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High Temperature Superconductivity Research at the IBM Thomas J. Watson and Almaden Research Centers

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Complementing the work of Bednorz and Müller, which started the field of high temperature oxide superconductivity, the IBM Research laboratories at Yorktown Heights in Almaden have made contributions also via many outside collaborations across the full scope of this field. Materials work includes the identification, separation and structural characterization of the $YBa_2Cu_3O_{7-x}$ phase, the detection of superconductivity and antiferromagnetism in La_2CuO_4, and the deposition of YBaCuO films with transition temperatures above 77 K by electron-beam deposition and plasma spraying. Characterization work includes measurement of the superconducting energy gap by far-infrared and tunneling measurements, study of Meissner and diamagnetic shielding, observation of superconducting fluctuations, correlation of $[Cu-O]^+$ complex concentration with T_c, and determination of valence electronic structure by photoemission. Theoretical work includes proposal of an interband scattering mechanism for superconductivity, a mean-field solution to an electron-interaction model, band-structure calculations, and a phenomenological model for lattice parameters and their influence on T_c. $YBa_2Cu_3O_{7-d}$ single crystals have been synthesized and shown to exhibit up to 70:1 magnetic anisotropy. In work of relevance to applications, the first thin film SQUIDs have been operated in temperatures up to 68 K, epitaxial films on $SrTiO_3$ have been found to sustain critical currents of more than 10^5 A/cm^2 at 77 K, and coatings, superconducting above 77 K, have been deposited by plasma spraying.

Introduction

High temperature oxide superconductivity was discovered last year at the IBM Zürich Research Laboratory, in the seminal work of Bednorz and Müller and their subsequent collaboration with Takashige [1–5]. Interest quickly spread to the IBM Research sites at Yorktown Heights and Almaden, which have contributed further to the explosive development of this amazing field. 38 papers [1–38] have so far been submitted from the IBM laboratories. Here we review briefly the principal contributions from researchers at Yorktown Heights and Almaden, which cover all major aspects of high temperature superconductivity and thus offer a kind of microcosm of the entire field.

Superconductors with the K_2NiF_4 Structure: Experiment and Theory

Initial work focused on the materials with K_2NiF_4 structure – $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$, which we henceforth denote for short by LaBaCuO and LaSrCuO. Although these materials lack the higher transition temperatures of the more recently discovered "123" materials (see below), they remain interesting from a fundamental point of view: Their simpler structure with a single type of copper-oxide plane offers insights into mechanisms of high temperature superconductivity.

Following on the Zürich work, Maletta et al. [7] showed that $La_{1.8}Sr_{0.2}CuO_4$ could be prepared essentially single-phase, showing 100% diamagnetic shielding as well as an over 40% Meissner effect. They pointed out the pitfalls in not distinguishing clearly between the two effects. The observation of essentially bulk superconductivity complemented fine work from other laboratories.

The observation of increased T_c with hydrostatic pressure in LaBaCuO by Chu and coworkers at the University of Houston [39] leads to the idea of using smaller ions to achieve an internal "lattice" pressure. But Bednorz, Takashige and Müller found that while Sr increased T_c, the smaller Ca decreased it [2, 4, 5]. Malozemoff [10] clarified this puzzle by noticing a concomitant anomaly in the basal-plane lattice parameter of LaCaCuO. In fact, for a given alkaline earth concentration, T_c correlates with the basal-plane lattice parameter. Ca did not work as expected, presumably because it substituted at least partially on the Cu site. By estimating the elastic constants, Malozemoff found he could account for the observed pressure dependence of T_c within the same phenomenological correlation.

A more fundamental understanding of the mechanism for superconductivity comes from a consideration of the band structure. Early theoretical work [41] had suggested that La_2CuO_4 was a semiconductor because of a Peierls or charge density wave instability arising from nesting of a half-filled antibonding $Cu-d-O\text{-}p$ band. This was based on the supposition that the tetragonal-to-orthorhombic transition, which occurs at about 500 K, opens a gap and is detrimental to superconductivity. Herman, working with Kasowski and Hsu of du Pont [21], found that band theory predicts no such gap, and indeed experimental data show no onset of an insulating tendency until much lower temperatures.

