PEROVSKITE-TYPE OXIDES - THE NEW APPROACH TO HIGH-T_c SUPERCONDUCTIVITY

Nobel lecture, December 8, 1987

by

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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, 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 Zurich 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 by 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 Megabar 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 create large 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 personal interest in the fascinating phenomenon of superconductivity was triggered in 1978 by a telephone call from Heinrich Rohrer, the manager of a new hire 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, 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 transpired 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 Zurich. His special interest was the field of granular superconductivity, an example being aluminum [1.6], 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 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 hardly had 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 on 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. This because since 1973 the highest T_c of 23.3 K [1.7] could not be raised. But nevertheless, the fact that superconductivity had been observed in several complex oxides evoked our special interest.

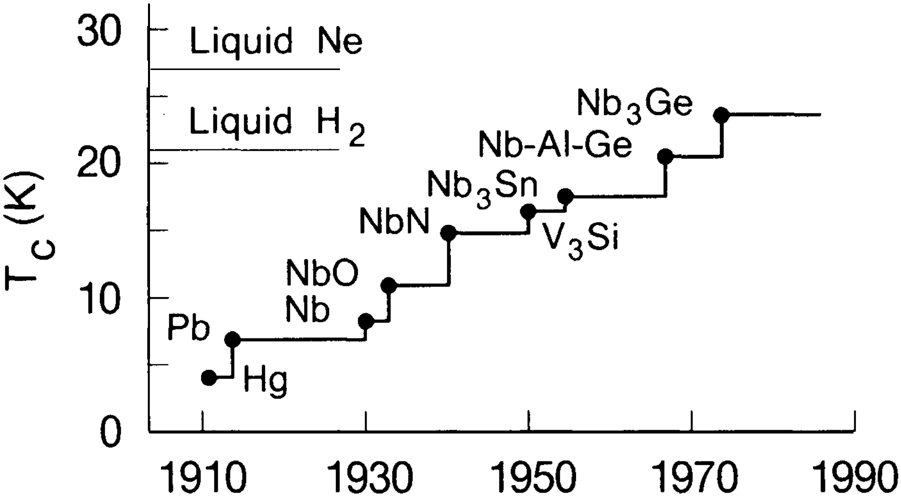

Figure 1.1. Development of the superconducting transition temperatures after the discovery of the phenomenon in 1911. The materials listed are metals or intermetallic compounds and reflect the respective highest T_c's.

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,. 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]

$$k_x T_c = 1.13\hbar\omega_D e^{-1/(N(E_F))xV^*},$$

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 V^*, 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, thus these attempts failed.

We in Rüschlikon felt and accepted the 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

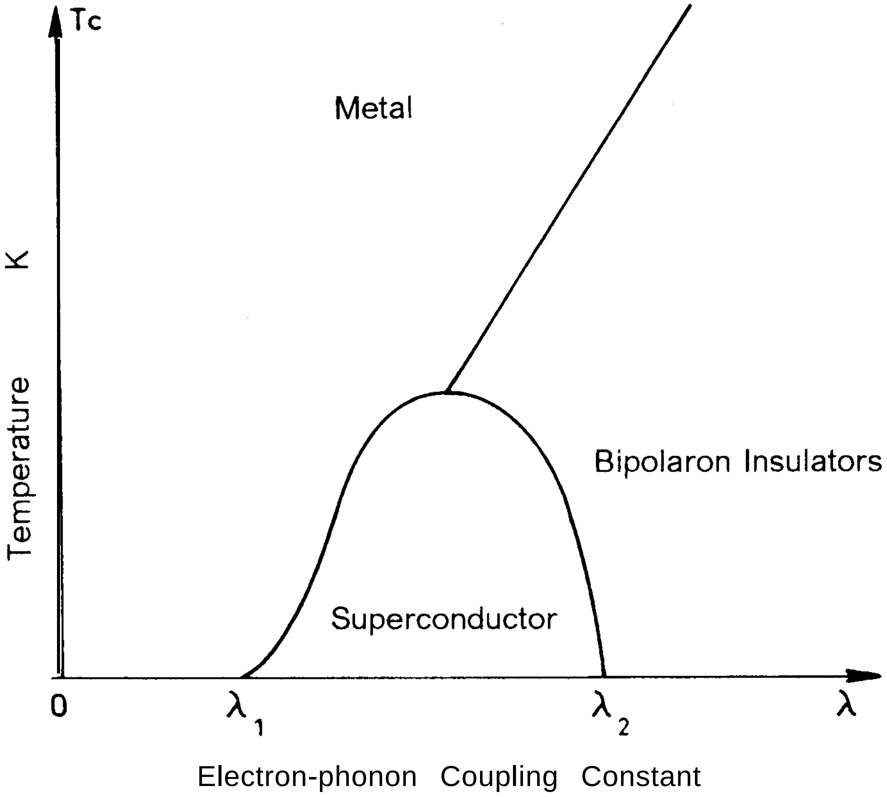

Figure 1.2. Phase diagram as a function of electron-phonon coupling strength. From [1.11], ©Les Editions de Physique 1979.

by the introduction of mixed valencies. The intuitive phase diagram of the coupling constant $\lambda = N(E_F)^x V^*$ 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, 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 units. 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 E_{JT} being of the magnitude of the bandwidth, the formation of JT polarons was proposed.

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 realize the Chakraverty phase diagram. Based on the experience from studies of isolated JT ions in the perovskite insulators, our assumption was that the model would

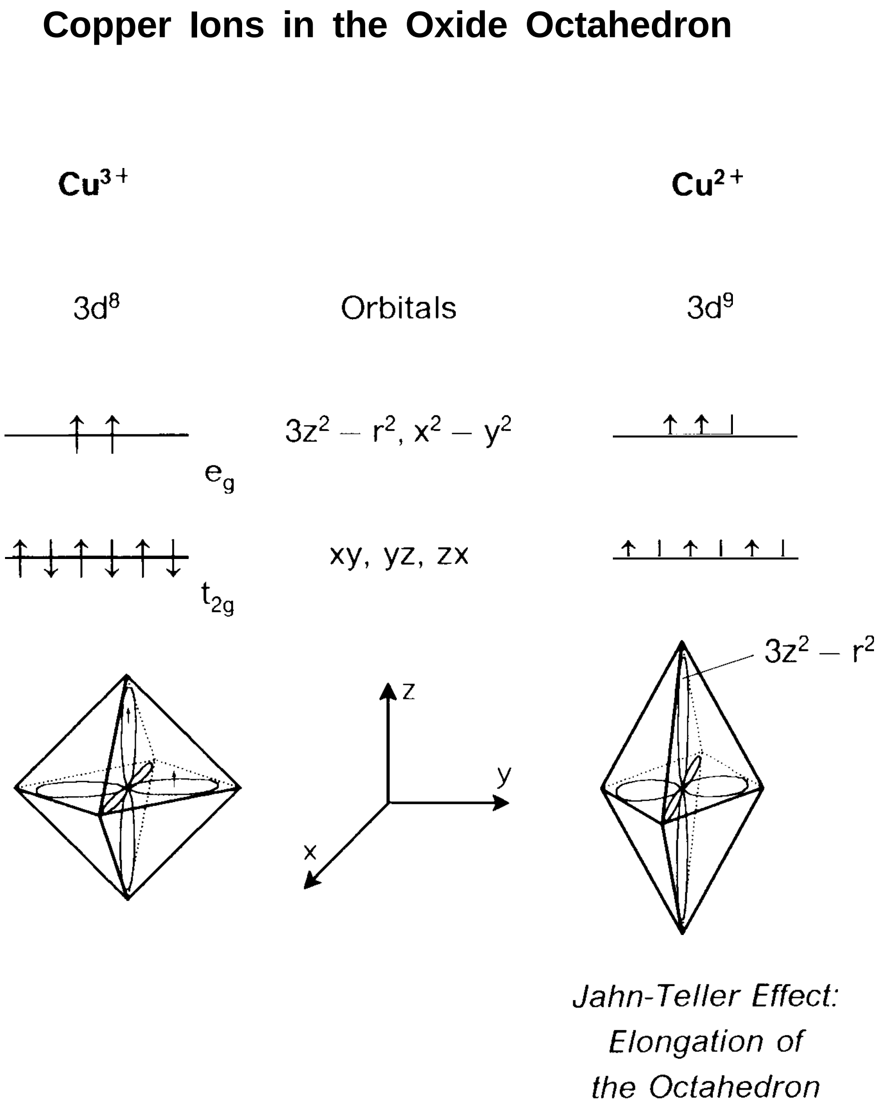

Figure 1.3. Schematic representation of electron orbitals for octahedrally coordinated copper ions in oxides. For Cu^{3}+ with 3d^{8} configuration, the orbitals transforming as base functions of the cubic e_g group are half-filled, thus a singlet ground state is formed. In the presence of Cu^{2+} with 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.

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, Figure 1.3, and we considered these as possible candidates for new superconductors.

The Search and Breakthrough

We started the search for high-T, 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, already the preparation of the pure compound brought some surprises, as the material obtained by our standard coprecipitation 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 substitute the trivalent Ni by trivalent Al to reduce the metallic bandwidth of the Ni ions and make it comparable to the Ni^{3+} Jahn-Teller stabilization energy. With increasing Al concentration, the metallic characteristics (see Figure 1.4) of the pure $LaNiO_3$ gradually changed, first giving 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. This we realized by replacing the La^{3+} ion by the smaller Y^{3+} ion, keeping the Ni site unaffected. The resistance behavior changed in a way we had already recorded 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?

