ADVANCED MATERIALS

Nobel Lecture

Perovskite-Type Oxides—the New Approach to High-T_c Superconductivity**

By J. Georg Bednorz* and K. Alex Müller*

Part 1: The Early Work in Rüschlikon

In our lecture, we take the opportunity to describe the guiding ideas and our effort in the search for high-T_c superconductivity. They directed the way from the cubic niobium-containing alloys to layered copper-containing oxides of perovskite-type structure. We shall also throw some light onto the circumstances and the environment which made this breakthrough possible. In the second part, properties of the new superconductors are described.

The Background

At IBM's Zürich Research Laboratory, there had been a tradition of more than two decades of research efforts in insulating oxides. The key materials under investigation were perovskites like $SrTiO_3$ and $LaAlO_3$, used as model crystals to study structural and ferroelectric phase transitions. The pioneering ESR experiments by *Alex Müller (KAM)*[1.1] and *W. Berlinger* on transition-metal impurities in the perovskite host lattice brought substantial insight into the local symmetry of these crystals, i.e., the rotations of the TiO_6 octahedra, the characteristic building units of the lattice.

One of us *(KAM)* first became aware of the possibility of high-temperature superconductivity in the 100 K range from the calculations of *T. Schneider* and *E. Stoll* on metallic hydrogen.[1.2] Such a hydrogen state was estimated to be in the 2-3 Mbar range. Subsequent discussions with *T. Schneider* on the possibility of incorporating sufficient hydrogen into a high-dielectric-constant material like $SrTiO_3$ to induce a metallic state led, however, to the conclusion that the density required could not be reached.

While working on my Ph.D. thesis at the Solid State Physics Laboratory of the ETH Zurich, I *(JGB)* gained my first experience in low-temperature experiments by studying the structural and ferroelectric properties of perovskite solid-solution crystals. It was fascinating to learn about the large variety of properties of these materials and how one could change them by varying their compositions. The key material, pure $SrTiO_3$, could even be turned into a superconductor if it were reduced, i.e., if oxygen were partially removed from its lattice.[1.3] The transition temperature of 0.3 K, however, was too low to cause much excitement in the world of superconductivity research. Nevertheless, it was interesting that superconductivity occurred at all, because the carrier densities were so low compared to superconducting NbO, which has carrier densities like a normal metal.

My (*JGB*'s) personal interest in the fascinating phenomenon of superconductivity was triggered in 1978 by a telephone call from *Heinrich Rohrer*, the manager of a new arrival at IBM Rüschlikon, *Gerd Binnig*. With his background in superconductivity and tunneling, *Gerd* was interested in studying the superconductive properties of $SrTiO_3$, especially in the case when the carrier density in the system was increased. For me (*JGB*), this was the start of a short but stimulating collaboration, as within a few days I was able to provide the IBM group with Nb-doped single crystals which had an enhanced carrier density compared to the simply reduced material. The increase in T_c was exciting for us. In the Nb-doped samples ($n = 2 \times 10^{20}$ cm^{-3}) the plasma edge lies below the highest optical phonon, which is therefore unshielded.[1.4] The enhanced electron-phonon coupling led to a T_c of 0.7 K.[1.5] By further increasing the dopant concentration, the T_c even rose to 1.2 K, but this turned out to be the limit, because the plasma edge passes the highest phonon. *Gerd* then lost his interest in this project, and with deep disappointment I realized that he had started to develop what was called a scanning tunneling microscope (STM). However, for *Gerd* and *Heinrich Rohrer*, it turned out to be a good decision, as everyone realized by 1986 at the latest, when they were awarded the Nobel Prize in Physics. For my part, I concentrated on my thesis.

It was in 1978 that *Alex (KAM)*, my second supervisor, took an 18-month sabbatical at IBM's T. J. Watson Research Center in Yorktown Heights, NY, where he started working in the field of superconductivity. After his return in 1980, he also taught an introductory course at the University of Zürich. His special interest was the field of granular superconductivity, an example being aluminum,[1.6]

---

[*] Dr. J. G. Bednorz, Prof. Dr. K. A. Müller
IBM Research Division
Zürich Research Laboratory
Säumerstrasse 4, CH-8803 Rüschlikon (Switzerland)

[**] Copyright © The Nobel Foundation 1988. – We thank the Nobel Foundation, Stockholm, for permission to print this article.

where small metallic grains are surrounded by oxide layers acting as Josephson junctions. In granular systems, the T_c's were higher, up to 2.8 K, as compared to pure Al with $T_c = 1.1$ K.

Involvement with the Problem

It was in the fall of 1983 that *Alex*, heading his IBM Fellow group, approached me and asked whether I would be interested in collaborating in the search for superconductivity in oxides. Without hesitation, I immediately agreed. *Alex* later told me he had been surprised that he had hardly needed to use any arguments to convince me; of course, it was the result of the short episode of my activities in connection with the superconducting $SrTiO_3$—he was knocking a door already open. And indeed, for somebody not directly involved in pushing T_c's to the limit and having a background in the physics of oxides, casual observation of the development of the increase of superconducting transition temperatures, shown in Figure 1.1, would naturally lead to the conviction that intermetallic compounds should not be pursued any further, as the highest T_c had remained since 1973 at 23.3 K.[1.7] But nevertheless, the fact that superconductivity had been observed in several complex oxides evoked our special interest.

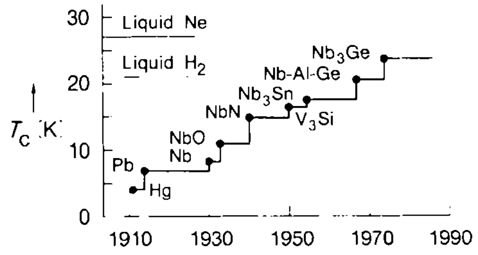

Fig. 1.1. Development of superconducting transition temperatures after the discovery of the phenomenon in 1911. The materials named are metals or intermetallic compounds and gave the highest T_c's at the time.

The second oxide after $SrTiO_3$ to exhibit surprisingly high T_c's of 13 K was discovered in the Li-Ti-O system by *Johnston* et al.[1.8] in 1973. Their multiphase samples contained a $Li_{1+x}Ti_{2-x}O_4$ spinel responsible for the high T_c. Owing to the presence of different phases and difficulties in preparation, the general interest remained low, especially as in 1975 *Sleight* et al.[1.9] discovered the $BaPb_{1-x}Bi_xO_3$ perovskite also exhibiting a T_c of 13 K. This compound could easily be prepared as a single phase and even thin films for device applications could be grown, a fact that triggered increased activities in the United States and Japan. According to the BCS theory[1.10] which gives

$$k \times T_c = 1.13\hbar\omega_D e^{-1/(N(E_F)) \times V^*}$$

both mixed-valent oxides, having a low carrier density $n = 4 \times 10^{21}$ cm^{-3} and a comparatively low density of states per unit cell $N(E_F)$ at the Fermi level, should have a large electron–phonon coupling constant, leading to the high T_c's. Subsequently, attempts were made to raise the T_c in the perovskite by increasing $N(E_F)$ via changing the Pb : Bi ratio, but the compound underwent a metal-insulator transition with a different structure, and thus all attempts failed.

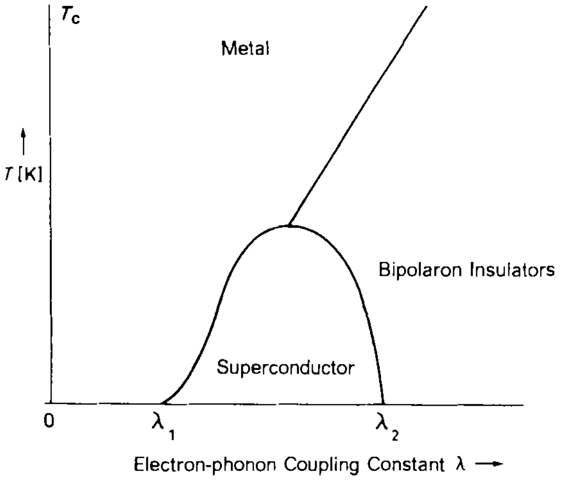

Fig. 1.2. Phase diagram as a function of electron-phonon coupling strength (adapted from [1.11]).

We in Rüschlikon took up this challenge, as we expected other metallic oxides to exist where even higher T_c's could be reached by increasing $N(E_F)$ and/or the electron–phonon coupling. Possibly we could enhance the latter by polaron formation as proposed theoretically by *Chakraverty*[1.11] or by the introduction of mixed valencies. The intuitive phase diagram of the coupling constant $\lambda = N(E_F) \times V^*$ versus T proposed by *Chakraverty* for polaronic contributions is shown in Figure 1.2. There are three phases, a metallic one for small λ and an insulating bipolaronic one for large λ, with a superconductive phase between them, i.e., a metal-insulator transition occurs for large λ. For intermediate λ, a high-T_c superconductor might be expected. The question was, in which systems to look for superconductive transitions.

The Concept

The guiding idea in developing the concept was influenced by the Jahn-Teller (JT) polaron model, as studied in a linear chain model for narrow-band intermetallic compounds by *Höck* et al.[1.12] The Jahn-Teller (JT) theorem is well known in the chemistry of complex states. A nonlinear molecule or a molecular complex exhibiting an electronic degeneracy will spontaneously distort to remove or reduce this degeneracy. Complexes containing specific transition metal (TM) central ions with special valency show this effect. In the linear chain model,[1.12] for small JT distortions with a stabilization energy E_{JT} smaller than the bandwidth of the metal, only a slight perturbation of the traveling electrons is present. With increasing E_{JT}, the tendency to localization is enhanced, and for the case where E_{JT} is comparable with the bandwidth, the formation of JT polarons was postulated.

These composites of an electron and a surrounding lattice distortion with a high effective mass can travel through the lattice as a whole, and a strong electron-phonon coupling exists. In our opinion, this model could fit the Chakraverty phase diagram perfectly. Based on the experience from studies of isolated JT ions in the perovskite insulators, our assumption was that the model would also apply to the oxides, our field of expertise, if they could be turned into conductors. We knew there were many of them. Oxides containing TM ions with partially filled e_g orbitals, like Ni^{3+}, Fe^{4+} or Cu^{2+} exhibit a strong JT effect (Fig. 1.3), and we considered these as possible candidates for new superconductors.

