Technology be established (*19*). Other, more limited proposals, with similar intent, include formation of a Department of Science, a National Technology Foundation, a National Institute for Research and Advanced Studies, and a National Applied Science Administration. As stated above, centralization is not synonymous with coordination or quality, and no good evidence can be drawn from the experiences of the countries examined to support the greater efficacy of more centralized versus more pluralistic systems. These countries run the gamut in this regard, and several countries have shifted along this spectrum in both directions (*1–3*).

Conclusions

This article demonstrates that there are many similarities and differences in the S&T policies, strategies, priorities, and practices among the six countries. In analyzing the comparative advantages and disadvantages it appears as if some of the advantages when carried to an extreme can become liabilities. For example, the U.S. reliance on project support contributes to greater flexibility, mobility, and market-orientation. It also results in less stability, less proportionate investment in infrastructure, and less general support for graduate students. Such advantages and disadvantages tend to be reversed in the other countries, although there are some notable exceptions.

It is not surprising that some of the more important recent changes appear to be designed to lessen the disadvantages while maintaining the advantages. In this way we can indeed learn from each other, adopt that which serves our individual country needs, while seeking to preserve our unique advantages.

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The Discovery of a Class of High-Temperature Superconductors

K. ALEX MÜLLER AND J. GEORG BEDNORZ

The exceptional interest in the new class of oxide superconductors and the importance of these materials are discussed together with the concepts that led to their discovery. The discovery itself and its early confirmation are summarized, including the work until the beginning of 1987. The observation of a superconductive glass state in percolative samples is also discussed.

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HIGH TRANSITION TEMPERATURE SUPERCONDUCTIVITY IN the Ba-La-Cu oxide system (*1*) was discovered by Bednorz and Müller at the IBM Zurich Research Laboratory and confirmed in early fall of 1986 (*2*). For this reason we were asked to review the progress for this special issue on "Science in Europe." Since this invitation, the work and interest in the field have been exceptional. Figure 1 shows the progression of the superconducting transition temperatures (T_c) from the discovery of the phenomenon in mercury by H. K. Onnes in 1911 (*3*) until February 1987. One notices a more or less linear increase in maximal T_c's until the 75th anniversary of the discovery. This led to the expectation of T_c's near

30 K in 1990. However, in the year of the anniversary this trend changed. By the beginning of 1987, T_c's had risen to 48 K for the original compound and its isomorphs (*4*). At the beginning of February 1987, the confirmed T_c's were over 90 K in a Ba-Y-Cu oxide found by Chu and collaborators (*5*) and nearly, but not simultaneously at Bellcore and the Academy in Beijing (*6*). Looking at Fig. 1, one notices the following: practically all of the high-T_c materials discovered until 1986 are cubic niobium compounds, and the new superconductors are layer-like copper oxides (*2, 7*), which form a new class per se. The exceptional interest is due to four factors: (i) these oxides are easy to fabricate, in contrast to the highly refractory niobates, and thus can be investigated at smaller laboratories and universities; (ii) their T_c's are very high, and so are their critical magnetic fields, H_{c2}, with estimates in the megagauss (*8*) range; (iii) they represent a considerable challenge to theoreticians, and various models have already been proposed; and (iv) they are of considerable technological importance, because in addition to the known applications (*9*) summarized in Fig. 2, they may allow cheap energy transport.

Owing to the large number of papers already submitted, nearing 100, it is not possible to review all of these efforts. Also, many of them have now been undertaken outside Europe. Rather, it was thought appropriate to summarize the achievements up to early 1987, including the original concept, which led to the discovery and which was followed by the early confirmations in Japan, the United States, and China.

The Concept

There has been a substantial effort to increase the transition temperature by alloying intermetallic compounds in many laboratories. However, for more than a dozen years, all efforts to enhance T_c over the 23.3 K reached by Gavaler (*10*) and Testardi *et al.* (*11*) in thin films of nearly stoichiometric Nb_3Ge failed. This situation and a study of representative reviews (*12*) led us in Rüschlikon to the conviction that the efforts in intermetallic compounds should not be pursued further.

The first superconducting metallic oxide was $SrTiO_3$, with a T_c of 0.3 K (*13*). Later studies in niobium-doped $SrTiO_3$ at Rüschlikon increased T_c to 0.7 K (*14*). For this T_c, the carrier concentration was only $n_c = 2 \times 10^{20}$ cm^{-3}, two orders of magnitude lower than in a metal, suggesting an extremely large electron-phonon coupling. The reason a large coupling is obtained at this small concentration is that the plasma edge lies below the highest optical phonon, which is important for Cooper-pair formation. Therefore, this phonon is unshielded. Upon increasing $n > n_c$, the plasma edge moves above the phonon and shields it, and the superconductivity disappears (*15*). However, in 1973, high-temperature superconductivity in the Li-Ti-O system with onsets as high as 13.7 K was reported by Johnston *et al.* (*16*). Their x-ray analysis revealed the presence of three different crystallographic phases, one of them with a spinel structure showing the high T_c (*17*). Two years later, superconductivity in the mixed-valence compound $BaPb_{1-x}Bi_xO_3$, a perovskite, was discovered by Sleight *et al.* (*18*). The highest T_c in homogeneous oxygen-deficient mixed crystals occurs at 13 K, with a comparatively low concentration of carriers, $n \simeq 2 \times 10^{21}$ to 4×10^{21} cm^{-3} (*19*). Therefore, according to the Bardeen-Cooper-Schrieffer (BCS) theory (*20*), a large electron-phonon coupling was present. Thus one could expect to find still higher T_c's in other metallic oxides if the electron-phonon interactions and the carrier densities, $n(E_F)$, at the Fermi level could be further enhanced. We were not aware that $n(E_F)$ is enhanced by going from three- to quasi–two-dimensional lattices, owing to the presence of a Kohn anomaly at E_F as calculated by Hirsch and Scalapino last year (*21*).

