

THE DEVELOPMENT OF SUPERCONDUCTIVITY RESEARCH IN OXIDES

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Starting with the first observation of superconductivity in an oxide, namely SrTiO_3 , the history of its development is traced. Basically, and consecutively, three kinds of oxide superconductors have been found: compounds with normal transition-metal-based conduction bands, oxides with cations exhibiting charge disproportionation, and finally the cuprates with large Coulomb on-site repulsion, U . The doped La_2CuO_4 was the first oxide discovered in this new class of materials. The discussion will then lead over to a characterization of the high- T_c materials, with regard to their main physical properties.

1 The Initial Two Decades of Superconductivity in Oxides

The first oxide in which superconductivity was found is reduced SrTiO_3 as reported by Schooley, Hosler and Cohen¹ in 1964. A $T_c \simeq 0.25$ K was observed with only $n = 3 \times 10^{19}$ electron carriers per cubic centimeter, i.e. at a carrier concentration three orders of magnitude below that of a normal metallic conductor, see Fig. 1. This phenomenon was clearly outside the accepted BCS

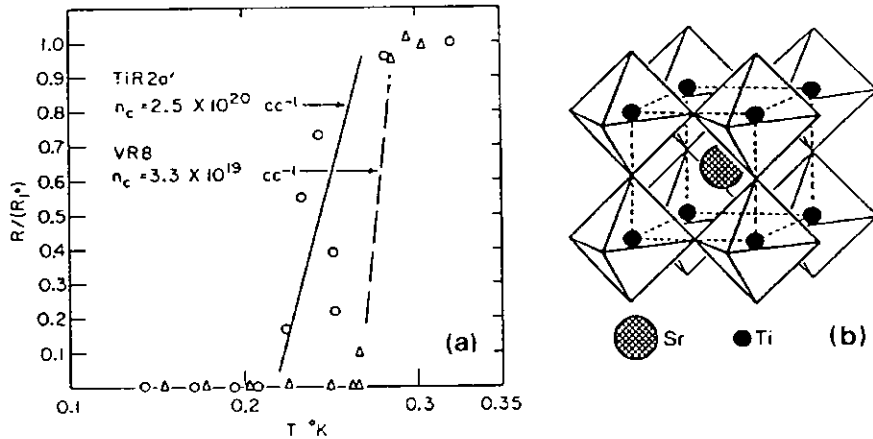


Figure 1: (a) Ratio of sample resistance at temperature T to that at 1 K, as function of temperature. From Ref. 1. (b) Perovskite lattice structure of SrTiO_3 . From Ref. 5.

picture of electron coupling by *shielded* phonons. Only recently — 17 years later — was the underlying process understood: because the carrier concentration is so low, the plasma edge is *below* the highest optical phonon branch in SrTiO₃. This phonon branch is therefore unshielded and the electron-phonon coupling parameter λ sufficiently large to induce superconductivity. Upon Nb doping of SrTiO₃, the electron concentration and the plasma edge increases, the edge passes this phonon branch which becomes shielded, and superconductivity vanishes at $n \simeq 10^{21} \text{ cc}^{-1}$ and $T_c \simeq 1.3 \text{ K}$.² Nine months after the SrTiO₃ discovery, Matthias' group reported superconductivity in the sodium tungsten bronze Na_xWO₃ with $x \simeq 0.3$, $n \simeq 10^{22} \text{ cc}^{-1}$ and a $T_c = 0.57 \text{ K}$.³ So it was clear that the phenomenon also occurred in another oxide, but with rather "normal" electron concentrations. Interestingly, in the Na_xWO₃ paper no reference to the over half a year older report on SrTiO₃ is given.