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, however the metallic character of the solid solutions was preserved down to 4 K [1.13]. But again, we observed no indication 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

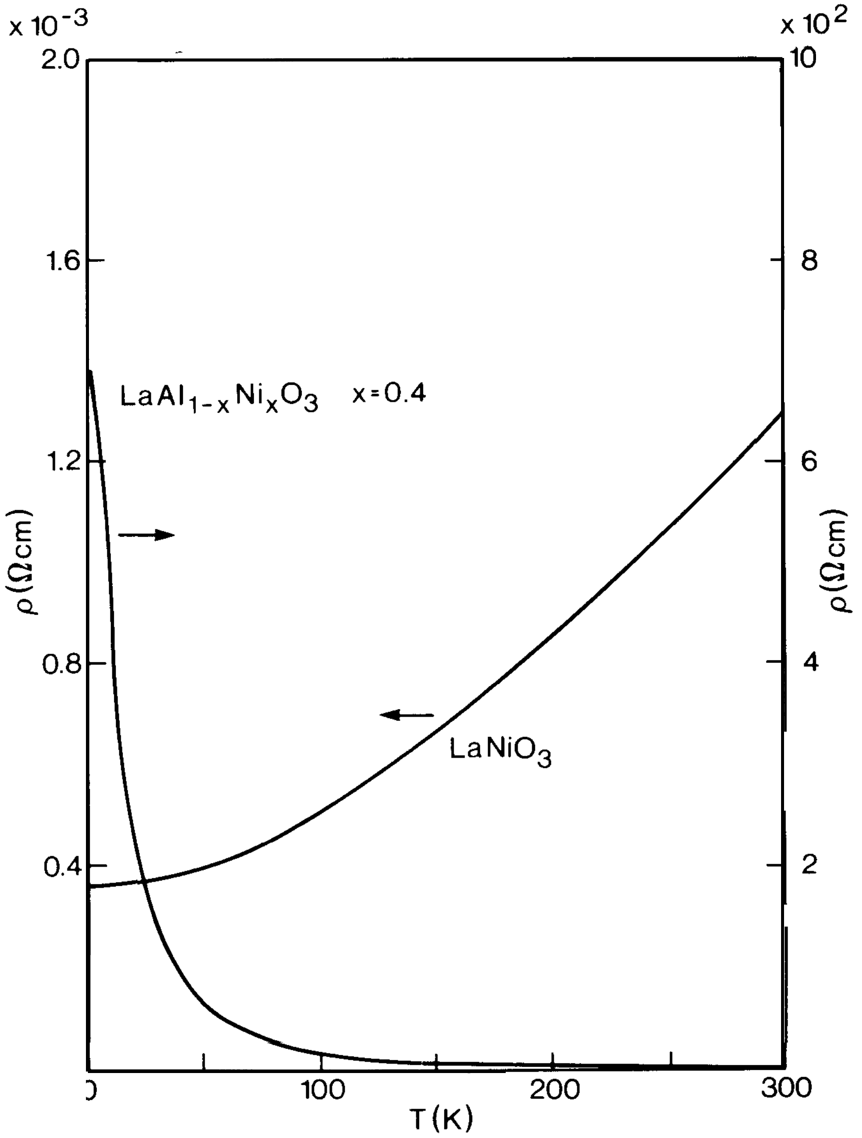

Figure 1.4. Temperature dependence of the resistivity for metallic $LaNiO_3$ and $LaAl_{1-x}Ni_xO_3$, where substitution of Ni^{3+} by Al^{3+} leads to insulating behavior for x = 0.4.

had investigated a Ba-La-Cu oxide with perovskite structure exhibiting metallic conductivity in the temperature range between 300 and - 100° C [1.16]. The special interest of that group was 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 decided to proceed to the ground-floor laboratory and start preparations for a series of solid solutions, as 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 had been performed, 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.

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 restart my activities in measuring the new compound. When performing the four-point

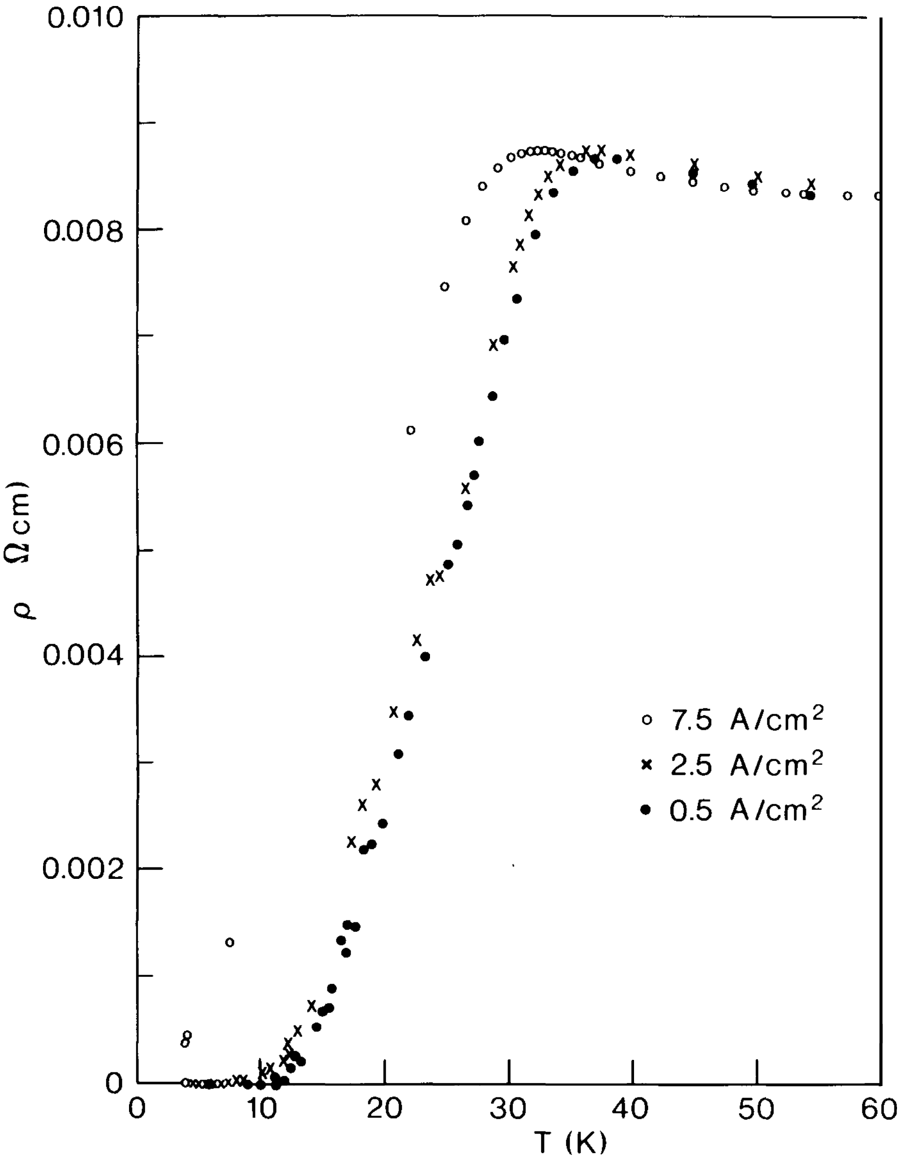

Figure 1.5. Low-temperature resistivity of a sample with x(Ba) = 0.75, recorded for different current densities. From [1.19], © Springer-Verlag 1986.

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 excluded. 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, Figure 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 irreproducible [1.7], therefore prior to the publication 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 lower temperatures. On the contrary, this behavior supported our interpretation that the drop in $\varrho(T)$ was related to the onset of

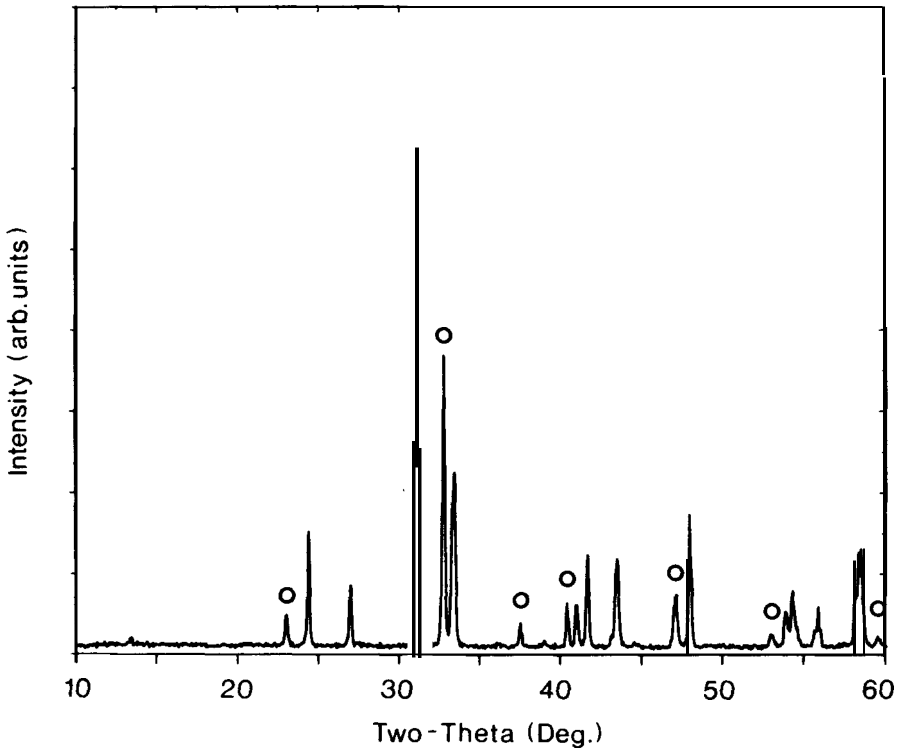

Figure 1.6. X-ray diffraction pattern of a two-phase sample with Ba:La = 0.08. The second phase occurring together with the K_2NeF,-type phase is indicated by open circles. From [1.20], © 1987 Pergamon Journals Ltd.

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 Figure 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 that of an oxygen-deficient perovskite with a three-dimensionally connected octahedra network. In both structures, La was partially replaced by Ba, as we learned from an electron microprobe analysis which Dr. Jürg Sommerauer at the ETH Zurich 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 realized how his careful comments of skepticism changed to supporting conviction while we were discussing the results. We had found our first companion.

Following this, while awaiting delivery of the magnetometer, we tried hard to identify the superconducting 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 Figure 1.8. The highest T_c’s were obtained with a Ba concentration close to this transition (Figure 1.9), whereas when the perovskite phase became dominant, the transition was suppressed and the samples showed only metallic characteristics.

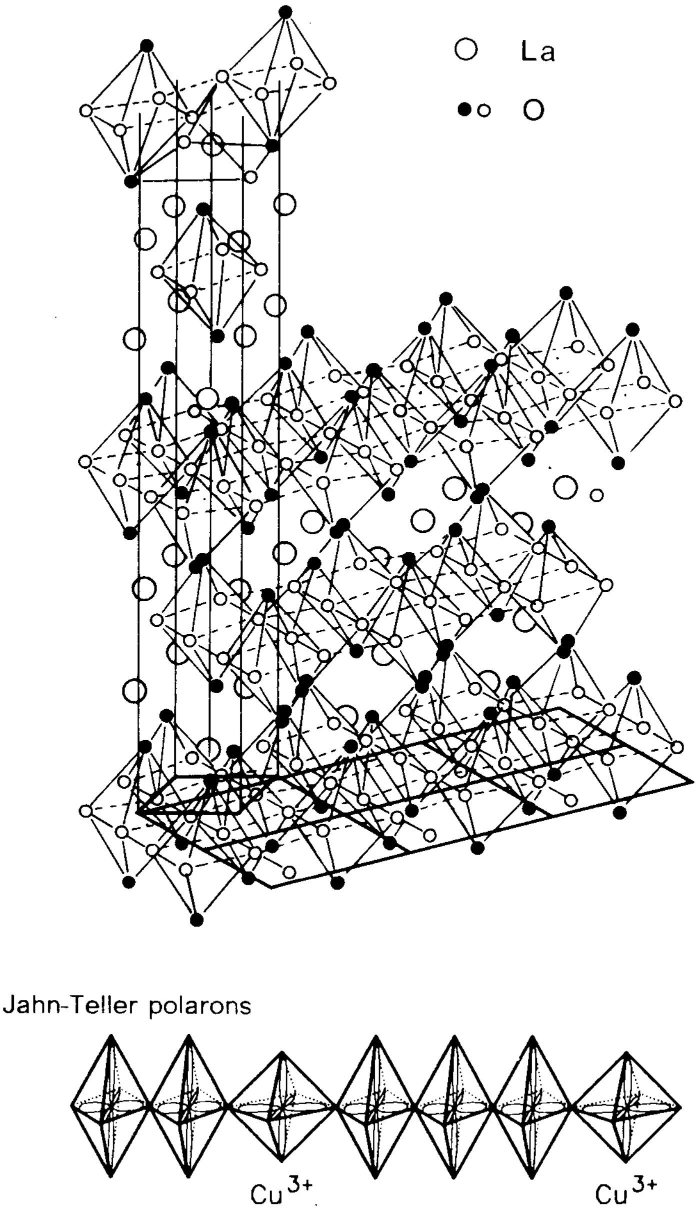

Figure 1.7. Structure of the orthorhombic La$_2$CuO$_4$ Large open circles represent the lanthanum atoms, small open and filled circles the oxygen atoms. The copper atoms (not shown) are centered on the oxygen octahedra. From [1.29], © 1987 by the American Association for the Advancement of Science.

