as Sm, Eu, Gd, Dy, Ho, and Yb does not greatly affect the high-temperature superconductivity.[23]

A unit cell of $YBa_2Cu_3O_7$ contains two CuO_2 layers and one CuO_3 chain. With the coordinate x, y, and z axes taken along the crystallographic a, b, and c axes, respectively, the CuO_2 layers are parallel to the xy plane while the copper–oxygen planes of the CuO_3 chains are parallel to the yz plane. Therefore, in the CuO_3 *chains*, it is the $z^2 - y^2$ orbital of Cu1 that plays the role which the $x^2 - y^2$ orbital of Cu2 plays in the CuO_2 *layers*. Figure 2a shows the dispersion relations of the top three d-block bands of $YBa_2Cu_3O_7$, where the dashed line refers to the Fermi level. The two nearly degenerate $x^2 - y^2$ bands (hence represented by a thick line) are solely derived from the CuO_2 layers, so they are 2D with almost equal dispersion along the a- and b-axis directions. The $z^2 - y^2$ band is solely represented by the CuO_3 chains and is dispersive only along the b-axis direction. The $z^2 - y^2$ band lies higher in energy than the $x^2 - y^2$ bands, because the $z^2 - y^2$ orbital of Cu1 is raised in energy due to the short Cu1–O4 distance (i.e., Cu1–O4 = 1.850 Å vs. Cu2–O4 = 2.303 Å).[7]

With two electrons to fill the three bands of Figure 2a, the two $x^2 - y^2$ bands are each half-filled and the $z^2 - y^2$ band is empty. The bottom of the last band lies 0.11 eV above the Fermi level. The Fermi surfaces of the two $x^2 - y^2$ bands are essentially identical, one of which is shown in Figure 2b. As expected, this Fermi surface is 2D in nature and shows a reasonably good Fermi surface nesting (with the nesting vector $\mathbf{q} \simeq a^*/2 \pm b^*/2$ as in the case of La_2CuO_4[8]). Shown in Figure 2c is the density of states (DOS), $n(e)$, calculated for the $x^2 - y^2$ and $z^2 - y^2$ bands. It is clear that this DOS profile is a superposition of the DOS for the 1D $z^2 - y^2$ band, which peaks at the top and the bottom of the band, and that for the 2D $x^2 - y^2$ bands, which peaks in the middle of the band. The Fermi level, e_f, occurs in the middle of the $x^2 - y^2$ bands, and the DOS value at e_f, $n(e_f)$, is calculated to be 8.85 electrons per unit cell/eV. According to Beno et al.,[7] the site occupancies of O1 and O2 are 0.92 (2) and 0.95 (2), respectively, so the refined stoichiometry of the superconducting Y–Ba–Cu–O phase is $YBa_2Cu_3O_{6.81}$. Thus the average oxidation number of copper in $YBa_2Cu_3O_{6.81}$ is smaller than that in $YBa_2Cu_3O_7$ by 0.127. Within the rigid band model, therefore, the Fermi level of nonstoichiometric $YBa_2Cu_3O_{6.81}$ may be estimated by putting 2.381 electrons (instead of 2) into the d-block bands in Figure 2a. This leads to a new Fermi level slightly higher than the one shown in Figure 2a, but still 0.06 eV below the bottom of the $z^2 - y^2$ band, and to a smaller $n(e_f)$ value (i.e., 7.80 electrons per unit cell/eV).

Since the $z^2 - y^2$ band is empty but the $x^2 - y^2$ bands are each half-filled, the oxidation state of copper is higher in the CuO_3 chains (Cu^{3+}) than in the CuO_2 layers (Cu^{2+}). The $x^2 - y^2$ bands do not have any orbital contributions from the CuO_3 chains. This implies that, within each superconducting $Ba_2Cu_3O_7{}^{3-}$ slab, the Cu2 atoms of one CuO_2 layer do not interact with those of the other CuO_2 layer although they are linked by the Cu2–O4–Cu1–O4–Cu2 bridges. This is rather puzzling in view of the long-range order (i.e., superconductivity) that occurs at a high temperature ($T_c > 90$ K). In essence, the partially filled bands of $YBa_2Cu_3O_7$ (i.e., the $x^2 - y^2$ bands) calculated for its equilibrium structure are identical in nature with the partially filled band of another superconducting phase, $La_{2-x}M_xCuO_4$.[8] Thus, one may wonder what electronic factors, if any, are responsible for the considerably higher superconducting transition temperature in $LBa_2Cu_3O_{7-y}$ (L = Y, Sm, Eu, Gd, Dy, Ho, Yb; 90 K < T_c < 100 K)[23] than in $La_{2-x}M_xCuO_4$ (M = Ba, Sr; 30 K < T_c < 40 K).[9-22] These questions will be probed in detail in our subsequent paper.[24]

