Electronic Band Structure of $CaBi_2Sr_2Cu_2O_8$

Mark S. Hybertsen and L. F. Mattheiss
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 25 February 1988)

The band structure for body-centered tetragonal $CaBi_2Sr_2Cu_2O_8$ has been calculated in the local-density-functional approach by the linearized muffin-tin-orbital method with the atomic-sphere approximation. This is the undistorted, stoichiometric parent compound to the recently reported 84-K superconductor. The main band features at the Fermi level include a pair of nearly half-filled two-dimensional Cu-O $3d$-$2p$ bands similar to those found in the previous Cu-O planar superconductors as well as a pair of slightly filled Bi $6p$ bands that provide additional carriers in the Bi-O planes.

PACS numbers: 71.25.Pi, 74.70.Ya

Superconductivity has been reported for Cu-O compounds containing bismuth with onsets exceeding 100 K.[1-3] The structure for a single-phase compound $Ca_{0.8}Bi_{2.2}Sr_2Cu_2O_{8+\delta}$ with zero resistance below 84 K and an onset above 100 K has now been deduced.[4,5] The actual structure is complex, consisting of a superlattice of orthorhombic subunits. However, the basic orthorhombic subunit of $CaBi_2Sr_2Cu_2O_8$ has essentially tetragonal symmetry with lattice parameters $a \approx b$. This pseudotetragonal subunit is closely approximated by a body-centered tetragonal structure whose primitive cell is shown in Fig. 1. The key elements of this structure are the presence of two Cu-O sheets similar to those in the previous 40- and 90-K materials as well as a double layer of edge-sharing Bi-O octahedra which fulfill a structural role that is analogous to the Cu-O chains in the compound $YBa_2Cu_3O_7$. The interesting question we address here is the effect of these Bi-O layers on the energy-band states near E_F, particularly the band filling within the Cu-O planes where it is generally believed that superconductivity occurs.

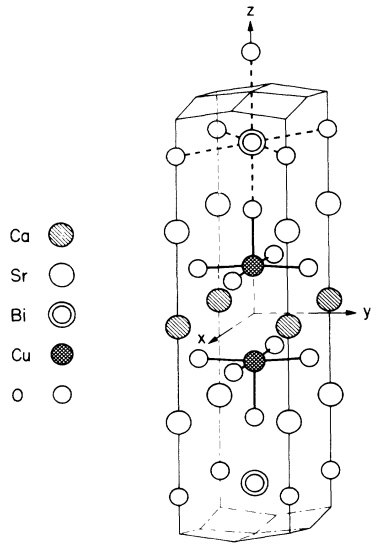

FIG. 1. Primitive cell for body-centered tetragonal $CaBi_2Sr_2Cu_2O_8$. O(1), O(2), and O(3) denote oxygens in the Cu, Bi, and Sr planes, respectively.

Two-dimensional band characteristics can be expected in this material because of the combined effects of the O vacancy in the central Ca plane and the body-centering translation that interchanges the central and corner atoms in adjacent cells along the c axis. While previous calculations for the perovskite-type $BaPb_{1-x}Bi_xO_3$ alloys[6] predict nearly degenerate Pb-Bi $6s$ and O $2p$ states and a single broad $6s$-$2p$ conduction band, the distorted BiO_6 octahedra in Fig. 1 have an average Bi—O bond distance ($\simeq$2.7 Å) which is about 25% greater than that in $BaPb_{1-x}Bi_xO_3$. Thus, it is unclear from the structure whether the Bi-O layers actively contribute to the transport properties of these materials.

