Physical Properties of the Quaternary Oxide Superconductor YBa$_2$Cu$_3$O$_7$[†]

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Introduction

Recently, two classes of copper oxides, La$_{2-x}$M$_x$CuO$_4$ (M = Ba,[1] Sr,[2-5] or Ca[6]) and RBa$_2$Cu$_3$O$_7$ (R = Y[7,8] or other lanthanides[9-12]), have been shown to exhibit high-temperature superconductivity. Scientists and engineers have become excited about the prospects of new technologies utilizing the novel properties of such superconductors. Prior to these discoveries, the highest known superconducting transition temperature, T_c, was ~23 K in Nb$_3$Ge.[13] Thus, liquid helium (4 K) or liquid hydrogen(!) (22 K) was required to cool Nb$_3$Ge to the superconducting state. With the new copper oxides, RBa$_2$Cu$_3$O$_7$, having T_c ~ 90 K, liquid nitrogen (77 K) can be used as the refrigerant. Because of the lower cooling costs, applications of these materials for power transmission and storage and in high-speed computers may be economical.

Temperature is not the only factor which defines the region of superconducting behavior for a given material. In general, a material will show superconductivity provided it is within the boundaries of a region rigidly defined by three parameters: the maximum critical temperature, T_c, critical magnetic field, H_c, and critical current density, J_c. If temperatures, applied magnetic fields, or electrical currents exceed these critical values, the superconductor will return to the normal state. Record holders prior to 1986 were T_c ~ 23 K for Nb$_3$Ge,[13,14] H_c ~ 600 kG for PbMo$_6$S$_8$,[15] and J_c ~ 10^7 A/cm^2 for V$_3$Ga.[14] YBa$_2$Cu$_3$O$_7$ is characterized not only by a high T_c but also by a large H_c. At 4 K, applied magnetic fields in excess of 1000 kG are necessary to destroy superconductivity.[16,17] However, while the critical current density, J_c, is >10^6 A/cm^2 in single crystals[18,19] and epitaxial films,[20] sintered pieces of these copper oxides remain superconducting only for current densities well below 10^4 A/cm^2.[21,22] This difference between single crystals and sintered materials indicates microstructural limitations to the current-carrying capacity. For many applications under consideration, the sintered material must carry at least 10^6 A/cm^2. Therefore, before RBa$_2$Cu$_3$O$_7$ can be brought into general application, an understanding of the interplay between synthesis, microstructure, and superconductivity

must be developed.

In this Account, the phenomenon of superconductivity is discussed from a chemist's point of view. We begin with a description of the electronic properties of superconducting oxides, including the related phenomenon of metal–insulator transitions. The methods used to prepare YBa$_2$Cu$_3$O$_7$ are described next along with a few synthetic caveats. In the following section, different experimental methods used to measure the superconducting properties are discussed and evaluated, together

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Table I.
Oxide Superconductor Systems

compound	T_c, K	no. of electrons	ref
SrTiO$_{3-x}$	1	<1 (3d)	28
A$_x$WO$_3$	7	<1 (5d)	29
Li$_{1+x}$Ti$_{2-x}$O$_4$	13	~1 (3d)	30
BaPb$_{1-x}$Bi$_x$O$_3$	13	~1 (5s)	27
La$_{2-x}$Sr$_x$CuO$_4$	37	~9 (3d)	1, 4–6
YBa$_2$Cu$_3$O$_{7-x}$	94	~9 (3d)	7–12

with a review of some techniques useful for gaining a better understanding of the inherent limitations of superconductivity in YBa$_2$Cu$_3$O$_7$. Finally, we present an interpretation of the observed electronic properties based on an examination of the microstructure of these high-temperature superconductors. At the present stage of study, it is extremely important to correlate microstructure and superconducting properties with methods used to synthesize YBa$_2$Cu$_3$O$_7$ in order to determine the origins of the low critical current of sintered materials. For a discussion of other important aspects of the synthesis, structure, and characterization of these high-temperature superconductors, the reader is referred to ref 23 and 24.
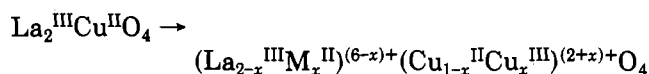
Metal–Insulator Transitions