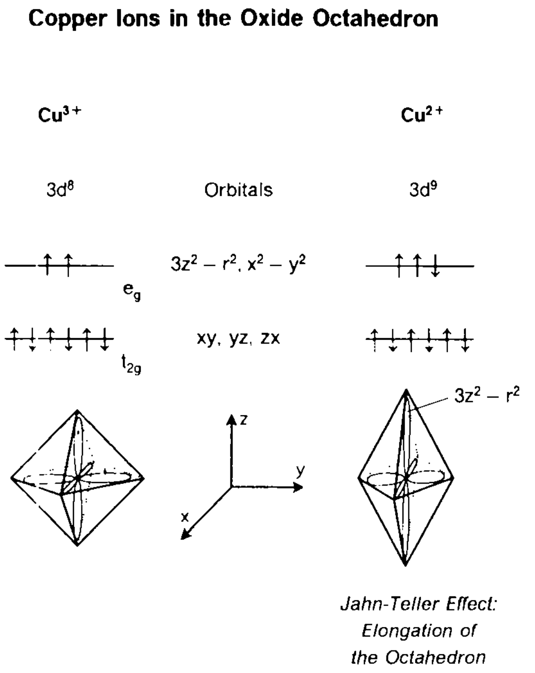

Fig. 1.3. Schematic representation of electron orbitals for octahedrally coordinated copper ions in oxides. For Cu^{3+} with $3d^8$ configuration, the orbitals transforming as base functions of the cubic e_g group are half-filled, thus a singlet ground state is formed. In the presence of Cu^{2+} with $3d^9$ configuration the ground state is degenerate, and a spontaneous distortion of the octahedron occurs to remove this degeneracy. This is known as the Jahn-Teller effect.

The Search and Breakthrough

We started the search for high-T_c superconductivity in late summer 1983 with the La-Ni-O system. $LaNiO_3$ is a metallic conductor with the transfer energy of the JT-e_g electrons larger than the JT stabilization energy, and thus the JT distortion of the oxygen octahedra surrounding the Ni^{3+} is suppressed.[1,13] However, even the preparation of the pure compound brought some surprises, as the material obtained by our standard co-precipitation method[1,14] and subsequent solid-state reaction turned out to be sensitive not only to the chemicals involved[1,15] but also to the reaction temperatures. Having overcome all difficulties with the pure compound, we started to partially replace Ni^{3+} by Al^{3+} to reduce the metallic bandwidth of the Ni^{3+} ions and make it comparable to the Ni^{3+} Jahn-Teller stabilization energy. With increasing Al^{3+} concentration, the metallic characteristics (see Fig. 1.4) of the pure $LaNiO_3$ gradually changed, first to give a general increase in the resistivity and finally with high substitution leading to a semiconducting behavior with a transition to localization at low temperatures. The idea did not seem to work out the way we had thought, so we considered the introduction of some internal strain within the $LaNiO_3$ lattice to reduce the bandwidth. We achieved this through replacing the La^{3+} ion by the smaller Y^{3+} ion, keeping the Ni^{3+} site unaffected. The resistance behavior changed in a way we had already observed in the previous case, and at that point we started wondering whether the target at which we were aiming really did exist. Would the path we decided to embark upon finally lead into a blind alley?

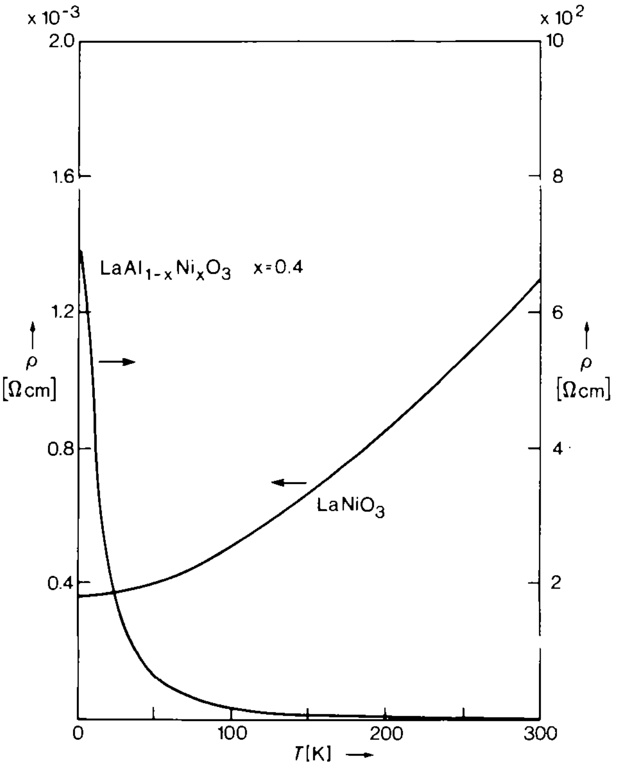

Fig. 1.4. Temperature dependence of the resistivity for metallic $LaNiO_3$ and $LaAl_{1-x}Ni_xO_3$, where substitution of Ni^{3+} by Al^{3+} leads to insulating behavior for $x = 0.4$.

It was in 1985 that the project entered this critical phase, and it probably only survived because the experimental situation, which had generally hampered our efforts, was improved. The period of sharing another group's equipment for resistivity measurements came to an end as our colleague, *Pierre Guéret*, agreed to my established right to use a newly set up automatic system. Thus, the measuring time was transferred from late evening to normal working hours. *Toni Schneider*, at that time acting manager of the Physics department, supported the plans to improve the obsolete X-ray analytical equipment to simplify systematic phase analysis, and in addition we had some hopes in our new idea, involving another TM element encountered in our search, namely copper. In a new series of compounds, partial replacement of the JT Ni^{3+} by the non-JT Cu^{3+} increased the absolute value of the resistance, although the metallic character of the solid solutions was preserved down to 4 K.[1.13] But again, we found no evidence of superconductivity. The time to study the literature and reflect on the past had arrived.

It was in late 1985 that the turning point was reached. I became aware of an article by the French scientists *C. Michel, L. Er-Rakho* and *B. Raveau*, who had investigated a Ba-La-Cu oxide with perovskite structure exhibiting metallic conductivity between 300 and −100°C.[1.16] That group studied the catalytic properties of oxygen-deficient compounds at elevated temperatures.[1.17] In the Ba-La-Cu oxide with a perovskite-type structure containing Cu in two different valencies, all our concept requirements seemed to be fulfilled.

I immediately went to the ground-floor laboratory and started preparations for a series of solid solutions, since by varying the Ba : La ratio one would have a sensitive tool to continuously tune the mixed valency of copper. Within one day the synthesis was complete, but the measurement had to be postponed, owing to the announcement of the visit of Dr. *Ralph Gomory*, our Director of Research. These visits always kept people occupied for a while, preparing their presentations.

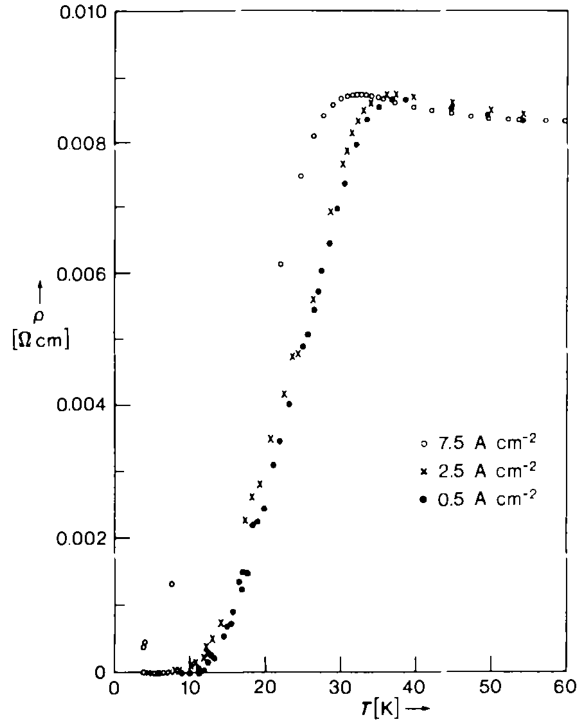

Fig. 1.5. Low-temperature resistivity of a sample with x(Ba) = 0.75, recorded for different current densities (adapted from [1.19]).

Having lived through this important visit, and returning from an extended vacation in mid-January 1986, I recalled that when reading about the Ba-La-Cu oxide, it had intuitively attracted my attention. I decided to resume my measurements on the new compound. When performing the four-point resistivity measurement, the temperature dependence did not seem to be anything special when compared with the dozens of samples measured earlier. During cooling, however, a metallic-like decrease was first observed, followed by an increase at low temperatures, indicating a transition to localization. My inner tension, always increasing as the temperature approached the 30 K range, started to be released when a sudden resistivity drop of 50% occurred at 11 K. Was this the first indication of superconductivity?

Alex and I were really excited, as repeated measurements showed perfect reproducibility and an error could be ruled out. Compositions as well as the thermal treatment were varied, and within two weeks we were able to shift the onset of the resistivity drop to 35 K (Fig. 1.5). This was an incredibly high value compared to the highest T_c in the Nb_3Ge superconductor.

We knew that in the past there had been numerous reports on high-T_c superconductivity, which had turned out to be non-irreproducible;[1.7] therefore before to the publishing of our results, we asked ourselves critical questions about its origin. A metal-to-metal transition, for example, was unlikely, owing to the fact that with increasing measuring current the onset of the resistivity drop was shifted to

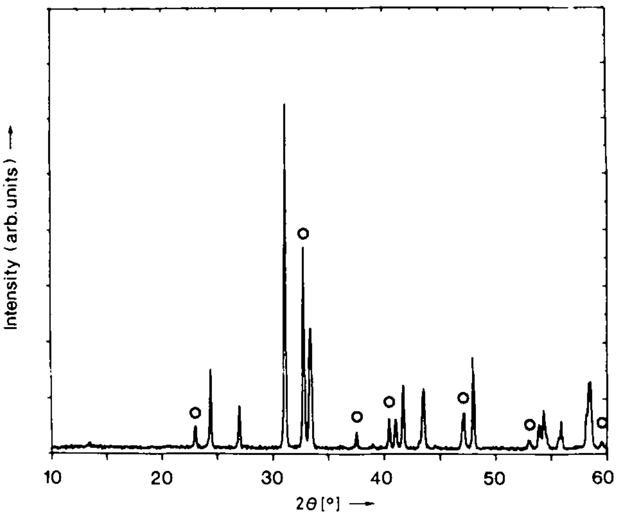

Fig. 1.6. X-ray diffraction pattern of a two-phase sample with Ba : La = 0.08. The second phase occurring together with the K_2NiF_4-type phase is indicated by open circles (adapted from [1.20]).

lower temperatures. On the other hand, this behavior supported our interpretation that the drop in $\rho(T)$ was related to the onset of superconductivity in granular materials. These are, for example, polycrystalline films of $BaPb_{1-x}Bi_xO_3$[1.18] exhibiting grain boundaries, or different crystallographic phases with interpenetrating grains as in the Li-Ti oxide.[1.7] Indeed, X-ray diffraction patterns of our samples revealed the presence of at least two different phases (see Fig. 1.6). Although we started the preparation process of the material with the same cation ratios as the French group, the wet-chemical process did not lead to the same result. This later turned out to be a stroke of luck, in the sense that the compound we wanted to form was not superconducting. The dominating phase could be identified as having a layered perovskite-like structure of K_2NiF_4-type as seen from Figure 1.7. The diffraction lines of the second phase resembled those of an oxygen-deficient perovskite with a three-dimensionally connected network of octahedra. In both structures, La was partially replaced by Ba, as we learned from an electron microprobe analysis which Dr. *Jürg Sommerauer* at the ETH Zürich performed for us as a favor. However, the question was "which is the compound where the mixed valency of the copper leads to the superconductive transition?"

