Inorg. Chem. **1987**, *26*, 1831–1832 **1831**

Band Electronic Structure of the High-Temperature (T_c > 90 K) Superconductor Orthorhombic $YBa_2Cu_3O_7$. 1. Partially Filled d-Block Bands of the Equilibrium Structure

Sir:

The report[1] of ambient-pressure superconductivity above 90 K in a multiphase sample of the Y–Ba–Cu–O system has stimulated numerous studies aimed at determining the identity of the superconducting phase and its structure.[2-6] Unfortunately, the X-ray diffraction studies[3-6] do not provide unambiguous oxygen atom positions, and occupancies, due to the weak X-ray scattering power of oxygen in the presence of heavy atoms such as Y, Ba, and Cu. Thus, Beno et al.[7] recently carried out a powder neutron diffraction study, in which all atoms have similar scattering amplitudes, on the superconducting Y–Ba–Cu–O phase (with a sharp superconducting transition at 92.5 K and a narrow transition width of 3 K), which revealed the superconducting phase to be orthorhombic $YBa_2Cu_3O_{7-y}$ ($y \simeq 0.19$). This structure differs in the oxygen atom positions and site occupancies from that derived in the single-crystal X-ray study of a tetragonal phase by Hazen et al.[6] In the present work, we describe the tight-binding band electronic structure of the stoichiometric composition $YBa_2Cu_3O_7$ calculated on the basis of its crystal structure determined by Beno et al.[7] Details of the tight-binding band calculations are described in our previous report[8] on orthorhombic La_2CuO_4 and tetragonal $La_{2-x}M_xCuO_4$ (M = Ba, Sr).

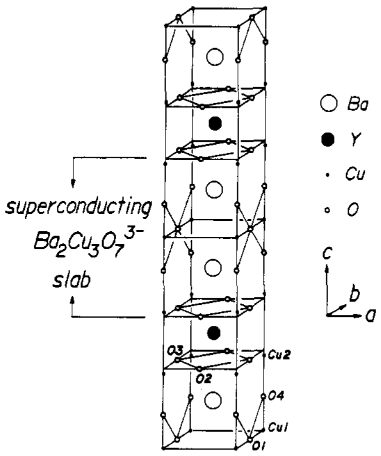
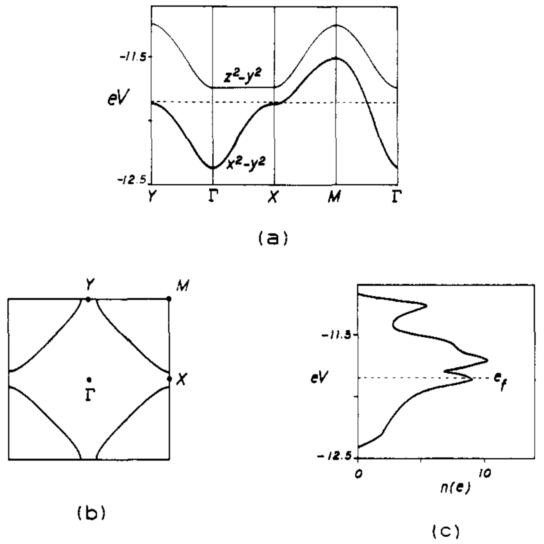


Figure 1. Crystal structure of $YBa_2Cu_3O_{7-y}$ ($y \simeq 0.19$) determined by neutron diffraction.[7]



(a)

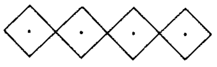
(b)

(c)

Figure 2. Electronic structure of $YBa_2Cu_3O_7$, where, in units of the reciprocal vectors a^*, b^*, and c^*, the wave vectors **Γ**, **X**, **Y**, and **M** are defined as $\mathbf{\Gamma} = (0, 0, 0)$, $\mathbf{X} = (a^*/2, 0, 0)$, $\mathbf{Y} = (0, b^*/2, 0)$, and $\mathbf{M} = (a^*/2, b^*/2, 0)$.

The crystal structure of $YBa_2Cu_3O_7$ is shown in Figure 1. The Cu1 atoms form CuO_3 chains (**1**) along the *b* axis, and the Cu2 atoms form dimpled CuO_2 layers (**2**) in the *ab* plane. The Cu2 atoms are out of the O2–O3 plane by 0.263 Å toward the side facing the Ba^{2+} cations. Each Cu2 atom of the CuO_2 layers is capped by the oxygen (O4) of the CuO_3 chains, thereby leading to a square-pyramidal coordination for Cu2. Each Y^{3+} cation has a square-prismatic coordination provided by two sandwiching CuO_2 layers, while each Ba^{2+} cation is located in an oxygen pocket made up of four oxygen atoms of a CuO_2 layer and six oxygen atoms of two CuO_3 chains. In turn, the Y^{3+} and Ba^{2+} cations form $(Y^{3+}\cdots Ba^{2+}\cdots Ba^{2+}\cdots)_\infty$ chains along the *c* axis. The structural unit of $YBa_2Cu_3O_7$ essential for high-temperature superconductivity is the two-dimensional (2D) slab $Ba_2Cu_3O_7^{3-}$, i.e., two CuO_2 layers that sandwich one CuO_3 chain and two Ba^{2+} ions per unit cell, which is referred to as a *superconducting* $Ba_2Cu_3O_7^{3-}$ slab in Figure 1. Substitution of Y by other lanthanide elements such

1



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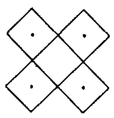

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as Sm, Eu, Gd, Dy, Ho, and Yb does not greatly affect the high-temperature superconductivity.[23]

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]

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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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