The principal results of the present band-structure calculations are as follows. The two Cu-O planes give rise to a pair of Cu $d_{x^2-y^2}$-O $p_{x,y}$ bonding-antibonding bands which are very similar to those in La_2CuO_4 and $YBa_2Cu_3O_7$.[7,8] The Fermi level is slightly below the center of the antibonding band. These bands are weakly coupled to a complex of planar Bi $p_{x,y}$-O $p_{x,y}$ bands which are slightly occupied near the [100] Brillouin-zone boundary, thereby reducing the filling of the Cu-O band complex. Thus, the Bi-O planes in effect dope the Cu-O planes with additional holes. The calculated bands indicate a low-carrier-density metal with a low Fermi-level density of states, similar to the previous Cu-O-based superconductors.[7,8]

Band-structure calculations for the parent compounds of the previous Cu-O-based superconductors (La_2CuO_4 and $YBa_2Cu_3O_6$) have yielded a metallic ground state.[7,8] However, these materials are, in fact, antiferromagnetic insulators.[9] This is widely thought to be a consequence of strong electron correlation in the Cu-O planes[10] not adequately described in the band picture. The Mott-Hubbard picture may be more appropriate from this point of view. Nonetheless, the band-structure approach is expected to describe correctly the overall chemical and electrostatic interactions in these systems. The super-

TABLE I. Atom position coordinates (in units of $a=3.83$ Å and $c=30.89$ Å) for $CaBi_2Sr_2Cu_2O_8$ (space group $I4/mmm$), based on the x-ray diffraction results of Ref. 4. The atomic-sphere radii used in the LMTO-ASA calculations are also listed.

	Type	x	y	z	S (Å)
Ca	2*b*	0.5	0.5	0.0000	1.935
Cu	4*e*	0.0	0.0	0.0543	1.244
Sr	4*e*	0.5	0.5	0.1091	2.113
Bi	4*e*	0.0	0.0	0.1989	1.884
O(1)	8*g*	0.5	0.0	0.0510	1.102
O(2)	4*e*	0.5	0.5	0.1980	1.102
O(3)	4*e*	0.0	0.0	0.1200	1.102

conducting phase has required the addition of extra carriers (holes) into the Cu-O planes by chemical substitution (e.g., Sr for La in La_2CuO_4) or nonstoichiometry (e.g., changes in O content in $YBa_2Cu_3O_{6+\delta}$). Indeed, evidence has been presented suggesting that the transition temperature is approximately proportional to the excess carrier density.[11] The unique feature introduced here is a reservoir of carriers (the Bi-O *p* bands) which is intrinsic and continuous. Furthermore, the Bi-O bands are not expected to exhibit strong correlation effects (in contrast to the Cu-O chains in $YBa_2Cu_3O_{6+\delta}$) and should be well described by the band approach. Hence, there may well be mobile carriers even in the stoichiometric compound.

The self-consistent energy bands for the body-centered tetragonal compound have been calculated in the local-density-functional approximation[12] by the linearized muffin-tin-orbital (LMTO) method in the atomic-sphere approximation (ASA).[13] Preliminary results[14] obtained with the linearized augmented-plane-wave method are in good agreement with the present results. The present calculation includes scalar-relativistic effects, and the correlation data of von Barth and Hedin[15] are used in the local exchange-correlation potential. Previous LMTO-ASA results[16] for analogous Cu-O superconductors have proven to be accurate in comparison to those obtained with the linearized augmented-plane-wave method.[7,8]

The structural coordinates used in the present calculation are derived from the x-ray diffraction results of Ref. 4 and are summarized in Table I. Similar results are reported in Ref. 5. The atomic spheres are centered at each atomic site (Table I) and no extra spheres are included. The relevant valence and conductions bands are expanded in terms of *s*, *p*, and *d* waves on each site. The effect of increasing this basis to include *f* waves in the large cation spheres (Ca, Bi, and Sr) is negligible. The Ca 3*p*, Sr 4*p*, and O 2*s* states are included as band states in a lower-energy panel with *s* and *p* waves on each site.