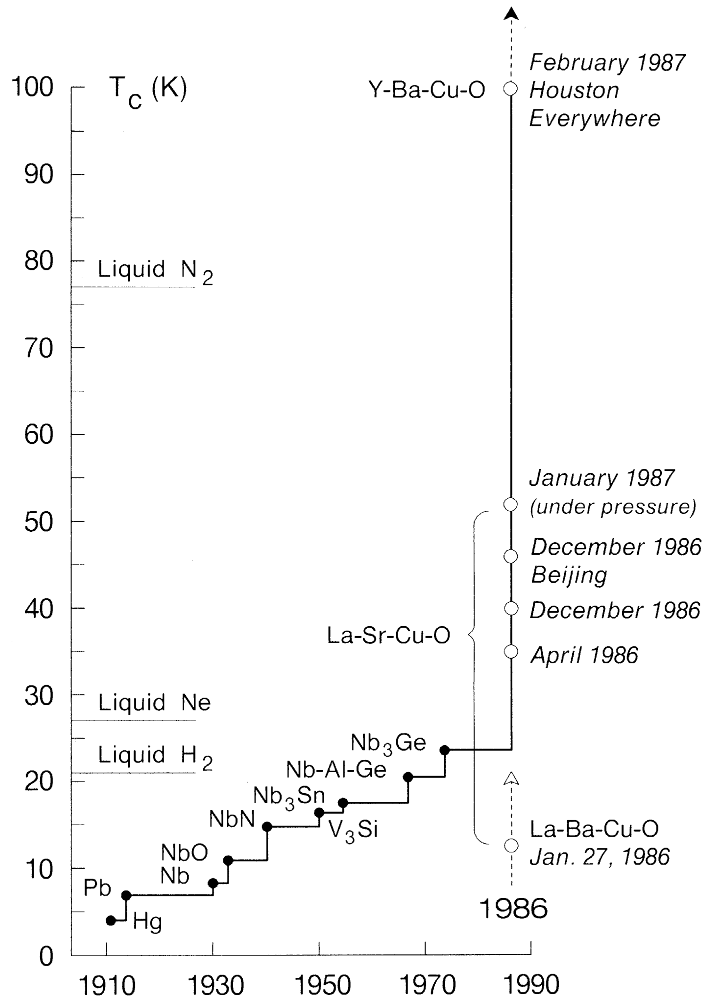


Fig. 1. Evolution of the superconductive transition temperature subsequent to the discovery of the phenomenon.

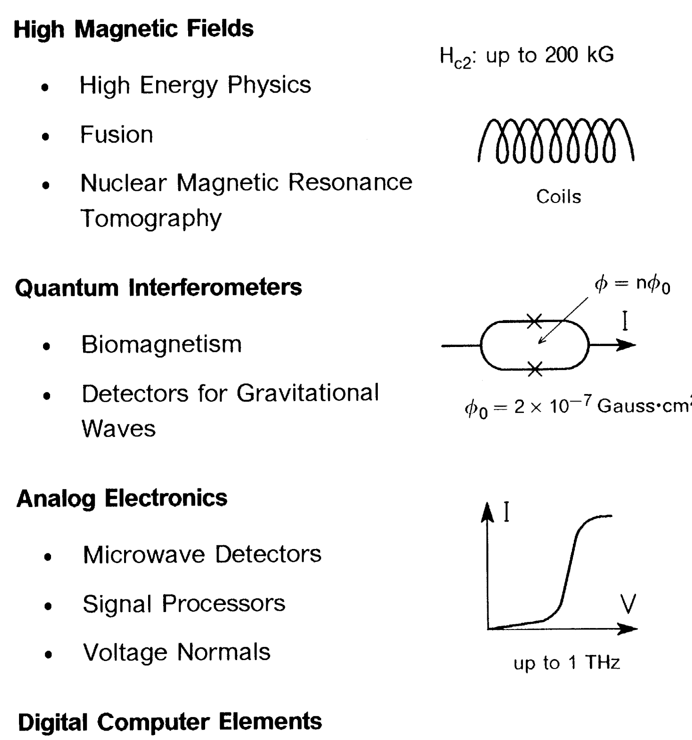


Fig. 2. Applications in superconductivity [see also (*9*)].

