Effect of Bismuth on High-T_c Cuprate Superconductors: Electronic Structure of $Bi_2Sr_2CaCu_2O_8$

Henry Krakauer
Department of Physics, College of William and Mary, Williamsburg, Virginia 23185

and

Warren E. Pickett
Condensed Matter Physics Branch, Naval Research Laboratory, Washington, D.C. 20375

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The electronic structure of the new Bi-based high-temperature superconductor, with T_c onsets above 110 K, is shown to be altered considerably from that of the other cuprate superconductors by the presence of Bi. There are Bi-O bands which cross the Fermi level, and the two-dimensional character of the bands is even greater than that of previous cuprates. As in the other cuprates, band critical points occur at the Fermi level.

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The discovery of high-critical-temperature (T_c) superconductivity[1-5] in a new material which contains no rare-earth element promises to provide useful insights into the pairing mechanism in these unusual cuprates. Bismuth is the new element which distinguishes the newest material, Bi-Sr-Ca-Cu-O, from the 40-K class, $La_{2-x}Sr_xCuO_4$ (2-1-4), and the 90-K class of $YBa_2Cu_3O_7$ (1-2-3). This new material shows a superconducting onset near 120 K, and does not require prolonged high-temperature processing. In ionic materials Bi usually assumes 3+ or 5+ states and if one assumes that the 3+ configuration occurs, it might be supposed that Bi acts much like the trivalent rare earths in providing electrons to the Cu-O complex and stabilizing a structure which is largely ionic in character. In this paper we provide evidence from density-functional calculations that Bi is qualitatively different from the RE (rare-earth) ions in these cuprates, which may account for the distinct properties exhibited by this new material.

The variation from magnetic behavior to high-T_c superconductivity as the oxygen or RE content is varied in the 2-1-4 and 1-2-3 materials suggests that these materials are qualitatively different from the more standard solids which are well described within the band picture. As a result there has been a large effort towards the treatment of these materials within a picture in which there is a large Hubbard repulsion U on the Cu atom, especially in the description of the antiferromagnetism. There are several cases, however, such as elemental Fe and Ni, where there is certainly a sizable on-site U and yet the local (spin-) density approach works surprisingly well. An even more remarkable example is the heavy-fermion metal UPt_3, which displays a variety of unusual properties including highly enhanced specific-heat coefficient and susceptibility, and yet its very complex many-sheeted Fermi surface is predicted[6] correctly by local-density theory. It is plausible that, in the regime where the material shows good metallic behavior, local-density calculations will provide realistic predictions of the electronic structure, bonding, and Fermi surface of the new Bi-based cuprate.

Several reports of a partial identification of the structure of the superconducting phase have been circulated. Tarascon *et al.*[3] have established that the phase can be indexed approximately to a quasitetragonal parent cell with one formula unit of stoichiometry near $Bi_2Sr_2CaCu_2O_8$ (referred to as 2-2-1-2). Their work is in general agreement with other structural studies[2-5] which show that the high-T_c phase is slightly distorted to an orthorhombic structure of dimension $\sqrt{2}a \times 5\sqrt{2}a \times c$, where $a = 3.814$ Å and $c = 8a = 30.52$ Å. In addition to the distortion, an incommensurate modulation of small amplitude seems to occur in the Bi-O subsystem. In this initial study we investigate the bonding and band structure for the parent tetragonal cell.

The structure, for which the internal parameters are given in Ref. 3, consists of alternating double layers of Cu-O1 planes and Bi-O3 planes, with Ca atoms between the Cu-O1 planes and Sr-O2 planes between the Cu-O1 and Bi-O3 planes. The space group is body-centered tetragonal *I4/mmm*. We have applied the linearized augmented-plane-wave method,[7] which provides a detailed and accurate description of the electronic structure within the local-density approximation. No approximations to the shape of the potential and the density have been made in these calculations, and well converged basis sets and k-point convergence are commensurate with our previous calculation[8] for the 1-2-3 structure.

The total and atom-projected densities of states (DOS) are shown in Fig. 1. As in the 2-1-4 and 1-2-3 materials, the occupied states consist primarily (but not totally; see below) of hybridized Cu d and O p states, and the Fermi level E_F falls in a region of relatively low density of states compared to "traditional" transition-