Most superconductors are elemental metals, intermetallic compounds, or alloys, such as the A15 phases (e.g., Nb$_3$Ge[13]) or the tetraborides (e.g., LuRh$_4$B$_4$[25]). In addition, there are a few transition-metal chalcogenides which exhibit superconductivity, such as the layered transition-metal dichalcogenides (e.g., NbSe$_2$[26]) and the Chevrel phases (e.g., PbMo$_6$S$_8$[15]). While many oxides are insulators, some exhibit metallic conductivity, and a few are superconductors (see Table I). It is not surprising that so few oxide superconductors are known because oxides remain superconducting only over a fairly narrow range of compositions; in order to discover new oxide superconductors, it is necessary to study a particular system carefully as a function of stoichiometry. Therefore, while oxide superconductors have stimulated some interest due to their anomalous superconducting properties, since so few were known it did not appear to be a promising area for superconductivity research. In addition, prior to 1986, the highest superconducting transition temperature for oxide materials was 13 K.[27,30] There was no reason to believe that copper oxides would exhibit such high transition temperatures, until the work of Bednorz and Muller.[1]

The behavior of the new high-T_c superconductors is similar to that observed for other oxide superconduc-

tors. All of these materials[1,6,27–30] are poor metals[31] at room temperature. Through relatively small variations in composition, such as changes in cation substitution (e.g., A$_x$WO$_3$ and La$_{2-x}$M$_x$CuO$_4$) or oxygen stoichiometry (e.g., SrTiO$_{3-x}$ and YBa$_2$Cu$_3$O$_{7-x}$), these materials become insulators and no longer exhibit superconductivity. For all the systems found prior to 1986, the d bands were near empty or, in the case of BaBi$_{1-x}$Pb$_x$O$_3$, the 5s band was near empty.[27] In each case, an insulating host material was doped in such a way as to add electrons to the empty d or s bands to produce a superconducting material.[32] The number of electrons, and thereby the electronic properties, of these oxides can be manipulated systematically by substituting cations or anions with lower formal charge, by inserting interstitial ions, or by increasing the number of anion or cation vacancies. Reduction of the insulating host material by any of these methods can result in a transition to metallic behavior; superconductivity is often observed at an optimum doping level near the metal-insulator transition, on the metallic side. For example, WO$_3$(d^0) is an insulator which becomes metallic when 0.33 mol of Na is inserted;[33] Na$_x$WO$_3$ materials exhibit superconductivity only for a narrow range of x, with x near but greater than 0.33.[29] NaWO$_3$(d^1), with x = 1, has a conductivity near that of copper metal, and neither NaWO$_3$ nor copper metal is a superconductor; only poor metals exhibit superconductivity.

The recently discovered high-T_c copper oxides differ from the earlier systems, containing not partially reduced host materials but highly oxidized ones. The formal copper oxidation states are greater than +2. Substitution of divalent alkaline earth atoms, M^{2+}, for La^{3+} in insulating La$_2$CuO$_4$[34] leads to superconducting materials La$_{2-x}$M$_x$CuO$_4$ for 0.05 < x < 0.30.[4–7] Cationic charge balance in the substituted material is maintained through formal oxidation of the copper

$$\text{La}_2{}^{\text{III}}\text{Cu}^{\text{II}}\text{O}_4 \rightarrow$$
$$(\text{La}_{2-x}{}^{\text{III}}\text{M}_x{}^{\text{II}})^{(6-x)+}(\text{Cu}_{1-x}{}^{\text{II}}\text{Cu}_x{}^{\text{III}})^{(2+x)+}\text{O}_4$$

Anion vacancies control superconductivity in the Y-Ba–Cu–O system. Formally, this material contains mixed-valent copper, YBa$_2$Cu$_2{}^{\text{II}}$Cu$^{\text{III}}$O$_7$. These mate-

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rials are highly oxidized and susceptible to reduction by loss of oxygen. Superconductivity, however, is observed only for $YBa_2Cu_3O_{7-x}$, with $0 \leq x \leq 0.5$. Removal of 0.5 oxygen atom per formula unit reduces the material by one electron and yields an insulating phase $YBa_2Cu_3^{II}O_{6.5}$.[35] This material can be reduced further by loss of another 0.5 oxygen atom to give $YBa_2Cu_2^{II}$-Cu^IO_6, also an insulator.[36,37] The existence of superconductivity over a narrow range of x in $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_{7-x}$ underscores the importance of rigorous synthetic control of the doping level and oxygen stoichiometry in these materials.