The lower part shows schematically 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+}.

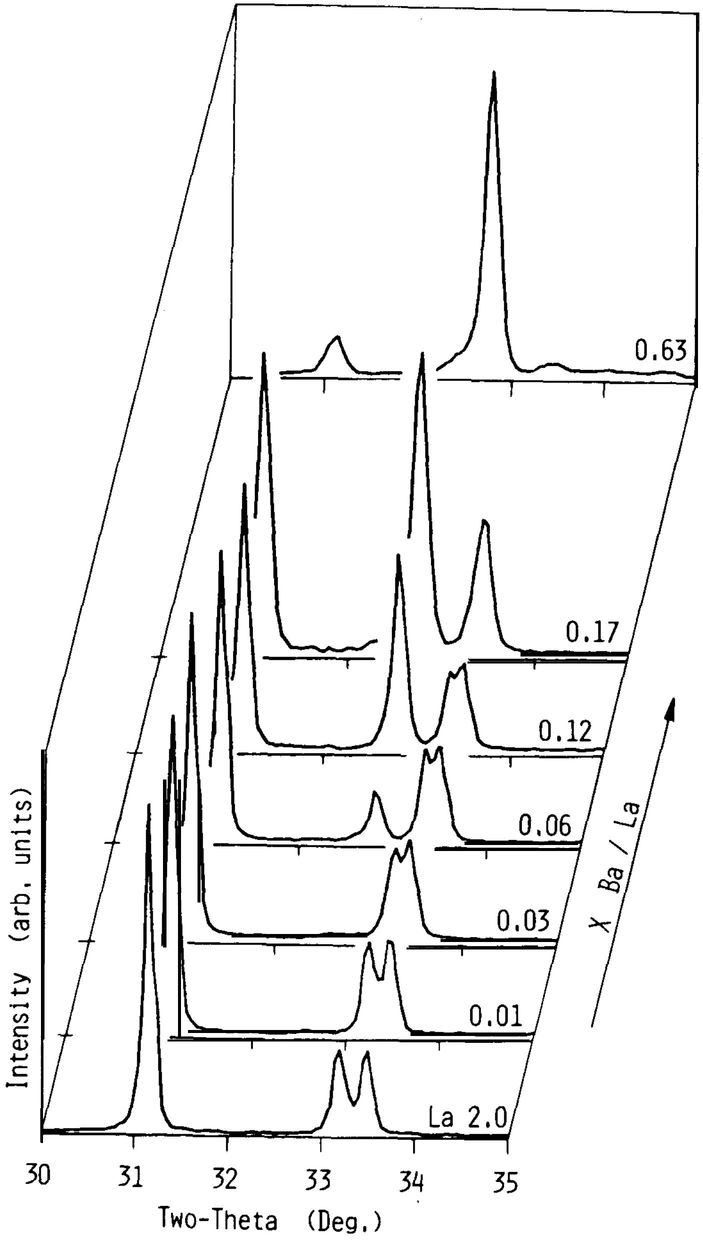

Figure 1.8. Characteristic part of the x-ray diffraction pattern, showing the orthorhombic-to-tetragonal structural phase transition with increasing Ba:La ratio. Concentration axis not to scale. From [1.20], © 1987 Pergamon Journals Ltd.

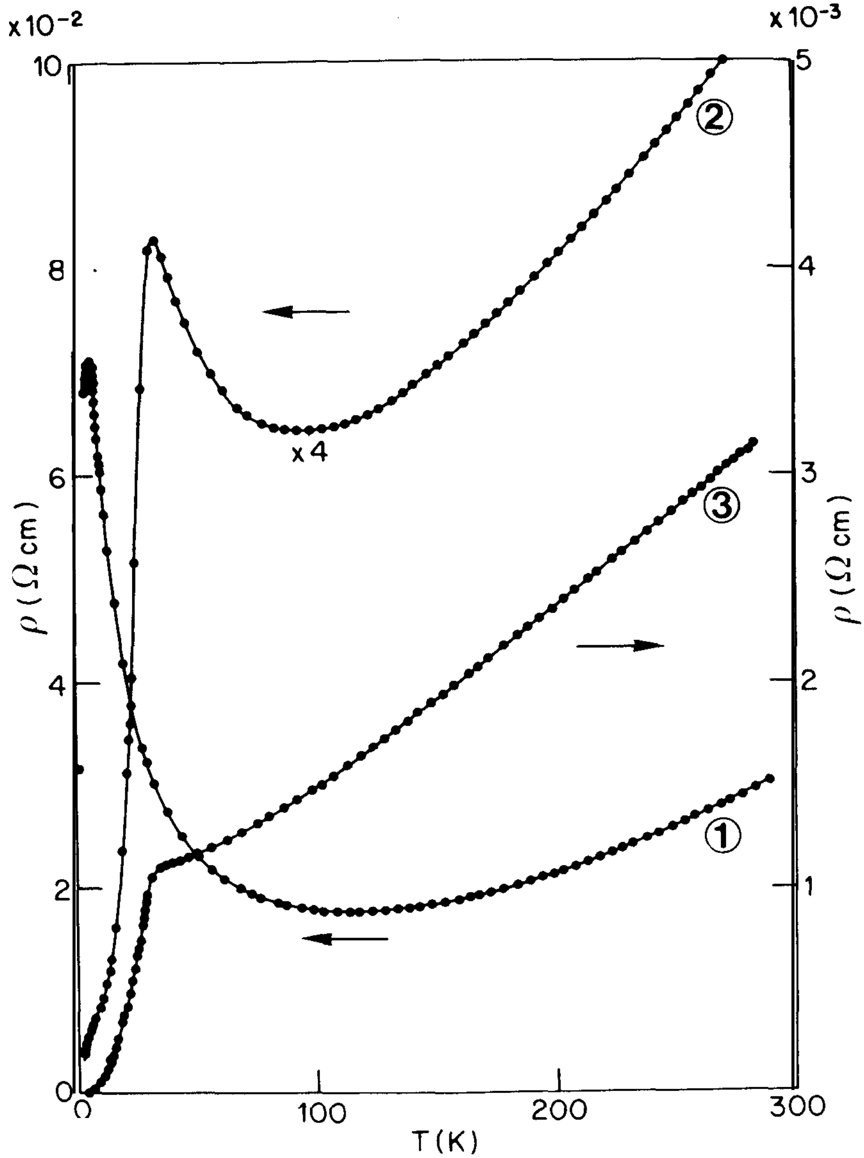

Figure 1.9. Resistivity as a function of temperature for La$_2$CuO$_{4-y}$: Ba samples with three different Ba:La ratios. Curves 1, 2, and 3 correspond to ratios of 0.03, 0.06, and 0.07, respectively. From [1.20], © 1987 Pergamon Journals Ltd.

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 like 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, within samples showing a resistivity drop, a transition from para- to diamagnetism occurred at slightly lower temperatures, see Figure 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

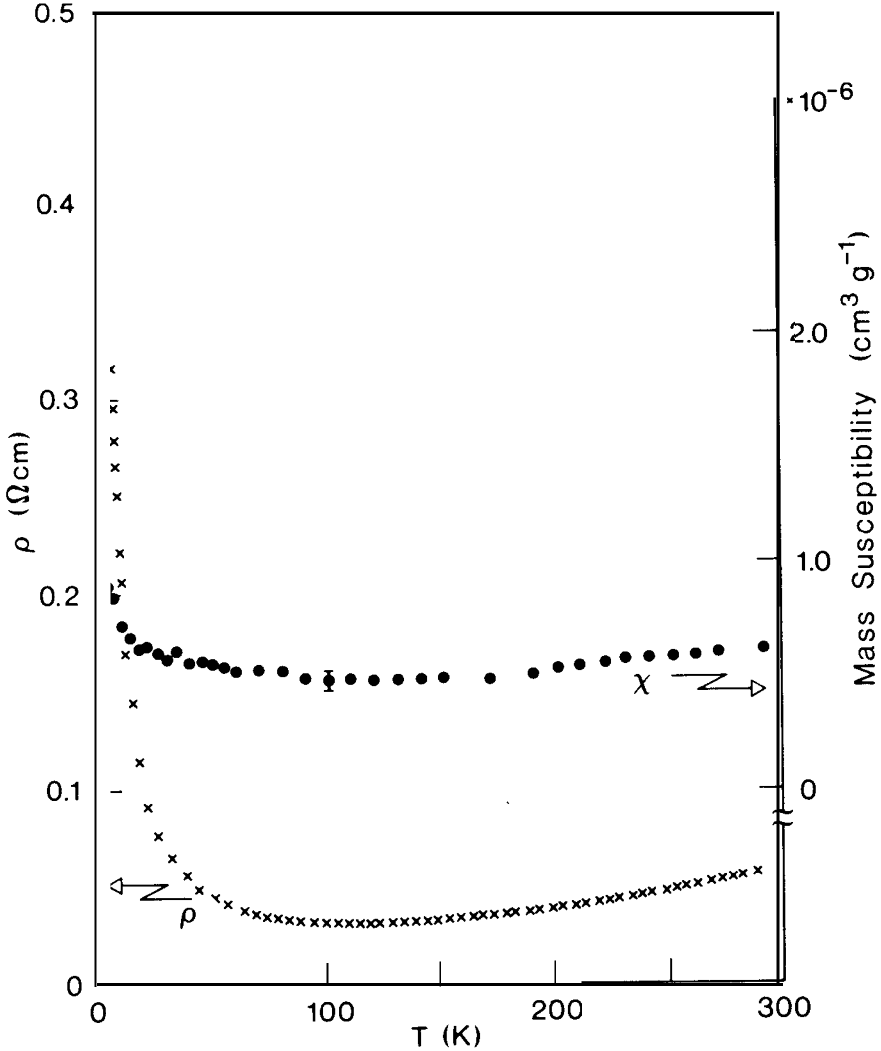

Figure ***1.10.*** Temperature dependence of resistivity (x) and mass susceptibility (●) of sample 1. From [1.23], © Les Editions Editions de Physique 1987.