In the following, we discuss some theoretical ideas complementary to the ones presented by Rice in the preceding short review (Z. Phys. B – Condensed Matter **67**, 141 (1987)).

An alternative explanation of the insulating tendency is in terms of strong electron correlations, as for example in a Hubbard insulator. Lee, in collaboration with Ihm from Bell Communication Research, carried this idea a step further [49]. Although the band calculations indicate only a single copper-oxygen band near the Fermi level, copper d_z^2 antibonding orbitals, which project charge density perpendicular to the CuO planes of the K_2NiF_4 structure, could have strong electron-correlation effects lifting them to the Fermi surface. The presence of two bands at the Fermi surface opens channels of interband scattering which could enhance T_c substantially, according to an earlier "two-band" model of superconductivity by Suhl, Matthias and Walker [40]. One possible origin of interband scattering is from phonons which tilt the CuO octahedra, in turn causing the tetragonal-to-orthorhombic structural transition. This would explain the coincidence of a structural transition and the maximum T_c at the same Sr concentration in $La_{2-x}Sr_xCuO_4$. The existence of a second band could also mediate electron pairing through plasmons or excitons.

Other evidence for electron correlations has come from experimental work of Greene et al. and Maletta et al. [19, 32] on the field dependent susceptibility of undoped La_2CuO_4. They observed a strong downward temperature shift with field of the previously known susceptibility cusp near 250 K, indicating an antiferromagnetic or spin-density-wave transition. They also found a large high temperature Pauli paramagnetic susceptibility in the Sr-doped material, significantly enhanced over values expected from band calculations. This suggests either an electron-correlation enhancement of effective mass or possibly evidence for another band at the Fermi energy, as suggested by Lee and Ihm [49].

Shafer, Penney and Olson [34] have studied the $La_{2-x}Sr_xCuO_{4-d}$ system using a chemical method for determining the electron deficiency or hole concentration. They found that oxygen deficiency increases dramatically above $x=0.15$, leading to a drop in the concentration of $[Cu-O]^+$ complexes. In fact, since the concentration of these complexes increases proportionally to the Sr substitution below $x=0.15$, they found a correlation between T_c and $[Cu-O]^+$ throughout the Sr concentration range, as shown in Fig. 1. The mechanism for the dropoff in T_c above $x=0.15$ had not previously been clear. In fact, the same authors found that $YBa_2Cu_3O_{7-d}$ in the "123" structure (see below) also correlates with this trend, although the detailed result depends on whether the $[Cu-O]^+$ complexes reside primarily on the chains or the planes of this structure.

These two clues – the role of electron-electron correlations and the simple proportionality of T_c to the $[Cu-O]^+$ concentration – motivate Newns [28] to treat a strongly correlated electron system in a nearly half-filled Hubbard band. In this mechanism for superconductivity originally investigated by Hirsch [41] and Anderson [42], electron pairing arises from a purely electronic single-site double-occupation mechanism. Newns' mean field solution of this problem gives the simple scaling of T_c with the quasiparticle Fermi level and hence with the hole concentration, as observed in the Shafer-Penney-Olson experiment.

The above discussion speaks of $[Cu-O]^+$ complexes rather than the more conventional Cu^{3+}. This is because photoemission and near-edge x-ray absorption fine structure (NEXAFS) by Yarmoff et al. [30]