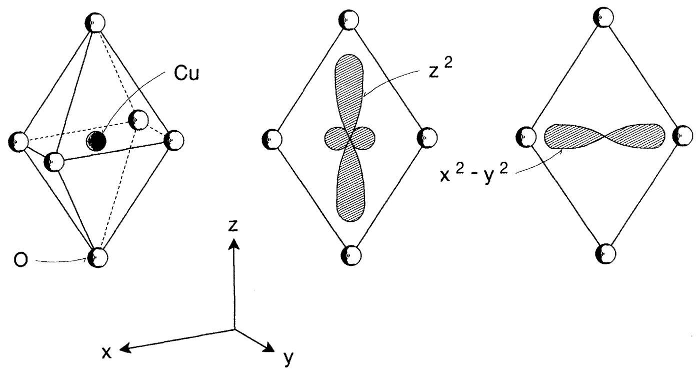


Fig. 3. The partially filled $3d$ wave functions of the Cu^{3+}/Cu^{2+} mixed-valence states. Positions of copper and oxygen atoms are shown at left.

Strong electron-phonon interactions can occur in oxides, owing to polaron formation as well as mixed-valence states. This can go beyond the standard BCS theory. A phase diagram with a superconducting to bipolaronic insulator transition was proposed early by Chakraverty (*22*) and has since been modified (*23*). A mechanism for polaron formation is the Jahn-Teller (JT) effect as studied by Höck *et al.* in a linear chain model (*24*). From it, one expects heavy polaron masses if the JT stabilization energy becomes comparable to the bandwidth of the degenerate orbitals. Isolated Fe^{4+}, Ni^{3+}, and Cu^{2+} in an octahedral oxygen environment show strong JT effects because their incompletely occupied e_g orbitals, transforming as $3z^2 - r^2$ and $x^2 - y^2$, point towards the negatively charged oxygen ligands (*25*) (Fig. 3). Although $SrFe^{4+}O_3$ is a distorted perovskite insulator, $LaNiO_3$ is a JT undistorted metal in which the transfer energy b_π of the e_g electrons of the Ni^{3+} is large enough to quench the JT distortion (*26*). On the other hand, $LaCuO_3$ is a metal containing only the non-JT Cu^{3+}. Therefore, it was decided to investigate and "engineer" nickel and copper-containing oxides, with reduced bandwidth $\sim b_\pi$, partially containing Ni^{3+} and Cu^{2+} states. Furthermore, in Rüschlikon, there was a tradition of more than two decades of research in insulating oxides that undergo structural and ferroelectric transitions, which was a strong motivation to pursue the program (*27*).

The Discovery of Superconductivity in Ba-La-Cu Oxide Ceramics

In our laboratory, the search for superconductivity was initiated in mid-summer of 1983. Our effort first concentrated on Ni^{3+}-containing perovskites, such as mixed crystals of $LaNiO_3$ and $LaAlO_3$. In these unpublished efforts, the metallic behavior of the various synthesized double or triple oxides was measured, and at low temperatures they exhibited localization upon cooling. This indicated the possible existence of JT polarons, however, without any signs of superconductivity (*28*). In late summer of 1985, the efforts were shifted to copper-containing compounds, such as $LaCuO_3$. Because Cu^{3+} has two electrons in the e_g subshell, the latter is half-filled. Thus, its ground state is not degenerate. It was clear that an oxide with mixed Cu^{2+}/Cu^{3+} or Cu^{3+}/Cu^{4+} valence had to be tried.

At this stage, we became aware of a paper by Michel, Er-Rakho, and Raveau (*29*) on the mixed perovskite $BaLa_4Cu_5O_{13.4}$, exactly meeting the requirements of mixed valency. The French authors had shown that this mixed oxide, a metal at room temperature and above, contained Cu^{2+} and Cu^{3+}. Thus, we tried to reproduce it, at the same time continuously varying the Cu^{2+}/Cu^{3+} ratio by changing the Ba concentration in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$, and we looked for superconductivity. At Rüschlikon, the samples were prepared by the coprecipitation method from aqueous solutions of Ba-La and Cu nitrates. When added to an aqueous solution of oxalic acid as precipitant (*30*), an intimate mixture of the corresponding oxalates was formed. Decomposition of the precipitate and solid-state reaction were carried out by heating at 900°C for 5 hours. The product was ground and pressed into pellets at 4 kbar, then reheated to 900°C for sintering. We performed dc measurements of the resistivity $\rho(T)$ by the four-point method with current densities around 0.5 A/cm^2. A typical set of data is reproduced in Fig. 4. In general, a high-temperature metallic behavior was observed, with an increase in resistivity at lower temperatures. Then upon further cooling, a sharp drop in $\rho(T)$ occurred that for higher currents was partially suppressed (Fig. 4, upper curves, left scale). The sharp drop was studied as a function of annealing conditions and barium content. The onset could be shifted by these means to 35 K (*1*).

At lower temperatures, the resistivity of some samples became three orders of magnitude smaller than the sensitivity of the apparatus, evidence for bulk superconductivity. Therefore, the onset of the drop in $\rho(T)$ was interpreted as possible high-T_c superconductivity of a percolative nature. The shift of the onset to lower temperatures with higher probing currents also supported this interpretation, as well as the comparison of the Ba-La-Cu-O data with those known for polycrystalline $BaPb_{1-x}Bi_xO_3$ (*31*). X-ray analysis revealed that the system consisted of three phases: CuO, the $Ba_xCu_{5-x}O_{5(3-y)}$ originally wanted, and a K_2NiF_4 phase containing perovskite layers (*2*). Owing to the presence of the latter, the possibility of two-dimensional superconducting correlations was also mentioned (*1*).