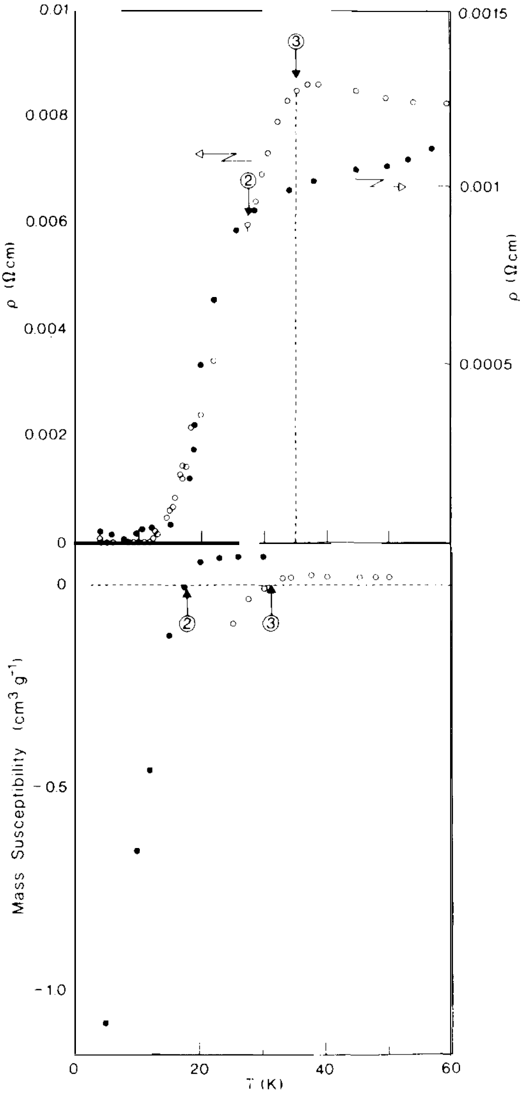

Figure 1.11. Low-temperature resistivity and susceptibility of (La-Ba)-Cu-O samples 2 (●) end 3 (○) from [1.23]. Arrows indicate the onset of the resistivity and the paramagnetic-to-diamagnetic transition, respectively. From [1.23], © Les Editions de Physiqe 1987.

been demonstrated. Combining the x-ray analysis, resistivity and susceptibility measurements, it was now possible to clearly identify the Ba-doped La$_2$CuO$_4$ as the superconducting compound.

First Responses and Confimations

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 appeared in the open literature, we rushed to get the results of our susceptibility data written up for publication.

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. The next day we were back to reality, and I started to prepare a set of samples for Richard Greene. Praveen Chaudhari, 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 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. Especially Sr^{2+} had the same ionic radius as La^{3+}. We began experiments on the new materials which indicated that for the Sr-substituted samples ‘I‘, was approaching 40 K and the diamagnetism was even higher, see Figure 1.12(a) and (b), [1.25]. It was just at that time that we learned from the Asahi-Shinbun International Satellite Edition [November 28, 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 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 Y^{3+}_{+} for the larger La^{3+} resulted in a giant jump of T_c to 92 K in multiphase samples [1.28], Figure 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, Figure 1.14, and even more impressive was the fact that the Meissner effect

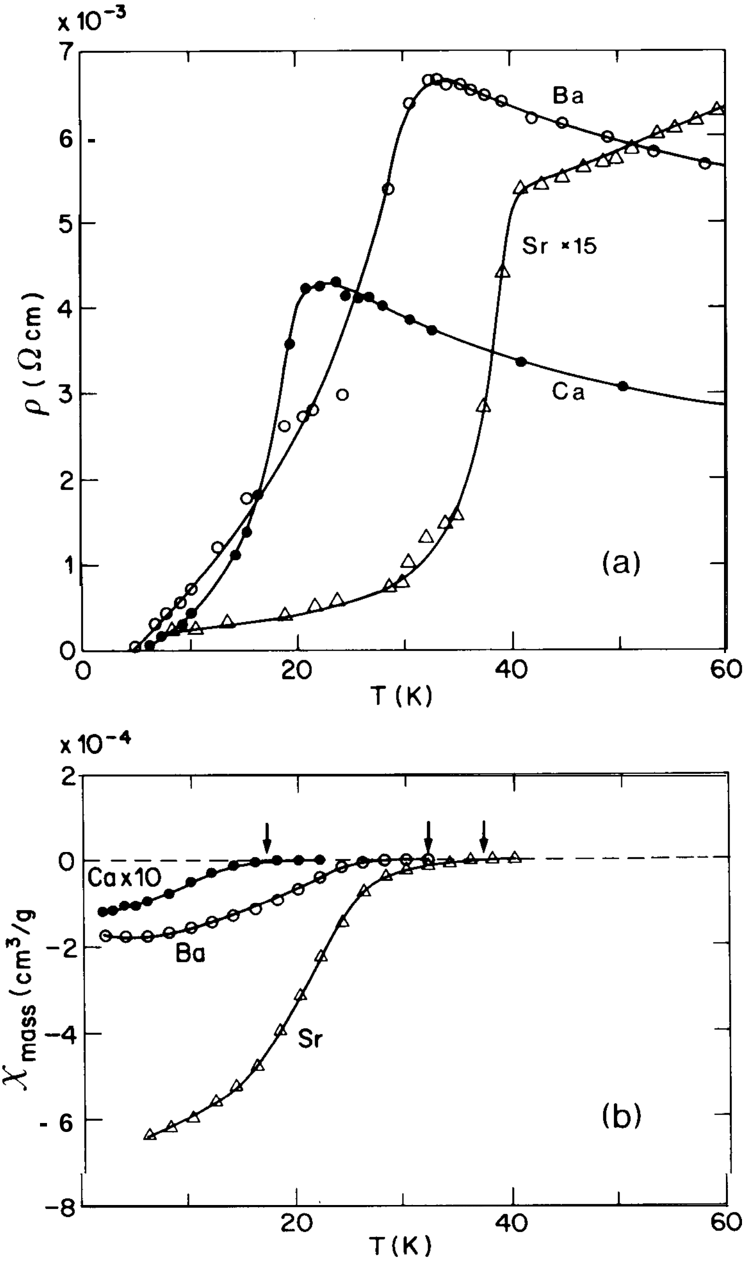

Figure 1.12. (a) Resistivity as a function of temperature for Ca (●), Sr (△), and Ba (○) substitution with substituent-to-La ratios of 0.2/1.8, # 0.2/1.8, 0.15/1.85, respectively. The Sr curve has been vertically expanded by a factor of 15. (b) Magnetic susceptibility of these samples. The substituents 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. From [1.25], © 1987 by the American Association for the Advancement of Science.

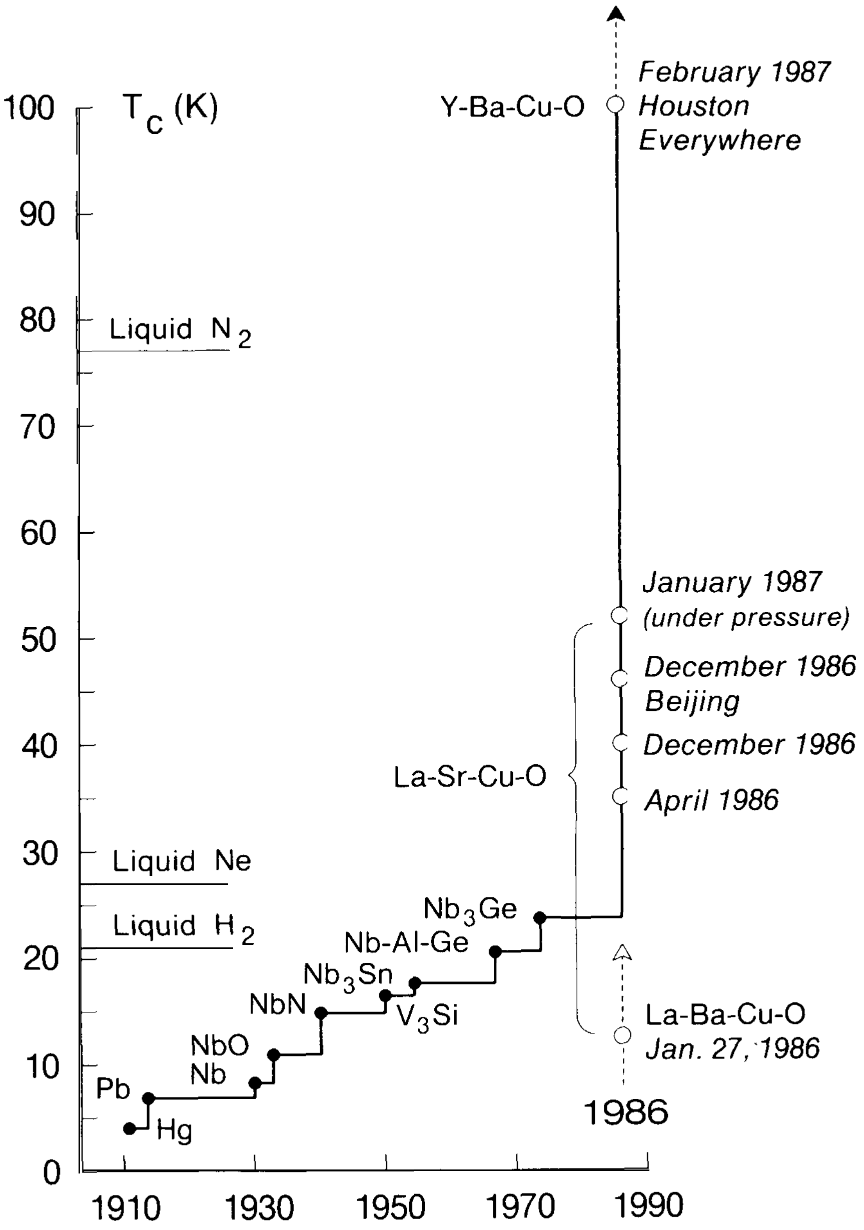

Figure 1.13. Evolution of the superconductive transition temperature subsequent to the discovery of the phenomenon. From [1.29], © 1987 by the American Association for the Advancement of Science.

could now be demonstrated without any experimental difficulties with liquid nitrogen as the coolant. Within a few months, the field of superconductivity had experienced a tremendous revival, with an explosive development of T_c's which 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].