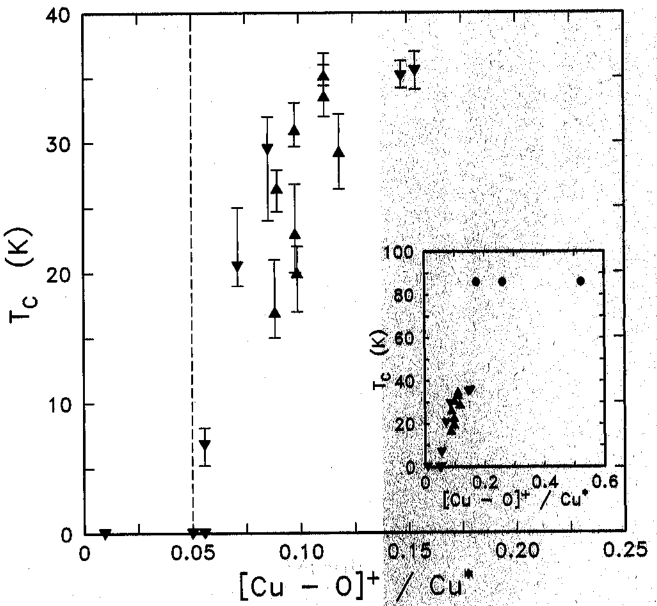

Fig. 1. Superconducting transition temperature versus $[Cu - O]^+$-concentration determined by chemical analysis in $La_{2-x}Sr_xCuO_4$ (triangles) and $YBa_2Cu_3O_{7-d}$ (circles in inset, corresponding to different choices of copper-oxide-complex location) (from Shafer et al. [34])

indicate that the holes in $YBa_2Cu_3O_{7-d}$ are localized predominantly on the oxygen rather than on the copper, and that these oxygens lie in the Cu−O chains (see below).

Perhaps the most surprising development is the discovery by Grant et al. [24] of superconductivity in undoped La_2CuO_4. The onset is near 40 K in resistivity and susceptibility measurements, but close to 100 K in thermopower. The effect is sensitive to stoichiometry and processing, and is apparently of a filamentary nature, since the diamagnetic susceptibility corresponds to only a small fraction of the sample. The possibility of a La deficiency would lead to $[Cu - O]^+$ complexes, much as described above. These results point to a remarkably general mechanism for high temperature superconductivity inherent in the *mixed valent* copper-oxide structures of these compounds.

Identification, Separation and Structure of $YBa_2Cu_3O_{7-d}$

When news of the discovery of a multiphase yttrium-barium cuprate superconducting above 90 K came from the Universities of Alabama and Houston and from the Academia Sinica in Peking [44–45], researchers in all three IBM laboratories began frenetic work to identify, separate and characterize the superconducting phase. Grant et al. [11] analyzed the green and black grains of the original ceramic mixture by electron microprobe and energy dispersive x-ray analysis, identifying the 2:1:1 and 1:2:3 composition ratios. Synthesis according to these ratios gave single phase material, insulating and superconducting in the two cases.

Initial x-ray analysis of the $YBa_2Cu_3O_{7-d}$ superconducting structure indicated a tripled perovskite-type unit cell with oxygen deficiency and regular layers of Y ions separated by two layers of Ba ions. This is a new structure not previously in the literature and quickly baptized "123". Its remarkable properties are still under intensive investigation. Henceforth, when we use the shorter YBaCuO, we mean the yttrium-barium cuprate with the 123 structure and composition.

The first lattice images, taken by Shaw and collaborators [12] and reproduced in Fig. 2, reveal the dramatic regularity and three-fold structure of this new phase. Subsequent close collaborative work between the Yorktown and Almaden groups refined the crystallography and microstructure [16, 29]. The unit cell was found to be orthorhombic, with oxygen deficiency (as compared to the full perovskite) accommodated by oxygen vacancies partially on the copper planes between the barium layers, and partially on the yttrium planes, as shown in Fig. 3. The vacancies on the copper planes order in a linear arrangement, forming Cu−O "ribbons" or "chains", in addition to the Cu−O "planes" evident in Fig. 3. The first insight into the chain-structure must be credited to Mattheiss and Hamann [46], but the process of pinning down this complex structure experimentally was an interactive and rapid-fire process between groups at many different laboratories.

