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## High Transition Temperature Inorganic Oxide Superconductors: Synthesis, Crystal Structure, Electrical Properties, and Electronic Structure

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"We stand today on a bright oasis of knowledge in an illimitable desert of the unknown."

Lord Salisbury

Since the discovery<sup>1</sup> in 1911 of superconductivity<sup>2</sup> in Hg with a superconducting transition temperature ( $T_c$ ) of 4.2 K, the holy grail of researchers in the field has been both to understand the mechanism involved and to increase  $T_c$  (high- $T_c$ !) to more manageable temperatures. The vast technological potential (zero resistance electrical power lines, magnetically levitated high-speed trains, superfast electrical circuits, and miniature computers, etc.) of high- $T_c$  materials has also greatly stimulated research. Thus, the search for high- $T_c$  superconductors has led to the synthesis of many novel superconducting materials including various "low-dimensional" systems, heavy fermion compounds, transition-metal compounds with the so-called A-15 structure such as Nb<sub>3</sub>Ge, and even organic superconductors. While the highest  $T_c$  obtained in the elements is 9 K in Nb, it has reached 8 K in S-based organic superconductors,<sup>3</sup> and a maximum  $T_c$  of 22.3 K was previously achieved over a decade ago<sup>4</sup> in the metal alloy Nb<sub>3</sub>Ge.

A relatively unexplored field of research in superconducting materials, in general, has been inorganic

oxide systems. Perhaps the best known example is mixed-valent BaPb<sub>1-x</sub>Bi<sub>x</sub>O<sub>3</sub> ( $0.05 \leq x \leq 0.30$ , maximum  $T_c = 13$  K at  $x = 0.3$ ).<sup>5</sup> In late 1986, an amazing breakthrough occurred with the discovery<sup>6</sup> by Bednorz and Müller of superconductivity in oxygen-deficient perovskite type compounds (vide infra) in the La-Ba-Cu-O (LBCO) system with overall composition La<sub>5-x</sub>Ba<sub>x</sub>Cu<sub>5</sub>O<sub>5(3-y)}</sub>. The original LBCO materials<sup>6</sup> were three-phase mixtures which exhibited broad superconducting transitions with an onset  $T_c$  of  $\sim 35$  K and with zero resistance achieved at  $\sim 13$  K. This remarkable

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(2) The electrical conductivity ( $\sigma$  in  $\Omega^{-1} \text{cm}^{-1}$ ) of solids has a range of values greater than 20 orders of magnitude with insulators having  $\sigma \approx 10^{-22}$ - $10^{-16} \Omega^{-1} \text{cm}^{-1}$ , semiconductors having thermally activated conductivity (conductivity rises with increased temperature,  $\sigma \approx 10^{-8}$ - $10^{-2} \Omega^{-1} \text{cm}^{-1}$ ), and metals having conductivity ( $\sigma \approx 10$ - $10^4 \Omega^{-1} \text{cm}^{-1}$ ) that increases with decreased temperature. The phenomenon of superconductivity is usually characterized by the following three physical properties: (i) sample electrical resistance ( $\rho$ ) drops to zero ( $\sigma \rightarrow \infty$ ), (ii) magnetic fields are expelled by the sample (the Meissner effect), and (iii) the sample specific heat rises exponentially upon the onset of superconductivity at  $T_c$ .

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The Argonne authors of this article are members of a group led by Dr. Williams and engaged in the synthesis, structure, electrical conductivity, and design of both inorganic and organic superconducting solids. Dr. Williams is an Associate Editor of *Inorganic Chemistry*. The North Carolina State authors are engaged in theoretical studies of conducting solids under the direction of Prof. Whangbo.

discovery of unprecedentedly high transition temperatures has triggered a virtual worldwide gold rush among scientists interested in superconductivity!

Very shortly after the original discovery it was shown<sup>7,8</sup> that the superconducting phase in the LBCO system was of composition  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  ( $x < 0.2$ ,  $y$  unspecified but small) which has the tetragonal  $\text{K}_2\text{NiF}_4$  layered perovskite structure. At the same time, Chu et al.<sup>9</sup> observed that the onset  $T_c$  could be increased to 40.2 K, and later to 52.5 K,<sup>10</sup> when samples were subjected to pressures of  $\sim 12$  kbar. These results suggested that the effect of pressure, which decreases lattice spacings, could be mimicked by replacing the La and/or Ba by smaller ionic species. By use of Sr (ionic radius  $\sim 1.13$  Å) in place of Ba (ionic radius  $\sim 1.35$  Å), it was subsequently demonstrated<sup>11,12</sup> that in  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  the  $T_c$  could be raised to  $\sim 36$  K with zero resistance achieved at  $\sim 34$  K or better.