Acknowledgment. Work at North Carolina State University and Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Grant DE-FG05-86-ER45259 and under Contract W31-109-ENG-38, respectively. We express our appreciation for computing time made available by DOE on the ER-Cray X-MP computer.

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Band Electronic Structure of the High-Temperature (T_c > 90 K) Superconductor Orthorhombic $YBa_2Cu_3O_7$. 2. Effect of the Capping-Oxygen Displacement on the Interaction of the CuO_2 Layers with the CuO_3 Chains, the Fermi Surface Dimensionality of the CuO_3 Chain Band, and the Valence Fluctuations of the Copper Atoms

Sir:

Recently, a number of synthetic and structural studies[1-8] have been reported on the high-temperature superconductors with T_c > 90 K, i.e., the Y–Ba–Cu–O system and its analogues. The recent powder neutron diffraction study of Beno et al.[7] identified the superconducting Y–Ba–Cu–O phase uniquely as orthorhombic $YBa_2Cu_3O_{7-y}$ ($y \simeq 0.19$), which contains two-dimensional (2D) structural units of composition $Ba_2Cu_3O_{7-y}{}^{3-}$, i.e., two CuO_2 layers that sandwich one CuO_3 chain and two Ba^{2+} cations per unit cell (see Figure 1 of ref 9). Within every $Ba_2Cu_3O_{7-y}{}^{3-}$ slab, each copper atom (Cu2 of the CuO_2 layers) is capped by the oxygen O4 (site fully occupied) of the CuO_3 chains in such a way that each copper atom (Cu1) of the CuO_3 chains forms a Cu2–O4–Cu1–O4–Cu2 bridge perpendicular to the $Ba_2Cu_3O_{7-y}{}^{3-}$ slab. The Y^{3+} cations of $YBa_2Cu_3O_{7-y}$ are sandwiched by the $Ba_2Cu_3O_{7-y}{}^{3-}$ slabs which alternate with layers of Y^{3+} cations along the c axis.