Shaw and Beyers observed the structure to be heavily twinned on the {110} planes, where the pseudotetragonal axis is taken to be [001]. A remarkable discovery was made as the heavily twinned lattice images were observed under heating in the transmission electron microscope: At about 700 C, the twinning contrast disappeared, indicating an orthorhombic-to-tetragonal transition confirmed by the high-temperature X-ray and neutron scattering results of LaPlaca, shown in Fig. 4.

This effect has provided a decisive clue for unraveling the mechanism for annealing enhancement of T_c in the YBaCuO. Above this temperature, the oxygen vacancies are disordered in the copper plane between the barium oxide layers, and quenching from this temperature freezes in a partially disordered arrangement with a reduced orthorhombic distortion. Annealing just below the transition promotes maximum ordering of the oxygen vacancies, resulting in

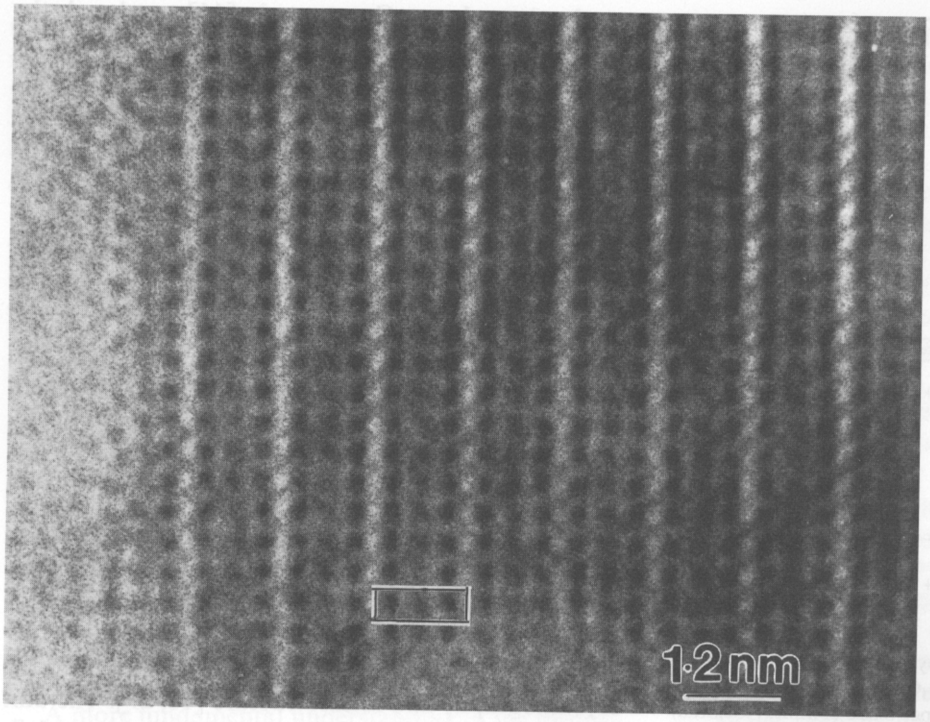

Fig. 2. TEM lattice image showing the two-dimensional structure of the layered perovskite $YBa_2Cu_3O_{7-d}$ (from Gallagher et al. [12])

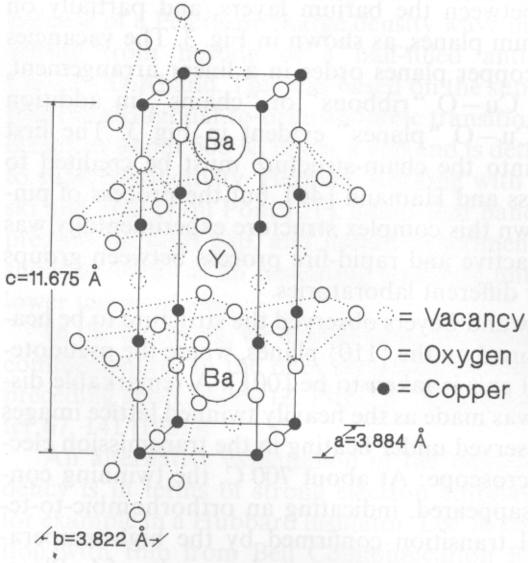

Fig. 3. Schematic structure of the "123" phase of $YBa_2Cu_3O_7$, showing copper-oxide "chains" and "planes" (from Beyers et al. [29])

superior superconducting properties. While this suggests that the ordered chains are the superconducting channels responsible for 90 K superconductivity, a more explicit confirmation awaits further work.