Another quantum jump in transition temperatures came with the report<sup>13</sup> of  $T_c \approx 93$  K at ambient pressure, again in multiphase samples derived from the Y-Ba-Cu-O (YBCO) systems. The superconducting phase, which has a structure different from that of the LBCO materials, was subsequently identified as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  ( $y \approx 0.19$ ) by numerous investigators.<sup>14-22</sup> Thus, for the first time,  $T_c$  exceeded the boiling point of liquid  $\text{N}_2$  (77 K), and sample cooling costs, which are an important consideration for technological applications, became relatively inexpensive. In the case of high- $T_c$  oxide superconductors, synthetic chemists play a vital role in devising new chemical routes, especially since the electrical and mechanical properties vary with processing conditions, and structural chemists have an essential role in unravelling the structure-property relationships, because the latter depend intimately on the

microstructure (see following article<sup>23</sup>). In this Account we focus on research on synthesis, structure, electrical properties (conductivity and superconductivity), and band electronic structure calculations of the newly discovered high- $T_c$  inorganic oxide superconductors.

## Synthesis

Perovskite oxides have traditionally been prepared by high-temperature solid-state reaction of the binary oxides or suitable oxide precursors such as carbonates, nitrates, oxalates, citrates, etc.<sup>24,25</sup> We have evaluated the coprecipitation of metal ion carbonates, oxalates, or citrates from solution followed by their decomposition, and we have found that the pH-adjusted carbonate route is advantageous because intimate component mixtures with the desired metal ratios are achieved and the final oxide is more homogeneous.<sup>26,27</sup> Decomposition of solid mixtures of metal nitrates or acetates has also been used, but these have serious limitations due to component volatility problems, thus making it difficult to maintain the desired metal ratios. Our studies and those of others demonstrate that the keys to the successful preparation of pure, single-phase perovskite oxides appear to be (i) the high purity of the starting materials, (ii) taking precautions to maintain the starting metal ratios, and (iii) maintaining high intimacy of the mixtures during the high-temperature solid-state reaction.

The oxygen stoichiometry in the 30–40 K superconductors  $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$  ( $M = \text{Ba}, \text{Sr}$ ) is close to 4 (i.e.,  $y \sim 0-0.1$ ) and appears to be fairly insensitive to the stoichiometry  $x$  of  $M$  (Ba or Sr). On the other hand, in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  and related perovskites, we<sup>27,28</sup> and others<sup>29,30</sup> have discovered that  $y$  is quite sensitive to annealing temperature, to atmosphere, and to the cooling rate subsequent to the annealing due to the reversible oxygen intercalation in these defect perovskites.<sup>24</sup> For oxygen determination, thermogravimetric<sup>29</sup> and iodometric titration methods<sup>28</sup> have been employed. Attempts at increasing oxygen stoichiometry above 7 under high oxygen pressures appear marginally successful in the sense that neither the oxygen content nor  $T_c$  can be raised substantially.<sup>29,30</sup>

## Substitution in LBCO and YBCO Materials

Although the parent compound  $\text{La}_2\text{CuO}_4$  was initially found to be semiconductive at low temperatures, it has recently been shown to become superconducting near 40 K if it is prepared by high-pressure  $\text{O}_2$  annealing.<sup>31,32</sup>

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The superconducting transition is more conveniently obtained by Ba<sup>6,7,8,12</sup> or Sr<sup>11,12</sup> doping. In La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> materials,  $T_c$  varies with  $x$  and reaches a maximum of  $\sim 36$  K for  $x \approx 0.15-0.2$ .<sup>33,34</sup> Beyond  $x \approx 0.25$  multiple phases are reported.<sup>26,33</sup> Ca doping results in much lower  $T_c$  (18 K).<sup>35</sup> Complete replacement of La by other Ln (Ln = lanthanide) elements in the LBCO materials results in the loss of superconductivity due, apparently, to changes in structure. However, replacing  $\sim 5-10\%$  La with other Ln elements produces only minor changes in properties. Replacing Cu at the 5% level by other first-row transition metals, however, depresses superconductivity substantially because the two-dimensional Cu-O conduction layer (discussed in the next section) is disrupted.<sup>36</sup>