The way the samples were prepared was of real importance for the discovery. Michel *et al.* (*29*) obtained a single-phase perovskite by mixing the oxides of lanthanum and copper and $BaCO_3$ in an

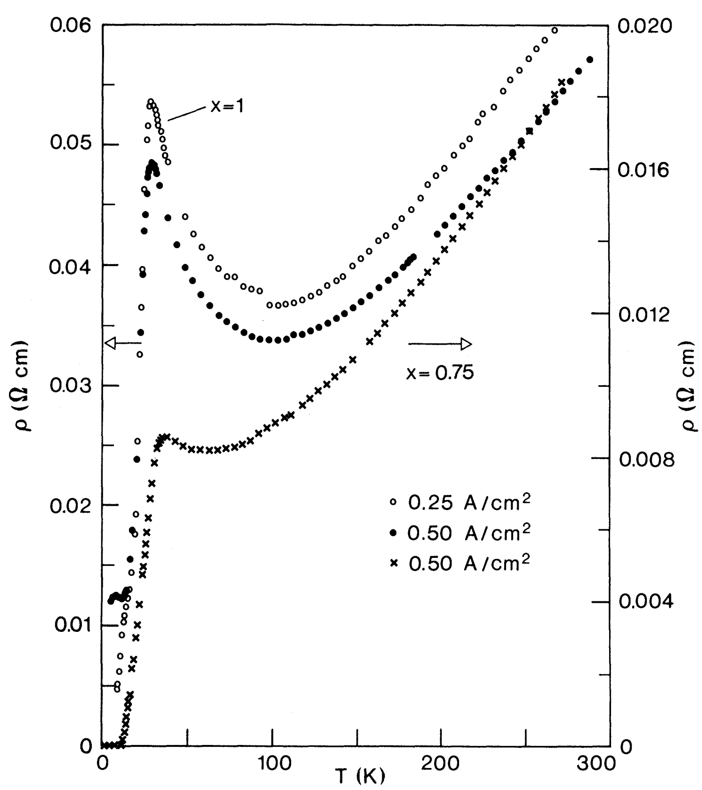


Fig. 4. Temperature dependence of resistivity in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ for samples with $x = 1$ (upper curves, left scale) and $x = 0.75$ (lower curve, right scale) (x nominal). The first two cases also show the influence of current density. [Reprinted from (*1*) with permission, copyright Springer-Verlag.]

appropriate ratio and subsequent annealing at 1000°C in air. By applying this annealing condition to our samples, which were obtained by the decomposition of the corresponding oxalates, no superconductivity was found. Thus, preparation from the oxalates and annealing below 950°C for a La/Cu ratio of 1 were necessary to obtain a layer-like, perovskite-related phase with a limited temperature range of stability. Because one of the three phases, CuO, is an insulator, only the K_2NiF_4 phase remained as a possible candidate for superconductivity, namely, the La_2CuO_4 double oxide. A detailed powder x-ray analysis combined with susceptibility measurements, discussed below, showed that the phase becoming superconducting was indeed the layer-like oxide La_2CuO_4. At this point, it should be mentioned that Michel and Raveau had investigated the structural and electrical properties of this phase shown in Fig. 5, and summarized their findings in their 1984 review (*32*). Thus, taking into account the determined search for superconductivity in Rüschlikon, this phase with its La/Cu ratio of 2 would, even without the lucky preparation conditions, have been found sooner or later. Of historical interest is the first synthesis of $LaSrCuO_4$ in 1973, a case in which the copper is fully trivalent (*33*), whereas a mixed Cu^{2+}/Cu^{3+} valence state is crucial for the occurrence of superconductivity.

To corroborate the existence of superconductivity, the susceptibility of Ba-La-Cu-O samples with various compositions and preparation histories was measured. It was expected that below T_c, grains coupled by Josephson junctions or the proximity effect might yield diamagnetic shielding currents and thus cause a change from Pauli-paramagnetic to diamagnetic susceptibility. The experiments carried out in late summer and fall of 1986 did indeed bear out this property in a systematic way (*2*), as shown in Figs. 6 and 7. Figure 6 shows experiments with a sample containing only 1% barium substituted for lanthanum. The resistivity exhibits a clear transition to localization when cooled, whereas its susceptibility is nearly temperature independent, metallic, and Pauli-like, except for a Curie-Weiss enhancement starting at 20 K. Such behavior has been termed a "Fermi glass" by Anderson (*34*), because for weakly correlated particles during localization (that is, mobility reduction) the Fermi-Dirac statistics still holds. In Fig. 7, the resistivity and susceptibilities of samples labeled 2 and 3 are shown. For sample 2, the onset in resistivity drop occurs near 26 K, and for 3 at 35 K (Fig. 7, upper part). For sample 2, a crossover from Pauli paramagnetic to a diamagnetic susceptibility at 20 K is seen on cooling, and for the latter at 32 K (Fig. 7, lower part). Owing to the absence of diamagnetism for sample 1 (Fig. 6) with no drop in resistivity and the existence of diamagnetism in samples 2 and 3 with conjoint increases of the onset in $\rho(T)$ and a diamagnetic crossover, evidence for high-T_c superconductivity was present. The diamagnetism measured was rather low, of the order of 1%, relative to a $-1/4\pi$ full-Meissner effect. As discussed then, the small diamagnetism reflects the percolative character of the early samples. Its suppression by external magnetic fields also led to a new aspect in superconductors: the existence of a superconducting glass state.