More recently the SrTiO₃ crystal showed another interesting property. Band calculations and experimental findings had been controversial until Mattheiss' calculations⁴ yielded two conduction bands 20 meV apart at the center of the Brillouin zone ($\vec{k} = 0$), the lower one having "starfish" shape. Thus, if he was correct, by increasing the doping one expected that after the first the second band would begin to fill. Consequently, one- and two-band superconductivity in the *same* material was expected and indeed observed by tunneling with In contacts in Rüschiikon,⁵ see Fig. 2. The progression of the observed two gaps is shown in Fig. 3 as a function of doping at helium temperature. One sees that the second gap appears at 32 meV, i.e. at a somewhat higher energy than the one calculated,⁴ but basically supporting it. The inset depicts the evolution of the two gaps in sample 8 as function of temperature T . It is very clear from it that the two gaps have the same transition temperature T_c . This is of relevance with respect to the controversy regarding the symmetry of the superconducting wave function in the copper oxides, namely, whether it is of "s" or rather "d" character.⁷ After having considered some of the best tunneling data, this author has recently suggested that also in certain cuprates two gaps with "s" and "d" character and the same T_c may be present.⁸

In 1965, superconductivity was also reported in TiO and NbO at temperatures of 0.68 and 1.25 K, respectively.⁹ However, these results did not meet with great interest because in NbN, with the same NaCl structure, a T_c of 16 K had already been observed back in 1941.¹⁰ After the superconducting bronzes had been found, the next substantial step forward in the oxides was the observation of a transition in the lithium titanium spinel LiTi₂O₄ with $T_c \simeq 11 \text{ K}$ by Johnston *et al.* in 1973 at San Diego,¹¹ Fig. 4. This represented already a quite respectable transition temperature. However, research in the spinel compound was not so intensive, probably because no single crystals became

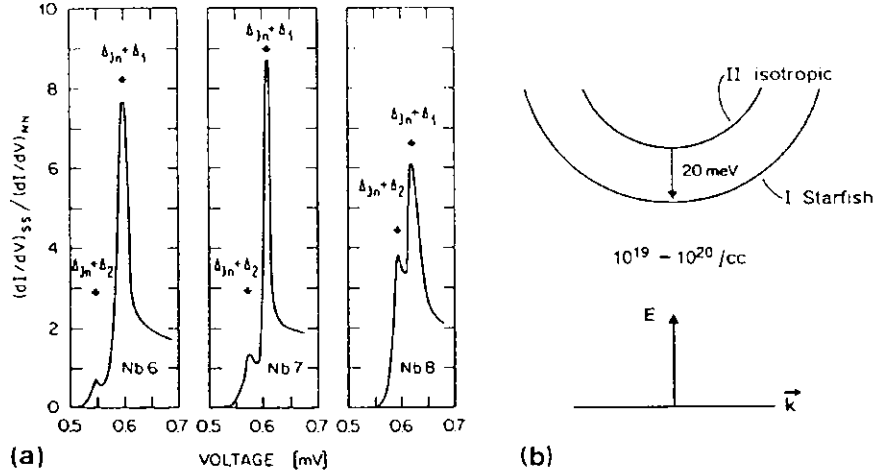


Figure 2: (a) Normalized tunneling conductance of Nb-doped SrTiO_3 -In junctions in the range of two-band superconductivity ($\mu_F > \mu_c \approx 32 \mu\text{eV}$) measured at $T = 100 \text{ mK}$. Only the portion of the voltage scale near the sum of the gaps of SrTiO_3 and In is shown. The latter could be determined within $\pm 2 \mu\text{eV}$ for a given sample and had a mean value of $\Delta_{In} = 535 \mu\text{eV}$. From Ref. 6. (b) Schematic of the conduction band structure.