In the YBCO<sup>13-21,37</sup> system, the ionic radii of Y<sup>3+</sup> and Ba<sup>2+</sup> are distinctly different (0.93 and 1.35 Å, respectively) so that Y does not substitute for Ba, in contrast to the LBCO system where a region of solid solution exists. In the YBCO system, replacing Y with Ln (except Ce, Pr, Tb) results in the same high  $T_c$ 's ( $\sim 90$  K).<sup>38-41</sup> Doping the Y<sup>3+</sup> sites with up to 50% Pr<sup>4+</sup> causes  $T_c$  to drop monotonically presumably due to a reduction of the Cu<sup>3+</sup> concentration.<sup>42</sup> Our attempts at replacing Y with other tetravalent cations (Zr<sup>4+</sup>, Hf<sup>4+</sup>, Pb<sup>4+</sup>) have led to multiphase mixtures.<sup>43</sup> Substitution of Ba, which prefers a high oxygen atom coordination number, by Sr (up to 50%) leads to a monotonic depression in  $T_c$  which is thought to be caused by oxygen deficiency due to the smaller Sr ions and decreased oxygen atom coordination number.<sup>44</sup> Our work on doping of Ba sites with alkali-metal ions (K, Rb, Cs) resulted in the formation of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub> along with other phases, and the mixture exhibits  $T_c \sim 90$  K without incorporation of alkali metal.<sup>43</sup> Replacing Cu by Ni or Co decreased  $T_c$  substantially.<sup>30</sup> Reports of much higher  $T_c$ 's in materials such as YBa<sub>2</sub>Cu<sub>3</sub>F<sub>2</sub>O<sub>y</sub> (155 K),<sup>45</sup> and unknown phases of the Y-Ba-Cu-O system<sup>46</sup>

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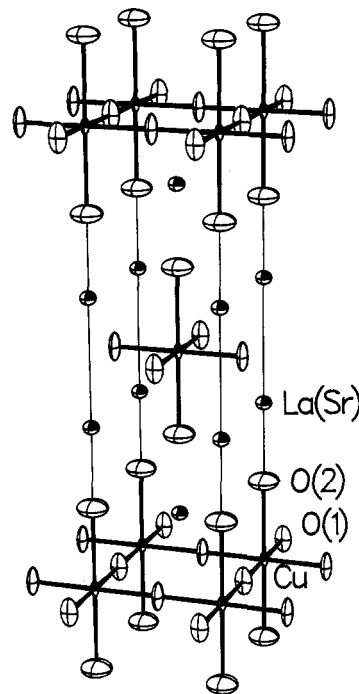


Figure 1. Crystal structure of La<sub>1.92</sub>Sr<sub>0.08</sub>CuO<sub>4</sub> as determined by X-ray diffraction<sup>49,50</sup> (90% thermal ellipsoids). Layers are formed by corner-sharing, tetragonally elongated CuO<sub>6</sub> octahedra.

(240 K), have not been confirmed nor duplicated,<sup>107</sup> but they have stimulated the search for new high- $T_c$  materials.

### Structural Aspects of LBCO and YBCO Materials

Most known superconducting oxides are closely related to the perovskite structure (ABO<sub>3</sub>) or one of its variants, the layered perovskite (A<sub>2</sub>BO<sub>4</sub>) or K<sub>2</sub>NiF<sub>4</sub> structure (Figure 1). These structure types are adopted by numerous mixed-metal oxides as well as a fair number of halides and sulfides. Both prototypes contain infinite planar nets of *corner-sharing* octahedra with the smaller metal ion (B) at the center of six oxygen atoms. The larger metal ions (A) are positioned in the oxygen pockets above and below the nets. The ABO<sub>3</sub> and A<sub>2</sub>BO<sub>4</sub> types differ in the relative arrangements of the layers: In the ABO<sub>3</sub> structure, adjacent layers combine so as to share the oxygen atoms and the A cations between the layers, and the resulting structure is cubic with linear B-O-B bridges in three dimensions. In the layered perovskite structure, the layers remain separated and are stacked in a staggered way so as to form a body-centered tetragonal structure with B-O-B bridges only in the two dimensions within the layers, but not between the layers.

La<sub>2-x</sub>M<sub>x</sub>CuO<sub>4-y</sub> (M = Sr or Ba). The strontium- or barium-doped LBCO materials belong to the layered A<sub>2</sub>BO<sub>4</sub> structural type.<sup>8</sup> The parent compound, La<sub>2</sub>CuO<sub>4</sub>, at room temperature possesses an orthorhombic superstructure of the tetragonal prototype with orthorhombic lattice constants<sup>47</sup>  $a_o \approx b_o \approx \sqrt{2}a_t$ ,  $c_o \approx c_t$ . The superstructure is due to a concerted washboard-like tilting of the Cu-O octahedra with respect to the  $c$  axis.