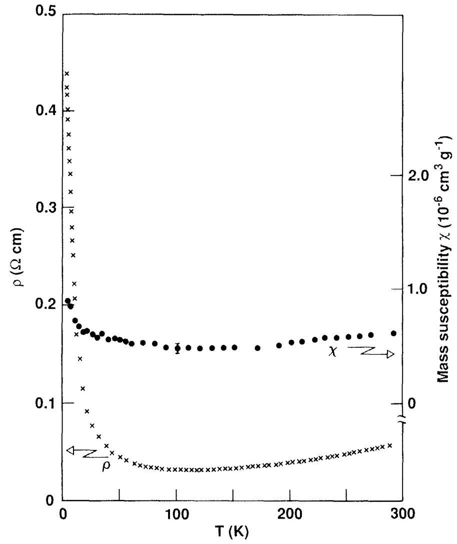


Fig. 6. Temperature dependence of resistivity ρ (x) and mass susceptibility χ (•) of sample 1 with 1% barium. [Reprinted from (*2*) with permission, copyright Éditions de Physique.]

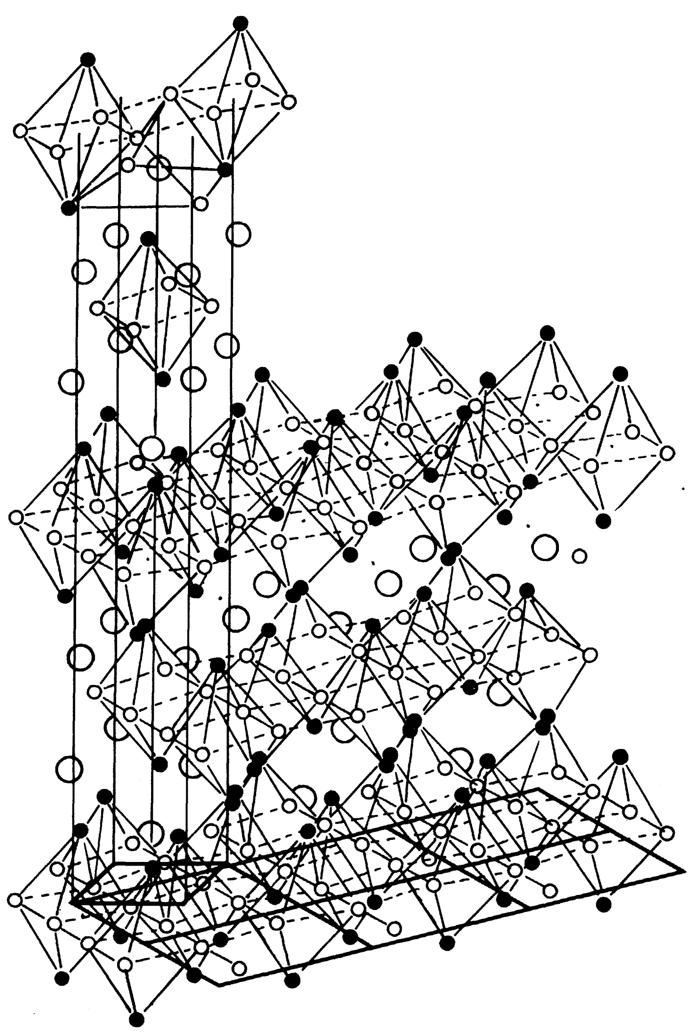


Fig. 5. Structure of the orthorhombic La_2CuO_4. Large open circles represent the lanthanum atoms, small open and filled circles represent the oxygen atoms. The copper atoms (not shown) are centered in the oxygen octahedra.

Early Confirmation and Progress

For more than a decade, the highest superconducting transition temperature had remained constant. Therefore, we expected that confirmation and acceptance of the Rüschlikon discovery could take as much as 2 to 3 years. In fact, subsequent events occurred very rapidly. We had not thought of the vigorous groups who had investigated the oxide superconductor $BaPb_xBi_{1-x}O_3$, such as the ones of Tanaka in Tokyo, Chu in Houston, and Batlogg at AT&T. These groups were reducing their efforts in 1986. This meant that their expertise in oxide superconductivity and equipment were still in place but rather idle. The new oxide ceramic was as easy to prepare as the earlier ones had been.