The subtle relationship between stoichiometry, metal–insulator instabilities, and superconductivity is representative of a variety of fascinating electronic properties observed for materials near a metal–insulator transition,[33] including charge density waves, magnetic ordering, and valence fluctuations. All of these phenomena are associated with the breakdown of the one-electron model of electronic structure. Near a metal–insulator transition, the evaluation of electron–electron interactions and interactions between electrons and phonons (lattice vibrations) is essential to understanding the electronic properties. For example, the electronic structure of $YBa_2Cu_3O_7$ cannot be described as independent electrons localized in discrete energy levels, nor as free electrons delocalized in broad energy bands.[38] $YBa_2Cu_3O_7$ is just on the metallic side of a metal–insulator transition, and the highest occupied energy levels are narrow bands, made up of copper d orbitals and oxygen p orbitals.[38] In these narrow bands, the electrons are delocalized but highly correlated, or strongly coupled, to each other.

It is not surprising to find that metallic compounds near metal–insulator transitions are often superconductors because electron–phonon and electron–electron interactions are important to superconductivity. The behavior of most known superconductors is best described by the BCS (Bardeen–Cooper–Schrieffer) model.[39] According to this model, the electrons are coupled as Cooper pairs in the superconducting ground state. Although the theory is derived for any pairing mechanism, for most superconductors this pairing is mediated by phonons. As one electron moves through the lattice, the ions move toward this electron. Since the ions move slowly compared with the electrons, a net polarization remains after the electron is long gone. A second electron can couple to the first through this polarization of the lattice. The most important lattice vibrations in this scheme will be those which are closely associated with electrons near the Fermi energy ϵ_f; in the case of these oxide systems, the important modes

are probably transition metal–oxygen stretching modes.

An important factor common to both the older near empty d band systems and the newer, nearly full d band transition metal oxide systems involves the presence of electronically degenerate states. Both d^1 and d^9 materials are susceptible to Jahn–Teller distortions; the soft (low energy) vibrational modes associated with Jahn–Teller distortions can lead to the strong electron–phonon coupling necessary for superconductivity. Judging from the analogous nearly empty d band systems, superconductivity in these nearly filled d band systems should not be too surprising. However, no superconducting d^{10-n} systems were known prior to April 1986. At that time, Bednorz and Muller submitted a paper presenting evidence for superconductivity above 30 K in a material consisting of La, Ba, Cu and O.[1] The superconducting phase in their multiphase mixture was later identified as $La_{2-x}Ba_xCuO_4$ with $x = 0.15$.[40,41] The formal oxidation state of copper in this material is +2.15 ($d^{8.85}$). In January 1987, just as scientists were becoming accustomed to superconductors with T_c above 30 K, Chu and co-workers reported superconductivity above 90 K in a material containing Y, Ba, Cu, and O.[7,8] The superconducting phase in their mixture was identified subsequently as $YBa_2Cu_3O_7$,[42-47] containing formally $Cu^{2.33+}(d^{8.67})$.

The unprecedentedly high transition temperature in $YBa_2Cu_3O_7$ has stimulated much discussion regarding the mechanism of superconductivity.[48] One experiment to test whether electron–phonon coupling is important to superconductivity in these materials is to determine whether T_c depends on the mass of the ions; changing the mass changes the frequency of the vibrational modes. Recent measurements indicate that a small shift in T_c is produced by substitution of ^{18}O for ^{16}O in $YBa_2Cu_3O_7$.[49] In keeping with the BCS model, the presence of this oxygen isotope effect demonstrates that lattice vibrations play an important role in the electron-pairing mechanism in these materials. However, if only electron–phonon interactions are involved, the coupling must be very strong to produce a T_c near 90 K. Since such strong electron–phonon coupling frequently leads to structural distortions which destroy superconductivity, many people believe that an additional interaction must be responsible for the high transition temperature observed for $YBa_2Cu_3O_7$.[48] In particular, an excitonic mechanism[50] and a dispropor-

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tionation mechanism,[51] both involving electron–electron interactions, have been proposed.

Synthesis

Almost anyone can make $YBa_2Cu_3O_{7-x}$ materials that are partly superconducting, enough to levitate a magnet. However, preparation of the homogeneous, well-ordered material necessary for technological applications or for the experimental studies of properties has proven to be a great synthetic challenge. Like most materials which exist near a metal–insulator instability, $YBa_2Cu_3O_{7-x}$ tends to phase separate[52] after formation, producing a mixture of superconducting, metallic, and insulating phases. In addition, it is difficult to prevent the formation of unwanted impurity phases, including non-superconducting copper oxides, hydroxides, and carbonates due to reaction with air, and products due to reactions with the crucibles used. Because many of these impurities reduce the critical current density, J_c, much of the work in the field now centers on these synthetic difficulties. Thus far, synthetic routes used have included methods typically employed for ceramic processing. The synthesis described below can be divided into a sequence of three steps: (1) preparation of a homogeneous starting mixture of the three metals in the appropriate stoichiometric ratio, (2) formation of single-phase oxygen-deficient $YBa_2Cu_3O_{7-x}$, and (3) annealing in oxygen to obtain the superconducting phase, with $0 \leq x \leq 0.5$.

