Linear muffin-tin-orbital atomic-sphere-approximation calculations of the electronic structure of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$

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Self-consistent linear muffin-tin-orbital atomic-sphere-approximation calculations have been performed for two new materials: the orthorhombic high-temperature superconductor $YBa_2Cu_3O_7$ and the tetragonal semiconductor $YBa_2Cu_3O_6$. The total density of states (DOS) at the Fermi energy is low in both compounds [51 states/(Ry unit cell) for the former and 30 states/(Ry unit cell) for the latter]. The DOS due to oxygen p electrons near the Fermi energy is significantly larger in $YBa_2Cu_3O_7$ than in $YBa_2Cu_3O_6$. This is due to the occupancy of O(1) electrons [i.e., oxygen on the one-dimensional Cu(1)-O(1) chain] and is probably important for the observed high value of T_c in $YBa_2Cu_3O_7$. The Fermi energy in $YBa_2Cu_3O_6$ lies in a region of very low density of states near the energy gap.

Since the recent discoveries[1,2] of superconductors with critical temperatures T_c, far above those previously considered possible for superconductivity, numerous studies have been made in order to try to understand the new phenomenon[3] and determine the mechanism responsible. The new superconductors have perovskite-derived structures which contain weakly coupled CuO_2 layers, e.g., doped $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$, where $0<\delta<\frac{1}{2}$.[4,5] The latter so-called 90-K superconductors feature one-dimensional CuO ribbons in addition to the two-dimensional CuO_2 layers. The observed superconductivity is sensitive to the oxygen vacancies at the O(1) sites on these ribbons (see Fig. 1). It is especially interesting that as the oxygen content is varied from $YBa_2Cu_3O_{6.9}$ (Refs. 4 and 5) to $YBa_2Cu_3O_{6.24}$ (Ref. 6), the material changes from an orthorhombic superconductor to a tetragonal semiconductor. To aid in our understanding of the new 90-K superconductors, we have performed band-structure calculations on both of these related compounds in order to try to identify the structural and electronic features responsible for the superconductivity. Since we cannot perform proper band-structure calculations for these compounds without using supercells with hundreds of atoms, we have made our calculations in each case for the unit cell with the closest total number of oxygens to the actual concentration, i.e., $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$. One can then extrapolate using the rigid-band-filling approximation.[7]

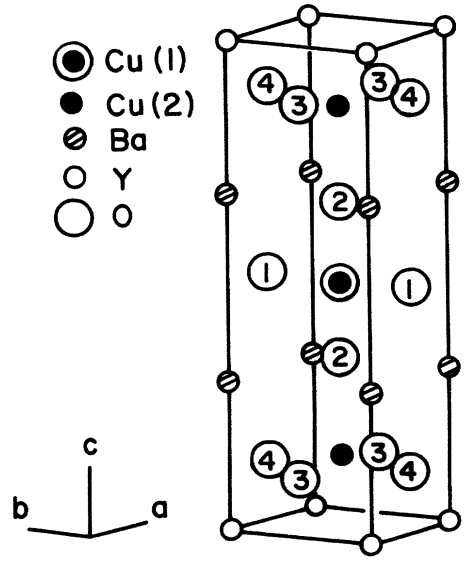


FIG. 1. Unit cell of $YBa_2Cu_3O_7$ according to Greedan, O'Reilly, and Stager (Ref. 4).

Our self-consistent non-spin-polarized calculations used the linear-muffin-tin orbital atomic-sphere-approximation (LMTO-ASA) method[8] with the von Barth–Hedin local exchange-correlation potential[9] and the neutron diffraction structure data due to Greedan *et al.*[4,6] $YBa_2Cu_3O_{7-\delta}$ has orthorhombic symmetry[4] with $a=3.8282$ Å, $b=3.889$ Å, and $c=11.6944$ Å (see Fig. 1). Since the difference between the lattice constants a and b is small, this structure has often been determined as quasitetragonal.[5,10] In our calculations we assume that $a=b=\sqrt{ab}$ but take into account that there is D_{2h} symmetry around the z axis due to occupation by oxygen [oxygen O(1) is in the x direction and the vacancy is in the y direction], and that summation over the two prisms (A and B in the inset of Fig. 2) in the Brillouin zone has to be performed in order to take into account the orthorhombic effect. In the calculations 56 K points were used in each prism. The notation for the Brillouin zone for tetragonal symmetry[11] is used in order to make discussion for both phases more transparent. Since a minimal valence basis set was employed, the oxygen $2s$ and barium $5p$ electrons might cause a schizophrenic effect on the band structure.[8] To avoid this, we chose an expansion level for these electrons very far from the initial one.