The $CaBi_2Sr_2Cu_2O_8$ energy bands are plotted along representative lines in the $k_z=0$ plane of the Brillouin zone in Fig. 2. Minimal dispersion (less than 0.1 eV for most bands) is found along the *z* direction. The occupied bands consist primarily of Cu 3*d* and O 2*p* states, whereas the unoccupied states have predominantly Bi 6*p* character. Two distinct types of bands intersect E_F. The first corresponds to a nearly degenerate pair of anti-

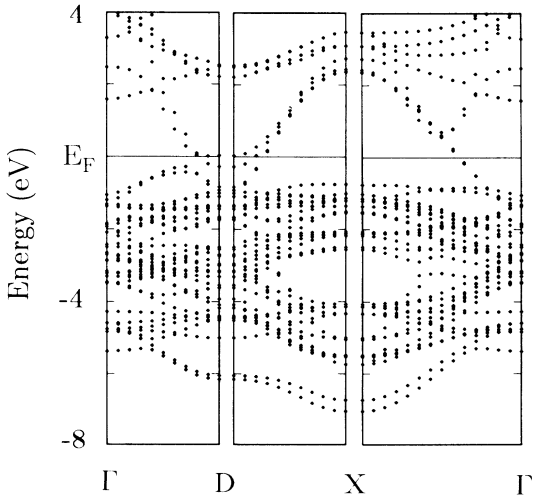

FIG. 2. Energy-band results for $CaBi_2Sr_2Cu_2O_8$ along representative lines in the $k_z=0$ plane of the Brillouin zone, where $D=(1,0,0)$ and $X=(1,1,0)$ in units of π/a.

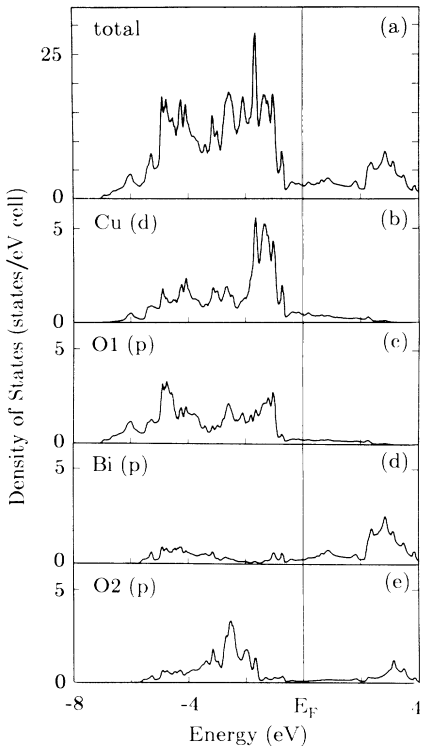

FIG. 3. Total and projected density-of-states results for atomic spheres in the Cu-O(1) and Bi-O(2) planes.

bonding Cu $d_{x^2-y^2}$-O(1) $p_{x,y}$ states that disperse above E_F toward the X point, leaving them less than half filled. The second represents the lowest pair of bands from the Bi-O(2) manifold that intersects E_F near D. The Bi 6s bands are located far below E_F at about -11 eV.

The total density of states (DOS) is shown in Fig. 3(a). This material has a low DOS at E_F (2.1 states/eV-formula unit), just as in the other Cu-O-based superconductors.[7,8] The partial DOS in the Cu, Bi, O(1), and O(2) spheres are shown in Figs. 3(b)-3(e). The states at E_F derive from the antibonding Cu-O(1) and Bi-O(2) bands. The shape of the Cu-O(1) DOS is similar to that in previous Cu-O-based superconductors.[7,8] The spectral weight of the Bi p states is primarily above E_F while that of the O(2) p states is below.