Homogeneous starting materials of extremely small particle size are important for the preparation of well-ordered single-phase materials.[53] Hand-grinding stoichiometric mixtures of Y_2O_3, $BaCO_3$, and CuO results in powdered material of average particle size ∼1 μm. More elegant coprecipitations of mixtures of complex metal salts, such as the carbonates,[54] nitrates,[55] or oxalates,[54] also have been used in attempts to obtain finer ($\leq 1 \mu$m) particle dispersions and better homogeneity than possible through grinding. Unfortunately, these precipitation routes are complicated by the dissimilar reaction chemistry of Y, Ba, and Cu. For most of the methods which have been tried, one salt precipitates selectively before the other two; e.g., $Ba(NO_3)_2$ precipitates first from concentrated HNO_3. Due to selective precipitation, materials prepared in this fashion are often no more homogeneous than hand-ground mixtures. It is clear that new synthetic routes to homogeneous powders must be developed.

Reaction of the starting materials at temperatures 800 °C $\leq T \leq$ 970 °C yields predominantly the oxygen-deficient $YBa_2Cu_3O_{7-x}$, where $0 < x < 1.0$. Brute force "heat and beat" methods, which use repeated heating and several intermediate grindings, have been necessary to obtain uniform products. Straight oxide starting
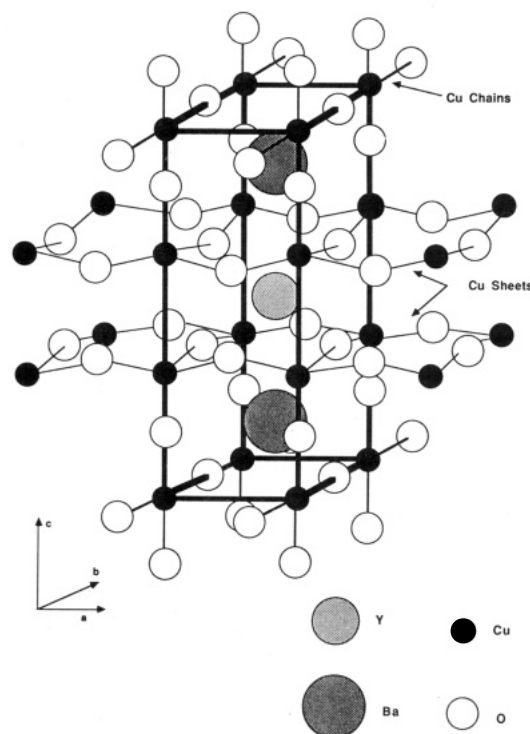
Figure 1. Structure of $YBa_2Cu_3O_7$. The superconducting phase is orthorhombic *Pmmm*, $a = 3.823$, $b = 3.886$, $c = 11.681$ (see ref 43–47). One-dimensional CuO chains run along the b axis, and two-dimensional CuO sheets lie in the a–b plane. These two features share a common oxygen, resulting in square-planar copper chains linked with 5-coordinate, square-pyramidal copper sheets. At high temperatures, oxygen loss produces vacancies along the CuO chain axis; this in turn leads to the tetragonal modification of $YBa_2Cu_3O_{7-x}$, *P4/mmm* (ref 35–37), with the oxygen vacancies disordering in the a–b plane between the chain units.

materials may be reacted directly at these high temperatures, while the precipitated salts need some extra care in heating because the decomposition rates of the various salts are different. It is important to heat the metal salt mixtures rapidly to temperatures above ∼800 °C, where $YBa_2Cu_3O_{7-x}$ is the dominant product formed. Decomposition at temperatures lower than ∼800 °C leads to the formation of substantial quantities of impurity phases such as $BaCuO_2$[56] and Y_2BaCuO_5.[57] Temperatures higher than 970 °C result in decomposition of $YBa_2Cu_3O_{7-x}$ to a multiphase mixture including Y_2BaCuO_5. In addition, $YBa_2Cu_3O_{7-x}$ reacts with most crucible materials, including silica, platinum, and alumina;[58] zirconia and gold are relatively inert. The best crucible to use is one made out of $YBa_2Cu_3O_{7-x}$! Also, we note that to date neither the straight oxide route nor the precipitation routes give product acceptable for most applications.