We had difficulties in finding a conclusive answer at the time; however, we rated the importance of our discovery so high that we decided to publish our findings, despite the fact that we had not yet been able to perform magnetic measurements to show the presence of the Meissner-Ochsenfeld effect. Thus, our report was cautiously entitled "Possible High T_c Superconductivity in the Ba-La-Cu-O System".[1.19] We approached *Eric Courtens*, my manager at the time, who in late 1985 had already strongly supported our request to purchase a dc SQUID magnetometer, and who is on the editorial board of *Zeitschrift für Physik*. In this capacity, we solicited his help to receive and submit the paper, although, admittedly, it did involve some gentle persuasion on our part!

Alex and I then decided to ask Dr. *Masaaki Takashige* whether he would be interested in our project. Dr. *Takashige*, a visiting scientist from Japan, had joined our Laboratory in February 1986 for one year. He was attached to *Alex*'s Fellowship group, and I had given him some support in pursuing his activities in the field of amorphous oxides. As he was sharing my office, I was able to judge his reaction, and noted how his careful sceptical comments changed to supporting conviction while we were discussing the results. We had found our first ally.

Following this, while awaiting delivery of the magnetometer, we tried hard to identify the superconducting

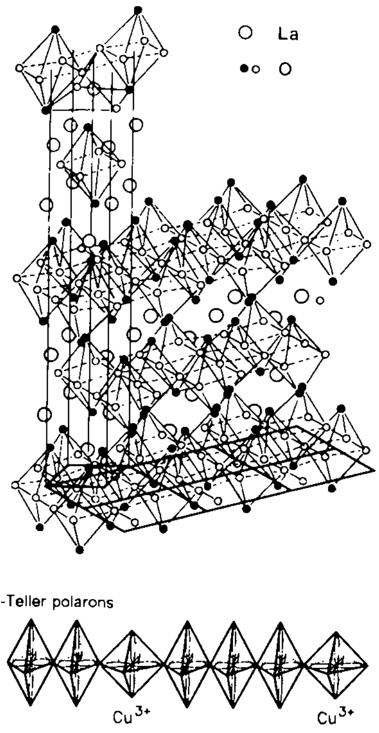

Fig. 1.7. Top: Structure of the orthorhombic La_2CuO_4. Large open circles represent the lanthanum ions, small open and filled circles the oxygen ions. The copper ions (not shown) are centered in the oxygen octahedra (from [1.29], © American Association for the Advancement of Science, 1987). Bottom: It is schematically shown how, in a linear chain, substitution of trivalent La by a divalent alkaline-earth element would lead to a symmetric change of the oxygen polyhedra in the presence of Cu^{3+}.

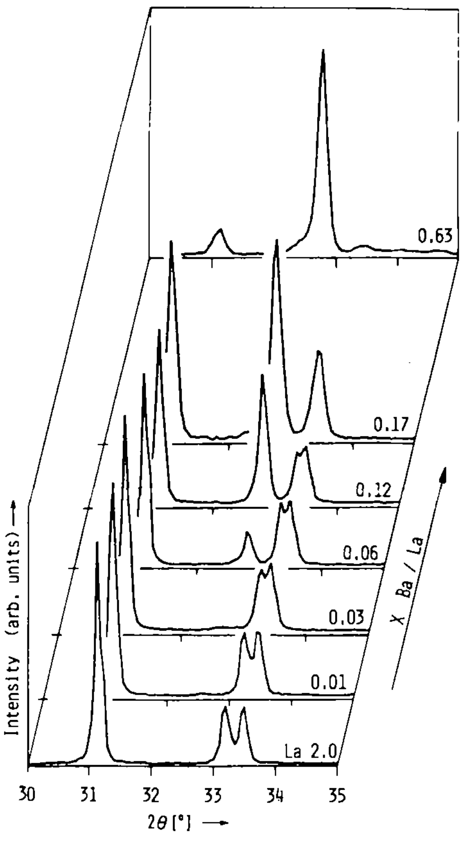

Fig. 1.8. Characteristic part of the X-ray diffraction pattern, showing the orthorhombic-to-tetragonal structural phase transition with increasing Ba : La ratio. Concentration axis not to scale (adapted from [1.20]).

phase by systematically changing the composition and measuring the lattice parameters and electrical properties. We found strong indications that the Ba-containing La_2CuO_4 was the phase responsible for the superconducting transition in our samples. Starting from the orthorhombically distorted host lattice, increasing the Ba substitution led to a continuous variation of the lattice towards a tetragonal unit cell[1.20] (see Fig. 1.8). The highest T_c's were obtained with a Ba concentration close to this transition (Fig. 1.9), whereas when the perovskite phase became dominant, the transition was suppressed and the samples showed only metallic characteristics.

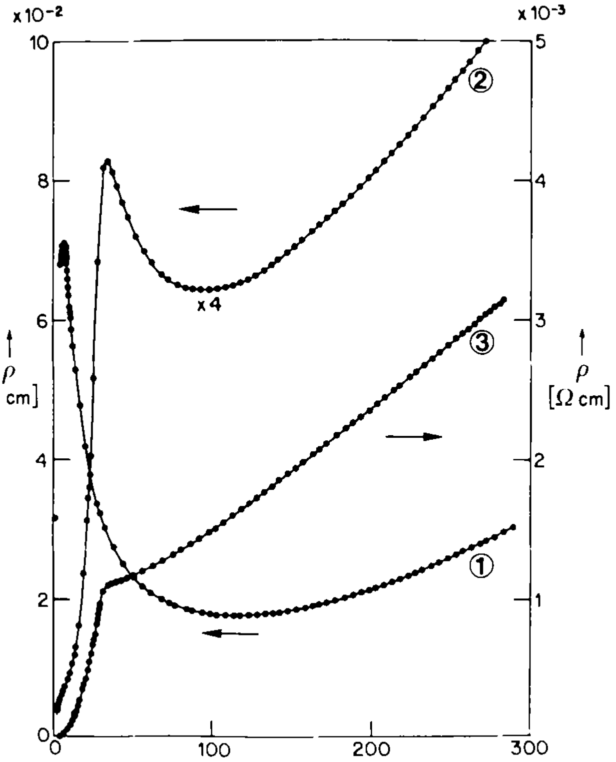

Fig. 1.9. Resistivity as a function of temperature for La_2CuO_{4-y} : Ba samples with three different Ba : La ratios. Curves ①, ②, and ③ correspond to ratios of 0.03, 0.06, and 0.07, respectively (adapted from [1.20]).

Finally, in September 1986, the susceptometer had been set up and we were all ready to run the magnetic measurements. To ensure that with the new magnetometer we did not measure any false results, *Masaaki* and I decided to gain experience on a known superconductor such as lead rather than starting on our samples. The Ba-La-Cu oxide we measured first had a low Ba content, where metallic behavior had been measured down to 100 K and a transition to localization occurred at lower temperatures. Accordingly, the magnetic susceptibility exhibited Pauli-like positive, temperature-independent and Curie-Weiss behavior at low temperatures, as illustrated by Figure 1.10. Most importantly, in samples showing a resistivity drop, a transition from para- to diamagnetism occurred at slightly lower temperatures (see Fig. 1.11) indicating that superconductivity-related shielding currents existed. The diamagnetic transition started below what is presumably the highest T_c in the samples as indicated by theories[1.21, 1.22] describing the behavior of percolative superconductors. In all our samples, the transition to the diamagnetic state was systematically related to the results of our resistivity measurements. The final proof of superconductivity, the presence of the Meissner-Ochsenfeld effect, had been demonstrated. Combining the X-ray analysis, resistivity and susceptibility measurements, it was now possible to clearly identify the Ba-doped La_2CuO_4 as the superconducting compound.

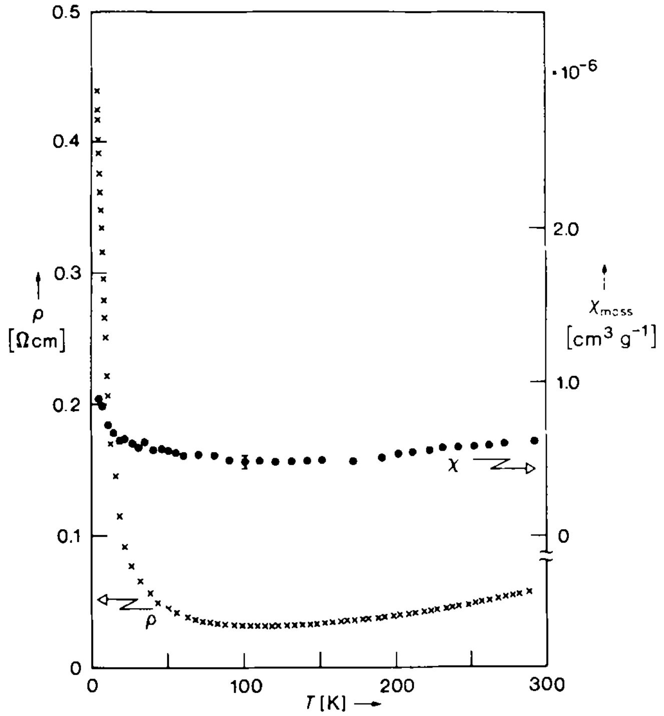

Fig. 1.10. Temperature dependence of resistivity (×) and mass susceptibility (●) of sample ① (adapted from [1.23]).

First Responses and Confirmations

The number of our troops was indeed growing. *Richard Greene* at our Research Center in Yorktown Heights had learned about our results and became excited. He had made substantial contributions in the field of organic superconductors and wanted to collaborate in measuring specific-heat data on our samples. We initiated an exchange of information, telefaxing the latest results of our research and sending samples. Realizing that our first paper had now appeared in the open literature, we rushed to get the results of our susceptibility data written up for publication.