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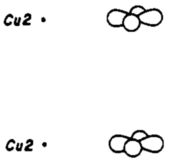
In our previous paper,[9] we reported the tight-binding band electronic structure of the stoichiometric composition $YBa_2Cu_3O_7$ calculated on the basis of its structure determined by Beno et al.[7] Within a rigid band model, the band electronic structure of nonstoichiometric $YBa_2Cu_3O_{7-y}$ ($y \simeq 0.19$) can be approximated by filling the top three d-block bands of stoichiometric $YBa_2Cu_3O_7$ with 2.381 electrons (instead of 2),[9] since the average oxidation state of copper in $YBa_2Cu_3O_{6.81}$ is smaller than that in $YBa_2Cu_3O_7$ by 0.127. Between two adjacent CuO_2 layers sandwiching the Y^{3+} cations, the $x^2 - y^2$ orbitals of Cu2 atoms have a δ-type overlap (see **1**), which is negligible. Therefore, the $x^2 - y^2$ and $z^2 - y^2$ bands of $YBa_2Cu_3O_7$ are dispersionless along the *c*-axis direction.[9] The $x^2 - y^2$ bands are solely represented by the CuO_2 layers, and the $z^2 - y^2$ band is solely represented by the CuO_3 chains.[9] Thus, within each $Ba_2Cu_3O_7^{3-}$ slab, the Cu2 atoms of one CuO_2 layer do not appear to interact with those of the other CuO_2 layer. This is apparently surprising, since superconductivity (i.e., a long-range order) occurs at a rather high temperature ($T_c > 90$ K). If the capping oxygen (O4) atoms remain on the Cu2–Cu1 line, as illustrated in **2**, all the orbitals of the O4 atom have zero overlap with the $x^2 - y^2$ orbital of the Cu2 atom due to the node of the $x^2 - y^2$ orbital along the Cu2–Cu1 axis. When the O4 atoms are displaced out of the Cu2–Cu1 line (e.g., see **3**), the *z* orbital of the O4 atom, which strongly overlaps with the $z^2 - y^2$ orbital of Cu1, can have nonzero overlap with the $x^2 - y^2$ orbital of Cu2. This could allow the Cu2 atoms of the two separated CuO_2 layers to interact via the Cu2–O4–Cu1–O4–Cu2 bridges. In addition, our previous paper[9] showed that the $z^2 - y^2$ band lies above the Fermi level, e_f, since the $z^2 - y^2$ orbital of Cu1 is raised due to the short Cu1–O4 distance (1.850 Å).[7] That is, the copper oxidation state is higher in the CuO_3 chains (Cu^{3+}) than in the CuO_2 layers (Cu^{2+}). Nevertheless, the bottom of the $z^2 - y^2$ band lies only 0.11 eV above the Fermi level,[9] so that the displacement of the O4 atom toward the Cu2 atom could lower the bottom of the $z^2 - y^2$ band below the Fermi level. Thus, even small displacements of the O4 atom from its equilibrium position (vide infra), and therefore lattice vibrational models involving the O4 atoms, might significantly affect the electronic structure of $YBa_2Cu_3O_7$. In the present report, we assess this effect of the O4 atom displacement by performing tight-binding band calculations as described earlier.[9,10]



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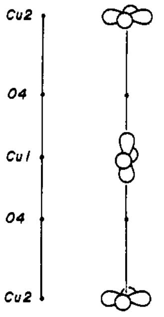

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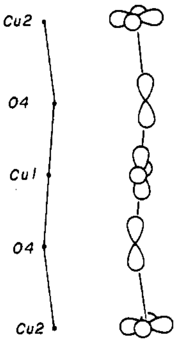

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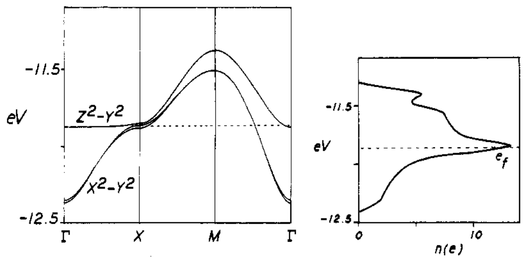
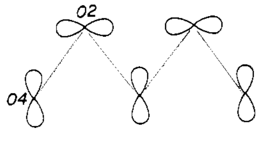


(a) (b)

Figure 1. Electronic structure of $YBa_2Cu_3O_7$ with the capping-oxygen displacement of $\Delta z = \Delta x = 0.04$ Å and $\Delta y = 0$, where, in units of the reciprocal vectors a^*, b^*, and c^*, the wave vectors $\mathbf{\Gamma}$, $\mathbf{X}$, $\mathbf{Y}$, and $\mathbf{M}$ are defined as $\mathbf{\Gamma} = (0, 0, 0)$, $\mathbf{X} = (a^*/2, 0, 0)$, $\mathbf{Y} = (b^*/2, 0)$, and $\mathbf{M} = (a^*/2, b^*/2, 0)$: (a) dispersion relations of the top three d-block bands. (b) density of states of the top three d-block bands.