A final anneal in oxygen results in the best superconducting materials.[59-63] Reacting the $YBa_2Cu_3O_{7-x}$

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powder at 400–500 °C in flowing oxygen yields the orthorhombic phase with x close to 0. However, the time and temperature required to obtain the best superconductors will vary with the grain size in a given sample and the density of the sintered piece. In addition, the rate at which the sample is cooled affects the product quality, in particular the ordering of the oxygen vacancies. Materials quenched from higher temperature are tetragonal with $x > 0.5$[64,65] and do not superconduct. In these materials, oxygen atoms are missing from the Cu–O chains (between the Cu–O layers) and disordered over adjacent sites which are vacant in the superconducting orthorhombic material.[64,65] The unit cell of the orthorhombic $YBa_2Cu_3O_7$ phase is shown in Figure 1. One further problem is that the material may not be stable under the conditions used for reoxidation. As discussed below, electron microscope experiments show some decomposition at the surfaces of the Y-$Ba_2Cu_3O_7$ grains upon annealing in either oxygen or vacuum at temperatures between 200 and 500 °C for several hours.[66] Therefore, the time and temperature conditions of the final oxygen anneal must be optimized in order to minimize decomposition but maximize the number of oxygen atoms ordered on the chain sites.

The reactivity of $YBa_2Cu_3O_7$ has been studied by flowing helium over the sample as the temperature is raised linearly;[67] the desorption products were monitored downstream with a quadrupole mass spectrometer. H_2O, CO, and CO_2 were found to desorb from $YBa_2Cu_3O_7$.[35,68] The H_2O, CO, and CO_2 are due to the formation of hydroxides and carbonates upon exposure to air, a consequence of the fact that these are highly oxidized, basic oxides. These inhomogeneities due to reaction with the atmosphere, as well as the inhomogeneities due to oxygen disorder and to impurity phases formed during synthesis, all contribute to the low critical current of sintered materials.

Characteristics of Superconductors

The measure of resistance vs temperature is a convenient method for the determination of the superconducting critical temperature, with the resistivity vanishing to exactly zero in the superconducting ground state. For $YBa_2Cu_3O_7$, a drop in resistance of 3–4 orders of magnitude is observed beginning near 92 K. For the best samples, the resistivity drops in 1 K to the typical detection limit of 10^{-8} $\Omega \cdot cm$.[69] This is equivalent to the resistivity of copper metal at 4 K. Given the difficulty in measuring zero resistance, a large drop in resistance is usually taken as an indication of a transition to the superconducting state. However, the measurement of a resistivity comparable to that of copper metal is not sufficient evidence to prove superconductivity. Mag-

Figure 2. Susceptibility versus temperature plot for two samples of $YBa_2Cu_3O_{7-x}$. The closed diamonds show a sample with a relatively sharp transition. For comparison, the open squares show data for a sample which was not annealed properly (from ref 68).

netic ordering, ferroelectricity, and piezoelectric effects all can produce a drop in resistivity of several orders of magnitude. In addition, there can be many experimental artifacts in sintered samples with some degree of heterogeneity, including drops in resistance due to poor contacts and unusual current loops.[69,70] More definitive proof of superconductivity is obtained by measuring the magnetic susceptibility of a sample.

When a superconductor such as $YBa_2Cu_3O_7$ is cooled in a small magnetic field, the magnetization changes from a small positive to a large negative value as the temperature falls below T_c. This corresponds to a transition from weak Pauli paramagnetism to strongly diamagnetic behavior and is known as the Meissner effect.[71] The diamagnetism arises from magnetic flux expulsion and surface currents which are set up to oppose the effects of the applied magnetic field.[72] These surface currents prevent penetration of the external field. Since no other known phenomena produce diamagnetism of a comparable magnitude, the Meissner effect is taken as sufficient evidence for superconductivity.