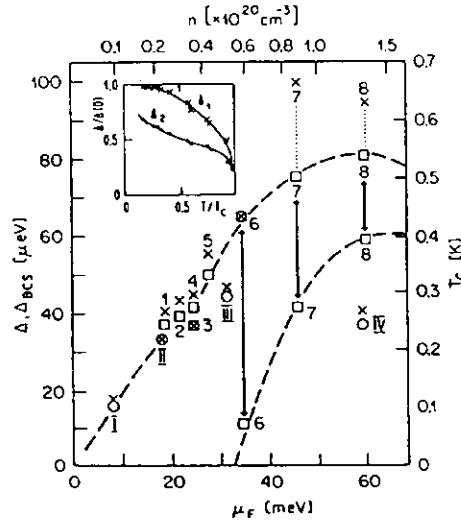


Figure 3: Superconducting order parameters Δ_1 and Δ_2 (inferred from peaks in the measured tunneling conductance of n -type SrTiO_3 -In junctions at $T \approx 0.2 T_c$: open circles, reduced samples; open squares, Nb doped. The inset shows the temperature dependence of both order parameters measured on sample Nb 8. From Ref. 6.

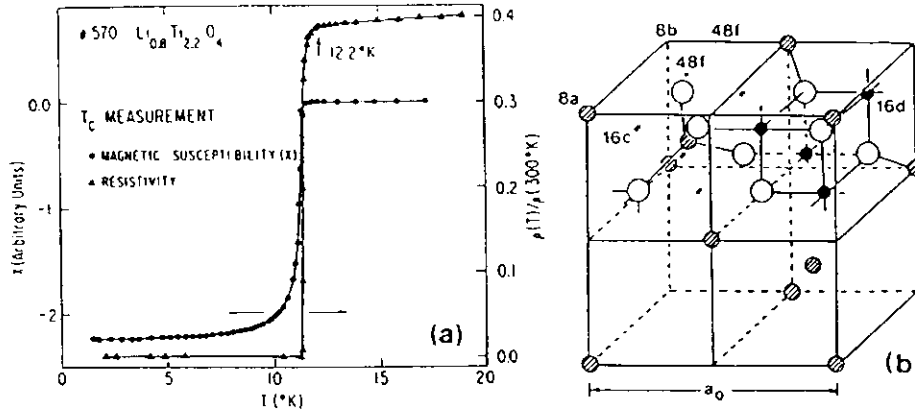


Figure 4: (a) Low-temperature magnetic susceptibility and resistivity data plotted vs. temperature for a sample prepared by sintering $\text{Li}_2\text{Ti}_2\text{O}_6$ and Ti_2O_3 at 800°C for one day. From Ref. 11. (b) Illustration of the cubic spinel $Fd\bar{3}m$, from Ref. 12.

available, despite the fact that a T_c of 13.7 K was reached in the mixed phase $\text{Li}_{1+x}\text{Ti}_{2-y}\text{O}_4$.¹³

Transition temperatures of comparable magnitude were reported only two years later in the perovskite $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system by Sleight *et al.*,¹⁴ Fig. 5. Remarkably this quaternary compound did not contain transition metals. Subsequent studies on hot-pressed ceramics,¹⁵ see Fig. 6, and single crystals¹⁶ allowed, in conjunction with expert band calculations,¹⁷ the characterization of its properties. The highest T_c was near 11.2 K with $x \simeq 0.25$ and a carrier concentration of $2.4 \times 10^{21} \text{cc}^{-1}$; correlations lengths were 60–70 Å, and the Ginzburg–Landau parameter $\chi \simeq 70$ –80. Therefore, according to the BCS theory, a large electron–phonon coupling was present. The transition temperature was found to be proportional to the *intensity* of a phonon band at 100cm^{-1} ,¹⁸ probably indicative of a substantial Bi(Pb)–O *anharmonicity* in σ -bonding. Thus one could expect to find still higher T_c 's in other metallic oxides if the electron–phonon interactions and the carrier densities, $n(E_F)$, at the Fermi level could be further enhanced. We were not aware at the time that $n(E_F)$ can be increased by going from three- to quasi-two-dimensional lattices, owing to the possible occurrence of a Kohn anomaly at E_F .¹⁹ More recently, by doping the charge-disproportionated insulator BaBiO_3 with K^+ on Ba^{2+} sites, an increase of T_c to near 30 K was realized,²⁰ Fig. 7. This is so far the oxide superconductor with the highest T_c that does not contain transition-metal ions. Its isotope effect is substantial, namely $\beta = 0.22$ to 0.4, i.e. nearly fully developed,²¹ indicating that dynamic atomic motion is responsible for the