Processing is important, as with other oxygen deficient perovskites. T_c can be degraded by annealing in inert atmosphere or vacuum. Schrott, Park and Tsuei [31] have studied these postannealing treatments of YBaCuO by ultraviolet und X-ray photoemission spectroscopy. They correlate changes in the oxygen 1*s* XPS peak with two degree of degradation in T_c. They suggest that a small degradation corresponds to removal of oxygen atoms from the apex of the pyramids (see Fig. 3) while a large degradation comes from removal of the oxygens in the linear Cu–O chains. Again this points of the important role of the chains in the high temperature superconductivity of 123-YBaCuO.

Herman and his collaborators at DuPont [38] have calculated the band structure of 123 as a function of oxygen occupation and ordering. They find that the density of states at the Fermi energy decreases as oxygen content and/or ordering decreases. Through the simple BCS formula assuming constant coupling, this observation can rationalize the observed decrease in T_c. Thus it may be that the dependency of T_c on average copper valency can be explained in single particle terms alone, though more work needs to be done to substantiate this quantitatively.

The identification of the 123-phase opened the door to the synthesis of a large number of other compounds, including a variety of alkaline earths and rare earths, see also Engler et al. [18]. It was discovered that the magnetic rare earths, such as Gd, has no

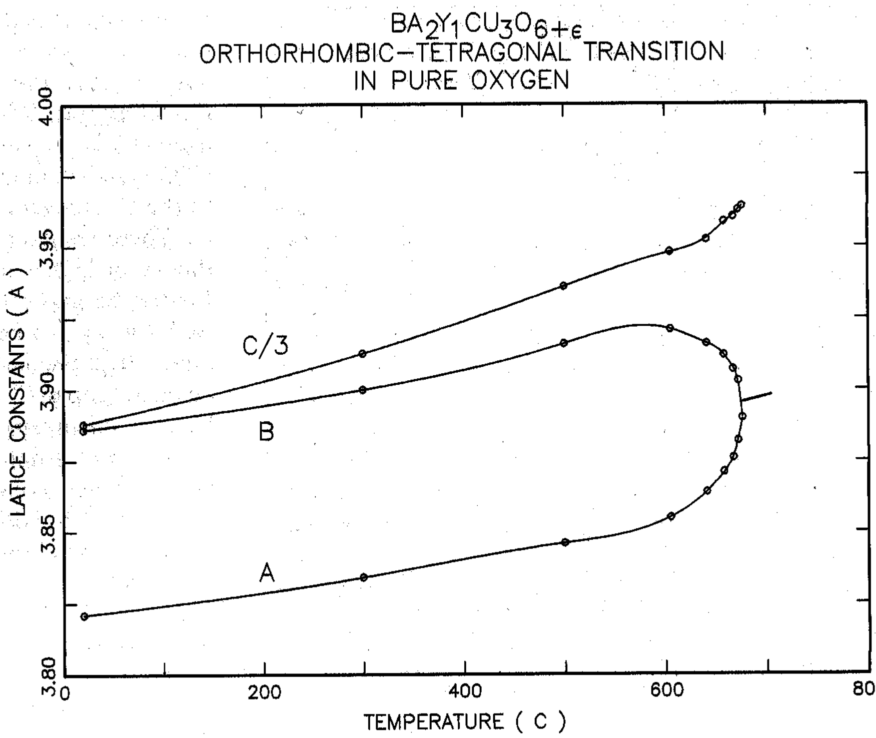

Fig. 4. Neutron diffraction determination of lattice parameters $YBa_2Cu_3O_{7-d}$, showing the orthorhombic to tetragonal transition near 700 C (from LaPlaca, to be published, see also Beyers et al. [29])