The first group to confirm the existence of high-T_c superconduc-

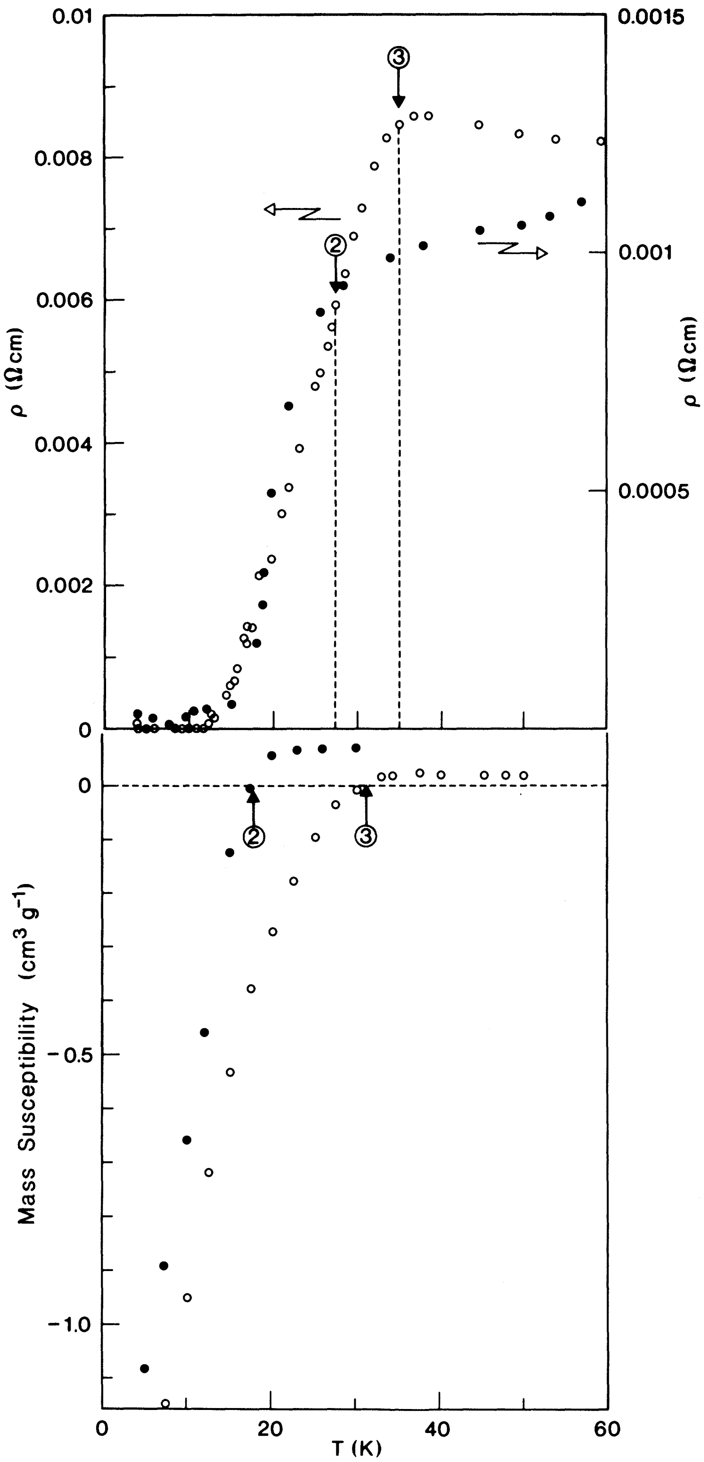


Fig. 7. Low-temperature resistivity and susceptibility of (La, Ba)-Cu-O samples 2 and 3. Arrows indicate the onset of the resistivity drop and the paramagnetic-to-diamagnetic transition, respectively. [Reprinted from (*2*) with permission, copyright Editions de Physique.]

tivity in the Ba-La-Cu-O system was at Tokyo University. Rather than argue whether our findings were true or "irreproducible," they decided to try to reproduce our results after the appearance of our first paper (*1*). They observed diamagnetism in their samples (*35*), prepared by reacting the oxides with a La/Cu ratio of 2. The onsets in $\rho(T)$ and diamagnetic crossovers were in the same temperature range as in our samples. Also, their independent structure analysis agreed with our x-ray study (*36*).

In fall of 1986, we conducted an x-ray study as a function of barium content at 300 K and found that the La_2CuO_4 underwent an orthorhombic-to-tetragonal structural phase transition (SPT) for higher barium concentrations. It could be that this orthorhombic-to-tetragonal SPT is related to the high-T_c superconductivity because it occurs near the barium concentration where the highest onsets are observed. This view is supported because, in doping our La_2CuO_4 also with Sr^{2+} and Ca^{2+}, we found the same relation between T_c and SPT on alkaline-earth substitution (*37*). The Sr^{2+}-containing samples yielded the sharpest onsets of superconductivity and largest diamagnetism (*38*). Our results on alkaline-earth doping proved the electronic origin of the superconductive enhancement, because the ionic radius r of Sr^{2+} is nearly the same as that of La^{3+}, with r = 1.14 Å, for which it presumably substitutes. The radius of Ba^{2+} is 0.22 Å larger, and the one of Ca^{2+} is 0.15 Å smaller than that of La^{3+}. Thus, these two ions produce local stresses. The alkaline-earth doping creates Cu^{3+} ions, which is essential for superconductivity to occur.