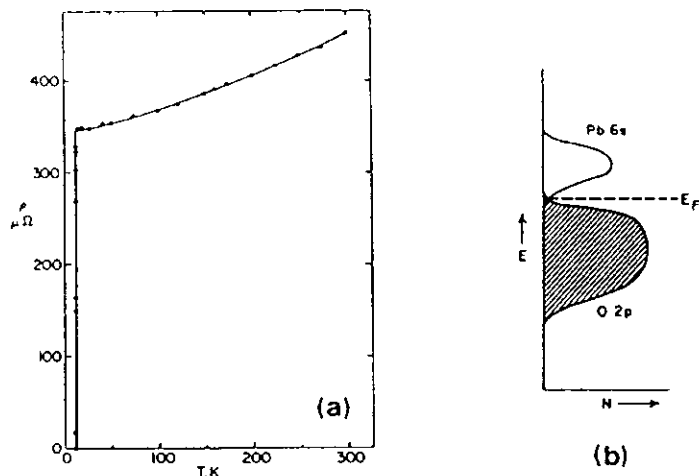


Figure 5: (a) Electrical resistivity vs. temperature for a crystal of $\text{BaPb}_{0.8}\text{Bi}_{0.2}\text{O}_3$.
 (b) Schematic energy level diagram for BaPbO_3 . From Ref. 14.

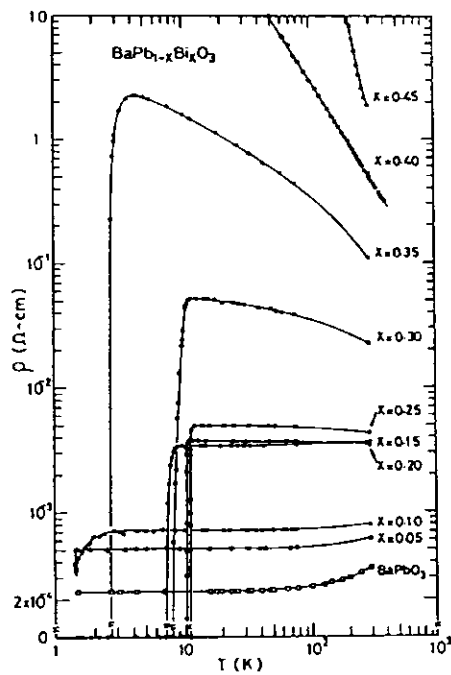


Figure 6: Temperature dependence of the electrical resistivity of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ with various Bi content. From Ref. 15, © by Springer-Verlag 1980.

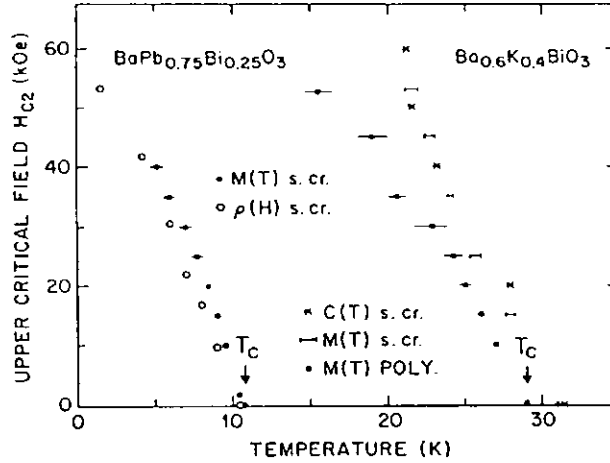


Figure 7: Upper critical field of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. From Ref. 20a.