The band electronic structures of $YBa_2Cu_3O_7$, calculated as a function of the O4 displacement along the *c* axis toward Cu2 (Δz), show that the bottom of the $z^2 - y^2$ band is lowered below the Fermi level only when $\Delta z \gtrsim 0.04$ Å. With $\Delta z \gtrsim 0.04$ Å, the O4 atom displacement either along the *a* axis (Δx) or along the *b* axis (Δy) by about 0.04 Å leads to appreciable mixing between the $z^2 - y^2$ and $x^2 - y^2$ bands in the wave vector region of **X**. As a representative example, Figure 1a shows the $x^2 - y^2$ and $z^2 - y^2$ bands obtained for $\Delta z = \Delta x = 0.04$ Å and $\Delta y = 0.0$. The corresponding density of states (DOS) is shown in Figure 1b. Since the bottom of the $z^2 - y^2$ band lies near the middle of the $x^2 - y^2$ bands, the resulting DOS has a large peak in the middle of the $x^2 - y^2$ bands where the Fermi level occurs. The DOS value at e_f, $n(e_f)$, is calculated to be 11.87 electrons per unit cell/eV, which is considerably greater than the corresponding value of 8.85 electrons per unit cell/eV calculated for $YBa_2Cu_3O_7$ with $\Delta x = \Delta y = \Delta z = 0$.

Figure 2 shows the Fermi surfaces for the three bands of Figure 1. The Fermi surfaces of the two $x^2 - y^2$ bands (Figure 2a,b) are 2D, as expected, but so is the Fermi surface (Figure 2c) of the $z^2 - y^2$ band although it is primarily of the CuO_3 chains in nature. This arises from the fact that the $z^2 - y^2$ band acquires a 2D character in the wave vector region of **X** by mixing with the $x^2 - y^2$ bands. As indicated in **4**, the *z* orbital of O4 interacts not only with the $x^2 - y^2$ orbital of Cu2 but also with the *x* orbital of O2 along the *a* axis (See Figure 1 of ref 9).



4

If the $z^2 - y^2$ band is further lowered by increasing the Δz value beyond 0.04 Å, the corresponding Fermi level is raised more from the bottom of the $z^2 - y^2$ band, eventually making it filled for all the wave vectors along $\mathbf{\Gamma} \rightarrow \mathbf{X}$. This makes the resulting Fermi surface of the $z^2 - y^2$ band one-dimensional (1D). Therefore, depending upon the extent of the capping oxygen atom displacement, the $z^2 - y^2$ band is empty, partially filled with a 2D

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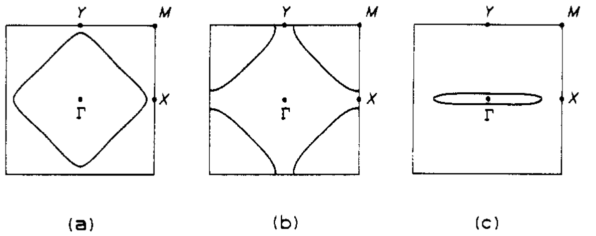

Figure 2. Fermi surfaces of the top three d-block bands with the same displacements as in Figure 1: (a) lower $x^2 - y^2$ band; (b) upper $x^2 - y^2$ band; (c) $z^2 - y^2$ band.

Fermi surface, or partially filled with a 1D Fermi surface. Of course, partial filling of the $z^2 - y^2$ band leads to partial emptying of the $x^2 - y^2$ bands. Thus upon any O4 atom displacement that lowers the $z^2 - y^2$ band below the Fermi level, the oxidation state of copper increases in the CuO_2 layers from +2 to +2 + Δ (Δ small) but decreases in the CuO_3 chains from +3 to +3 − Δ. Therefore, certain lattice vibrational modes involving the O4 atom displacement will lead to slight valence fluctuations of the copper atoms.

Thus, slight displacement of the capping oxygen atom O4 from its equilibrium position gives rise to crucial changes in the band electronic structure of $YBa_2Cu_3O_7$. At room temperature the root-mean-square (rms) deviation of the O4 atom from its equilibrium position is about 0.09 Å,[7] and similar values have been reported at approximately 80 K.[11,12] Therefore, the O4 atom displacement on the order of $\Delta x = \Delta y = \Delta z = 0.05$ Å should be easily accessible via the lattice vibration modes involving the O4 atoms. In the CuO_3 chains, the rms deviation of the other oxygen atom (i.e., O1) is highly anisotropic and is much greater than that of the O4 atom[7,12] in the plane perpendicular to the Cu1–O1–Cu1 axis (e.g., 0.17, 0.06, and 0.16 Å, respectively, along the *a*, *b*, and *c* axes at room temperature[7]). Our band calculations on $YBa_2Cu_3O_7$ show that O1 atom displacements as large as 0.10 Å along either the *a* or the *c* axis hardly lower the $z^2 - y^2$ band. Since O4 is much closer to Cu1 than is O1 (i.e., Cu1–O1 = 1.943 Å vs. Cu1–O4 = 1.850 Å[7]), the position of the $z^2 - y^2$ band is primarily governed by the O4 atom displacement.