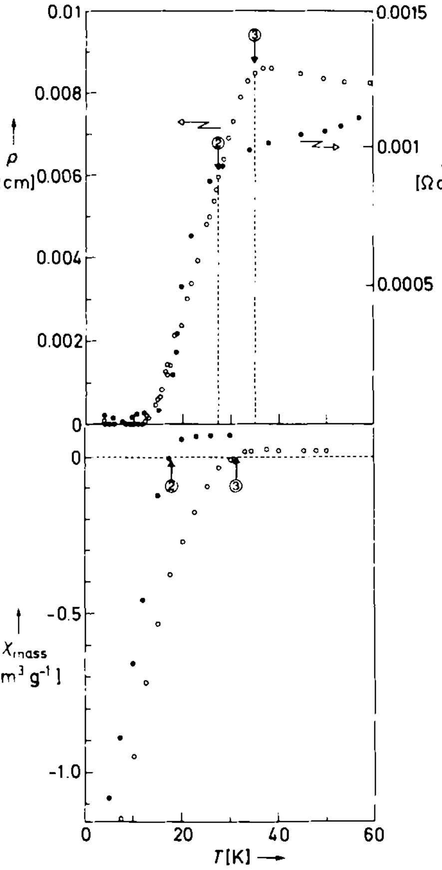

Fig. 1.11. Low-temperature resistivity (top) and mass susceptibility (bottom) of (La-Ba)-Cu-O samples ② (●) and ③ (○). Arrows indicate the onset of the resistivity and the paramagnetic-to-diamagnetic transitions, respectively (adapted from [1.23]).

The day we made the final corrections to our report turned out to be one of the most remarkable days in the history of our Laboratory. *Alex, Masaaki* and I were sitting together, when the announcement was made over our P.A. system that the 1986 Nobel Prize for Physics had been awarded to our colleagues *Gerd Binnig* and *Heinrich Rohrer*. With everything prepared for the submission of our paper,[1.23] for one more day we could forget about our work, and together with the whole Laboratory celebrate the new laureates. One day later we were back to reality, and I started to prepare a set of samples for *Richard Greene*. *Praveen Choudhari*, our director of Physical Science in Yorktown Heights, took them with him the same evening.

Later in November, we received the first response to our latest work from Professor *W. Buckel*, to whom *Alex* had send a preprint with the results of the magnetic measurements. His congratulations on our work were an encouragement, as we began to realize that we would probably have a difficult time getting our results accepted. Indeed, *Alex* and I had started giving talks about our discovery and, although the presence of the Meissner effect should have convinced people, at first we were met by a skeptical audience. However, this period turned out to be very short indeed.

We continued with the magnetic characterization of the superconducting samples and found interesting properties related to the behavior of a spin glass.[1.24] We then intensively studied the magnetic field and time dependences of the magnetization, before finally starting to realize an obvious idea, namely, to replace La also by other alkaline-earth elements like Sr and Ca. In particular Sr^{2+} had the same ionic radius as La^{3+}. We started experiments on the new materials, which indicated that for the Sr-substituted samples T_c was approaching 40 K and the diamagnetism was even higher (see Fig. 1.12).[1.25] It was just at that time that we learned from the Asahi-Shinbun International Satellite Edition [28 November 1986] that the group of Professor *Tanaka* at the University of Tokyo had repeated our experiments and could confirm our result.[1.26] We were relieved, and even more so when we received a letter from Professor *C. W. Chu* at the University of Houston, who was also convinced that within the Ba-La-Cu-O system superconductivity occurred at 35 K.[1.27] Colleagues who had not paid any attention to our work at all suddenly became

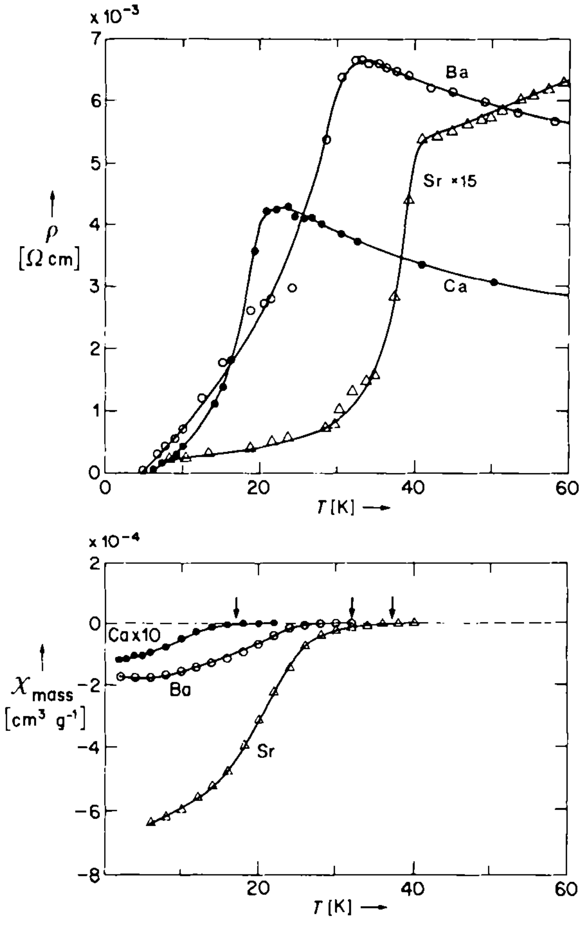

Fig. 1.12. Top: Resistivity as a function of temperature for Ca (●), Sr (△), and Ba (○) substitution with substituent to La ratios of 0.2/1.8, 0.2/1.8, 0.15/1.85, respectively. The Sr curve has been vertically expanded by a factor of 15. Bottom: Magnetic susceptibility of these samples. The substituents are Ca (●), Sr (△), and Ba (○), with total sample masses of 0.14, 0.21, and 0.13 g, respectively. The Ca curve has been expanded by a factor of 10. Arrows indicate onset temperatures (adapted from [1.25]).

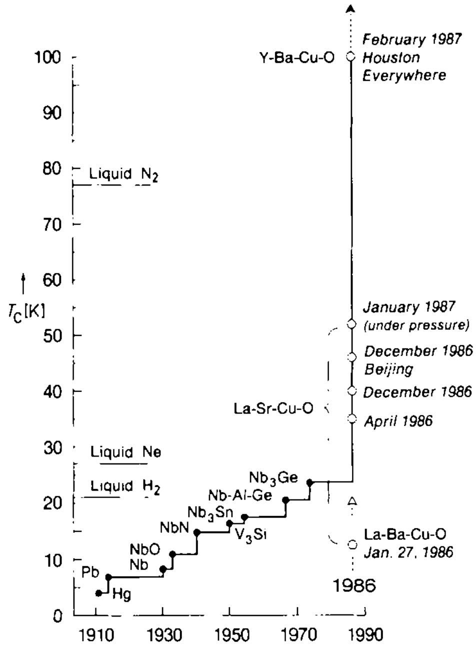

Fig. 1.13. Evolution of the superconductive transition temperature subsequent to the discovery of the phenomenon (adapted from [1.29]).

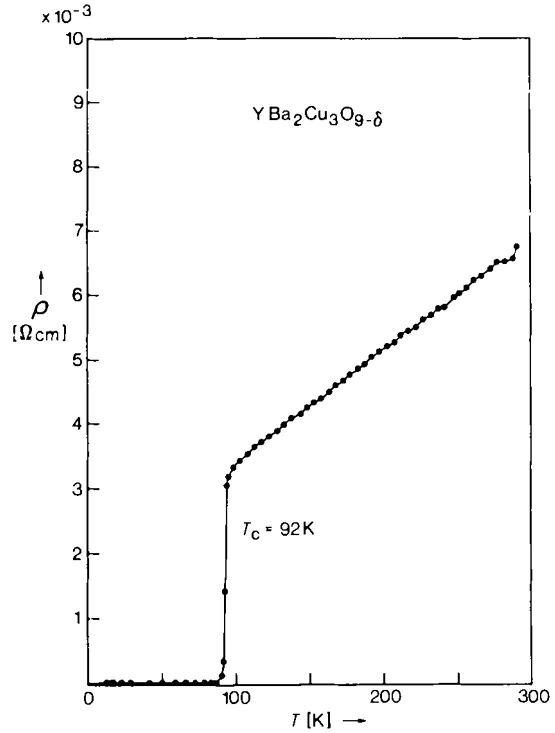

Fig. 1.14. Resistivity of a single-phase $YBa_2Cu_3O_7$ sample ("123 compound") as a function of temperature.

alert. By applying hydrostatic pressure to the samples, Professor *Chu* was able to shift the superconductive transition from 35 to almost 50 K.[1.27] Modification of the original oxides by introducing the smaller yttrium for the larger lanthanum ion resulted in a giant jump of T_c to 92 K in multiphase samples[1.28] (Fig. 1.13). At a breathtaking pace, dozens of groups now repeated these experiments and after an effort of only a few days the new superconducting compound could be isolated and identified. The resistive transition in the new $YBa_2Cu_3O_7$ compound was complete at 92 K (Fig. 1.14), and even more impressive was the fact that the Meissner effect could now be demonstrated without any experimental difficulties with liquid nitrogen as the coolant. Within several months, the field of superconductivity had experienced a tremendous revival, with an explosive development of T_c's such that nobody can predict where it will end.

An early account of the discovery appeared in the September 4 1987 issue of *Science*, which was dedicated to science in Europe.[1.29]

References Part 1

[1.1] K. A. Müller in E. J. Samuelsen, E. Andersen, J. Feder (Eds.): *Structural Phase Transitions and Soft Modes*, Universitetsforlayet, Oslo 1971, p. 85.

[1.2] T. Schneider, E. Stoll, *Physica (Amsterdam) 55* (1971) 702.

[1.3] J. F. Schooley, H. P. R. Frederikse, W. R. Hosler, E. R. Pfeiffer, *Phys. Rev. 159* (1967) 301.

[1.4] A. Baratoff, G. Binnig, *Physica (Amsterdam) 108B+C* (1981) 1335; A. Baratoff, G. Binnig, J. G. Bednorz, F. Gervais, J. L. Servoin in W. Buckel, W. Weber (Eds.): *Superconductivity in d- and f-Band Metals, Proc. 4th Conf.*, Kernforschungszentrum Karlsruhe 1982, p. 419.

[1.5] G. Binnig, A. Baratoff, H. E. Hoenig, J. G. Bednorz, *Phys. Rev. Lett. 45* (1980) 1352.

[1.6] K. A. Müller, M. Pommerantz, C. M. Knoedler, D. Abraham, *Phys. Rev. Lett. 45* (1980) 832, and references cited therein.

[1.7] M. R. Beasley, T. H. Geballe, *Phys. Today 36* (1984) No. 10, p. 60; J. Mueller, *Rep. Prog. Phys. 43* (1980) 663.