In order to elucidate more clearly the orbital character of the key bands that intersect E_F, those states with appropriate wave-function character have been projected out and plotted separately in Figs. 4 and 5. Figure 4 includes those states with Cu $d_{x^2-y^2}$-O(1) $p_{x,y}$ character for which the squared amplitude of the LMTO wave function is at least 5% per basis function. For comparison, the results of a simple two-parameter ($E_p = E_d = -2.6$ eV, $pd\sigma = -1.8$ eV) tight-binding model for these states are illustrated by the continuous curves. This simple model summarizes the essential features of the Cu $d_{x^2-y^2}$-O(1) $p_{x,y}$ manifold, particularly the antibonding band near E_F.

Figure 5 contains an analogous plot for the Bi $p_{x,y}$ and O(2) $p_{x,y}$ states with the same 5% cutoff criterion. Here, a more elaborate tight-binding scheme is required to model the LMTO results. Namely, both Bi-Bi ($pp\sigma = 0.5$ eV, $pp\pi = -0.25$ eV) and Bi-O ($pp\sigma = 2.0$ eV) hopping integrals are required, along with a Bi 6p orbital energy ($E_p = 0.7$ eV) which is somewhat above that of O ($E_p = -2.0$ eV). It is noteworthy that the pair of Bi 6p band edges at D are about 1 eV below E_F, mainly because of direct Bi-Bi interactions. although one might have concluded from Fig. 2 that the Bi-O(2) bands near E_F were higher. Although spin-orbit splittings are large ($\simeq 2$ eV) for the atomic Bi 6p states, spin-orbit coupling is expected to increase rather than decrease the filling of the Bi 6p bands at D.

The number of excess carriers compared to half filling is important for superconductivity, as noted above. The interesting feature is that the Cu-O(1) bands are below half filling because of the electron pockets in the Bi-O2 p bands. Thus the stoichiometric compound is self doped in this picture. The number of extra holes ($\simeq 0.1$ per Cu) is comparable to that introduced by optimal Sr doping ($x = 0.18$) in $La_{2-x}Sr_xCuO_4$. The $CaBi_2Sr_2Cu_2O_8$ samples are reported to have excess oxygen,[4,5] $\simeq 0.2$ per formula unit. Tarascon *et al.*[5] suggest that the extra oxygen is incorporated between the Bi-O layers with a corresponding distortion. The presence of extra O may transfer more electrons from the Cu-O(1) planes to the Bi-O octahedra, an additional doping effect. Excess Bi^{3+}, as reported in the as-grown superconducting material,[4] will counter dope. Finally, Pb substitution appears to enhance the superconducting onset.[4] This may be a doping effect with the assumption that the Pb substitutes on the Bi site.

The novel feature in the band structure of $CaBi_2Sr_2Cu_2O_8$ is the presence of a conducting reservoir of carriers, the Bi-O planes, which are not themselves expected to exhibit strong correlation effects. The important question is whether these carriers remain in the actual superconducting material. Two relevant issues are the following. First, the indication of a superstructure in the x-ray diffraction data may reflect either a structural

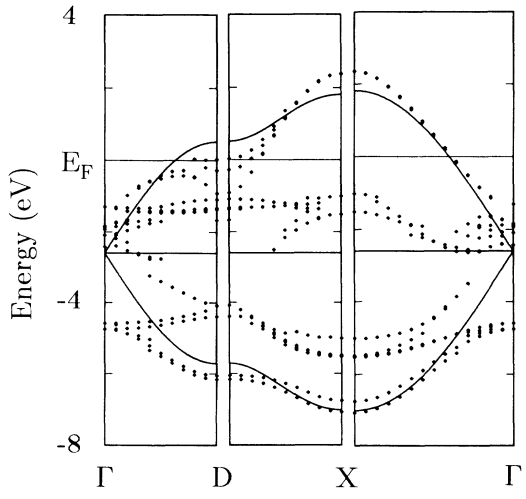

FIG. 4. Selected band dispersion results for the Cu $d_{x^2-y^2}$-O(1) $p_{x,y}$ derived states. The continuous curves represent a tight-binding description of these states, as discussed in the text.