noticeable effect on the superconducting transition temperature. This is surely one of the most unique properties of these new high temperature superconductors, because in all known superconductors, magnetic ions act as "pair-breakers" and rapidly reduce the transition temperature with increasing concentration. Recent results also show that this effect persists not just for a chemically ordered compound like $GdBa_2Cu_3O_{7-d}$ but also for mixed rare earth substitutions in the yttrium plane of Fig. 3 (e.g. $Gd_{1-y}Y_y$ or $Ho_{1-y}Y_y$). This implies that T_c is also remarkably unaffected by certain kinds of chemical disorder.

Frase, Liniger and Clarke [20] have filled out the understanding of the $Y_2O_3-BaO-CuO$ pseudoternary phase diagram at 950 C. They have confirmed the phase compatibility field for 123, and have found a number of new compounds: a 132 ABO_3 perovskite phase and two binary phases between barium oxide and $BaCuO_2$, one of which (Ba_2CuO_3) is a K_2NiF_4-type of defect perovskite, so far not superconducting.

Single Crystals of $YBa_2Cu_3O_{7-d}$

Dinger et al. [26] grew small single crystals of $YBa_2Cu_3O_{7-d}$ from a sintered powder using an oxidizing atmosphere during a 975 C anneal to promote the growth of crystallites already present in the particle compact. The crystals approached 0.5 mm in size and had a somewhat smaller orthorhombic distortion than the earlier-studied ceramics. Correspondingly the transition temperatures were somewhat lower, typically around 85 K rather than in the 90's. While the crystals twinned under mechanical grinding, they appeared not to be twinned as-grown.

Both lower critical field and magnetic hysteresis measurements showed large anisotropy perpendicular and parallel to the copper-oxide planes. An example is shown in Fig. 5, where there is a 30:1 anisotropy in the hysteresis at 4.5 K. This hysteresis can be used to determine a minimum possible value of the critical current density, which exceeds 2×10^6 A/cm^2 parallel to the copper-oxide planes. A more direct measurement of the current density in epitaxial films is described below.

Further work is progressing on the anisotropy of upper critical field as well as anisotropy in the pseudotetragonal basal plane. This information will be exceedingly important in defining the highly anisotropic parameters, and this in turn will be decisive in identifying the mechanism for high temperature superconductivity in this complex phase.

The availability of even these small single crystals opens the door to a variety of other important measurements. Dinger, Cook and Clarke [26] have determined the fracture toughness of 123-YBaCuO by indentation crack length measurements. The toughness