For $YBa_2Cu_3O_6$ we used the lattice parameters measured by Greedan[6] for tetragonal symmetry: $a=b=3.862$ Å, $c=11.787$ Å. We neglected the oxygen atom $(\frac{1}{2},0,\frac{1}{2})$ which, according to Greedan,[6] has occupancy 0.24 in $YBa_2Cu_3O_{6.24}$. This atom is related to O(1) in $YBa_2Cu_3O_7$. Since the volume of the unit cell of

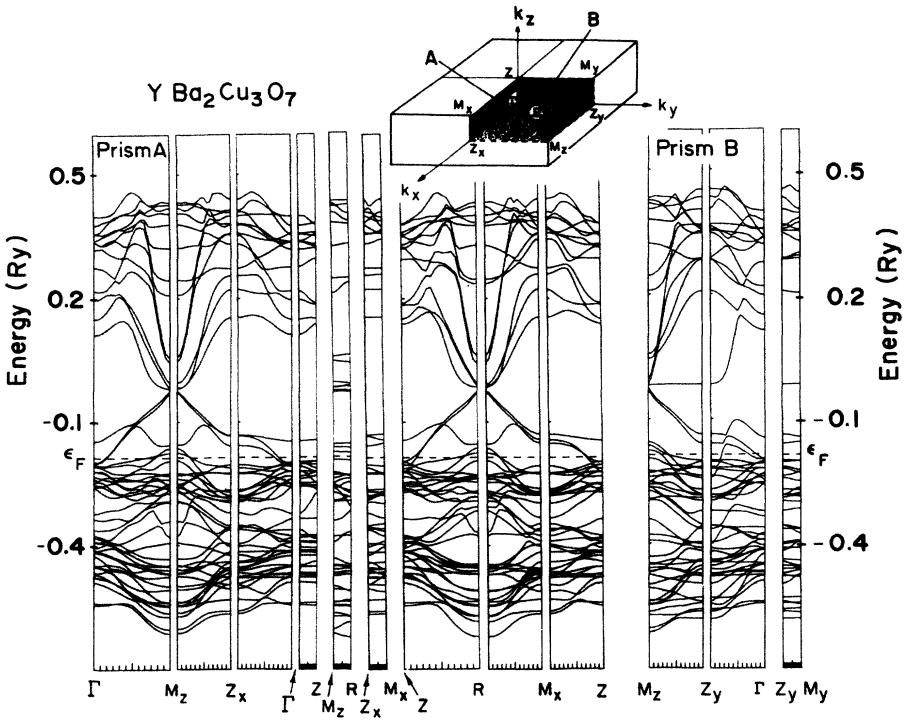


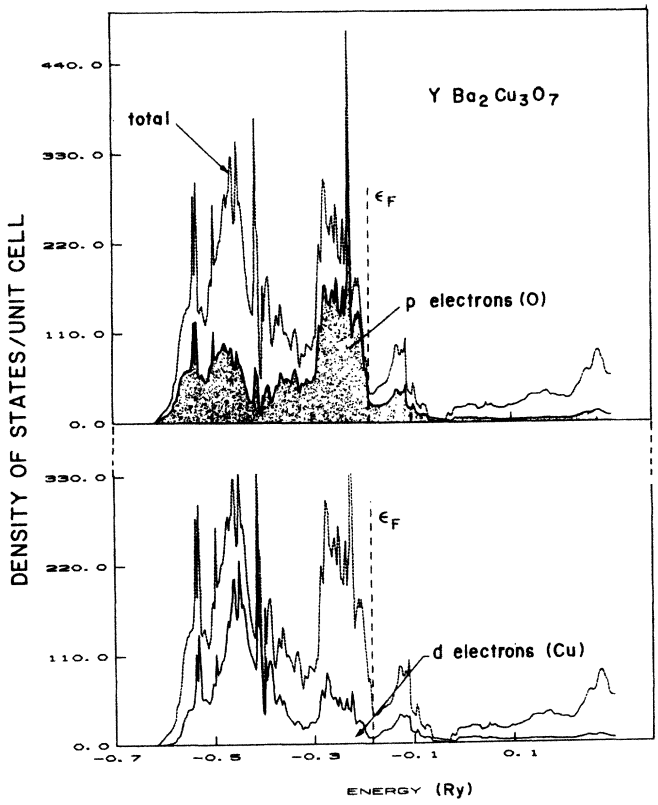
FIG. 2. The calculated band structure for $YBa_2Cu_3O_7$ along symmetry points in prism A and prism B. The Brillouin zone is shown in the inset.