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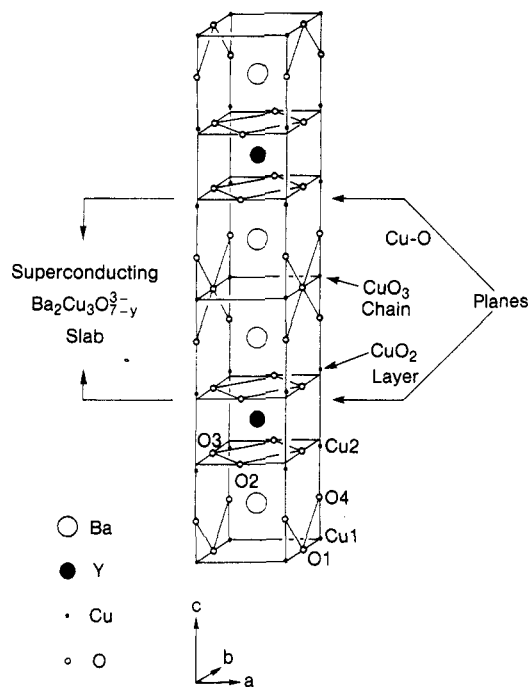
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At elevated temperatures the crystals become tetragonal,<sup>48</sup> with an undistorted  $K_2NiF_4$  structure.

Doping of  $La_2CuO_4$  with the alkaline earth metals Sr or Ba suppresses the orthorhombic-tetragonal phase transition to below room temperature. The results of our single-crystal X-ray diffraction<sup>49,50</sup> investigation of  $La_{1.92}Sr_{0.08}CuO_4$  (Figure 1) are in good agreement (same structure, etc.) with powder neutron diffraction results<sup>51</sup> on samples with twice the doping levels of Sr or Ba. The lattice parameters depend on the doping level  $x$ , so that for  $x < 0.2$  a steady increase of the  $c/a$  ratio with increasing  $x$  is observed.<sup>26,33,52</sup> The  $c/a$  ratio also correlates with  $T_c$  such that the higher the value of  $c/a$  (up to  $\sim 3.50$ ), the higher<sup>33</sup> the  $T_c$ .

A phase transition to lower symmetry has been detected in our single-crystal X-ray diffraction study,<sup>50</sup> and in other studies involving synchrotron X-ray diffraction,<sup>53</sup> high-resolution X-ray powder diffraction,<sup>54</sup> and powder neutron diffraction<sup>55,56</sup> for both the Sr- and Ba-doped systems. The transition temperature depends on the doping level<sup>54</sup> and is about 190 K for  $La_{1.85}Sr_{0.15}CuO_4$ . We observed that single crystals exhibit extensive twinning upon cooling through the phase transition but become single again when warmed to room temperature.<sup>50</sup> The structure of the low-temperature phase, as determined by neutron powder diffraction,<sup>55,56</sup> is essentially that of the parent orthorhombic compound  $La_2CuO_4$  at room temperature. Thus, the effect of the alkaline earth metal is to depress the phase transition temperature, probably through a decrease of unfavorable electrostatic interactions in the tetragonal phase.<sup>57,58</sup> A high-resolution synchrotron X-ray powder diffraction study<sup>53</sup> indicates the presence of more than one perovskite-like phase at low temperature and monoclinic symmetry below  $\sim 150$  K. In  $La_{1.85}Ba_{0.15}CuO_4$ , a sudden decrease of the orthorhombic splitting ratio,  $(b-a)/(b+a)$ , at 75 K, in addition to the tetragonal-orthorhombic phase transition at 180 K, indicated the possibility of a second transition.<sup>55</sup>

**$YBa_2Cu_3O_{7-y}$ .** The structure of the high-temperature ( $T_c > 90$  K) superconductor  $YBa_2Cu_3O_{7-y}$ , as determined by several neutron powder diffraction studies,<sup>14,20,21,59-61</sup> can be regarded as an oxygen-deficient supercell of an  $ABO_3$  cubic perovskite (see Figure 2). The resultant orthorhombic unit cell comprises three



**Figure 2.** Structure of  $YBa_2Cu_3O_{7-y}$  as determined by neutron diffraction investigations. Two  $CuO_2$  planes are linked by  $CuO_3$  one-dimensional chains and enclose two  $Ba^{2+}$  to form a  $Ba_2Cu_3O_{7-y}^{3-}$  conducting slab.

cubic perovskite blocks stacked along the crystallographic  $c$  axis with copper atoms at the B sites and with the A sites occupied by  $Ba^{2+}$  cations in the first and third blocks and  $Y^{3+}$  in the central perovskite unit. The result is an ordering of the A site cations in the sequence  $Y^{3+}Ba^{2+}Ba^{2+}Y^{3+}Ba^{2+}Ba^{2+}$ ....