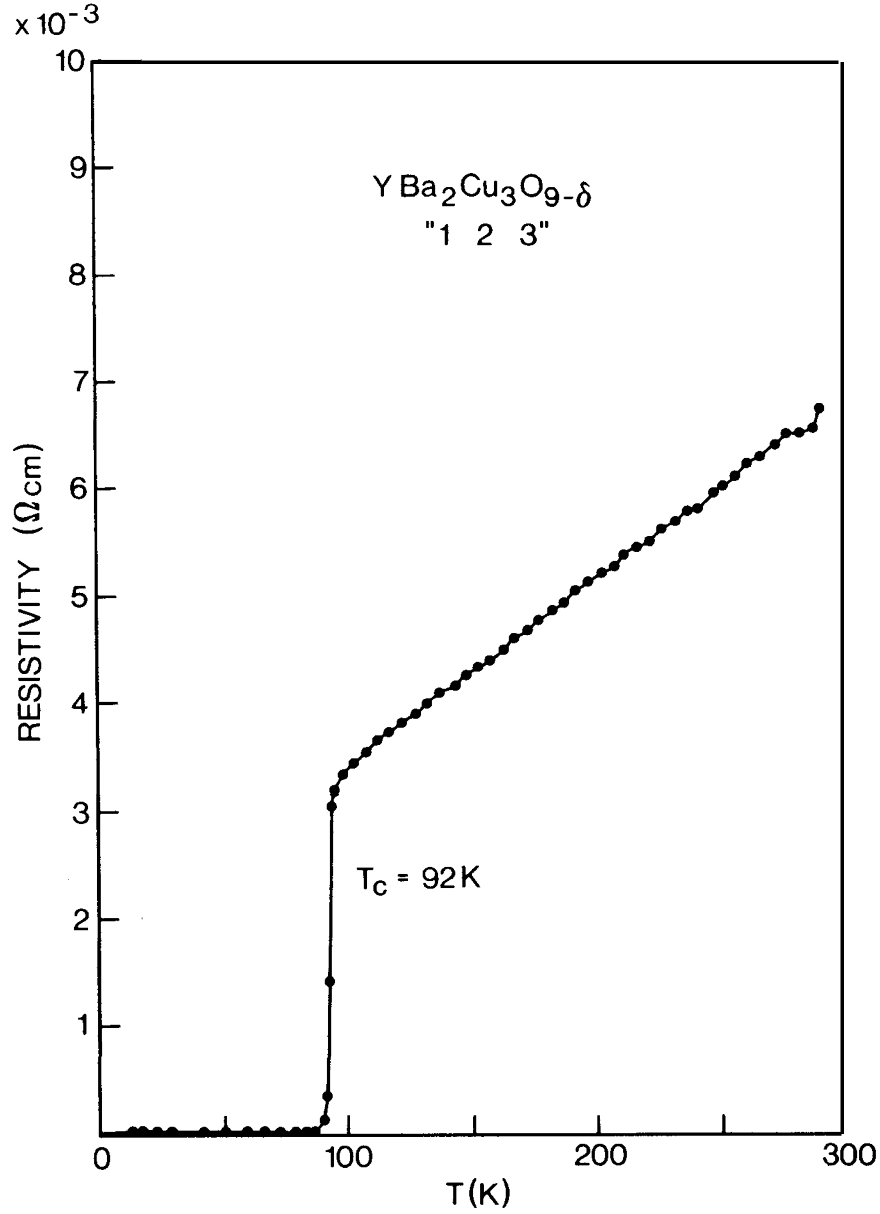

Figure 1.14. Resistivity of a single-phase $YBa_2Cu_3O_7$ sample as a function of temperature.

References Part 1

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

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

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

[1.4] Baratoff, A. and Binnig, G. (1981) Physica *108B,* 1335; Baratoff, A., Binnig, G., Bednorz, J. G., Gervais, F., and Servoin, J. L. (1982) in: *Superconductivity in d- and f-Band Metals, Proceedings IV Conference on Superconductivily in d- and f-Band Metals,* editors W. Buckel and W. Weber (Kernforschungszentrum Karlsruhe) p. 419.

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

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

[1.7] Beasley, M. R. and Geballe, T. H. (1984) Phys. Today 36(l0), 60; Muller, J. (1980) Rep. Prog. Phys. 43, 663.

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

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

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

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

[1.12] Höck, K.-H., Nickisch, H., and Thomas, H. (1983) Helv. Phys. Acta 56, 237.

[1.13] Goodenough, J. B. and Longo, M. (1970, “Magnetic and other properties of oxide and related compounds” In: *Landoldt-Boernstein New Series. Vol. III/4a: Crystal and Solid State Physics,* editors K. H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, Heidelberg, New York), p. 262, Fig. 73.

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

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

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

[1.17] Michel, C. and Raveau, B. (1984) Rev. Chim. Min. *21,* 407. It is ofinterest that back in 1973, Goodenough, J. B., Demazeaux, G., Pouchard, M., and Hagenmüller, P. (1973) J. Solid State Chem. 8, 325, in Bordeaux, and later Shaplygin, I. S., Kakhan, B. G., and Lazarev, V. B. (1979) Russ. J. Phys. Chem. 24(6), 1478, pursued research on layered cuprates with catalysis applications in view.

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

[1.19] Bednorz, J. G. and Müller, K. A. (1986) ‘Z. Phys. B 64, 189.

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

[1.21] Bowman, D. R. and Stroud, D. (1984) Phys. Rev. Lett. 52, 299.

[1.22] Ebner, C. and Stroud, D. (1985) Phys. Rev. B 31, 165, and references therein.

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

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

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

[1.26] Takagi, H., Uchida, S., Kitazawa, K., and Tanaka, S. (1987) Jpn. J. Appl. Phys. 26, L123; Uchida, S., Takagi, H., Kitazawa, K., and Tanaka, S. (1987) *ibid.,* L151.

[1.27] Chu, C. W., Hor, P. H., Meng, R. L., Gao, I,., Huang, Z. J., and Wang, Y. Q. (1987) Phys. Rev. Lett. 58, 405.
[1.28] Wu, M. K., Ashburn, J. R., Torng, C. J., Hor, P. H., Meng, R. L., Goa, I.., Huang, Z. J., Wang, Y. Q., and Chu, C. W. (1987) Phys. Rev. Lett. 58. 908; Hor, P. H., Gao, L., Meng, R. L., Huang, Z. J., Wang, Y. Q., Forster, K., Vassilious, J., Chu, C. W., Wu, M. K., Ashburn, J. R., and Torng, C. J. (1987) ibid., 91 1.
[1.29] Müller, K. A. and Bednorz, J, G. (1987) Science 237, 1133.

PART 2: PROPERTIES OF THE NEW SUPERCONDUCTORS

In the second part, properties of the new layered oxygen superconductors were described. Since their discovery, summarized in the first part, a real avalanche of papers has been encountered; thus it would be beyond the scope of this Lecture to review all of them here. A forthcoming international conference in Interlaken, Switzerland, in February 1988, is intended to fulfill this task and will be chaired by one of us. Therefore, only a selected number of experiments were presented 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 unbeknown 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, 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 subsequently revert. Then they applied microwaves at $\varkappa$ = 9.4 GHz and observed Shapiro steps [2.3] at V_s = 19 µV intervals. From the well-known Josephson formula [2.4]

$$V_s = h\varkappa/q, \tag{2.1}$$

they obtained q = 2e, i.e., Cooper pairs were present. Figure 2.1 illustrates these steps. From the fundamental London equations, the flux ϕ through a ring is quantized [2.5]

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

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

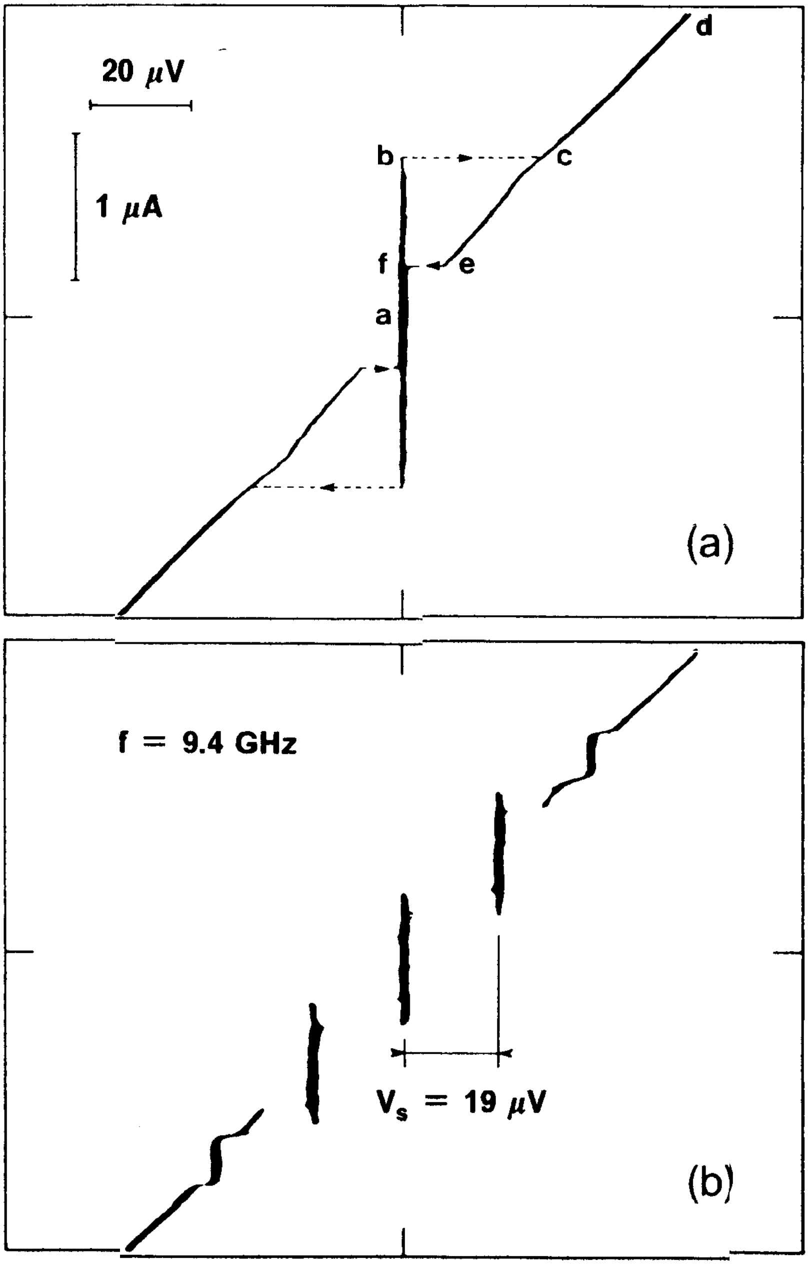

Figure 2.1. (a) Oscilloscope trace of a current-voltage characteristic obtained at 4.2 K with an aluminum tip on a $La_{1.85}Sr_{0.15}CuO_4$ sample. Letters a through f indicate sense of trace. Dashed lines have been added to indicate the switching between the two branches. (b) Steps induced by a microwave irradiation at frequency f = 9.4 GHz. All other experimental conditions identical with those of (a). From [2.2] © Les Editions de Physique 1987.

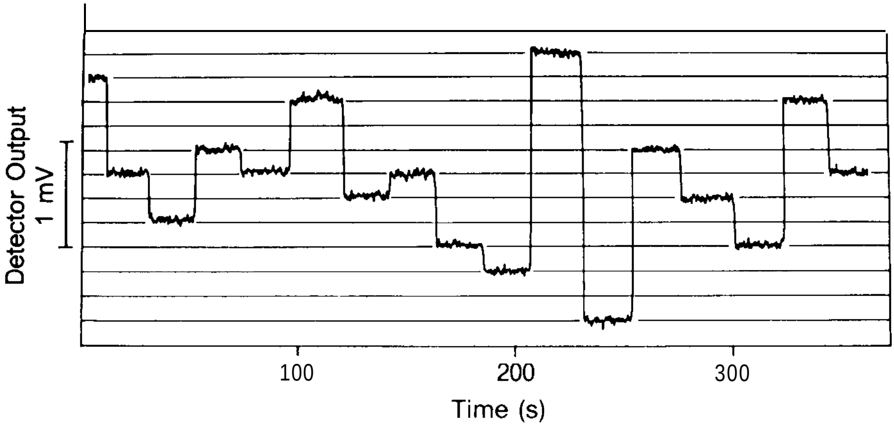

Figure 2.2. Output of the r.f.-SQUID magnetometer showing small integral numbers of flux quanta jumping in to and out of a ring. Reprintcd by permission from [2.6], copyright © 1987 Macmillan Magazines Ltd.

