarons (11), rather than Ti, V, or Cr ions. Therefore, from 1983 onwards, composite metallic oxides with Ni and Cu were systematically investigated. At the end of January 1986, a strong decrease in resistivity upon cooling a barium-lanthanum-copper-oxide ceramic (BaLaCuO) was observed. The onset of the decrease occurred in the best samples at 35 K, a very substantial (Fig. 2) enhancement above the 23.3 K in Nb_3Ge, and a paper was submitted to *Zeitschrift für Physik B* in April (12). X-ray investigations revealed that the ceramics contained three phases: the insulating CuO, the metallic $La_{1-x}Ba_xCuO_3$, and the layer structure $La_{2-x}Ba_xCuO_4$, which exhibited the superconducting properties. The former and latter mixed-valent phases have been investigated above 300 K in France by Michel and Raveau (13). The layer structure of La_2CuO_4 consists of alternating layers of corner-linked CuO_6 octahedra and LaO layers. In the fall of 1986, for

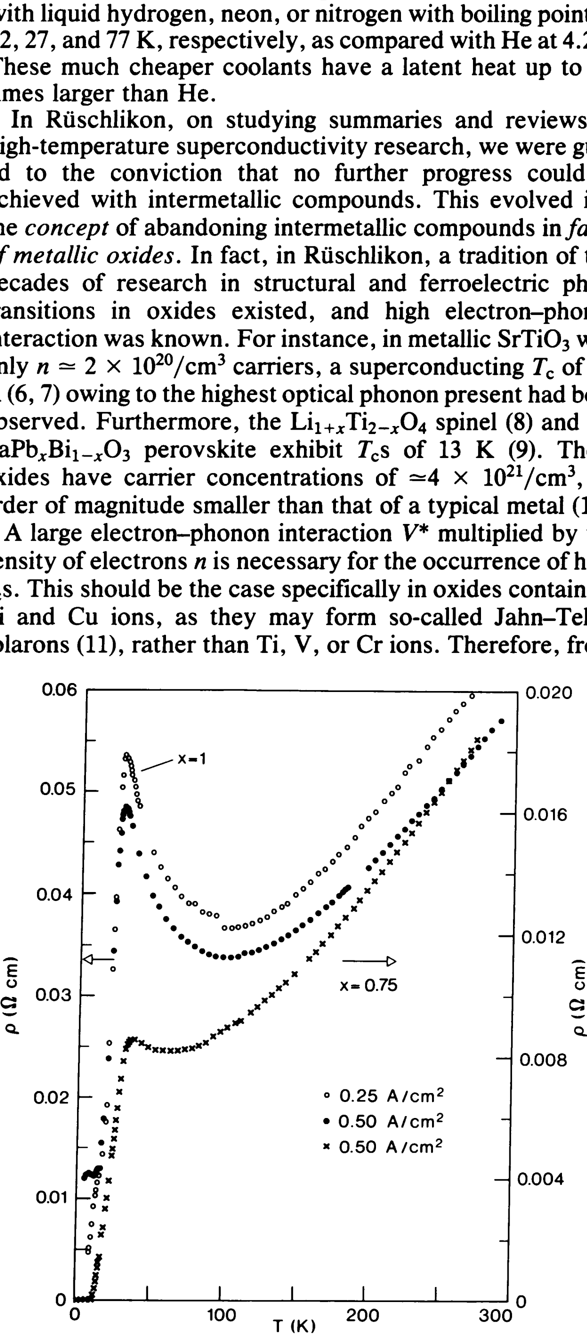

FIG. 2. Temperature dependence of resistivity in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ for samples with x(Ba) = 1 (○ and ●, left scale) and x(Ba) = 0.75 (×, right scale). The first two cases also show the influence of current density. (Reproduced with permission from ref. 12; copyright Springer-Verlag.)