The Japanese confirmation "fanned the fire" in the United States. Both Chu's and Batlogg's groups, as well as that at Bellcore, not only confirmed, but had by the end of the year surpassed the Rüschlikon results in two ways. At AT&T, they started directly with Sr^{2+} substitution for lanthanum (*39*). Their expertise in oxide ceramics allowed AT&T to obtain sharper onsets, with full super-

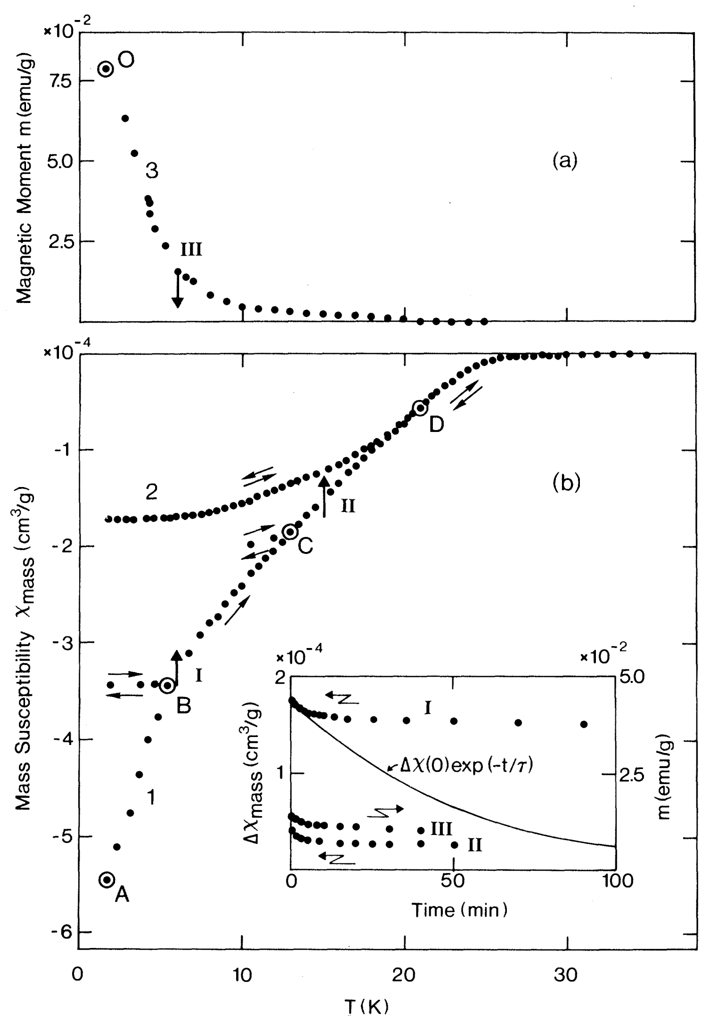
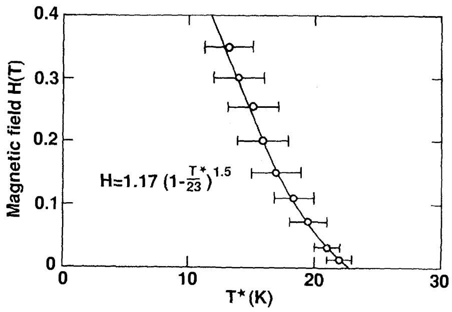


Fig. 8. (**a**) Flux trapping curve (*3*) and (**b**) nonergodic values versus ergodic behavior of the susceptibility after zero-field and field cooling, respectively, as discussed in the text. Inset: Decay of metastable states, τ = 39 min. [Reprinted from (*48*) with permission, copyright American Physical Society.]

Fig. 9. Experimentally determined $H(T^*)$ line that separates ergodic from nonergodic areas, together with an analytic expression for the quasi–de Almeida–Thouless line. [Reprinted from (*48*) with permission, copyright American Physical Society.]



conductivity reached a few degrees below onset, and up to 30% Meissner effect at low temperatures, thus proving the presence of three-dimensional superconductivity. Tarascon *et al.* at Bellcore achieved a transition width of only 2 K with T_c very near 40 K (*40*). At Houston, first the Rüschlikon results (*41*) were confirmed, and then resistivity measurements under hydrostatic pressure revealed onsets up to 52 K (*42*). Therefore, Chu *et al.* foresaw still higher T_c's for the future (*42*), which they did indeed find (*5, 6*). At the Academy of Science in China, a long tradition of research in oxide ceramics exists. The scientists there also optimized the barium-strontium replacement of lanthanum and had reached a T_c of 48 K by the end of 1986 (*4*).

Thus, after our first results became public, independent results were obtained at various research institutes all over the world, which in general agree with one another experimentally. The known structure of La_2CuO_4 allowed Mattheiss (*43*) to perform electronic structure calculations for the tetragonal La_2CuO_4 lattice. A half-filled Cu($3d$)-O($2p$) band of $3d$, $x^2 - y^2$, two-dimensional character with nearly square Fermi surfaces was found, as expected (*21*). This electronic structure is of help in understanding the occurrence of superconductivity in the material.