Magnetic experiments provide a representative measure of the behavior of the entire sample, leading to additional information about sample quality. The transition width, ΔT, measured from 10% to 90% of the diamagnetic signal, is a good measure of the homogeneity of the sample. For one of our best samples, shown in Figure 2, ΔT is $\sim$5 K. Broader transitions are observed most commonly in the cases of low sample purity and those with incomplete sample oxidation, ($x > 0$ in $YBa_2Cu_3O_{7-x}$[68,73]) and incomplete oxygen ordering. A resistivity experiment on a comparable sample would show a much sharper superconducting transition width, on the order of 1 K. The resistivity experiment is not representative of the bulk of the ma-

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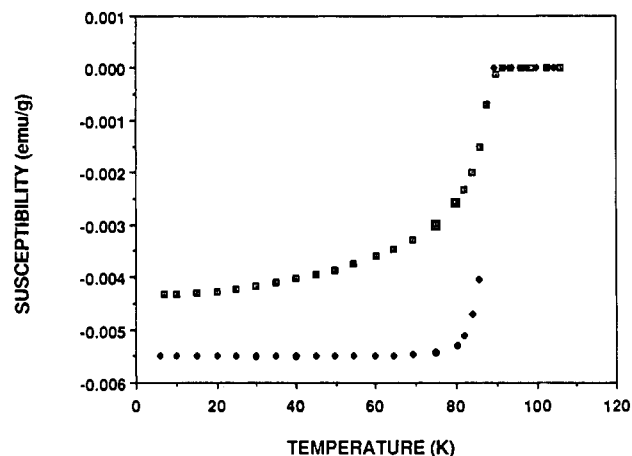
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terial, since the current path between the electrical connections is through the strand of material with the lowest resistivity.

An ideal superconductor, in the shape of a long thin needle, will give a volume susceptibility of $-^1/_{4\pi}$ emu/cm^3. Experimentally measured susceptibilities can be compared to this ideal value in order to establish the degree of nonideality for a given superconducting sample. For our best samples, the gram susceptibility after cooling in a field of 12 G is $\sim$$-5.5 \times 10^{-3}$ emu/g at 4 K. If one uses the theoretical density of 6.3 g/cm^3, the volume susceptibility is -3.5×10^{-2} emu/cm^3. An estimate of the Meissner effect is 44%; i.e., roughly half of the expected magnetization is realized. Since X-ray powder diffraction indicates purities in excess of 95%, this low Meissner effect cannot be attributed to low sample purity but must instead be due to incomplete expulsion of magnetic flux from the sample or flux trapping.[74,75] Both of these effects can arise through the presence of microstructural defects known as Josephson junctions.

A Josephson junction is a thin resistive barrier (on the order of 10 Å) which separates two pieces of superconducting material.[72] Resistive barriers can arise from impurities at the grain boundaries, as well as other defects such as twinning and intergrowths. The maximum current density which can pass through a Josephson junction is small.[72,76-78] While the surface currents which screen magnetic fields from penetration into a superconductor are confined to a very thin (<1 Å) region near the surface, screening currents penetrate deep into Josephson junctions because of their low current-carrying capacity. The result is a decrease in the amount of material from which flux is excluded, and hence there is a lower volume fraction of superconducting material. The low Meissner effect is related to the penetration of magnetic fields into Josephson junctions, as is the low critical current in sintered pieces of YBa$_2$Cu$_3$O$_7$.

In addition to these thin resistive barriers, there are thick resistive barriers (>100 Å) which also reduce the critical current of sintered pieces. The presence of such barriers separating superconducting regions can be detected via a measure of the persistent current in a ring of superconducting material.[73,79] In this experiment, the sample is cooled in a weak magnetic field to $T < T_c$, and then the field is turned off. The magnetization is measured for two orientations, one with the ring axis parallel to the applied field and the other with the axis perpendicular to the field. In both cases, the magnetic flux is expelled from superconducting regions. However, in the parallel case, the field passes through the center of the ring. When the field is turned off, this flux is trapped due to the supercurrent around the ring, and a net magnetization can be measured in the di-

rection of the formerly applied field. No such supercurrent should be present in the perpendicular orientation, since no flux has been trapped. When this experiment is performed on a ring of YBa$_2$Cu$_3$O$_7$, a net positive magnetic moment is obtained in the parallel orientation, just as predicted. However, a net positive moment of a similar magnitude is obtained also for the perpendicular orientation. This implies the presence of many tiny, isolated current loops within the ring, rather than one connected loop around the ring. Therefore, not only is there a significant number of thin, Josephson-type junctions in YBa$_2$Cu$_3$O$_7$, but the persistent current experiment shows that resistive junctions of a larger scale might also play an important part in isolating regions of superconducting material from one another.