Oxygen vacancies occur on the yttrium atom plane (at  $z = 1/2$ , resulting in a layered structure) and along the  $a$  axis between adjacent Cu1 atoms (at  $z = 0$ ). The latter vacant sites are responsible for the orthorhombic distortion of the unit cell, since partial population of this site with oxygen atoms results in a tetragonal unit cell.<sup>62</sup> In the stoichiometric compound ( $y = 0$ ), the distorted square-planar coordination observed for Cu1 results in the formation of one-dimensional (1D)  $CuO_3$  chains along the  $b$  axis. The coordination of Cu2 is square-pyramidal, resulting in dimpled  $CuO_2$  layers in which the Cu2 atoms are capped by the O4 atoms of the  $CuO_3$  chains. Each  $Y^{3+}$  cation has square-prismatic coordination while the  $Ba^{2+}$  cations are 10-coordinate. Since there is no direct path for electronic transport along the crystallographic  $c$  axis, the structural unit in  $YBa_2Cu_3O_{7-y}$  responsible for high- $T_c$  superconductivity is the two-dimensional (2D) slab  $Ba_2Cu_3O_{7-y}^{3-}$  formed by two  $CuO_2$  layers which sandwich one  $CuO_3$  chain and two  $Ba^{2+}$  cations per unit cell.

For values of  $y$  ranging from 0.0<sup>21,59</sup> to 0.4<sup>61</sup> partial oxygen vacancies may occur at the O1 and O2 positions. At values of  $y \geq 0.5$ , a transition from the orthorhombic phase to a tetragonal phase is observed.<sup>62</sup> This phase,

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initially identified by high-temperature X-ray powder diffraction<sup>63-66</sup> and by electron microscopy,<sup>18,67</sup> also occurs at ambient temperatures<sup>27,29,68</sup> in samples which are rapidly quenched from temperatures  $>700$  °C and is probably nonsuperconducting.<sup>69</sup> Neutron powder diffraction studies at high temperatures<sup>62</sup> on quenched samples<sup>68,70</sup> demonstrate that at  $y = 0.5$  the O1 atoms partially occupy the position at  $(1/2, 0, 0)$ , which is completely vacant in the orthorhombic phase. In the tetragonal phase with  $y \geq 0.5$ , the O1 and  $(1/2, 0, 0)$  site positions are equivalent by symmetry and are observed to be  $\leq 25\%$  occupied. Thus, the 1D  $\text{CuO}_3$  chains found in orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  no longer exist in the tetragonal phase and are replaced by highly oxygen deficient Cu-O layers which, in the limit of  $y \approx 1.0$  ( $\text{YBa}_2\text{Cu}_3\text{O}_6$ ),<sup>68</sup> contain 2-coordinate  $\text{Cu}^+$  atoms. These findings suggest that the  $\text{CuO}_3$  chains are essential to the occurrence of superconductivity at  $T_c > 90$  K.

### Normal-State and Superconducting Properties

$\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ). The normal-state conductive properties of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$  are typical of this class of oxide superconductors. Room-temperature resistivities,  $\rho(300 \text{ K})$ , are reported<sup>11,26,34</sup> to be of the order of  $1000 \mu\Omega \text{ cm}$  but vary widely from sample to sample, and the temperature dependence of  $\rho$  ranges from metallic-like ( $d\rho/dT > 0$ ) to semiconductive, depending on compositional variables and, probably, sample inhomogeneities. The balance between metallic and semiconductive behavior has been attributed to the  $\text{O}_2$  partial pressures during the annealing process such that oxygen deficiencies (from low partial pressures) favor the semiconductive behavior along with lower values of  $T_c$  and broader superconducting transitions.<sup>8,11,30</sup> The principal charge carriers between room temperature and the superconducting transition temperature are holes (positive carriers),<sup>6,71</sup> and there generally is little, if any, change in the resistivity arising from the tetragonal-to-orthorhombic phase transition near 200 K.

Zero resistances within instrument resolution for Ca-, Sr-, and Ba-doped derivatives of  $\text{La}_2\text{CuO}_4$  have been reported to be as high as  $\sim 16, 34,$  and  $28$  K, respectively, for optimum concentrations of the dopants.<sup>11,72</sup>

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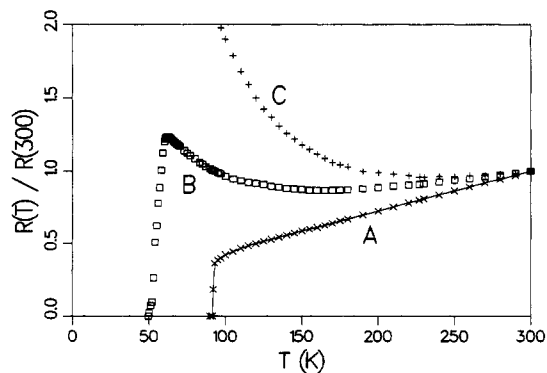
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**Figure 3.** Relative resistivities as a function of temperature for the orthorhombic phase (curve A,  $y \approx 0.19$ ) and tetragonal phase (curves B and C,  $y \approx 0.5$ ) of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ . The semiconductive behavior in curve C extends to the lowest temperature measured,  $\sim 12$  K.