$YBa_2Cu_3O_6$ (175.8 Å^3) is larger than that of $YBa_2Cu_3O_7$ (174.1 Å^3), major modification of the electronic structure should be expected.

The atomic-sphere-approximation (ASA) with combined corrections[8] was used. In the present calculations the Y, Cu, and O atomic-sphere radii were assumed to be the same in both compounds: $r_A(Y)=3.41$ a.u., $r_A(Cu)=2.55$ a.u., $r_A(O)=2.45$ a.u. Different atomic-sphere radii on barium were used in $YBa_2Cu_3O_7$ (3.5 a.u.) and $YBa_2Cu_3O_6$ (3.75 a.u.).

We observe in Fig. 3 that the main contribution to the total density of states (DOS) for $YBa_2Cu_3O_7$ comes from the p electrons on oxygen and the d electrons on copper, with the oxygen p character dominating near the Fermi energy. This result is in keeping with the photoemission results of Johnson *et al.*[12] There are a few notable peaks in the oxygen p electron DOS near the Fermi energy which become quite small in $YBa_2Cu_3O_6$ (Fig. 4). In these figures, we shaded the area of the oxygen p electron DOS in order to show clearly the large modification of the shape of the DOS by the removal of the O(1) oxygen. In particular, the DOS near the Fermi energy is lowered in going from $YBa_2Cu_3O_7$ [$n(\epsilon_F)=51$ states/(Ry unit cell)] to $YBa_2Cu_3O_6$ [$n(\epsilon_F)=30$ states/(Ry unit cell)]. This suggests the importance of the O(1) oxygen atoms for the observed superconductivity. This effect is not dependent on the assumed relative atomic-sphere radii of oxygen and copper.

The primary role of barium and yttrium is to stabilize the crystal structure in which oxygen and copper atoms are the only ones which interact together through p-d hybridization as has been noticed by other authors[7,13] in the



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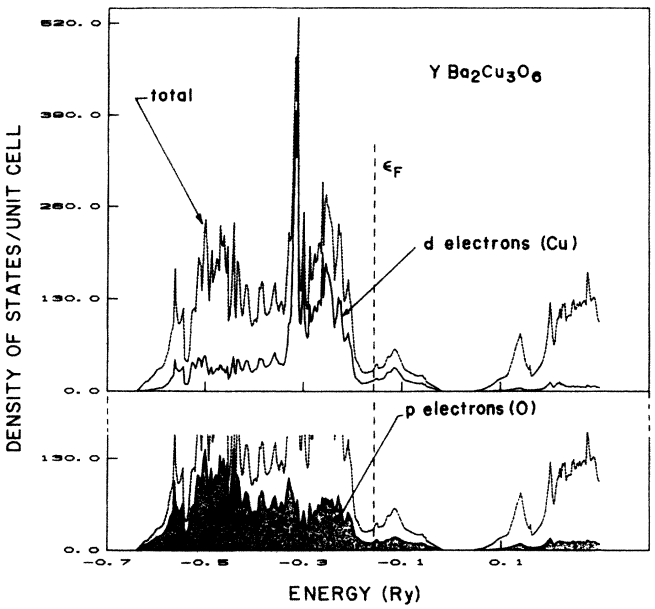

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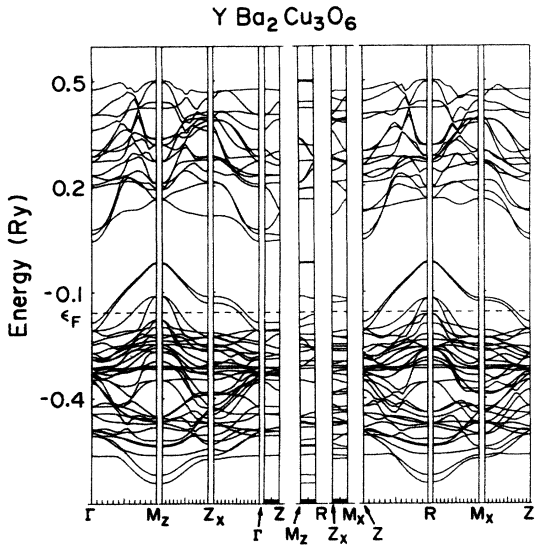

FIG. 5. The calculated band structure for $YBa_2Cu_3O_6$ along symmetry points in prism A (see inset of Fig. 2).