coupling. The third class of oxide superconductors was found in 1986 with the Ba^{2+} -doped La_2CuO_4 .²²

2 The Concept and Discovery of Superconductivity in Ba-La-Ca Oxide Ceramics

Strong electron-phonon interactions can occur in oxides, owing to polaron formation as well as mixed-valence states. This can go beyond the standard BCS theory. A phase diagram with a superconducting to bipolaronic insulator transition was proposed early by Chakraverty.²³ A mechanism for polaron formation is the Jahn-Teller (JT) effect as studied by Höck *et al.* in a linear chain model.²⁴ From it, one expects heavy polaron masses if the JT stabilization energy becomes comparable to or larger than the bandwidth of the degenerate orbitals, and thus localization. Intermediate polarons are expected if the JT energy is not too large compared to the bandwidth. We recall that the JT theorem states the following: A nonlinear molecule or a defect in a crystal lattice exhibiting an electron degeneracy will spontaneously distort in lowering its symmetry, thereby removing its degeneracy. Isolated Fe^{4+} , Mn^{3+} , Ni^{3+} and Cu^{2+} in an octahedral oxygen environment show strong JT effects because their incompletely occupied e_g orbitals, transforming as $3z^2 - r^2$ and $x^2 - y^2$, point towards the negatively charged oxygen ligands²⁵ (Fig. 8). Although $\text{SrFe}^{4+}\text{O}_3$ is a distorted perovskite insulator, LaNiO_3 is a JT undistorted metal in which

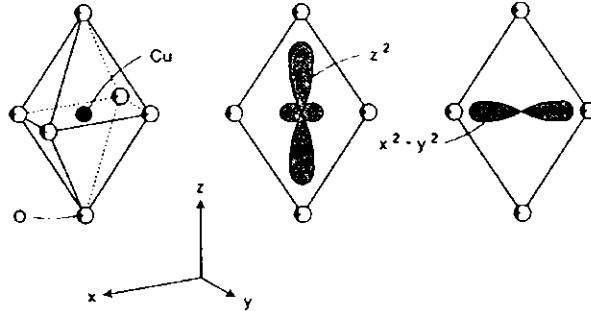


Figure 8: The partially filled 3d wave functions of the mixed-valence states. Positions of copper and oxygen atoms are shown at left. From Ref. 26, © 1987 by the AAAS.

the transfer energy b_{π} of the e_g electrons of the Ni^{3+} is large enough to quench the JT distortion.²⁷ On the other hand, LaCuO_3 is a metal containing only the non-JT Cu^{3+} . Therefore, it was decided to investigate and “engineer” nickel- and copper-containing oxides, with reduced bandwidth $\simeq b_{\pi}$, partially containing Ni^{3+} or Cu^{2+} states. The JT polaron proposed in 1983²⁴ was one envisaged to lead to a heavy mass of the particle; an intermediate, mobile polaron suited for superconductivity was not considered. However, in the ferromagnetic conductor $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, a giant oxygen isotope effect has been discovered most recently and ascribed to the presence of intermediate JT polarons due to the Mn^{3+} ions present in the oxide.²⁸ This important and new evidence for the existence of intermediate JT polarons is quite in favor of the original concept.²²

In Rüschnikon, there was a tradition of more than two decades of research in insulating oxides that undergo structural and ferroelectric transitions, which was a strong motivation to pursue the program. Furthermore, in 1979 the present author had started to work in the field of granular superconductors in which small Al grains are surrounded by amorphous Al_2O_3 .²⁹ In these systems T_c 's had been reported to be as high as 5 K, compared to pure Al with a T_c of 1.1 K. In our laboratory, the search for superconductivity was initiated together with J.G. Bednorz in mid-summer of 1983. Our efforts first concentrated on Ni^{3+} -containing perovskites, such as mixed crystals of LaNiO_3 and LaAlO_3 . In these unpublished efforts, the metallic behavior of the various synthesized double and triple oxides was measured, and at low temperatures they exhibited localization upon cooling. This indicated the possible existence of JT polarons, however, without any signs of superconductivity. In Fig. 9, results of these efforts are reproduced, see Ref. 30. In late summer of 1985, the efforts were shifted to copper-containing compounds, such as LaCuO_3 . Because Cu^{3+} has