Microstructure

A thorough microstructural characterization of YBa$_2$Cu$_3$O$_7$ is necessary in order to gain a better understanding of the impurities and inhomogeneities implied by the magnetic experiments. It is of additional importance that this approach be applied extensively to sintered pieces of superconductor, since in all likelihood they will make up the bulk of technologically useful material. Energy dispersive X-ray (EDX) analysis in the SEM has shown that typical YBa$_2$Cu$_3$O$_7$ samples exhibit uniform distributions of Y, Ba, and Cu down to the limit of resolution, or 1 μm. However, higher resolution EDX studies performed in an analytical electron microscope showed chemical inhomogeneities at the 0.05-μm scale. There appears to be some degree of decomposition of the product, sometimes within a single 1-μm particle, to CuO and a Ba-Cu-O phase (BaCuO$_2$ or a low melting Ba-Cu-O eutectic). The absence of significant amounts of chemical inhomogeneities above the 1-μm level, and the presence of some heterogeneities at the submicron level, indicate that the major cause of the low critical current and the flux trapping observed in the magnetism experiments must occur on a scale of order <1000 nm.

High-resolution transmission electron microscopy (HREM) studies of YBa$_2$Cu$_3$O$_7$ reveal a large number of different structural defects occurring at the 50–500-nm scale.[62,69,80-87] While large regions of particle interiors are well-ordered, with structures in good agreement with published X-ray and neutron diffraction experiments, there is frequent twinning and complicated grain boundary formations. Twinning involving a-into-b axes is especially common. The presence of twinning is not surprising considering that some strain

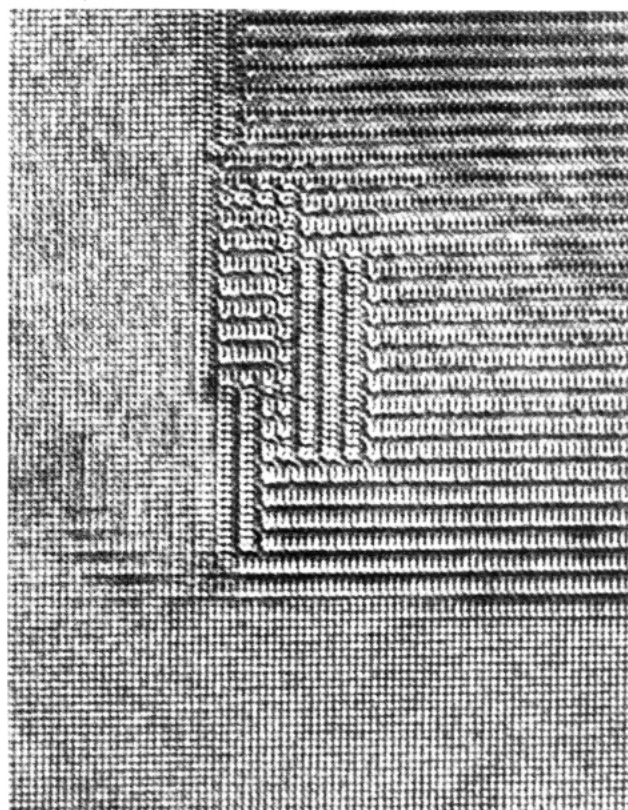(74) Muller, K. A.; Takashige, M.; Bednorz, J. G. *Phys. Rev. Lett.* **1987**, *58*, 1143.

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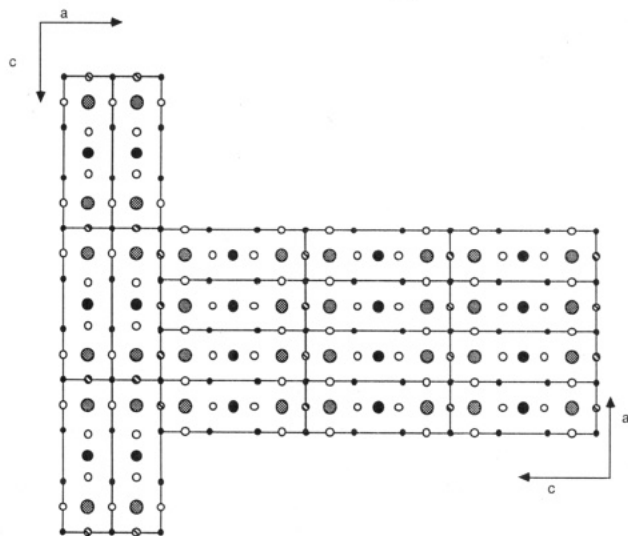(76) de Gennes, P. G. *C.R. Acad. Sci., Ser. 2* **1981**, *292*, 9, 279.