case of the 35 K superconductor $La_{2-x}M_xCuO_4$. The peak in the DOS above 0.0 Ry is due to d electrons of Ba in both compounds. Below this peak the DOS from Y and Ba is negligible. The most important feature of the new superconductor is that the number of important nearest neighbors of oxygen is reduced to only two copper atoms which, as is well known from tight-binding model calculations on surface atoms, causes a sharpening in the DOS.[7,14]

In Fig. 2 the energy-band structure is presented along the symmetry lines of prism A for $YBa_2Cu_3O_7$. It is dominated by quite flat bands of p and d electrons. Above the Fermi energy there is a region of low DOS which becomes the semiconductor energy gap for the lower oxygen occupancy in $YBa_2Cu_3O_6$. In Fig. 2 the band structure for prism B is shown as well in order to demonstrate the effect of oxygen [O(1)] occupancy. Comparison of the band structure for prisms A and B shows significant differences in the shape of some of the bands around and above the Fermi energy. This strong dependence on the x or y direction is a demonstration of the one-dimensionality of the bonding between O(1)(p) and Cu(1)(d) electrons. In the case of $YBa_2Cu_3O_6$ (Fig. 5), these bands disappear. Another significant difference between these two compounds is a modification of the yttrium and barium d bands above the Fermi energy (Figs. 2 and 5), and the energy gap is more extended in $YBa_2Cu_3O_6$ than in the superconductor. Below the Fermi energy the electronic band structure for $YBa_2Cu_3O_6$ in Fig. 5 is not very different from that of $YBa_2Cu_3O_7$ in Fig. 2. There are strongly hybridized p-d bands which, around the Fermi energy, change from dominant oxygen p type in $YBa_2Cu_3O_7$ to copper d type in $YBa_2Cu_3O_6$. The other bands below the Fermi energy are not sensitive to the x and y directions. They are primarily O(p)-Cu(d) two-dimensional (2D) bands. The Fermi energy in $YBa_2Cu_3O_6$ is in an area of low DOS but is not zero. The extended gap in the energy above -0.0175 Ry obtained in these non-spin-polarized calculations for the oxygen-deficient O_6 compound may shift towards the Fermi energy in spin-polarized calculations. This would lead to agreement with the observed semiconducting behavior in $YBa_2Cu_3O_6$.

The position of the Fermi energy is quite uncertain in these compounds due to valence fluctuations which are not taken into account properly in band-structure calculations. There is also an inherent error due to the use of the local-density approximation. Another approximation which might influence the location of the Fermi energy is the neglect of hybridization with the Ba ($5p$), O ($2s$), and Y ($4p$) electrons in our minimal valence basis set approximation. However, experimental measurements (XPS) of the valence-band energies[15] for $YBa_2Cu_3O_7$ show that these bands lie well below the Fermi energy, i.e., ~ -14, ~ -20, and ~ -24 eV, respectively. Our non-spin-polarized calculations also do not take into account possible antiferromagnetic ordering in these compounds. It should be realized that the LMTO approximation is not ideal for these compounds as some of them qualify as open structure compounds[11] and the full potential linearized augmented plane wave (FLAPW) method, for example, is more suitable in this case.[7] The LMTO method is a good approximation[16] as long as space filling in the atomic spheres is above 60% and the spheres do not overlap more than 20% which was fulfilled in our calculations.

Our LMTO-ASA calculations show clearly the important features of the electronic structure of these new materials. However, less approximate methods such as FLAPW should reveal much better the details but they are more time consuming than those using the simpler LMTO-ASA and ASW methods. This means that it can be very useful to employ the latter methods to explore the

electronic structure of newer materials with comparatively large unit cells and then to use more precise methods for the important finer details.

Several calculations of the band structure $YBa_2Cu_3O_7$ have now appeared. Ours is more complex around the Fermi energy than that of Freeman and collaborators[17] possibly due to our assumption that the lattice constants a and b are equal and inherent errors due to the LMTO-ASA approximation. Herman, Kasowski, and Hsu[18] have discussed the electronic structure variation in $YBa_2Cu_3O_x$ with oxygen content $x=6$, 7, and 8. Our results agree with theirs for $x=6$ and 7 but the variation of the energy gap above the Fermi energy is not shown in their work.