[1.8] D. C. Johnston, H. Prakash, W. H. Zachariasen, R. Viswanathan, *Mater. Res. Bull. 8* (1973) 777.

[1.9] A. W. Sleight, J. L. Gillson, F. E. Bierstedt, *Solid State Commun. 17* (1975) 27.

[1.10] J. Bardeen, L. N. Cooper, J. R. Schrieffer, *Phys. Rev. 108* (1957) 1175.

[1.11] B. K. Chakraverty, *J. Phys. Lett. 40* (1979) L99; *J. Phys. 42* (1981) 1351.

[1.12] K.-H. Höck, H. Nickisch, H. Thomas, *Helv. Phys. Acta 56* (1983) 236.

[1.13] J. B. Goodenough, M. Longo, *"Magnetic and other properties of oxide and related compounds"* in K. H. Hellwege, A. M. Hellwege (Eds.): *Landoldt-Börnstein New Series, Vol. III/4a: Crystal and Solid State Physics*, Springer, Berlin 1970, p. 262, Fig. 73.

[1.14] J. G. Bednorz, K. A. Müller, H. Arend, H. Gränicher, *Mater. Res. Bull. 18* (1983) 181.

[1.15] N. Y. Vasanthacharya, P. Ganguly, J. B. Goodenough, C. N. R. Rao, *J. Phys. C: Solid State Phys. 17* (1984) 2745.

[1.16] C. Michel, L. Er-Rakho, B. Raveau, *Mater. Res. Bull. 20* (1985) 667.

[1.17] C. Michel, B. Raveau, *Rev. Chim. Miner. 21* (1984) 407. It is of interest that back in 1973, J. B. Goodenough, G. Demazeaux, M. Pouchard, P. Hagenmüller (*J. Solid State Chem. 8* (1973) 325) in Bordeaux, and later I. S. Shaplygin, B. G. Kakhan, V. B. Lazarev (*Russ. J. Phys. Chem. 24* (1979) 1478) pursued research on layered cuprates with catalysis applications in view.

[1.18] M. Suzuki, T. Murakami, T. Inamura, *Shinku 24* (1981) 67; Y. Enomoto, M. Susuki, T. Murakami, T. Innukai, T. Inamura, *Jpn. J. Appl. Phys. 20* (1981) L661.

[1.19] J. G. Bednorz, K. A. Müller, *Z. Phys. B64* (1986) 189.

[1.20] J. G. Bednorz, M. Takashige, K. A. Müller, *Mater. Res. Bull. 22* (1987) 819.

[1.21] D. R. Bowman, D. Stroud, *Phys. Rev. Lett. 52* (1985) 299.

[1.22] C. Ebner, D. Stroud, *Phys. Rev. B31* (1985) 165, and references cited therein.

[1.23] J. G. Bednorz, M. Takashige, K. A. Müller, *Europhys. Lett. 3* (1987) 379.

[1.24] K. A. Müller, M. Takashige, J. G. Bednorz, *Phys. Rev. Lett. 58* (1987) 1143.

[1.25] J. G. Bednorz, K. A. Müller, M. Takashige, *Science 236* (1987) 73.

[1.26] H. Takagi, S. Uchida, K. Kitazawa, S. Tanaka, *Jpn. J. Appl. Phys. Lett. 26* (1987) L 123; S. Uchida, H. Takagi, K. Kitazawa, S. Tanaka, *ibid. 26* (1987) L 151.

[1.27] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, *Phys. Rev. Lett. 58* (1987) 405.

[1.28] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Goa, Z. J. Huang, Y. Q. Wang, C. W. Chu, *Phys. Rev. Lett. 58* (1987) 908; P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y. Q. Wang, K. Forster, J. Vassilious, C. W. Chu, M. K. Wu, J. R. Ashburn, C. J. Torng, *ibid. 58* (1987) 911.

[1.29] K. A. Müller, J. G. Bednorz, *Science 237* (1987) 1133.

Part 2: Properties of the New Superconductors

In the second part, properties of the new layered oxygen superconductors are described. Since their discovery, summarized in the first part, a real avalanche of papers has appeared; thus it would be beyond the scope of this lecture to review all of them here. A forthcoming international conference in Interlaken, Switzerland, in late February 1988, is intended to fulfill this task and will be chaired by one of us *(KAM)*[*]. Therefore, only a selected number of experiments was discussed in Stockholm—those judged of importance at this time for the understanding of superconductivity in the layered copper oxides. In some of them, the laureates themselves were involved, in others not. Owing to the frantic activity in the field, it may be possible that equivalent work with priority existed unknown to us. Should this indeed be the case, we apologize and propose that the following be read for what it is, namely, a write-up of the lecture given, including the transparencies shown.

After the existence of the new high-T_c superconductors had been confirmed, one of the first questions was "What type of superconductivity is it?" Does one again have Cooper pairing[2.1] or not? This question could be answered in the affirmative. The earliest experiment to come to our knowledge was that of the Saclay-Orsay collaboration. *Estève* et al.[2.2] measured the I-V characteristics of sintered $La_{1.85}Sr_{0.15}CuO_4$ ceramics using nonsuperconducting Pt-Rh, Cu or Ag contacts. In doing so, they observed weak link characteristics internal to the superconductor, to which we shall return later. They then applied microwaves at $\nu = 9.4$ GHz and observed Shapiro steps[2.3] at $V_s = 19$ µV intervals. From the well-known Josephson formula[2.4]

$$V_s = h\nu/q, \qquad (2.1)$$

they obtained $q = 2e$, i.e., Cooper pairs were present. Figure 2.1 illustrates these steps.

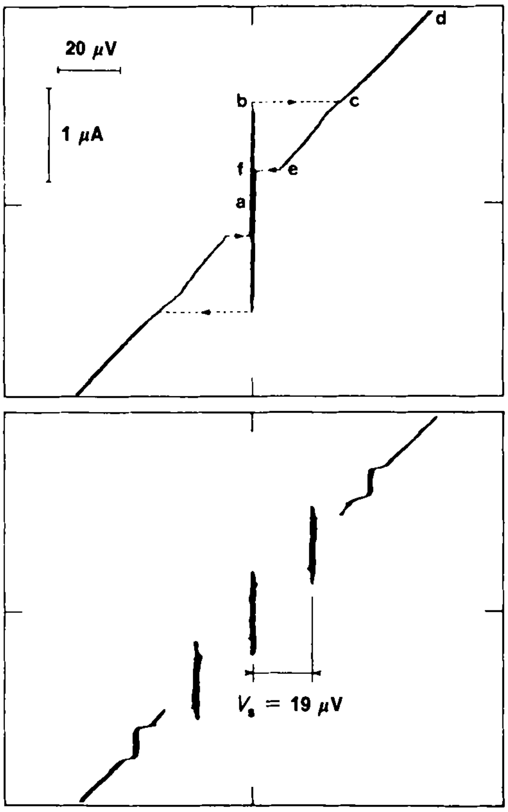

Fig. 2.1. Top: Oscilloscope trace of a current-voltage characteristic obtained at 4.2 K with an aluminum tip on a $La_{1.85}Sr_{0.15}CuO_4$ sample. Letters a through f indicate direction of trace. Dashed lines have been added to indicate the switching between the two branches. Bottom: Steps induced by microwave irradiation at frequency $\nu = 9.4$ GHz; all other experimental conditions identical (adapted from [2.2]).

From the fundamental London equations, the flux ϕ through a ring is quantized:[2.5]

$$\begin{aligned} \phi &= n\phi_0 \\ \phi_0 &= hc/q \end{aligned} \qquad (2.2)$$

The clearest experiment, essentially following the classical experiments in 1961, was carried out in Birmingham, England, by *C. E. Gough* et al.[2.6] They detected the output of an r.f.-SQUID magnetometer showing small integral numbers of flux quanta ϕ_0 jumping in and out of the ring of $Y_{1.2}Ba_{0.8}CuO_4$ (see Fig. 2.2). The outcome clearly confirmed that $q = 2e$.

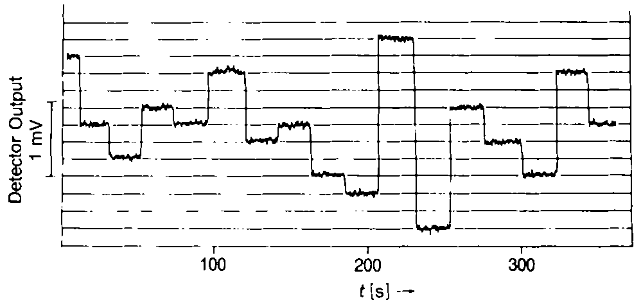

Fig. 2.2. Output of the r.f.-SQUID magnetometer showing small integral numbers of flux quanta jumping in and out of a ring (adapted from [2.6]).

---

[*] See conference report on page 771 of this issue.

To understand the mechanism, it was of relevance to know the nature of the charge carrier present. In La_2CuO_4 with very little doping, the early measurements[1.23] showed localization upon doping with divalent Ba^{2+} or Sr^{2+} and Ca^{2+}; it was most likely that these ions substituted for the trivalent La^{3+} ions. Thus, from charge-neutrality requirements, the compounds had to contain holes. Subsequent thermopower measurements confirmed this assumption.[2.7] The holes were thought to be localized on the Cu ions. Because the copper valence is two in the stoichiometric insulator La_2CuO_4, doping would create Cu^{3+} ions. Thus a mixed Cu^{2+}/Cu^{3+} state had to be present. By the same argument, this mixed-valence state ought also to occur in $YBa_2CuO_{7-\delta}$ ($\delta \approx 0.1$). Early photoelectron core-level spectra (XPS and UPS) by *Fujimori* et al.[2.8] and *Bianconi* et al.[2.9] in $(La_{1-x}Sr_x)_2CuO_{4-y}$ and $YBa_2La_3Cu_{6.7}$ did not reveal a 2p $3d^8$ final state arising from a Cu^{3+} $3d^8$ state (the underlining indicates a hole). However, the excitation was consistent with the formation of holes $\underline{L}$ in the oxygen-derived band, i.e., a predominant $3d^9$ L configuration for the formal Cu^{3+} state. Photo-X-ray absorption near the edge structure was also interpreted in the same manner by comparison with other known Cu compounds. Emission spectra by *Petroff*'s group[2.10] pointed in the same direction, since the excitation thresholds were compatible with the presence of holes in Cu-O hybrid bands. From their data, both groups concluded that strong correlation effects were present for the valence carriers. However, these results were challenged by other groups working in the field, partly because the spectra involved the interpretation of Cu-atom satellites. A beautifully direct confirmation of the presence of holes on the oxygen p-levels, like $\underline{L}$, was carried out by *Nücker* et al.[2.11] These authors investigated the core-level excitation of oxygen 1s electrons into empty 2p states of oxygen at 528 eV. This is an oxygen-specific experiment. If no holes are present on the p-level, no absorption will occur. Figure 2.3 summarizes their data on $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$. It is shown that for $x=0$ and $\delta=0.5$, no oxygen p-holes are present and thus no absorption is observed, whereas upon increasing x or reducing δ, a 2$\underline{p}$ hole density at the Fermi level is detected in both compounds.