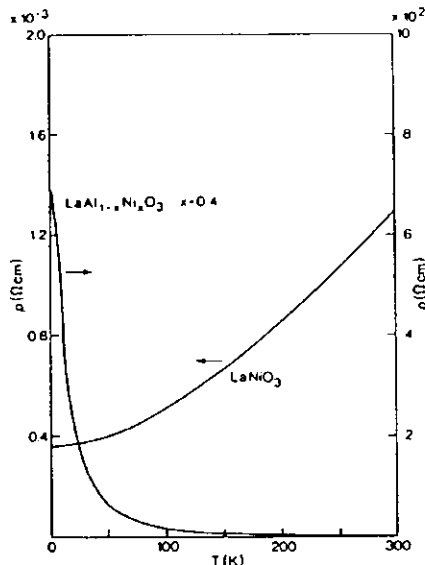


Figure 9: Temperature dependence of the resistivity for metallic LaNiO_3 and $\text{LaAl}_{1-x}\text{Ni}_x\text{O}_3$, where substitution of Ni^{3+} by Al^{3+} leads to insulating behavior for $x = 0.4$. From Ref. 30.

two electrons in the e_g subshell, the latter is half-filled. Thus, its ground state is not degenerate. It was clear that an oxide with mixed $\text{Cu}^{2+}/\text{Cu}^{3+}$ or $\text{Cu}^{3+}/\text{Cu}^{4+}$ valence had to be tried.

At this stage, Georg became aware of a paper by Michel, Er-Rakho and Raveau³¹ on the mixed perovskite $\text{BaLa}_4\text{Cu}_5\text{O}_{13.4}$, exactly meeting the requirements of mixed valence. The French authors had shown that this mixed oxide, a metal at room temperature and above, contained Cu^{2+} and Cu^{3+} . Thus, we tried to reproduce it, at the same time continuously varying the $\text{Cu}^{2+}/\text{Cu}^{3+}$ ratio by changing the Ba concentration in $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$, and we looked for superconductivity. A representative and concise account of the discovery of superconductivity in $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$ and the relevant superconducting phase present appeared in the September 4, 1987, issue of *Science*³⁶ and, in more detail, in the first of the two Nobel lectures in 1987,³⁰ and would exceed the scope of this contribution.

In Fig. 10 original data are shown as they were submitted for publication in April 1986.²² Upon cooling the resistivity first decreases near linearly, then shows a minimum and increases towards localization as in the case of $\text{LaAl}_{0.6}\text{Ni}_{0.4}\text{O}_3$ in Fig. 9. Then, upon further cooling, a sharp drop in $\rho(T)$ to very low values occurs that for higher currents is partially suppressed (upper

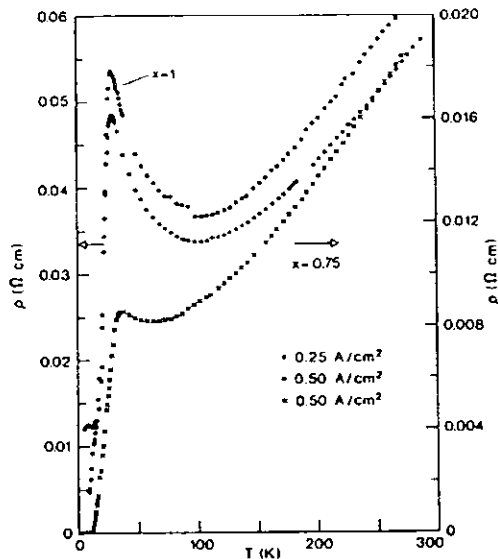


Figure 10: Temperature dependence of resistivity in $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$ for samples with $x = 1$ (upper curves, left scale) and $x = 0.75$ (lower curve, right scale) (x nominal). The first two cases also show the influence of the current density. From Ref. 22, © by Springer-Verlag 1986.