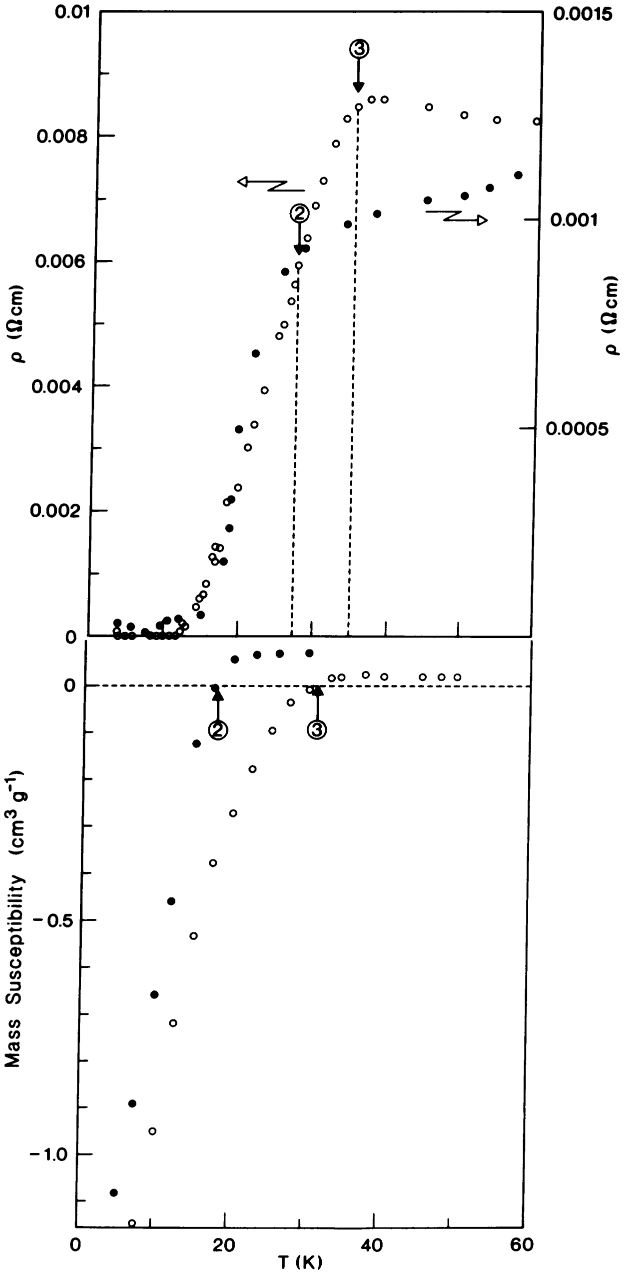

FIG. 3. Low-temperature resistivity and susceptibility of (La,Ba)-Cu-O samples 2 (●) and 3 (○) from ref. 14. Arrows indicate the onset of the resistivity drop and the paramagnetic-to-diamagnetic transition, respectively. (Reproduced with permission from ref. 14; copyright Les Editions de Physique.)

the first time, the above-mentioned magnetic-field exclusion could be detected in the superconducting $La_{2-x}Ba_xCuO_4$. These confirmatory data (14) are shown in Fig. 3.

More Recent Work

The Rüschlikon results at first met with skepticism in the USA and Europe, except for the president of the European Physical Society, W. Buckel. However, in November 1986, they were confirmed at the University of Tokyo by Professor Tanaka's group (15), who also determined the structure of La_2CuO_4 independently (16). Its production from La_2O_3, BaO, and CuO oxides by calcination at 900–1100°C is quite easy, which is also of technological importance. About a month later in the USA at the AT&T Laboratories (17) and in Professor Chu's group (18), positive results were obtained. The onset of superconductivity could be enhanced to 40 K by substituting strontium Sr^{2+} for La^{3+} instead of Ba (17). Then a group at the Chinese Academy of Science in Beijing reached an onset temperature of 46 K (19). Under hydrostatic pressure, the Houston group, still working with the IBM-Rüschlikon oxide, reached 52 K at 13 kbar (20). This finding indicated the possibility of reaching temperatures above 77 K with a modified oxide. If this could be achieved, then it would be possible to cool the conductors with the cheap liquid nitrogen, and use of superconductivity for energy transfer would become feasible if the critical currents were sufficiently high. A recent *New York Times* (21) article carried the message that 98 K has been reached in Houston, and a preprint from Bell Communications Research independently also found the same onset temperature (21–24). The enthusiasm created for high-temperature superconductivity has attracted hundreds of scientists into the field, which in the USA has been termed as "exploding" and in France as creating a "revolution." Thus, one could say that the discovery of the new class of oxide superconductors can be considered as a breakthrough worldwide. Much experimental and theoretical work has already been done to understand why this high-temperature superconductivity occurs. To review these is beyond the scope of the present article but will be done in a future one. Recent measurements indicate that the critical field H_{c_2} to destroy superconductivity could be well over a megagauss (25)!

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