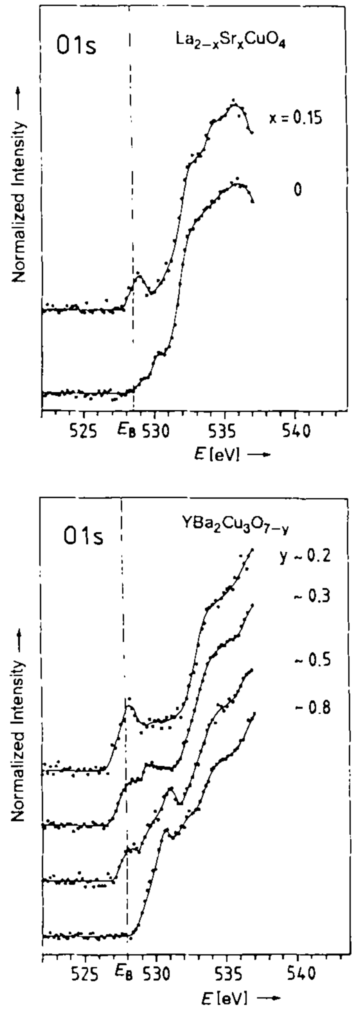

Fig. 2.3. Oxygen 1s absorption edges of $La_{2-x}Sr_xCuO_4$ (top) and $YBa_2Cu_3O_{7-x}$ (bottom) measured by energy-loss spectroscopy. The binding energy of the O 1s level, as determined by X-ray induced photoemission, is shown by the dashed line. In the framework of an interpretation of the spectra in terms of the density of unoccupied states, this line would correspond to the Fermi energy (adapted from [2.11]).

Of considerable interest is the dependence of the transition temperature on the hole concentration. The electron deficiency is hereafter written in the form $[Cu\text{-}O]^+$ as a peroxide complex in which the probability of the hole is about 70% $3d^9$ 2$\underline{p}$, as discussed above, and 30% $3d^8$ as recently inferred from an XPS study.[2.12] Hall-effect data are difficult to analyze in the presence of two-band conduction, which is possible in these copper oxide compounds, owing to the well known compensation effects. Therefore, *M. W. Shafer, T. Penney*, and *B. L. Olson*[2.13] determined

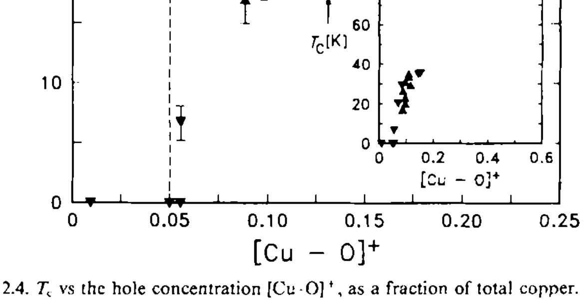

Fig. 2.4. T_c vs the hole concentration $[Cu\text{-}O]^+$, as a fraction of total copper. Down triangles are for compositions with $x<0.15$, up triangles for $x>0.15$. Insert shows same data plus points for a single $YBa_2CuO_{6.6}$ sample as discussed in the text (adapted from [2.13]).

the concentration by wet chemistry according to the reaction $[Cu-O]^+ + Fe^{2+} \rightleftarrows Cu^{2+} + Fe^{3+} + O^{2-}$ in the $La_{2-x}Sr_xCuO_{4-\delta}$ compound. Figure 2.4 shows a plot of T_c vs $[Cu-O]^+$ concentration with a maximum of 35 K at 15% total copper present. There is also a clear threshold at about 5%. From the study, it is apparent that 15-16% $[Cu-O]^+$ is the maximum number of holes the La_2CuO_4 structure accepts. Beyond this concentration, oxygen vacancies are formed. The relationship between T_c and $[Cu-O]^+$ in $La_{2-x}Sr_xCuO_4$ was extended to $YBa_2Cu_3O_{7-\delta}$. The insert of Figure 2.4 illustrates the results under the assumption that two layers in the 123 compound are active for $\delta \approx 0.1$ and $\delta \approx 0.3$, i.e., T_c's of 92 K and 55 K.[2.14] The latter transition, first reported by *Tarascon* et al., was confirmed by near-room-temperature plasma oxidation of the oxygen-deficient Y-compound.[2.14]

The $La_{2-x}Sr_xCuO_{4-y}$ with its less complicated structure allows easier testing of models. Its magnetic properties below the hole threshold concentration, $x = 0.05$, are of special interest. For $x = 0$, the susceptibility $\chi(T) = M(T)/H$ exhibits a maximum at low fields of $H \approx 0.05$ T below 300 K. This maximum increases in height and shifts to lower temperatures for higher magnetic fields up to 4.5 T[2.15] as seen in Figure 2.5a. Such behavior is indicative of spin density waves or antiferromagnetic fluctuations. Indeed, neutron diffraction experiments by *Vaknin* et al.[2.16] proved three-dimensional (3-D) antiferromagnetic ordering up to 240 K depending on oxygen stoichiometry (i.e., hole concentration). The structure is shown in Figure 2.5b. Subsequent neutron scattering experiments on a single crystal revealed a novel two-dimensional (2-D) antiferromagnetic correlation well above and also *below* the 3-D Néel temperature T_N as shown in Figure 2.6. This instantaneous (not time-averaged) ordering, seen even above room temperature, was termed a quantum spin fluid (Q.S.F.).[2.17] The existence of antiferromagnetism (A.F.) supports models in which holes lead either to localization or to pairing in the strong-coupling limit as proposed by *Emery*[2.18] and others.[2.19] The resonant valence-band state is also related to the A.F. state.[2.20]

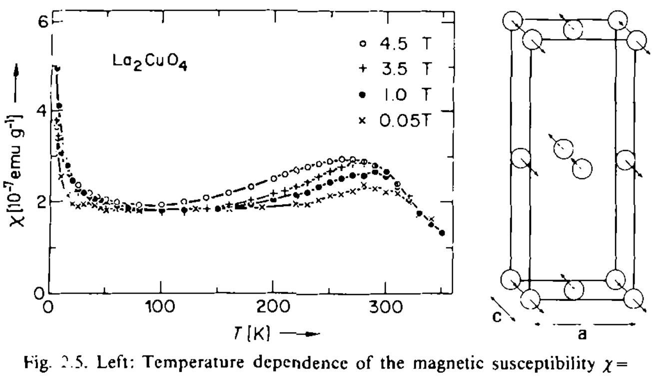

Fig. 2.5. Left: Temperature dependence of the magnetic susceptibility $\chi = M/H$ of La_2CuO_4 in different fields H (adapted from [2.15]). Right: Spin structure of antiferromagnetic La_2CuO_4. .. Only copper sites in the orthorhombic unit cell are shown for clarity (adapted from [2.16]).

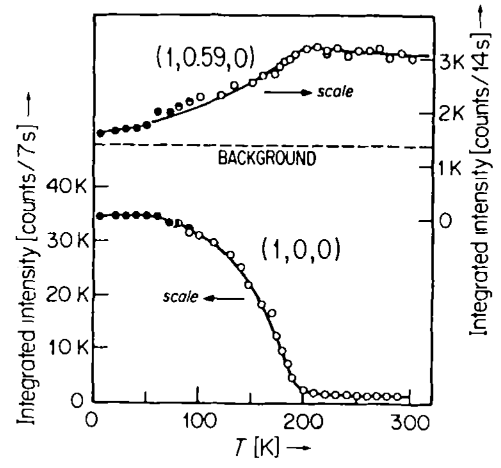

Fig. 2.6. Integrated intensities of the (100) 3-D antiferromagnetic Bragg peak and the (1,0.59,0) 2-D quantum spin fluid ridge. The open and filled circles represent separate experiments (adapted from [2.17]).

From the prevalence of magnetic interactions as a primary cause for the occurrence of high-T_c superconductivity, one would expect the isotope effect to be absent, since it occurs when the Cooper pairing is mediated by phonon interaction, as found in most of the metallic superconductors previously known. Indeed, substituting O^{16} by O^{18} in the $YBa_2Cu_3O_{7-\delta}$ compound at AT&T did not reveal a shift in T_c.[2.21] However, substitution experiments in $La_{2-x}Sr_xCuO_{4-y}$ oxide carried out shortly thereafter did reveal an isotope effect with $0.14 < \beta < 0.35$[2.22] as compared with the full effect of $\beta = 0.5$ deduced from the weak-coupling formula[1.10]

$$T_c = 1.13\,\Theta_D \exp - (1/N(E_F) \times V^*), \qquad (2.3)$$

with the Debye temperature $\Theta_D \propto 1/M^{1/2}$, where M is the reduced mass. Thus in the lanthanum compound, oxygen motion is certainly present. As it is highly unlikely that the mechanism is substantially different in the 123 compound, oxygen motion should also be there. This is because absence of the isotope effect does not necessarily exclude a phonon mechanism, which has to be present if Jahn-Teller polarons participate. Indeed, a subsequent, more accurate experiment did show a weak isotope effect in $YBa_2Cu_3O_{7-\delta}$ with $\Delta T_c \approx 0.3$ to 0.5 K.[2.23] From these results, it appears likely that there is more than one interaction present which leads to the high transition temperatures, the low quasi-2D properties certainly being of relevance.

The X-ray and photoemission studies mentioned earlier had indicated strong correlation effects. Cooper pairing having been ascertained, it was therefore of considerable interest whether the new superconductors were of the strong- or the weak-coupling variety. In the latter case, the ratio of the gap 2Δ to kT_c is:[1.10]

$$\frac{2\Delta}{kT_c} = 3.52 \qquad (2.4)$$

whereas in the former it is larger.

Tunneling experiments have been widely used to determine the gap in the classical superconductors. However, the very short coherence length yields too low values of 2Δ, as will be discussed later.[2.24] Infrared transmission and reflectivity measurements on powders were carried out at quite an early stage. With the availability of $YBa_2Cu_3O_7$ single crystals, powder infrared data are less relevant, but are quoted in the more recent work. A beautiful example is the reflectivity study by *Schlesinger* et al.[2.25] of superconducting $YBa_2Cu_3O_7$ and a Drude fit to the nonsuperconducting $YBa_2Cu_3O_{6.5}$ data. From the Mattis-Bardeen enhanced peak in the superconducting state, these authors obtained $2\Delta_{ab}/kT_c \approx 8$, i.e., strong coupling in the Cu-O planes (see Fig. 2.7). NMR relaxation experiments by *Mali* et al.,[2.26] although not yet completely analyzed, yield two gaps with ratios 4.3 and 9.3, respectively, the latter being in the range of the infrared data.