To understand the mechanism, it was of relevance to know the nature of the carrier charge present. In La_2CuO_4 doped very little, 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 and Hall-effect 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-,(6 ~ 0.1). Early photo-electron core-level spectra (XPS and UPS) by Fujimori el al. [2.8] and Bianconi et al. [2.9] in $(La_{1-x}Sr_x)_2CuO_{4-y}$ and $YBa_2La_3Cu_{6\cdot7}$ did not reveal a $\underline{2p}$ $3d^8$ final state owing to a Cu^{3+} $3d^8$ state (the underlining indicates a hole). However, the excitation was consistent with the formation of holes L in the oxygen-derived band, i.e., a predominant $3d^9L$ configuration for the formal Cu^{3+} state. Photo-x-ray absorption near the edge structure was also interpreted in the same manner by comparison to 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, partially 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 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 $x \approx 0$ and6 = 0.5, no

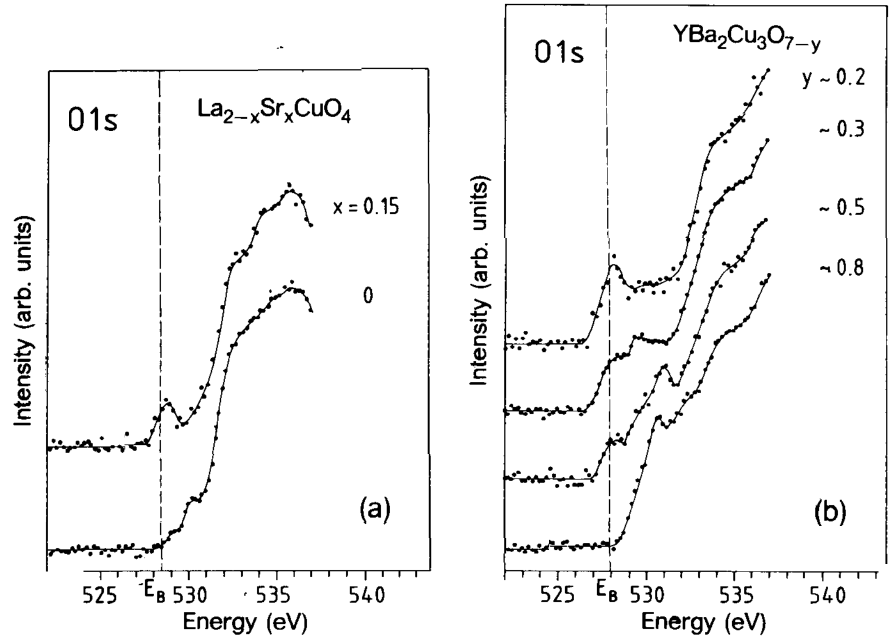

Figure 2.3. Oxygen ls absorption edges of (a) $La_{2-x}Sr_xCuO_4$ and (b) $YBa_2Cu_3O_{7-y}$ measured by energy-loss spectroscopy. The binding energy of the O ls level, as determined by x-ray induced photoemission, is shown by the dashed line. In the framework of an interpretation of the spectra by the density of unoccupied states, this line would correspond to the Fermi energy. From [2.11], © 1988 The American Physical Society.

oxygen p-holes are present and thus no absorption is observed, whereas upon increasing x or reducing δ, a $\underline{2p}$ hole density at the Fermi level is detected in both compounds.

Of substantial interest is the dependence of the transition temperature on the hole concentration. The electron deficiency is hereafter written in the form $[Cu-O]^+$ as a peroxide complex in which the probability of the hole is about 70% $3d^9\,\underline{2p}$, 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 conductivity, 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 the concentration by wet chemistry according to the reaction $[Cu-O]^+ + Fe^{2+} \leftrightharpoons Cu^{2+} + Fe^{3+} + O^{2-}$ 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 of 15% total copper present. There is also a clear threshold at about 5%. From the study, it is apparent that 15-16% $[Cu-0]^+$ 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 inset 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

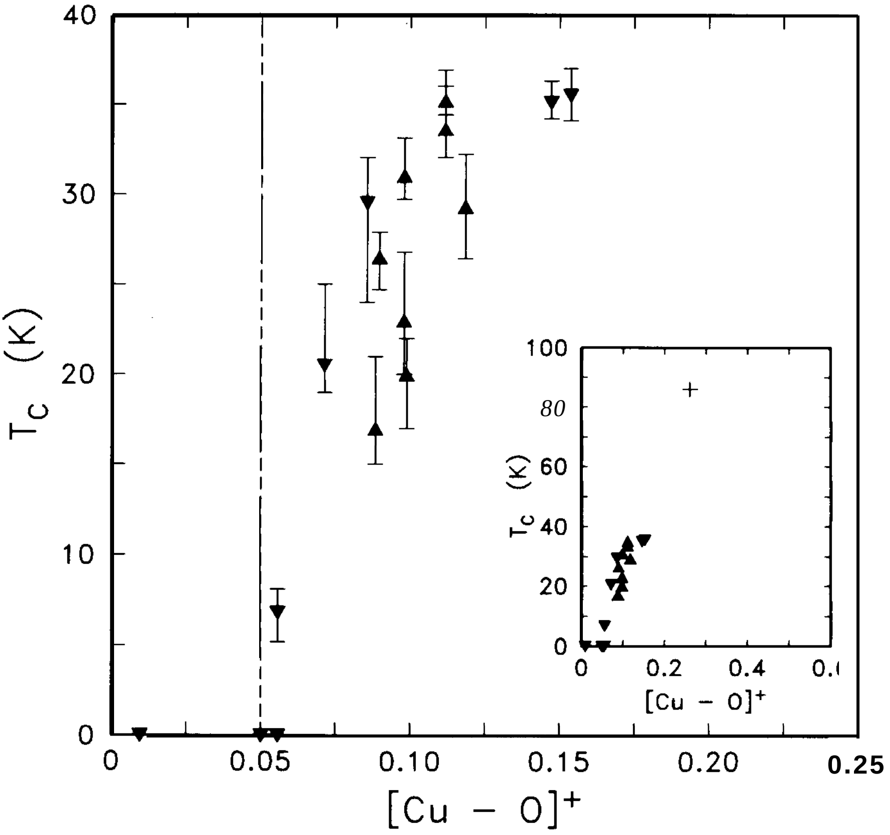

Figure 2.4. T_c vs the hole concentration $[Cu\text{-}O]^+$, as a fraction of total copper. Down triangles are for compositions with $x<0.15$, up triangles for $x>0.15$. Inset shows same data plus points for single $YBa_2Cu_3O_{6.6}$ sample as discussed in the text. From [2.13], ©1987 The American Physical Society.

and coworkers, could be well evidenced 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 $H = 0.05$ Tesla 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 2.5(a). 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 2.5(b). 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 of T_N as shown in Figure 2.6. This instantaneous (not time-averaged) ordering was seen even above room temperature [2.17]. The existence of antiferromagnetism (A.F.) supports models in which holes lead either

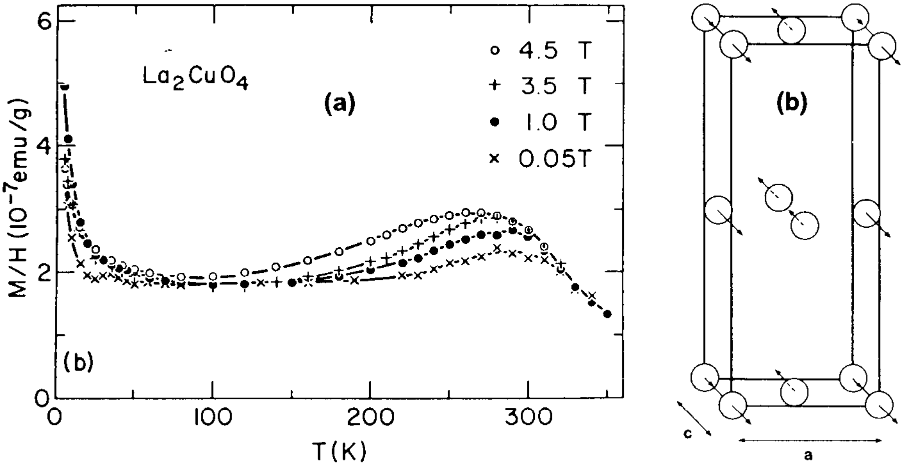

Figure 2.5. (a) Temperature dependence of the magnetic susceptibility $\chi = M/H$ of La_2CuO_4 in different fields H. From [2.15], © 1987 Pergamon Journals Ltd. (b) Spin structure of antiferromagnetic La_2CuO_{4-y}. Only copper sites in the orthorhombic unit cell are shown for clarity. From 12.16], © 1987 The American Physical Society.

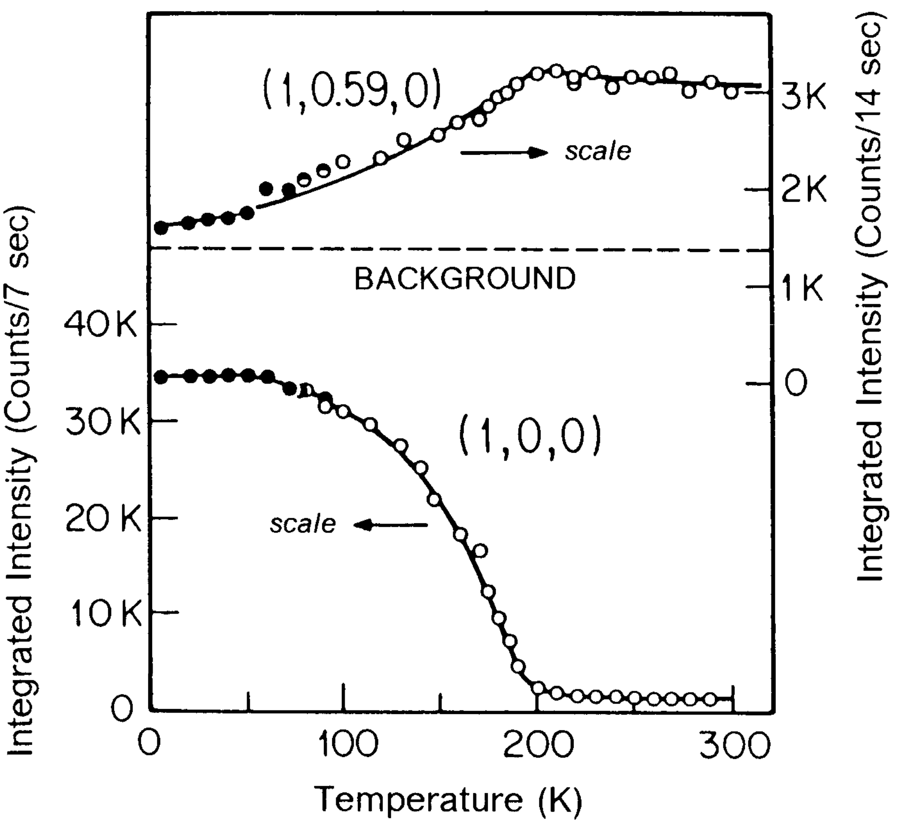

Figure 2.6. Integrated intensities of the (100) 3-D antiferromagnetic Bragg peak and the (1,0.59,0) 2-D quantum spin fluid ridge. The open and filled circles represent separate experiments. From [2.17], © 1987 The American Physical Society.