curves, left scale). The maximum onset could be shifted to 35 K by sample preparation. It was interpreted as a percolative onset to superconductivity. X-ray analysis revealed that the system consisted of three phases: CuO_2 , the $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$ originally wanted, and a K_2NiF_4 phase containing perovskite layers. A detailed powder X-ray analysis combined with susceptibility measurements showed that the phase becoming superconducting was indeed the layer-like oxide La_2CuO_4 ,³² which Michel and Raveau had characterized by X-rays earlier.³³ The La_2CuO_4 crystal contains a *checkerboard-type* CuO_2 layer that so far is present in all high- T_c superconductors. Furthermore, the doping with Ba^{2+} — or another two-valent ion — on the La site was crucial for inducing a mixed-valent hole conductivity, found also in all other copper-oxide highest- T_c superconductors.

The first to confirm our discovery were researchers from those laboratories that had investigated the oxide superconductor $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_3$ until 1986. This meant that their expertise in oxide superconductivity and equipment were still in place, and ready. The earliest confirmation of the existence of high- T_c superconductivity in the Ba-La-Cu-O came from Tanaka's group at Tokyo University.³⁴ Their onsets in $\rho(T)$ and diamagnetic crossovers were in the same

temperature range as those for the samples investigated in Rüsçhlikon. Moreover, their independent structure analysis also showed good agreement.³⁵ The Japanese confirmation stimulated research work in the United States. Both Chu's and Batlogg's groups, as well as that at Bellcore, not only confirmed, but had by the end of the year 1986 surpassed the Rüsçhlikon results in two ways. At AT&T, they started directly with Sr²⁺ substitution for lanthanum.³⁶ Their expertise in oxide ceramics allowed AT&T to obtain sharper onsets, with full superconductivity reached a few degrees below onset, and up to 30% Meissner effect at low temperatures, thus proving the presence of three-dimensional superconductivity. Tarascon *et al.* at Bellcore achieved a transition width of only 2 K with T_c very near 40 K.³⁷ At Houston, first the Rüsçhlikon results were confirmed,³⁸ and then resistivity measurements under hydrostatic pressure revealed onsets up to 52 K.³⁹ Therefore, Chu *et al.* foresaw still higher T_c 's for the future,³⁹ which they did indeed find,^{40, 41} and are reviewed in his contribution in these proceedings. At the Academy of Science in China, a long tradition of research in oxide ceramics exists. The scientists there also optimized the barium–strontium replacement of lanthanum and had reached a T_c of 48 K by the end of 1986.⁴²

3 Three Classes of Oxide Superconductors

Characteristic of this last class of oxide superconductors is their layered structure containing perovskite Cu–O planes. These planes can be stacked singly, doubly, triply or quadruply with either Cu–O chains, planes or single-double planes of other oxides (La, Bi, Tl, etc.) between them. More than two dozens of such compounds have been synthesized, with a confirmed maximum of 133 K for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ ⁴³ and of 163 K at high pressure.⁴⁴ The compounds with the highest T_c 's are all *hole* superconductors despite the fact that electron ones have also been found.⁴⁵ The coherence length ξ is highly anisotropic, 10 to 30 Å along the planes and 1 to 7 Å perpendicular to them. The Ginzburg–Landau parameter χ is of the order of 100 in plane and perpendicular to it over 1000. This is relevant for applications concerning both critical currents and magnetic fields. The latter become very high in the megagauss range, because $H_{c2} = \phi_2/\pi\xi^2$. The flux pinning observed is atypical. Their carrier concentration is of the order of a few times 10^{21}cc^{-1} ,³⁰ substantially lower than that of the earlier high- T_c superconductors, which were all Nb intermetallic alloys or compounds. So far, no other class of high- T_c superconductors has been found — which makes one wonder whether the copper oxides are unique.