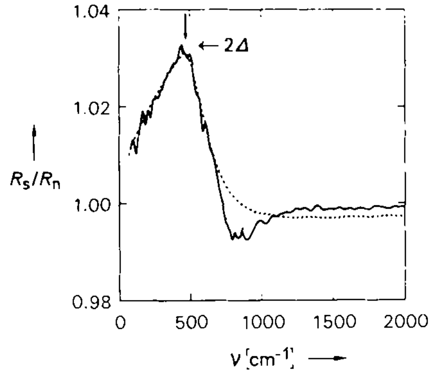

Fig. 2.7. Normalized infrared reflectivity of a single crystal of $YBa_2Cu_3O_7$ and fitted Mattis-Bardeen form of $\delta(\omega)$ (dotted line) in the superconducting state. The arrow shows the peak occurring at $2\Delta \approx 480$ cm $^{-1}$, hence $2\Delta \approx 8kT_c$ with $T_c = 92$ K (adapted from [2.25]).

NMR relaxation experiments were among the first at the time to prove the existence of a gap.[2.27] They also appear to be important for the new class of superconductors.

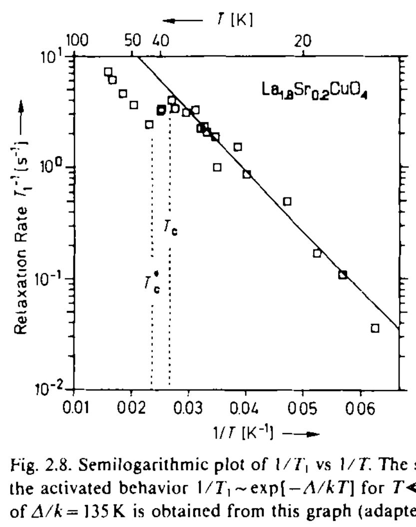

Fig. 2.8. Semilogarithmic plot of $1/T_1$ vs $1/T$. The straight line demonstrates the activated behavior $1/T_1 \sim \exp[-\Delta/kT]$ for $T \ll T_c^*$. An activation energy of $\Delta/k = 135$ K is obtained from this graph (adapted from [2.28]).

Zero-field nuclear spin lattice relaxation measurements on ^{139}La in $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ below T_c follow the relationship $1/T_1 \propto \exp(-\Delta/kT)$ (see Fig. 2.8) with activation energy $\Delta = 1.1$ meV; at low temperatures $kT \ll 2\Delta$ due to a $T_c = 38$ K. A ratio of $2\Delta/kT_c = 7.1$ was obtained.[2.28] Therefore, strong coupling is also present in the La compound. The value of Δ probably has to be attributed to the gap parallel to the planes. In fact, it has been shown that infrared reflectivity data on powders measure the gap along the c-axis, and a ratio of $2\Delta_c/kT_c \approx 2.5$ was given.[2.29] Thus the coupling between the planes appears to be weak. Such a substantial anisotropic property was not previously found in other superconductors.

From the first measurements of resistivity as a function of magnetic field, the slopes dH_{c_2}/dT near T_c could be obtained, and from them very high critical fields at low temperatures were extrapolated. From the many papers published, we quote that of *Decroux* et al.,[2.30] also because this was the first paper to report a specific-heat plateau at T_c. The group at the University of Geneva found $dH_{c_2}/dT = -2.5\,\mathrm{T\,K^{-1}}$, yielding an extrapolated $H_{c_2}(T=0) = 64$ T.

From the well-known formula for the critical field in type-II superconductors

$$H_{c_2} = \frac{\phi_0}{2\pi\xi^2} \tag{2.5}$$

one calculates that the coherence length ξ is of the order of the lattice distances. Actually the coherence lengths evaluated have become smaller; recent results on single crystals by an IBM group in Yorktown Heights[2.31] and on epitaxial layers by the Stanford group [2.32] are of the order $\xi_c \approx 3$-4 Å for the coherence length parallel to c and $\xi_{ab} \approx 20$-30 Å perpendicular to c.

Such short coherence lengths could be expected when one considers the relationship between ξ, the gap and the Fermi energy E_F. *Weisskopf*[2.33] deduced

$$\xi \approx \frac{E_F}{\Delta} d \tag{2.6}$$

from the Heisenberg uncertainty principle. In equation (2.6), d is the screening length, which one can assume to be of the order of a unit cell distance. The ratio E_F/Δ is near unity owing to the large Δ and the small E_F, the latter resulting from the low carrier density and the sizeable electron mass. Therefore in oxides, ξ is considerably smaller than in metals. Because Δ is anisotropic, so is ξ. The comparable size of E_F and Δ indicates that most of the carriers participate in the superconductivity of the new oxides for temperatures $T < T_c$, in contrast to the classical superconductors, where $E_F \gg \Delta \approx 1.7\,kT_c$.

The short coherence lengths in the layered copper oxide superconductors are important theoretically, experimentally, and applicationwise: The short ξ's and carrier concentrations of the order of $n = 10^{21}$ cm^{-3} make one wonder whether boson-condensation approaches are not more appropriate, i.e., real-space Cooper pairing in contrast to the wave-vector space pairing of classical BCS theory,[1.10] which applies so well for metals with large ξ's and concentrations n. Actually, *Schafroth*[2.34] back in 1955 was the first to work out a superconducting theory with boson condensation. Referring to *Chakraverty*'s phase diagram in Figure 1.2,[1.11] one may regard the metal superconducting phase line as BCS with weak coupling, and the superconductor-insulator boundary for large coupling constants λ as the Schafroth line.

The short coherence lengths induce considerable weakening of the pair potential at surfaces and interfaces, as emphasized by *Deutscher* and *Müller*.[2.24] Using an expression for the "extrapolation length" b[2.35] for the boundary condition at the superconductor-insulator interface, the $\Delta(x)$ profile was deduced as shown in Figure 2.9 for $T \lesssim T_c$ and $T \ll T_c$.

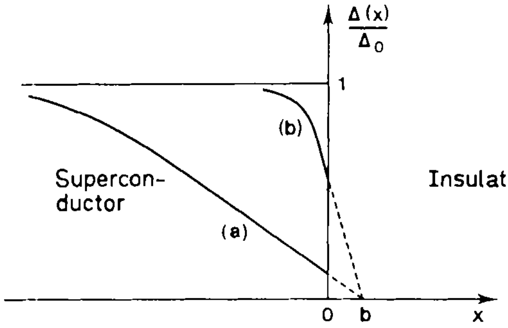

Fig. 2.9. Profile of the pair potential in a short-coherence-length superconductor near a superconductor-insulator boundary. Curve (a): $T \lesssim T_c$; curve (b): $T \ll T_c$ (adapted from [2.24]).

Analogous behavior of $\Delta(x)$ will also be present at superconducting-normal (SN) interfaces. Thus, the depressed order parameter involving experiments of SIS and SNS will result in tunneling characteristics[2.24] with a marked reduction in the observed value of Δ. In consequence, such experiments are less suitable than infrared and NMR studies to determine Δ, and actually lead to erroneous conclusions regarding gapless superconductivity also in point-contact spectroscopy.[2.36] $YBa_2Cu_3O_7$ undergoes a tetragonal-to-orthorhombic phase transition near 700°C. Thus upon cooling, (110) twin boundaries are formed, separating the orthorhombic domains and inducing *intragrain* Josephson or weak-link junctions. These junctions form a network dividing the crystallites into Josephson-coupled domains, with the possibility of fluxon trapping as well. Therefore even single crystals form a superconducting glass *in the presence* of a sizeable magnetic field.

The basic Hamiltonian regarding the phases is[1.22]

$$\beta \mathscr{H} = -\sum J_{ij} \cos(\phi_i - \phi_j - A_{ij}) \qquad (2.7)$$

Here, J_{ij} is the Josephson coupling constant between domains. The phase factors $A_{ij} = K_{ij} H$ introduce randomness for $H \neq 0$ because K_{ij} is a random geometric factor. A review of the superconducting glass state has recently appeared.[2.37]

The first evidence indicating the presence of superconducting glassy behavior was deduced from field-cooled and zero-field-cooled magnetization data[1.24, 2.38] in $La_{2-x}Ba_xCuO_4$ ceramics. In addition to the twin-boundary-induced *intragrain* junctions, such a material also has junctions resulting from the *intergrain* boundaries. The latter J_{ij}'s are much weaker and uncouple at lower magnetic fields and currents j_c. Consequently, the critical currents observed in the ceramics are more of the order of 10^3 to 10^4 A cm^{-2},[2.39] whereas those in epitaxial layers[2.40] and single crystals[2.1] are of the order of 10^6 to 10^7 A cm^{-2}.[2.41] The latter work, carried out by two IBM groups, is a major breakthrough in the field.

The decay lengths of the superconducting wave functions at SNS and SIS junctions are both of the order of $\xi(0)$. This entails an anomalous temperature dependence $J_c \propto (T - T_c)^2$. Such behavior is seen in the mid-temperature range for $J_c(T)$ in the $YBa_2Cu_3O_{7-\delta}$ epilayer on $SrTiO_3$ of Figure 2.10.[2.40] Such critical currents are acceptable for thin film applications at 77 K for low magnetic fields (Fig. 2.10), whereas in the ceramics the much lower J_c's indicate a need for further development work, or, perhaps better still, the discovery of a new type of high-T_c superconductor that should exist.

The geometrical critical magnetic field $H^*_{c_1}$ is of the order of[1.22]

$$H^*_{c_1} = \phi_0 / 2S \qquad (2.8)$$

where S is the projected area of the superconducting loop with uniform phase. In single crystals, the S of domains is of the order of 100 µm^2, whereas that of grains in ceramics is 1–10 µm^2. In agreement with equation (2.8), $H^*_{c_1}$ is of the order of 0.5 G for the penetration of H into twinned crystals, and 5 to 100 G to disrupt intergranular nets in ceramics.