Somewhat lower transition temperatures (by several kelvin) are frequently observed, and the resistive transition widths (defined as the temperature interval between the onset of superconductivity and zero resistance) are typically  $\sim 4-5$  K or even larger for specimens which exhibit semiconductive behavior near the onset temperature. Applied hydrostatic pressure (up to 20 kbar) increases the temperatures for zero resistance by  $\sim 0.2$  K/kbar and more dramatically increases the onset temperatures for superconductivity.<sup>10,73,74</sup> The Meissner effect (see following article<sup>23</sup> for more details), which is the expelled magnetic flux as a fraction of that expelled by a perfect superconductor (volume diamagnetic susceptibility is  $-1/4\pi$ ), amounts to  $\sim 30-40\%$  at 5 K,<sup>11,34</sup> indicating a large fraction of bulk superconducting phase. Magnetic susceptibility studies demonstrate that bulk superconductivity begins near the resistive superconducting transition temperatures.<sup>34</sup>

Measurements of the lower and upper critical magnetic fields,  $H_{c1}$  and  $H_{c2}$ , respectively, indicate that these materials are extreme type II superconductors with considerable anisotropy of the fields.<sup>12,75-77</sup> The anisotropy is consistent with the two-dimensional-layer-like nature of the structures. Determinations of the superconducting energy gap,  $\Delta$  (the energy to break a Cooper pair and a quantity which is important for establishing the superconducting mechanism), by infrared reflection and transmission experiments,<sup>78-80</sup> as well as point-contact tunneling measurements,<sup>81</sup> have yielded values from less than the weak-coupling BCS<sup>82</sup> limit ( $2\Delta/kT_c = 3.5$ ) to values much larger by about a factor

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of 2. These variations may be the result of considerable anisotropy in the gap.

**YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub>.** Room-temperature resistivities of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub> are of the order of 1000 μΩ cm<sup>16,83,84</sup> but may be an order of magnitude larger for samples with substantial amounts of impurities. The samples are p-type (hole) conductors.<sup>16</sup> The temperature dependence of ρ, even for impure samples and various rare earth ions, is typically metallic-like with an essentially linear behavior down to the onset of superconductivity.<sup>13,16,17,27,40,83</sup> However, semiconductive behavior has also been observed<sup>17</sup> as a result of the presence of the tetragonal phase.<sup>27,63,69</sup>

Figure 3 illustrates the temperature dependence of resistivities that we have measured for the orthorhombic and tetragonal phases obtained by slow cooling in O<sub>2</sub> or by quenching in air, respectively.<sup>27</sup> The orthorhombic phase gives metallic behavior and a sharp superconducting transition near 90 K. The two tetragonal samples give a semiconducting behavior for one sample (curve C) and mixed metallic-semiconductive behavior for another (curve B) which exhibits a broad superconducting transition near 60 K. As for the LBCO superconductors, O<sub>2</sub> partial pressure in annealing and, therefore, the oxygen stoichiometry, are regarded to be important factors in obtaining the highest T<sub>c</sub> in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub>.<sup>17,27,30,64</sup>

The highest quality orthorhombic materials have resistive transition midpoint T<sub>c</sub>'s of 91–93 K with narrow transition widths of 1–2 K. Inductive measurements on ceramic specimens,<sup>16</sup> as well as single crystals,<sup>85</sup> show that diamagnetism (superconductivity) begins very near the same values of T<sub>c</sub>. In contrast to the LBCO materials, applied pressure has little effect on T<sub>c</sub>.<sup>86,87</sup> Meissner effect measurements, with values typically in the range 20–80%,<sup>13,16,17,85</sup> indicate that orthorhombic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub> is a bulk superconductor. On the other hand, our studies of the tetragonal phase represented in Figure 3 yield Meissner effects of <4%, indicating little bulk superconductivity and possibly the presence of orthorhombic phase impurity (curve B).<sup>28</sup> Measurements of the critical magnetic fields show extreme type II behavior.<sup>13,84,98</sup> The superconducting energy gap, as determined from infrared reflectance<sup>89,90</sup> and point-contact tunneling measurements,<sup>91</sup> ranges from the weak-coupling BCS<sup>82</sup> limit to exceptionally large values, 2Δ/kT<sub>c</sub> ≈ 13.