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].

From the prevalence of magnetic interactions as primary cause for the occurrence of the high-T, superconductivity, one would expect the isotope effect to be absent. This, because the latter effect is found 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 the $La_{2-x}Sr_xCuO_{4-y}$ carried out shortly thereafter did reveal an isotope effect with $0.14< \beta < 0.35$ [2.22] as compared with the full effect of $\beta = 1/2$ deduced from the weak-coupling formula [1. 10]

$$T_c = 1.13\Theta_D \exp-(1/N(E_F)_x V^*), \tag{2.3}$$

with the Debye temperature $\Theta_D \propto 1/M^{1/2}$ of 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, 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 $YBa_2Cu_3O_7$ with AT, ≈ 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 gap 2A to kT_c, ratio is [1. 10]

$$\frac{2\Delta}{kT_c} = 3.52, \tag{2.4}$$

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. An interesting example is the reflectivity study by Schlesinger *et al*. [2.25] of superconducting $YBa_2Cu_3O_7$ and a Drude tit 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 Figure 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 i.e., the latter in the range of the infrared data.

NMR relaxation experiments were among the first at the time to prove the

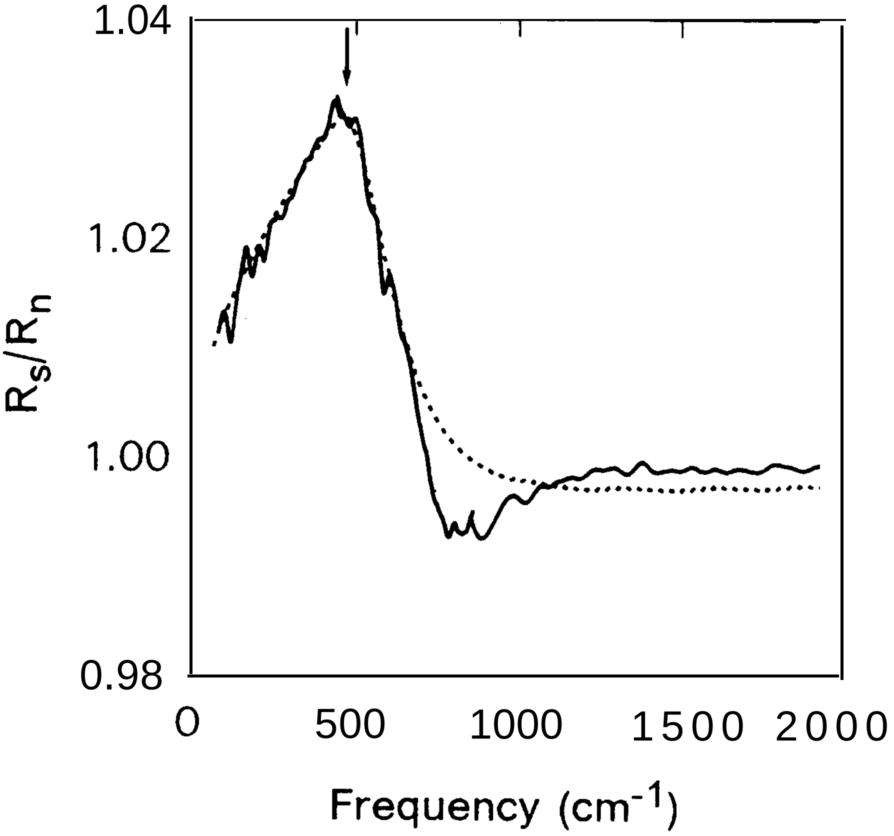

Figure 2.7. Normalized infrared reflectivity of a single crystal of $YBa_2Cu_3O_7$ and fitted Mattis-Bardeen form of $\delta(\omega)$ (dotted line) in the superconducting state. The arrow shows the peak occurring at 2A ~ 480 cm^{-1}, hence 2A ≈ $8kT_c$, with T_c = 92 K [2.25]. Courtesy of Z. Schlesinger et al.

existence of a gap [2.27]. They also appear to be important for the new class of superconductors. Zero-field nuclear spin lattice relaxation measurements of ^{139}La in $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ below T_c, behave like 1/T, ∝ exp(-A/kT), see Figure 2.8, with activation energy Δ = 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 appears to be 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 could be 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 would 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_{c2}/dT near T_c, could be obtained, and from them very high critical fields at low temperatures were extrapolated. From the many works published, we quote that of Decroux et *al.* [2.30], also because this was the first paper to

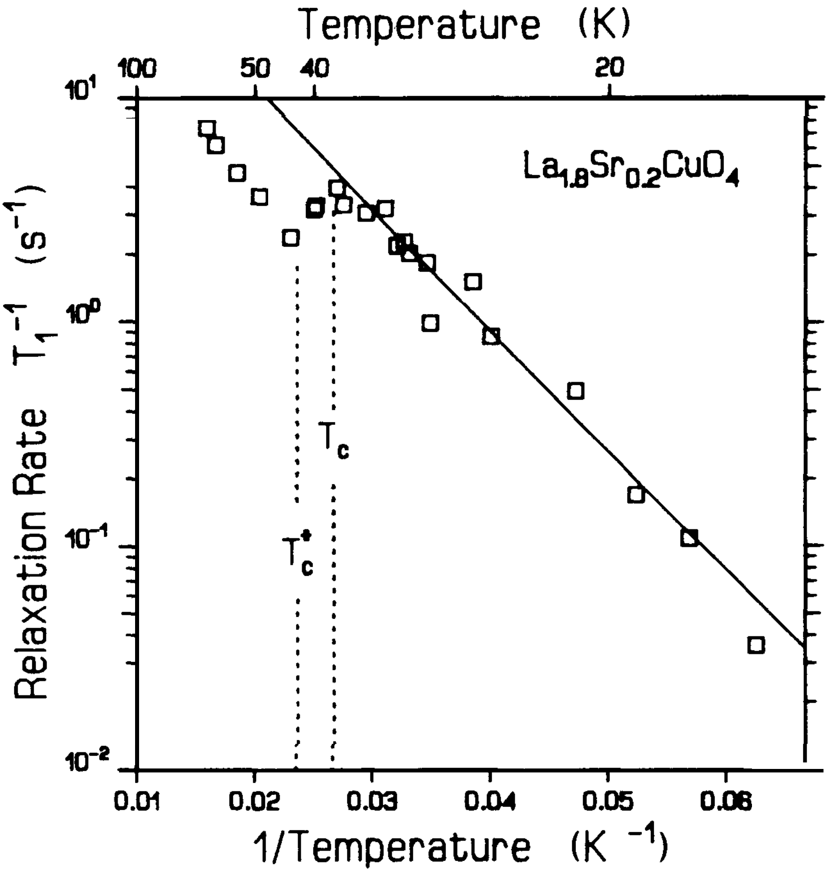

Figure 2.8. Semilogarithmic plot of $1/T_1$ vs $1/T$. The straight line demonstrates the activated behavior $1/T_1 \sim \exp[-\Delta/kT]$ for $T \ll T_c$. An activation energy of $\Delta/k = 135$ K is obtained from this graph. From [2.28], ©Les Editions de Physique 1988.

report a specific-heat plateau at T_c. The group at the University of Geneva found $dH_{c2}/dT = -2.5$ T/K, yielding an extrapolated $H_{c2}(T = 0) = 64$ T.

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

$$H_{c2} = \frac{\phi_0}{2\pi\xi^2}, \tag{2.5}$$

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 IBM's group in Yorktown Heights [2.31] and the Stanford group on expitaxial layers [2.32] are of the order $\xi_c \approx 3 - 4\,\Omega$ for the coherence length parallel to c and $\xi_{ab} \approx 20 - 30\Omega$ perpendicular to c.

Such short coherence lengths could be expected when one considers the relation of ξ with 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 Eq. (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 classic 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 $n = 10^{21}/\text{cm}^3$ make one wonder whether boson-condensation approaches arc 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 superconductivity theory with boson condensation. Referring to Chakraverti's phase diagram in Figure 1.2 [1.11], one may regard the metal superconducting phase line as BCS with weak coupling, and the superconducting 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 superconducting-insulator interface, the $\Delta(x)$ profile was deduced as shown in Figure 2.9 for 1' $\lesssim T_c$ and $T \ll T_c$.

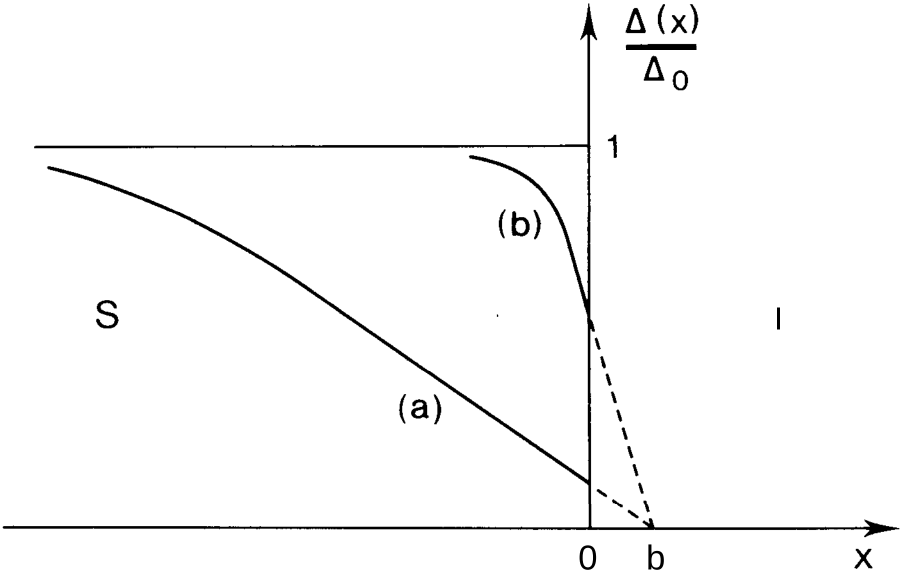

Figure 2.9. Profile of the pair potential in a short-coherence-length superconductor near a superconductor-insulator boundary. Curve a: $T \lesssim T_c$; curve b: $T \ll T$,. From [2.24], © 1987 The American Physical Society.

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 reduced value of the A observed. In consequence, such experiments are less suitable than infrared and NMR 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 possibility of fluxon trapping as well. Therefore even single crystals can form a superconducting glass in the presence of a sizeable magnetic field.