In order to make progress, an understanding of the microscopic mechanism is quite relevant. This is reflected in the still large research effort world-wide.

Of course, development for use in industry is the other motor. Industrial applications can now progress empirically and do so successfully, based on the experimental findings and expert materials research. These have so far advanced the field, and allowed certain microscopic mechanisms to be excluded: on the conservative side those using *harmonic* electron-phonon interactions, on the exotic side the original resonance valence bond and the fractional quantum state theories.⁴⁶ Central to all attempts is the insight that a sizeable *atomic* coulomb repulsion U is operative at the copper ions in order to exclude hole carriers on the same site. Thus the ratio U/t , where t stand for the transfer integral, is substantial compared to the ratio Δ/t , where Δ is the energy needed to transfer Cu d -charge onto the neighboring oxygen p orbitals. This is opposite to the process in d - d oxide superconductors with low Hubbard U discovered first.⁴⁷ Figure 11 is a modified version of a figure that appeared in the reference cited, and shows the accepted picture. One notes that on both sides of the diagonal, $U \simeq \Delta$, there is a large area in which the transition-metal oxides are insulators. This is true for most oxides containing 3d metals from V to Ni. The d - d metals are mainly titanates, tungstates or molybdates, but there are exceptions.

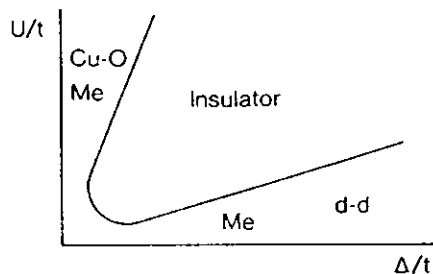


Figure 11: Modified metal-insulator diagram of the reduced Hubbard electron correlation energy, U , vs. reduced charge transfer energy Δ . t : transfer matrix element ($\propto W$, the bandwidth). Adapted from Ref. 47.

Therefore, one can categorize three classes of known oxide superconductors as follows: The first ranges from SrTiO_3 to LiTi_2O_4 and T_c 's from 0.2 to 13 K, with $\Delta > U$. In the second class are the "valence skippers," bismuthates with T_c 's from 13 to 32 K. The third, with $U \gg \Delta$, comprises *layered* compounds with T_c 's from 35 K as in La_2CuO_4 to well over 100 K. Regarding their transition temperatures, we therefore note that *each of the three categories has its own transition temperatures adjacent to those of next one*: the first up to 13 K, valence skippers up to 32 K, and cuprates above them up to 165 K so far (Fig. 12). Is there perhaps a fourth category?

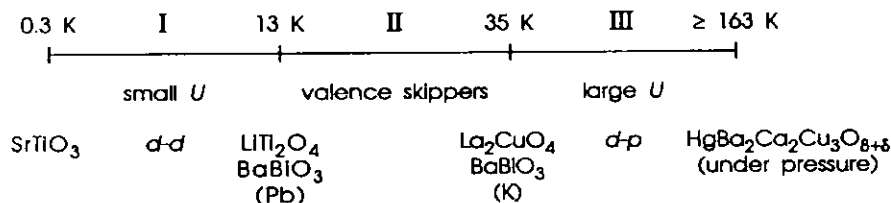


Figure 12: The development of superconductivity in oxides. U : on-site d -Coulomb repulsion.

The author thanks Ch. Bolliger for her help in editing and finalizing this paper, the topic of which has been addressed under the same title in the form of a long abstract without figures elsewhere.⁴⁸ Some of the context that led to the discovery of the copper oxide superconductors and the early confirmation²⁶ has also been included.

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