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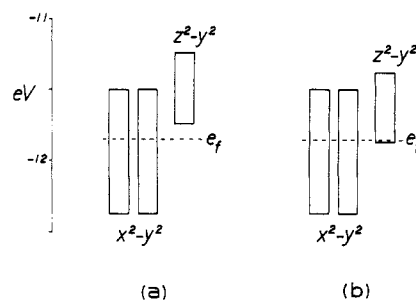
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**Figure 4.** Top three d-block bands calculated for the orthorhombic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> phase with (a) the Cu1–O4 distance of 1.850 Å and (b) the Cu1–O4 distance of 1.890 Å. In (a) the CuO<sub>2</sub> layer,  $x^2 - y^2$  bands are each half-filled, and in (b) they are slightly less than half-filled because the bottom of the CuO<sub>3</sub> chain band is below the Fermi level.

### Crystal Structure–Band Electronic Structure Correlation

**La<sub>2</sub>CuO<sub>4</sub> and La<sub>2-x</sub>M<sub>x</sub>CuO<sub>4</sub> (M = Sr or Ba).** Band electronic structure calculations<sup>92–94</sup> on tetragonal La<sub>2</sub>CuO<sub>4</sub> reveal that its  $x^2 - y^2$  band (i.e., the highest-lying d-block band) is half-filled as expected from the formal oxidation Cu<sup>2+</sup>(d<sup>9</sup>), that the Fermi surface (FS) of this band is well-nested, and that this FS nesting is quickly destroyed as electrons are removed from the  $x^2 - y^2$  band. In general, the electronic instability associated with an FS nesting gives rise to either a Peierls distortion or an antiferromagnetic (AFM) ordering. Due to the twofold screw rotation symmetry along the *c* axis of orthorhombic La<sub>2</sub>CuO<sub>4</sub>, the tetragonal-to-orthorhombic (T → O) distortion of La<sub>2</sub>CuO<sub>4</sub> at 533 K<sup>48</sup> cannot open a band gap at the Fermi level.<sup>92</sup> Thus, band electronic structure calculations on orthorhombic La<sub>2</sub>CuO<sub>4</sub> show the FS of its half-filled  $x^2 - y^2$  band to be well-nested as in tetragonal La<sub>2</sub>CuO<sub>4</sub>, and consequently the T → O distortion is not a Peierls distortion.<sup>92</sup>

At high temperatures the electrical conduction of La<sub>2</sub>CuO<sub>4</sub> is poorly metallic,<sup>51,95</sup> while the low-temperature properties of La<sub>2</sub>CuO<sub>4</sub> are strongly affected by oxygen and lanthanum atom vacancies.<sup>96–98</sup> Thus, a sample of La<sub>2</sub>CuO<sub>4</sub> exhibits either AFM ordering<sup>99–101</sup> or high-T<sub>c</sub> superconductivity<sup>32,102</sup> as in La<sub>2-x</sub>M<sub>x</sub>CuO<sub>4</sub>. This observation may be rationalized in terms of the  $x^2 - y^2$  band occupancy, *f*, by writing the accurate composition of “La<sub>2</sub>CuO<sub>4</sub>” as La<sub>2-x</sub>CuO<sub>4-y</sub>. Within a rigid band model,  $f = 0.5 - 1.5x + y$  for La<sub>2-x</sub>CuO<sub>4-y</sub>. Since the FS nesting responsible for an AFM ordering occurs when  $f = 0.5$ ,<sup>92</sup> the presence of an AFM ordering in La<sub>2-x</sub>CuO<sub>4-y</sub> implies that  $1.5x = y$ . Such an La<sub>2-x</sub>CuO<sub>4-y</sub> sample can be made superconducting by annealing it under oxygen.<sup>31,32,102</sup> The resulting sample

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is close to  $\text{La}_{2-x}\text{CuO}_4$  in stoichiometry, and therefore,  $f$  deviates from 0.5 (i.e.,  $f \simeq 0.5 - 1.5x < 0.5$ ). In a similar manner, suppression of the AFM ordering by decreasing the  $x^2 - y^2$  band occupancy to slightly less than 0.5 would be the primary role of the alkaline earth cations  $\text{M}^{2+}$  in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  (i.e.,  $f = 0.5 - 0.5x < 0.5$ ).