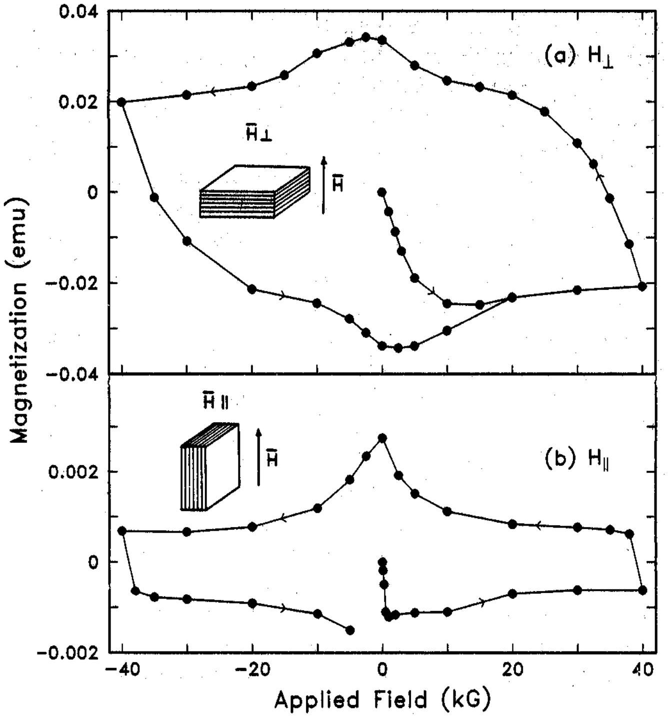

Fig. 5. Magnetization hysteresis loops at 4.5 K for a single crystal of $YBa_2Cu_3O_{7-\delta}$ with Cu−O planes oriented a) perpendicular and b) parallel to the applied magnetic field (from Dinger et al. [26]). The difference indicates a 30:1 anisotropy in critical current density in the two directions

of 1 MPa $\mathrm{m}^{\frac{1}{2}}$ is a bit higher than, but comparable to that of, silicon. The brittleness and moisture enhanced sub-critical crack growth will pose problems for certain applications. Further measurements on single crystals will be discussed below.

Gap Measurements and Other Characterization of YBaCuO

One of the most important characteristics of any superconductor is its energy gap, and this has been probed in a series of experiments on both LaSrCuO and YBaCuO using far-infrared spectroscopy and point-contact tunneling, by Schlesinger, Collins, Kirtley and coworkers [6, 9, 13, 15, 33, 35]. Far-infrared results on randomly oriented ceramic material indicates a gap-to-critical-temperature ratio $2\Delta/kT_c$ of about 2.5, while tunneling indicates a distribution of values around 4.3.

Recent far-infrared measurements [35] on epitaxial YBaCuO films (see below) show a much higher gap ratio of 5, removing the previous discrepancy with tunneling. The difference between ceramic and epitaxial-film results is intriguing. Since high temperature superconductors have much larger gaps than any previously studied superconductors, phonons may affect the far-infrared absorption more strongly and may obscure the true superconducting gap. Recent tunneling into YBaCuO single crystals gives a range from 4.5 to 6.0 for tunneling perpendicular to the CuO layers, and from 3.9 to 4.8 for tunneling parallel to the CuO layers [33].

These results have important implications for the theory of high temperature oxide superconductivity. Firstly the gap ratios indicate strong-coupling in the BCS theory (3.5 being the ratio for the weak-coupled limit [46]). Secondly, the presence of the gap argues against "gapless" theories. Thirdly, there is evidence for gap anisotropy.

Another point concerns the linear background in the tunneling conductance-voltage curve. According to a model by Zeller and Giaever [47], this can be caused by granular superconductivity with small interparticle capacitance. Fitting gives particle sizes of order 10 nm, puzzling smaller than typical grain sizes in these materials.

Both conductivity and magnetic measurements show a curvature setting in at temperatures above the main superconducting transition. Many earlier authors have pointed to such effects as evidence of yet higher temperature superconductivity. Freitas, Tsuei and Plaskett [23] have found that the conductivity and magnetic curvature fits a three-dimensional Aslamazov-Larkin theory of superconducting fluctuations with no adjustable parameters. Because of YBaCuO's large normal state resistivity and the small coherence length which enter the theory in a proportional and inverse way respectively, these effects are of order 10^4 times as large as in conventional superconductors. The three-dimensionality poses a problem for theories which attribute superconductivity to the linear copper-oxide chains.

Thin Films, Squids and Critical Current

Laibowitz et al. were the first to report YBaCuO films superconducting above 77 K [14]. Their rapid success was based on the quick communication of the initial structure findings from the Almaden group. The films were prepared by electron-beam deposition from three metal targets in an oxygen partial pressure of up to 1 m Torr, onto sapphire or MgO substrates heated typically to 450 C. After removal from the vacuum system, the films were annealed in oxygen and became fully superconducting by 87 K. These 1 µm-thick films were slightly off-stoichiometry and remained polycrystalline with micron-sized grains.