It has been proposed recently[19,20] that due to a possible electronic-enhanced mechanism for superconductivity, the gap above the Fermi energy should be studied as a parameter related to the value of T_c. As discussed above our calculations show a drastic change in the direct gap at the M_z point which for $YBa_2Cu_3O_7$ is 0.13 eV and for $YBa_2Cu_3O_6$ is 2.42 eV. However, note that this gap above the Fermi energy is very sensitive to the assumed approximations in the calculations. This gap varies in different calculations for $YBa_2Cu_3O_7$: 2.17,[21] 1.93,[19,20] and 1.12 eV.[17] The corresponding value for La_2CuO_4 varies from 1.35 eV (Ref. 13) to 0.82 eV.[7] The gap above the Fermi energy demonstrates that the interlayer interactions are very sensitive to the assumed approximations in these open structures. Our calculations exaggerate the interlayer interactions due to the LMTO-ASA approximation.

In conclusion, the most interesting result of our calculations is that the lack of one oxygen [O(1)] in the nonsuperconductor $YBa_2Cu_3O_6$ causes dramatic changes in the electronic structure in comparison with that of $YBa_2Cu_3O_7$. As a result, we expect that these O(1) oxygen atoms and the high density of states in the vicinity of the Fermi energy due to the oxygen p electrons are important for the observed superconductivity. It should be noted that the more mobile p electrons might lead to a possible excitonic mechanism. Emery[22] has argued that the conduction mechanism is due to oxygen p holes.

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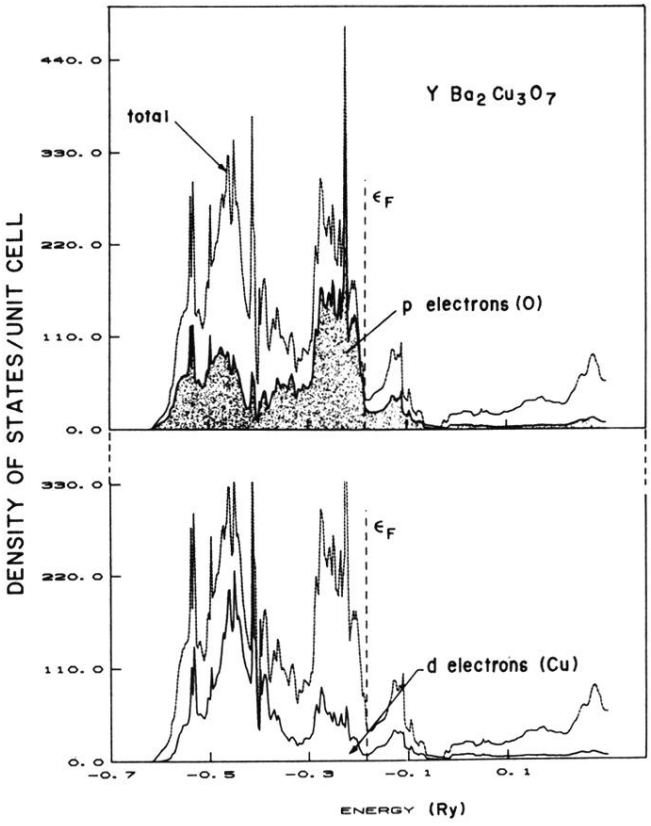

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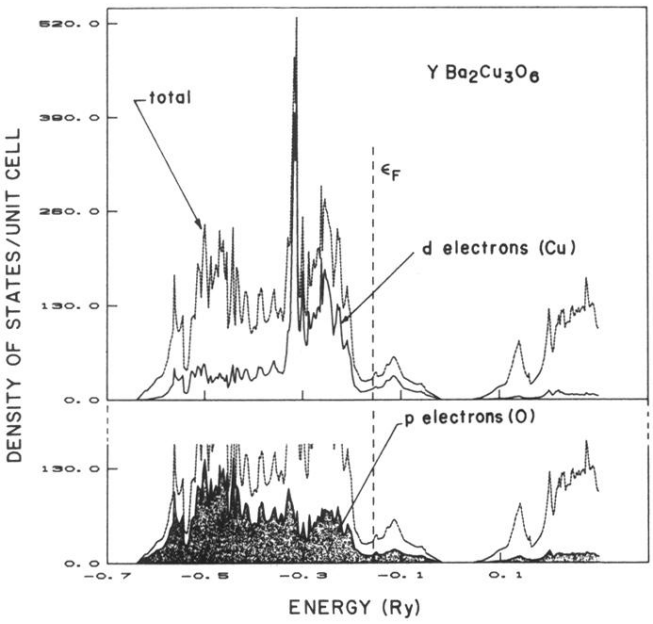

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