**$\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ .** Within a rigid band model, the electronic structure of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  ( $y \simeq 0.19$ ) is simulated by that of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  upon adding  $2y$  electrons to the d-block bands of the latter.<sup>103-105</sup> As illustrated in Figure 4a, the band electronic structure calculated for the equilibrium structure of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  shows<sup>103,106</sup> that the top three d-block bands consist of two half-filled  $x^2 - y^2$  bands solely derived from the  $\text{CuO}_2$  layers and one empty  $z^2 - y^2$  band solely derived from the  $\text{CuO}_3$  chains. Although the chain Cu1 atom has a lower coordination number than does the layer Cu2 atom, the chain  $z^2 - y^2$  band lies higher in energy than the layer  $x^2 - y^2$  bands because the  $z^2 - y^2$  orbitals are raised in energy due to the strong antibonding character in the short Cu1-O4 distance.<sup>103</sup> Thus, the copper oxidation state is higher in the chains (close to  $\text{Cu}^{3+}$ ) than in the layers (close to  $\text{Cu}^{2+}$ ). In essence, the  $x^2 - y^2$  bands of the  $\text{CuO}_2$  layers in orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  are identical in nature with those of the  $\text{CuO}_4$  layers in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ .<sup>103</sup> Nevertheless, the  $T_c$  of the former is higher than that of the latter by about 60 K. Therefore, orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  must possess some special electronic features not present in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ .<sup>103,104</sup>

Within each  $\text{Ba}_2\text{Cu}_3\text{O}_{7-y}^{3-}$  slab (see Figure 2), the Cu2 atoms of one  $\text{CuO}_2$  layer do not interact with those of the other  $\text{CuO}_2$  layer, if the capping oxygen atoms O4 remain on the Cu2-Cu1 line.<sup>104</sup> The O4 atom orbitals have zero overlap with the Cu2 atom  $x^2 - y^2$  orbital due to the node of the  $x^2 - y^2$  orbital along the Cu2-Cu1 axis. When the O4 atoms are slightly displaced (on the order of 0.04 Å) out of the Cu2-Cu1 line, the O4 atom  $z$  orbital can have nonzero overlap with the Cu2 atom  $x^2 - y^2$  orbital, thereby allowing the Cu2 atoms of the two separated  $\text{CuO}_2$  layers to interact via the Cu2-O4-Cu1-O4-Cu2 linkages.<sup>104</sup> Figure 4b shows the top three d-block bands of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in which the capping oxygen atoms O4 are slightly displaced away from their equilibrium positions.<sup>104,106</sup> A small increase in the Cu1-O4 distance ( $\sim 0.04$  Å) lowers the bottom of the chain  $x^2 - y^2$  band below the Fermi

level, so that some electrons flow from the  $\text{CuO}_2$  layers into the  $\text{CuO}_3$  chains. Thus, lattice vibrational modes involving the O4 atom displacement would give rise to slight valence fluctuations of the copper atoms and hence strong electron polarization.<sup>104</sup> As the Cu1-O4 distance increases, the p orbitals of the chain O4 atoms overlap better with those of the layer O2 atoms so that the chain  $z^2 - y^2$  band acquires a two-dimensional character.<sup>104</sup> In addition, the lowering of the chain  $z^2 - y^2$  band bottom to the Fermi level enhances the density of states at the Fermi level.<sup>104</sup> All of those special electronic properties of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ , brought about by a slight displacement of the capping oxygen atom O4, are absent in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ .

The electronic structure of tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  ( $y \gtrsim 0.5$ ) can be simulated by that of ordered  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  structures which contain no  $\text{CuO}_3$  chains.<sup>106</sup> This study suggests that, in the tetragonal phase, random distributions of the O1 atoms in the plane of the Cu1 atoms, and the low average coordination number of the Cu1 atoms, cause all the d-block levels of the Cu1 atoms to lie below the bottom portion of the  $\text{CuO}_2$  layer  $x^2 - y^2$  bands. Consequently, in tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  ( $y \gtrsim 0.5$ ) the d-block levels of the Cu1 atoms with low coordination number are all filled so that the oxidation state of such Cu1 atoms is +1. Therefore, tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  ( $y \gtrsim 0.5$ ) does not possess the special electronic properties of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  ( $y \simeq 0.19$ ).

### Concluding Remarks

The remarkable discovery of high- $T_c$  superconductivity at temperatures exceeding 90 K has generated a large amount of attention, both in the public press, where possible technological developments are emphasized, and in the scientific community, where well over 1200 journal publications and submissions have appeared since January 1987. However, in spite of this attention, we still do not yet have an accurate theory nor do we understand the mechanism involved and why these copper oxide perovskites have such high superconducting transition temperatures. In addition, we do not know to what extent these materials are unique or if there are other classes of compounds yet to be discovered with even higher  $T_c$ 's. What we can confidently predict, as suggested in the epigraph, is that this is a field which will remain highly active and exciting for years to come. Finally, whatever the eventual theory that explains high- $T_c$  superconductivity, it will owe an enormous debt to solid-state chemists because their synthetic and structural studies are propelling the current revolution in superconductivity.

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