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a-c Twinning

Figure 3. (a, top) High-resolution electron micrograph showing a–c twins in a tetragonal modification of $YBa_2Cu_3O_{7-x}$ (ref 87). (b, bottom) Schematic representation of a–c twinning. Similar oxygen environments in both orientations, necessitating minimal local reorganizations at the twin plane, and closely related cell parameters, i.e., $c/a \sim 3$, favor the formation of this defect.

must be involved in the tetragonal-to-orthorhombic phase transition which occurs as the samples are cooled from high temperature. At these twin planes, the Cu–O chain directions are rotated by approximately 90°. If the oxygen stoichiometry at these twin boundaries deviates from that in the bulk, a thin resistive (Josephson) junction could result. An important area for further research is to correlate the presence of various defects with the critical current.

A second common defect type is shown in Figure 3,[87] where two grains growing along mutually perpendicular

Figure 4. Schematic of one possible structure resulting from the insertion of a CuO plane parallel to c. This insertion may include some structural rearrangements in order to avoid formation of coordinatively unsaturated copper. In this schematic, CuO layer insertion along c is accompanied by a shift of $b/2$.

c axes meet at a rather well-defined grain boundary. Here, the short a axis merges neatly into the long c axis (note $c = 3a$). Minimal restructuring is needed for this defect to form because of the similar arrangement of oxide anions along each axis. Since the conductivity is larger in the a–b plane compared with the c direction, this defect is anticipated to be detrimental to the current-carrying capacity.

Amorphous regions are observed frequently on the surfaces of the grains.[62,86] These amorphous regions are due mainly to reaction with H_2O and CO_2, to amorphous impurity phases, and to disorder induced by the crushing and grinding procedures used to prepare the samples for microscopy. Certainly these amorphous regions isolate the superconducting grains and limit the critical current density. Studies of materials handled exclusively under inert conditions will be extremely valuable.

Although the amorphous region is usually joined directly to well-ordered regions, sometimes an unusual defect with a spreading of the layers along the c axis is observed between the two regions, as shown in Figure 4.[62] The c axis spreading, or layer insertion, typically originates at an amorphous layer coating the outer fringe of the particle and then propagates into the ordered bulk. Atomic resolution microscopic imaging, together with careful image simulations, has shown that the insertion is composed of an extra Cu–O layer in the form of the Cu–O chains running along the b axis.[62] This insertion mechanism suggests that the amorphous surface layer near this defect should be comparatively rich in Y and Ba.[69]

This insertion of an extra Cu–O layer has been shown to be the product of a very efficient decomposition mechanism for the superconducting $YBa_2Cu_3O_7$ mate-

rial. Thermal treatments of YBa$_2$Cu$_3$O$_7$ at temperatures as low as 150 °C for several hours, in atmospheres ranging from pure O$_2$ to a static vacuum, all lead to decomposition of the particle surfaces[62] and formation of insertion layers. Continued degradation, with an increase in the number of insertion layers, as well as the amount of amorphous material, is observed after annealing for extended periods of time. Since this decomposition reaction occurs in pure O$_2$ and under vacuum, this is evidence that YBa$_2$Cu$_3$O$_7$ is not stable at temperatures between ~100 and ~500 °C. However, it is difficult to rule out completely decomposition due to reaction with trace quantities of water. If these materials are metastable, this should not discourage successful applications. (Diamonds are metastable!) It appears that decomposition is limited to the surfaces of the grains, and even this surface decomposition is slow relative to the time needed to anneal the sample at elevated temperatures. Furthermore, the surfaces of the grains appear kinetically stable at room temperature and below, provided H$_2$O and CO$_2$ are rigorously excluded. It is very important to investigate this issue of metastability further to determine the optimum processing conditions to avoid the production of large quantities of decomposition products; these decomposition products isolate the superconducting grains and severely limit the critical current.

Summary

The quality of superconducting YBa$_2$Cu$_3$O$_{7-x}$ is dependent on a number of synthetic parameters related to the dissimilar chemistry of Y, Ba, and Cu and to the difficulty of preparing materials whose electronic properties are near a metal–insulator transition. Even the most carefully prepared samples are best described as superconducting grains separated and isolated from one another by insulating barriers. Improved synthetic procedures are necessary in efforts to obtain more homogeneous, well-ordered YBa$_2$Cu$_3$O$_7$. Much interdisciplinary work between synthesis and microstructural characterization will be required to develop methods to control the microstructure and obtain the critical currents necessary for most applications.