This work opened the door to fabrication of the first thin-film devices operating in the liquid nitrogen temperature range, by Koch et al. [25]. These were superconducting quantum interference devices, or SQUIDs, consisting of a 40 × 40 μm loop separating two 17 μm-wide weak links. The patterning was achieved using an ion-implantation technique developed by Clark et al. [22], in which implanted oxygen and arsenic ions were found to suppress T_c and eventually drive the YBaCuO film amorphous. The desired superconducting lines were protected from the implantation by a lithographically patterned gold layer, leaving a planar YBaCuO structure for the SQUIDs.

SQUID operation persisted up to 68 K, somewhat lower than the original film transition temperature, presumably because of a small amount of ion penetration through the gold. The flux-periodicity of the voltage confirmed the conventional superconducting flux quantum of $h/2e$. While the flux noise was estimated to be higher than that of helium-temperature SQUIDs, it is still in a range to be of considerable use in applications like magnetometry.

Surprising in this work was the fact that weak links could be made out of lines 17 μm wide, especially in view of the very small estimated BCS coherence length in these oxide superconductors. The likely explanation is the presence of barriers and occasional Josephson contacts between grains, as originally proposed by Müller, Takashige and Bednorz [3].

These barriers are also the likely reason for rather low critical currents widely reported in randomly oriented ceramic YBaCuO. In principle, current density is fundamentally limited by a "depairing current density", at which the pair kinetic energy equals the superconducting condensation energy [48]. An estimate from standard formulae gives a value above 10^8 A/cm^2 for YBaCuO, and about 10^7 at 77 K for a 95 K superconductor (where the Ginzburg-Landau theory is used to estimate the temperature dependence near T_c). In practice, however, the critical current density is determined by flux-line pinning in Type II superconductors, because flux motion generates loss. Achieving strong pinning and hence large current density is decisive for most applications of superconductivity, including high field magnets, cost-efficient magnets, cost-efficient power transmission and interconnect lines in superconducting or semiconducting electronics.

A major step in demonstrating high critical current density was made by Chaudhari et al. [27], who electron-beam-deposited YBaCuO films onto $SrTiO_3$ substrates and annealed them to form preferentially oriented or epitaxial films. These films, fully superconducting at 90 K, showed critical current density above 10^5 A/cm^2 at 77 K, and an indirect determination from magnetic hysteresis measurements indicated current density above 10^6 at 4 K, similar to that in the single crystals described earlier. The nature of the pinning defects is under investigation, but apparently the preferential orientation has served to eliminate grain-boundary barriers which limited critical current density in earlier work. The importance of this result is that it lays to rest any doubts about the ability of YBaCuO to carry large current density, and this opens the door to many possible applications, although clearly new techniques will have to be devised to orient grains in applications incompatible with single-crystal substrates.

The ability to use these materials also depends on convenient ways to deposit them. For covering large areas or complex shapes, plasma spraying has been a widely used industrial technique. Cuomo et al. [37] have succeed in plasma spraying YBaCuO onto a variety of substrates, achieving coating from 10 to 250 μm thick. A fine powder of YBaCuO is fed with a carrier gas into an Ar–He plasma and propelled against the desired surface. With a subsequent oxygen anneal, the material has been made superconducting up to 84 K. The ability of the material to withstand this kind of "punishment" augurs well for its flexibility in various application environments.

Conclusion

Great though the progress has been in understanding and applying high temperature superconductivity, one can confidently predict as much excitement in the months and years to come. While many proposals have been made, there is as yet no detailed comparison of theory with experiment sufficient to establish the mechanism of superconductivity in either the K_2NiF_4 or 123 structures. The kind of data described above on single crystals and epitaxial films is heralding a new generation of effort in this direction. Another exciting area is the possibility of superconductivity at yet higher temperatures. One can surely expect the discovery of new structures conductive to high temperature superconductivity. Work on applications has also barely started and their impact on technology could be dramatic. The program of research and development at the three IBM research laboratories will continue to pursue these goals.

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