The basic Hamiltonian regarding the phases is [1.22]

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

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 experimental 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 ***intragrain*** 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 length of the superconducting wave functions at SNS and SIS junctions are both of the order of $\xi(0)$. This entails an anomalous temperature dependence of $J_c \propto (T-T,)^2$. Such behavior is seen in the mid-temperature range for J,(T) in the $YBa_2Cu_3O_{7Pd}$ 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 (Figure 2.10), whereas in the ceramics much lower J_c's require substantial inventiveness or, perhaps better still, a new type of high-T, superconductor that should exist.

The geometrical critical magnetic field $H^{\star}_{c1}$ is of the order of [1.22]

$$H^{\star}_{c1} = \phi_0/2S, \tag{2.8}$$

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 S = 100 µm^2, whereas that of grains in ceramics is S = 1 - 10 µm^2. In agreement with Eq. (2.8), $H^{\star}_{c1}$ is of

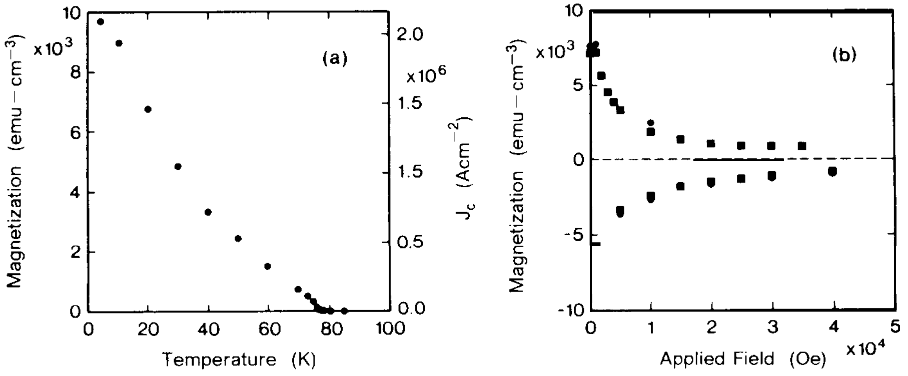

Figure ***2.10.*** (a) The volume magnetization vs increasing temperature for an epitaxial sample. The y-axis scale on the right was obtained with the use of the Bean formula $J_c = 30$ M/d and with the mean radius of the sample of d = 0.14 cm. (b) The volume magnetization vs applied field at 4.2 K for two samples. From [2.40], © 1987 The American Physical Society.

the order of 0.5 Gauss for the penetration of H into twinned crystals, and 5 to 100 Gauss 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 (Figure 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 glassy 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 large magnetic-field applications for example in beam bending in accelerators and plasma containment in fusion.

References Part 2

[2.1] Cooper, L. N. (1956) Phys. Rev. 104, 1189.

[2.2] Estève, D., Martinis, J. M., Urbina, C., Devoret, M. H., Collin, G., Monod, P., Ribault, M., and Revcolevschi, A. (1987) Europhys. Lett. 3, 1237.

[2.31 Shapiro, S. (1963) Phys. Rev. Lett, *11, 80.*

[2.4] Josephson, B. D. (1962) Phys. Lett, 1, 251.

[2.5] London, F. *(1950) Superfluids,* Vol. I. (John Wiley and Sons, Inc., New York), p. 152.

[2.6] Gough, C. E., Colclough, M. S., Forgan, E. M., Jordan, R. G., Keene, M., Muirhead, C. M., Rae, A. I. M., Thomas, N., Abell, J. S., and Sutton, S. (1987) Nature (London) 326, 855.

[2.7] Steglich, F., Bredl, C. D., De Boer, F. R., Lang hf., Rauchschwalbe, U., Rietschel, H., Schefzyk, R., Sparn, G., and Stewart, G. R. (1987) Physica Scripta *T19, 253.*

[2.8] Fujimori, A., Takayama-Muromachi, E., Uchida, Y., and Okai, B. (1987) Phys. Rev. B 3.5, 8814.

[2.9] Bianconi, A., Castellano, A. C., De Santis, M., Delogu, P., Gargano, A., and Giorgi, R. (1987) Solid State Commun. 63, 1135; Bianconi, A., Castellano, A. C., De Santis, M., Politis, C., Marcelli, A., Mobilio, S., and Savoia, A. (1987) Z. Phys. B 67, 307.

[2.10] Thiry, P., Rossi, G., Petroff, Y., Revcolevschi, A., and Jegoudez, J. (1988) Europhys. Lett, 5, 55.

[2.11] Nücker, M., Fink. J., Fuggle, J. C., Durham, P. J., and Temmerman, W. M. (1988) Phys. Rev. B 37, 5158.

[2.12] Steiner, P., Hüfner, S., Kinsinger, V., Sander, I., Sirgwart, B., Schmitt, H., Schulz, R., Junk, S., Schwitzgebel, G., Gold, A., Politis, C., Müller, H. P., Hoppe, R., Kemmler-Sack, S., and Kunz, C. (1988) Z. Phys. B 69, 449.

[2.13] Shafer, M. W., Penney, T., *and Olson,* B. L. (I 987) Phys. Rev. B 36, 4047.

[2.14] Tarascon, J. M., McKinnon, W. R., Greene, L. H., Hull, G. W., and Vogel, E. M. (1987) Phys. Rev. B 36, 226; see also Bagley, B. G., Greene, L. H., Tarascon, J. M., and Hull, G. W. (1987) Appl. Phys. Lett. *51, 622.*

[2.15] Greene, R. L., Maletta, H., Plaskett, T. S., Bednorz, J. G., and Müller, K. A. (1987) Solid State Commun, 63, 379.

[2.16] Vaknin, D., Sinha, S. K., Moncton, D. E., Johnston, D. C., Newsam, J, M., Safinya, C. R., and King, H. E., Jr. (1987) Phys. Rev. Lett. 58, 2802.

[2. 17] Shirane, G., Endoh, Y., Birgeneau, R. J., Kastner, M. A., Hidaka, Y., Oda, M., Suzuki, M., and Murakami, T. (1987) Phys. Rev. Lett. 59, 1613.

[2.18] Emery, V. J. (1987) Phys. Rev. Lett. 58, 2794; *idem* (1987) Nature (London) 328, 756.

[2.19] Hirsch, J. E. (1987) Phys. Rev. Lett. 59, 228; Cyrot, M. (1987) Solid State Commun. 62, 821, and to be published.

[2.20] Anderson, P. W. (1987) Science 235, 1196; Anderson, P. W., Baskaran, G., Zou, Z., and Hsu. T. (1987) Phys. Rev. Lett. 58, 2790.

[2.21] Batlogg, B., Cava, R. J., Jayaraman, A., Van Dover, R. B., Kourouklis, G. A., Sunshine, S., Murphy, D. W., Rupp, L. W., Chen, H. S., White, A., Short, K. T., Mujsce, A. M., and Rietman, E. A. (1987) Phys. Rev. Lett. 58, 2333; Bourne, L. C., Crommite, M. F., Zettl, A., zur Loye, H.-C., Keller, S. W., Leary, K. L., Stacy, A. M., Chang, K. J., Cohen, M. L., and Morris, D. E. (1987) *ibid, 2337.*

[2.22] Faltens, T. A., Ham, W. K., Keller, S. W., Leary, K. J., Michaels, J. N., Stacy. A. M., zur Loye, H.-C., Morris, D. E., Barbee III, T. W., Bourne, L. C., Cohen, M. L., Hoen, S., and Zettl, A. (1987) Phys. Rev. Lett. 59,915; Batlogg , B., Kourouklis, G., Weber, W., Cava, R. J., Jayaraman, A., White, A. E., Short, K. T., Rupp, L. W., and Rietman, E. A. (1987) *ibid,* 912.

[2.23] Leary, K. J., zur Loye, H.-C., Keller, S. W., Faltens, T. A., Ham, W. K., Michaels, J. N., and Stacy, A. M. (1987) Phys. Rev. Lett. 59, 1236.

[2.24] Deutscher, G. and Müller, K. A. (1987) Phys. Rev. Lett. 59, 1745.

[2.25] Schlesinger, Z., Collins, R. T., Kaiser, D. L., and Holtzberg, F., (1987) Phys. Rev. Lett. 59, 1958.

[2.26] Mali, M., Brinkmann, D., Pauli, L., Roos, J., Zimmermann, H., and Hulliger, J. (1987) Phys. Lett. A 124, 112, and references 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] Hebel, L. C. and Slichter, C. P. (1959) Phys. Rev. *113*, 1504.

[2.28] Seidel, H., Hentsch, F., Mehring, M., Bednorz, J. G., and Müller, K. A. (1988) Europhys. Lett. 5, 647.

[2.29] Schlesinger, Z., Collins, R. T., and Shafer, M. W‘. (1987) Phys. Rev. B 35, 7232.

[2.30] Decroux, M., Junod, A., Bezinge, A., Cattani, D., Cors, J., Jorda, J. L. Stettler, A., Francois, M., Yvon, K., Fischer, Ø., and Muller, J. (1987) Europhys. Lett. 3, 1035.

[2.31] Worthington, T. K., Gallagher, W. J., and Dinger, T. R. (1987) Phys. Rev. Lett. 59, 1160.

[2.32] Kapitulnic, A., Beasley, M. R., Castellani, C., and Di Castro, C. (1988) Phys. Rev. B 37, 537.

[2.33] Weisskopf, V. F. (1979) “The Formation of Cooper Pairs and the Nature of Superconducting Currents,” CERN, Geneva, Memorandum No. CERN 79-12, Theoretical Studies Division, Dec. 2 1, 1979.

[2.34] Schafroth, M. R., (1954) Phys. Rev. 96, 1149 and 1442; *idem* (1955) Phys. Rev. *100, 463.*

[2.35] de Gennes, P. *G.* (1968) *Superconductivity of Metals and Alloys* (Benjamin, New York) p. 229.

[2.36] Yanson, I. K., Rybal’chenko, L. F., Fisun, V. V., Bobrov, N. L., Obolenskii, M. A., Brandt, N. B., Moshchalkov, V. V., Tret’yakov, Yu. D., Kaul’, A. R., and Graboi, I. É. (1987) Fiz. Nizk. Temp. 13,557 [Sov. J. Low Temp. Phys. 13, 315 (1987)]

[2.37] Müller, K. A., Blazey, K. W., Bednorz, J. G., and Takashige, M. (1987) Physica 148 B, 149.

[2.38] Razavi, F. S., Koffyberg, F. P., and Mitrović, B. (1987) Phys. Rev. B 35, 5323.

[2.39] Kwak, J, F., Venturini, E. L., Ginley, D. S., and Fu, W. (1987) Novel *Superconductiviy, Proceedings of the International Workshop on Novel Mechanisms in Superconductivity,* editors, S. A. Wolf and V. Z. Kresin (Plenum Press, New York) p. 983.

[2.40] Chaudhari, P., Koch, R. H., Laibowitz, R. B., McGuire, T. R., and Gambino, R. J, (1987) Phys. Rev. Lett. 58, 2684.

[2.41] Dinger, T. R., Worthington, T. K., Gallagher, W. J., and Sandstrom, R. L. (1987) Phys. Rev. Lett. 58, 2687.