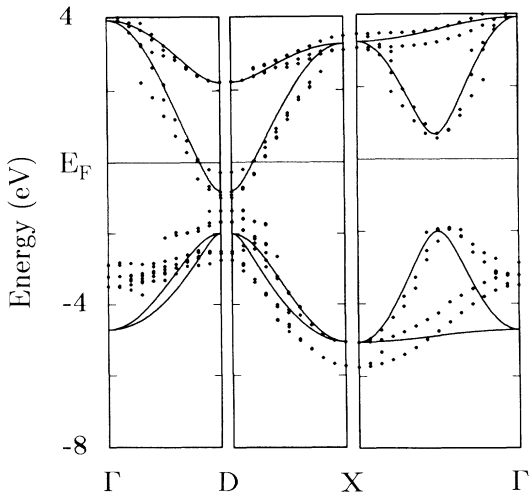

FIG. 5. Same as Fig. 4 for the Bi $p_{x,y}$-O(2) $p_{x,y}$ derived states.

distortion or chemical fluctuations. It is unclear whether this is intrinsic to the superconducting properties. If so, the Bi-O p-band filling may be eliminated if the bond distances are severely changed. Second, the strong correlation of the electrons in the Cu-O planes will lead to a gap in the Cu-O states. The carriers in the Bi-O complex may be transferred back into the Cu-O planes if the lowest Hubbard band for holes in the Cu-O planes does not overlap the Bi-O p bands. This, however, would be countered by the electrostatic dipoles set up by such transfer.

If the Bi-O bands do indeed provide a reservoir of carriers, this should have observable consequences. The stoichiometric compound will be metallic and may be superconducting. The presence of electron pockets near the Brillouin-zone edge may be probed by standard Fermi-surface techniques, e.g., positron annihilation. The presence of carriers in the Bi-O planes will influence relaxation rates in nuclear resonance experiments on Bi. Finally, the degree of doping of the Cu-O planes may well depend on pressure since the position of the Bi-O bands relative to the Cu-O bands will change.

We wish to thank S. A. Sunshine, T. Siegrist, and the other authors of Ref. 4 for making their structural results available to us prior to publication. It is a pleasure to acknowledge useful discussions with M. Schlüter and D. R. Hamann during the course of this work.

[1]C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

[2]H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. Lett. (to be published).

[3]R. M. Hazen *et al.*, Phys. Rev. Lett. **60**, 1174 (1988).

[4]S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. van Dover, R. M. Fleming, S. H. Glarum, S. Nakahara, R. Farrow, J. J. Krajewski, S. M. Zahurak, J. V. Waszczak, J. H. Marshall, P. Marsh, L. W. Rupp, Jr., and W. F. Peck, to be published.

[5]J. M. Tarascon, Y. Le Page, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Hwang, to be published.

[6]L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **28**, 4227 (1983).

[7]L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987); L. F. Mattheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1987), and unpublished.

[8]J. Yu, A. J. Freeman, and J.-H. Xu, Phys. Rev. Lett. **58**, 1035 (1987); S. Massidda, J. Yu, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987).

[9]G. Shirane *et al.*, Phys. Rev. Lett. **59**, 1613 (1987); J. M. Tranquada *et al.*, Phys. Rev. Lett. **60**, 156 (1988).

[10]See, in general, the papers in *Novel Superconductivity*, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987).

[11]M. W. Shafer, T. Penney, and B. L. Olson, Phys. Rev. B **36**, 4047 (1987); K. Takita, to be published.

[12]P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[13]O. K. Anderson, Phys. Rev. B **12**, 3060 (1975); H. L. Skriver, *The LMTO Method* (Springer-Verlag, New York, 1984).

[14]L. F. Mattheiss and D. R. Hamann, unpublished.

[15]U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[16]W. M. Temmerman, G. M. Stocks, P. J. Durham, and P. A. Sterne, J. Phys. F **17**, L135 (1987).