The present work shows that slight displacement of the capping oxygen atom (O4) from its equilibrium position gives rise to slight valence fluctuations of the copper atoms, interactions between two separated CuO_2 layers within each $Ba_2Cu_3O_7^{3-}$ slab, and a change in the Fermi surface dimensionality of the CuO_3 chain band. For the long-range order such as superconductivity to occur at a high temperature in each $Ba_2Cu_3O_7^{3-}$ slab, the copper atoms of the two separated CuO_2 layers must interact effectively. Our study suggests that this can be easily achieved via the Cu2–O4–Cu1–O4–Cu2 bridges with the help of the lattice vibrational modes involving the capping oxygen atoms O4.

Acknowledgment. Work at North Carolina State University and Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Grant DE-FG05-86-ER45259 and under Contract W31-109-Eng-38, respectively. We express our appreciation for computing time made available by DOE on the ER-Cray X-MP computer.

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High-T_c Superconductors: Selective Preparation and Characterization of Tetragonal and Orthorhombic (93 K Superconductor) Phases of $YBa_2Cu_3O_{7-x}$

Sir:

Dramatic milestones in terms of greatly increased superconducting transition temperatures have been achieved recently, resulting in T_c's well above 90 K.[1-3] The materials in question were prepared from mixtures of Y_2O_3, $BaCO_3$, and CuO, and the superconducting phase was subsequently identified as having the composition $YBa_2Cu_3O_{9-\delta}$ ($\delta \sim 2$).[4] X-ray powder patterns indicated that the compound had a perovskite-like structure,[4,5] similar to that found in some compositions of the La–Y–Ba–Cu–O system.[6] However, some confusion has arisen because two *different* structures, both presumably superconducting, have been reported for this material: a tetragonal phase ($a = 3.85$ Å, $c = 11.72$ Å, space group $P\bar{4}m2$) by means of single-crystal X-ray diffraction,[7] and an orthorhombic phase ($a = 3.823$ Å, $b = 3.886$ Å, $c = 11.681$ Å, space group *Pmmm*)[8] from powder neutron diffraction studies.[8-10] Both structures are derived from a regular ABX_3 perovskite by tripling the *c* axis concurrent with the ordering ···Y–Ba–Ba–Y–Ba–Ba··· on the A site, but they differ in the specific oxygen vacancy arrangement, which, in turn, may depend on the method of preparation. Slow furnace cooling is reported to produce superconducting materials[4,5,11] with high T_c's (~90 K), and the structure of this material is reportedly orthorhombic.[8] In this communication we report (i) the advantages of the coprecipitation method for the preparation of $YBa_2Cu_3O_{7-x}$ ($x \simeq 0.1$) and also report (ii) that the two phases can be selectively obtained, i.e., orthorhombic or tetragonal, depending on the sample cooling rate subsequent to oxygen annealing, (iii) that *superconductivity at 93 K* exists only in the *orthorhombic phase*, and (iv) that the electrical properties of the tetragonal phase exhibit sample-to-sample variations ranging from a semiconductor to a lower T_c superconductor with a broad transition at ~60 K.

For the preparation of $YBa_2Cu_3O_{7-x}$, we chose the "pH-adjusted carbonate route"[12] over the commonly used Y_2O_3–$BaCO_3$–CuO calcination method. The advantages of the former are several: (i) Y:Ba:Cu ratios in the final oxide are very close to the starting ratios (see below); (ii) better sample homogeneity (of the Y, Ba, Cu dispersion) results from this solution method than by grinding; (iii) virtually single-phase materials (with respect to composition) are obtained.

Synthesis. An aqueous solution (triply distilled water) of high purity $Y(NO_3)_3$ (prepared from Y metal (99.99%) and concen-

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