Since the publication on the existence of this new class of materials, the interest and work have far exceeded the expectations of the laureates, whose aim was primarily to show that oxides could "do better" in superconductivity than metals and alloys. Due to this frenzy, progress on the experimental side has been rapid and is expected to continue. This will also assist in finding new compounds, with T_c's reaching at least 130 K (Fig. 2.4). Quantitative theoretical models are expected in the not too distant future, first perhaps phenomenological ones. On this rapidly growing tree of research, separate branches are becoming strong, such as glass aspects, growth techniques for single crystals, epitaxial films, and preparation of ceramics, the latter two being of crucial importance for applications. The former will dominate the small-current microelectronics field, while the latter will have to be mastered in the large-current field. Here the hopes are for energy transport, and

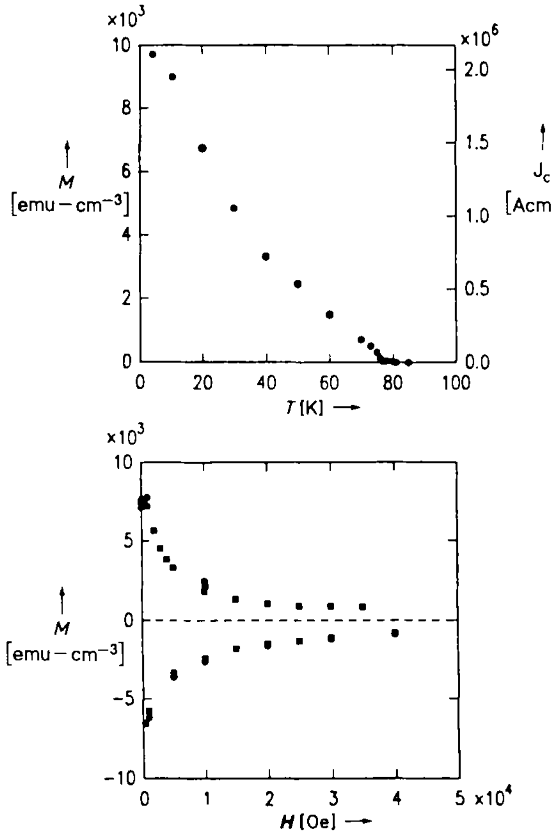

Fig. 2.10. Top: The volume magnetization M vs temperature for an epitaxial sample. The y-axis scale on the right was obtained with the use of the Bean formula $J_c = 30\ M/d$, with the mean radius of the sample $d = 0.14$ cm. Bottom: The volume magnetization M vs applied field H at 4.2 K for two samples (adapted from [2.40]).

later large magnetic field applications, for example in beam bending in accelerators and plasma containment in fusion.

References Part 2

[2.1] L. N. Cooper, *Phys. Rev. 104* (1956) 1189.
[2.2] D. Estève, J. M. Martins, C. Urbina, M. H. Devoret, G. Collin, P. Monod, M. Ribault, A. Revcolevschi, *Europhys. Lett. 3* (1987) 1237.
[2.3] S. Shapiro, *Phys. Rev. Lett. 11* (1963) 80.
[2.4] B. D. Josephson, *Phys. Lett. 1* (1962) 251.
[2.5] F. London: *Superfluids. Vol. 1*, Wiley, New York 1950, p. 152.
[2.6] C. E. Gough, M. S. Colclough, E. M. Forgan, R. G. Jordan, M. Keene, C. M. Muirhead, A. I. M. Rae, N. Thomas, J. S. Abell, S. Sutton, *Nature (London) 326* (1987) 855.
[2.7] F. Steglich, C. D. Bredl, F. R. de Boer, M. Lang, U. Rauchschwalbe, H. Rietschel, R. Schefzyk, G. Sparn, G. R. Stewart, *Phys. Scr. T19* (1987) 253.
[2.8] A. Fujimori, E. Takayama-Muromachi, Y. Uchida, B. Okai, *Phys. Rev. B35* (1987) 8814.
[2.9] A. Bianconi, A. C. Castellano, M. De Santis, P. Delogu, A. Gargano, R. Giorgi, *Solid State Commun. 63* (1987) 1135; A. Bianconi, A. C. Castellano, M. De Santis, C. Politis, A. Marcelli, S. Mobilio, A. Savoia, *Z. Phys. B67* (1987) 307.
[2.10] P. Thiry, G. Rossi, Y. Petroff, A. Revcolevschi, J. Jegoudez, *Europhys. Lett. 5* (1988) 55.
[2.11] M. Nücker, J. Fink, J. C. Fuggle, P. J. Durham, W. M. Temmerman, *Phys. Rev. B*, (1988), in press.
[2.12] P. Steiner, S. Hüfner, V. Kinsinger, I. Sander, B. Siegwart, H. Schmitt, R. Schulz, S. Junk, G. Schwitzgebel, A. Gold, C. Politis, H. P. Müller, R. Hoppe, S. Kemmler-Sack, C. Kunz, *Z. Phys. B69* (1988) 449.
[2.13] M. W. Shafer, T. Penney, B. L. Olson, *Phys. Rev. B36* (1987) 4047.
[2.14] J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, E. M. Vogel, *Phys. Rev. B36* (1987) 226; see also B. G. Bagley, L. H. Greene, J. M. Tarascon, G. W. Hull, *Appl. Phys. Lett. 51* (1987) 622.
[2.15] R. L. Greene, H. Maletta, T. S. Plaskett, J. G. Bednorz, K. A. Müller, *Solid State Commun. 63* (1987) 379.
[2.16] D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, H. E. King, Jr., *Phys. Rev. Lett. 58* (1987) 2802.
[2.17] G. Shirane, Y. Endoh, R. J. Birgeneau, M. A. Kastner, Y. Hidaka, M. Oda, M. Suzuki, T. Murakami, *Phys. Rev. Lett. 59* (1987) 1613.
[2.18] V. J. Emery, *Phys. Rev. Lett. 58* (1987) 2794; *Nature (London) 328* (1987) 756.
[2.19] J. E. Hirsch, *Phys. Rev. Lett. 59* (1987) 228; M. Cyrot, *Solid State Commun. 62* (1987) 821, and unpublished results.
[2.20] P. W. Anderson, *Science (Washington) 235* (1987) 1196; P. W. Anderson, G. Baskaran, Z. Zou, T. Hsu, *Phys. Rev. Lett. 58* (1987) 2790.
[2.21] B. Batlogg, R. J. Cava, A. Jayaraman, R. B. Van Dover, G. A. Kourouklis, S. Sunshine, D. W. Murphy, L. W. Rupp, H. S. Chen, A. White, K. T. Short, A. M. Mujsce, E. A. Rietman, *Phys. Rev. Lett. 58* (1987) 2333; L. C. Bourne, M. F. Crommie, A. Zettl, H.-C. zur Loye, S. W. Keller, K. L. Leary, A. M. Stacy, K. J. Chang, M. L. Cohen, D. E. Morris, *ibid. 58* (1987) 2337.
[2.22] T. A. Faltens, W. K. Ham, S. W. Keller, K. J. Leary, J. N. Michaels, A. M. Stacy, H.-C. zur Loye, D. E. Morris, T. W. Barbee III, L. C. Bourne, M. L. Cohen, S. Hoen, A. Zettl, *Phys. Rev. Lett. 59* (1987) 915; B. Batlogg, G. Kourouklis, W. Weber, R. J. Cava, A. Jayaraman, A. E. White, K. T. Short, L. W. Rupp, E. A. Rietman, *ibid. 59* (1987) 912.
[2.23] K. J. Leary, H.-C. zur Loye, S. W. Keller, T. A. Faltens, W. K. Ham, J. N. Michaels, A. M. Stacy, *Phys. Rev. Lett. 59* (1987) 1236.
[2.24] G. Deutscher, K. A. Müller, *Phys. Rev. Lett. 59* (1987) 1745.
[2.25] Z. Schlesinger, R. T. Collins, D. L. Kaiser, F. Holtzberg, *Phys. Rev. Lett. 59* (1987) 1958.
[2.26] M. Mali, D. Brinkmann, L. Pauli, J. Roos, H. Zimmermann, J. Hulliger, *Phys. Lett. A 124* (1987) 112, and references cited therein. It should be noted that analysis of the relaxation data $1/T_c \propto T^3$ is also possible, as one expects in the presence of anisotropic gaps.
[2.27] L. C. Hebel, C. P. Slichter, *Phys. Rev. 113* (1959) 1504.
[2.28] H. Seidel, F. Hentsch, M. Mehring, J. G. Bednorz, K. A. Müller, *Europhys. Lett. 5* (1988) 647.
[2.29] Z. Schlesinger, R. T. Collins, M. W. Shafer, *Phys. Rev. B35* (1987) 7232.
[2.30] M. Decroux, A. Junod, A. Bezinge, D. Cattani, J. Cors, J. L. Jordan, A. Stettler, M. François, K. Yvon, Ø. Fischer, J. Muller, *Europhys. Lett. 3* (1987) 1035.
[2.31] T. K. Worthington, W. J. Gallagher, T. R. Dinger, *Phys. Rev. Lett 59* (1987) 1160.
[2.32] A. Kapitulnic, M. R. Beasley, C. Castellani, C. Di Castro, *Phys. Rev. B37* (1988) 537.
[2.33] V. F. Weisskopf: *The Formation of Cooper Pairs and the Nature of Superconducting Currents*, CERN, Geneva, Memorandum No. CERN 79-12, Theoretical Studies Division, 21 December 1979.
[2.34] R. Schafroth, *Phys. Rev. 96* (1954) 1149, 1442; *100* (1955) 463.
[2.35] P. G. de Gennes: *Superconductivity of Metals and Alloys*, Benjamin, New York 1968, p. 229.
[2.37] I. K. Yanson, L. F. Rybal'chenko, V. V. Fisun, N. L. Bobrov, M. A. Obolenskii, N. B. Brandt, V. V. Moshchalkov, Yu. D. Tret'yakov, A. R. Kaul', I. É. Graboi, *Fiz. Nizk. Temp. (Kiev) 13* (1987) 557 [*Sov. J. Low Temp. Phys. 13* (1987) 315].
[2.37] K. A. Müller, K. W. Blazey, J. G. Bednorz, M. Takashige, *Physica (Amsterdam) 148 B* (1987) 149.
[2.38] F. S. Razavi, F. P. Koffyberg, B. Mitrović, *Phys. Rev. B35* (1987) 5323.
[2.39] J. F. Kwak, E. L. Venturini, D. S. Ginley, W. Fu in S. A. Wolf, V. Z. Kresin (Eds.): *Novel Superconductivity. Proc. Int. Worksh. Novel Mechanisms in Superconductivity*, Plenum, New York 1987, p. 983.
[2.40] P. Chaudhari, R. H. Koch, R. B. Laibowitz, T. R. McGuire, R. J. Gambino, *Phys. Rev. Lett. 58* (1987) 2684.
[2.41] T. R. Dinger, T. K. Worthington, W. J. Gallagher, R. L. Sandstrom, *Phys. Rev. Lett. 58* (1987) 2687.

Received: March 25, 1988