The Superconductive Glass State

The early samples with their percolative nature and small diamagnetism qualitatively resembled the behavior in the layer compounds $TaSe_3$ and $NbSe_3$. However, in the latter compound, the T_c and the magnetic fields suppressing the diamagnetism are substantially lower (*44*). This was attributed to Josephson or proximity junctions becoming normal. The existence of frustration was pointed out theoretically for such a situation (*45*). A larger cluster can support many supercurrent-carrying states of nearly equal energy. It has been said that "the presence of a hierarchy of loops is crucial in defining its behavior in high magnetic fields" (*46*, p. 1542). Recently, Stroud and collaborators presented calculations of diamagnetic response of coupled superconducting clusters in the presence of high magnetic fields (*47*). In their model, superconducting grains, each small compared to the London penetration depth, are weakly coupled into closed loops. The picture they arrived at, in agreement with earlier calculations by themselves and others (*47*), corresponds to a spin glass, hereafter called a superconductive glass state.

Some essential features of the glass state are (i) the difference in field-cooled and zero-field-cooled responses, (ii) the existence of a de Almeida–Thouless line separating metastable from stable regions, and (iii) nonexponential time dependences (*48*). Figure 8 shows typical sequences on the early ceramics supporting statement (i). After zero-field cooling the sample and then switching on of a 0.03-T field, the susceptibility χ is measured at point A. On heating the sample, point B on curve 1 is reached. On cooling, a nearly temperature-independent susceptibility is measured. With further heating, point B is passed until point C is reached. On cooling from C, a temperature-dependent slope smaller than that of curve 1 is followed. On continued heating, curve 1 becomes reversible past point D. The same value D is reached by field cooling from 35 K. In field cooling past D, curve 2 is followed reversibly on a time scale of 2 hours.

Figure 8b shows that on this time scale a reversible and an irreversible trajectory of the system are present. Point D at temperature $T^* = 21 \pm 1$ K and magnetic field $H = 0.03$ T marks the ergodic limit. From measurements with different fields H, a quasi–de Almeida–Thouless line in the H-T plane is obtained, corresponding well to a curve $H = 1.17[1 - T^*(H)/T(0)]^{3/2}$, for $T(0) = 23$ K (Fig. 9). Theoretically, de Almeida and Thouless (*49*) derived the line separating ergodic and nonergodic regions, from the Sherrington-Kirkpatrick model with infinite-range spin interaction, to be $H = H_0[1 - T_g(H)/T_g(0)]^\gamma$, $\gamma = 3/2$ where T_g is the glass temperatures. That $H(T^*)$ for the superconductive glass fits the exponent $\gamma = 1.5$ so well may be related to the longer range of forces present in a superconductor as compared to a magnetic system. Figure 9 is evidence for statement (ii).

When the sample was field-cooled, following curve 2 to low temperature and then switching off the field, a positive remanent magnetization was observed, shown as point O in Fig. 8a. This remanent magnetization results from flux trapping and was a proof of superconductivity in its own right. On heating the sample at a rate of 0.3 K/min, the magnetism follows curve 3. After a monotonic decrease, the magnet movement $m(t)$ disappears around T^*, that is, where the irreversibility of the susceptibility also disappears and curves 1 and 2 merge at point D. This shows the consistency of all the data in Fig. 8, since above T^* reversibility exists and no flux trapping can occur.

When the superconductor is in a nonequilibrium state, as for χ on curve 1 below T^* or for m on curve 3 (Fig. 8), it is metastable. Therefore, it tends to relax toward the stable state. The system can do that through a hierarchy of relaxational paths via phase slips (*45–47, 49*). The measured decay of χ at points I and II of curve 1 and III of curve 3 is shown in the inset. The long time decay is slow, proportional to log t, and arises from the fact that after a certain time larger clusters with superconductive phase coherence have fewer relaxation paths.

An important aspect is whether this phase coherence has to occur between the La_2CuO_{4-y}:Ba grains or within them. In the experiments, grain sizes reached a volume $V = 50\ \mu m^3$. According to earlier calculations (*47*), the low-field limit to maintain complete field exclusion is $H^*_{c1} = \phi_0/2S$, where ϕ_0 is the flux quantum and S is the homogeneous superconducting area. The probing field H of 300 G did not reach the valve of H^*_{c1}, and thus $S > \phi_0/2H = 0.03\ \mu m^2$. This means that the single-phase areas were smaller than that of a single grain with $S = V^{2/3} = 14\ \mu m^2$. Therefore, the superconductive glass state was present in the La_2CuO_{4-y}:Ba grains. However, it should be noted that samples prepared differently show no tendency to carrier localization on cooling; a sharp onset of superconductivity and a much higher diamagnetism below T_c are seen in Figs. 7 and 8. Therefore, in those samples S is still larger and the superconductive glass features are considerably reduced.

Conclusions

The young "tree" of layer-oxide superconductors already appears to have grown a side branch: the existence of a superconductive glass state. This new class of materials found at the IBM Zurich Research Laboratory are hole rather than electron superconductors. The finding of the layered copper oxide superconductors can already now be foreseen to prompt many investigations in the sectors detailed in the introduction. The authors hope to contribute to some of them and keep informed of the others.

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