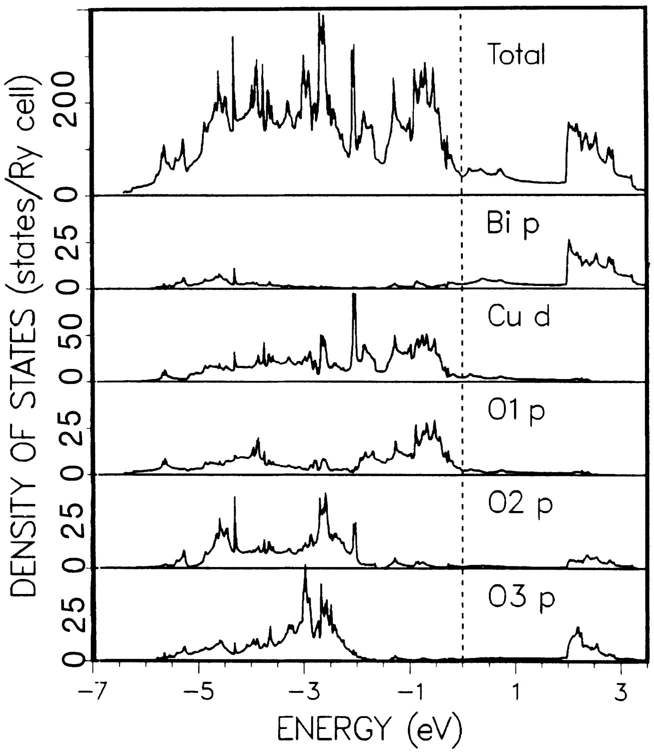

FIG. 1. Total and partial densities of states. Note the Bi, O3, and O2 peaks at 2 eV above E_F (taken as zero), tailing off to E_F and below.

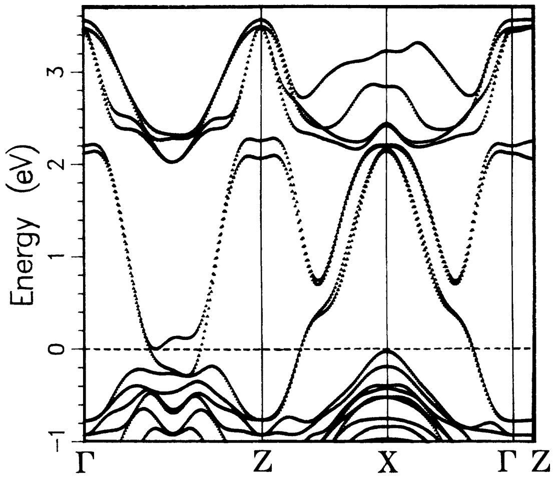

FIG. 2. Band structure in the high-symmetry directions (for $k_z=0$) near and above E_F. Bi-O bands which lie primarily 2-4 eV above E_F disperse downward strongly near the zone boundary (midway between Γ and Z) and cross E_F.

metal superconductors. Unlike the other cuprates, however, (1) there is a significant density of states of the O2 and O3 atoms well above E_F, and (2) the Bi p DOS, which as expected lies primarily above E_F, extends downward to the Fermi level and even below. The density of states at E_F is 2.88 eV/cell, with contributions from the Bi p, Cu d, O1 p, O2 p, and O3 p states of 0.17, 0.33, 0.16, 0.07, and 0.07 eV/atom, respectively.

The origin of the Bi-O DOS tail can be seen in Fig. 2, where the bands near E_F are shown along the high-symmetry directions. The occupied bandwidth for the complex Cu-O bands is 6.5 eV, compared to about 7.0 eV in the 1-2-3 material.[8] As might be expected, the Cu-O layers give rise to bands near E_F which are similar to those in the 2-1-4 system. There are two sets of such bands, one for each Cu-O layer, which are nearly degenerate, which remain completely filled along the ⟨100⟩ direction, but which disperse strongly across E_F in going to the $X=(100)$ corner of the zone. A lower Cu-O band just contacts the Fermi level at the X point.

In addition to these antibonding Cu-O states, however, there are two Bi-O bands 2-3 eV above E_F which disperse strongly *downward* away from the high-symmetry points. Along the (100) direction one of these bands dips below E_F, becomes occupied, and hybridizes with the Cu-O bands in this region. The other Bi-O band just contacts E_F from above. It is striking that this Bi-O band and the Cu-O band at X (mentioned above) tend to pin E_F between them. This feature may be sensitive to oxygen and bismuth concentration. As a result of one Bi-O band's dipping below E_F the Bi, unlike the Sr and Ca ions, is not fully ionized, but retains a small but potentially important amount of valence charge. This bismuth density bonds in a covalent-metallic fashion with the neighboring O2 and O3 ions, and as a result there is a definite peak of unoccupied O3 p states, and to a lesser degree O2 p states, about 2 eV above E_F. The resulting partially covalent character of the Bi-O subsystem may account for the distinct properties of the 2-2-1-2 compound compared to the more ionic 2-1-4 and 1-2-3 materials, such as its comparative softness[3] and the achievement of superconductivity around 80 K without

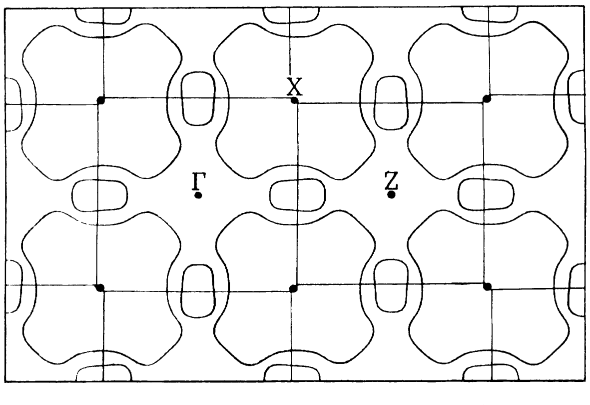

FIG. 3. Calculated Fermi surfaces in the (001) plane. For clarity, we show only one of the two large, nearly degenerate X-centered sheets arising from the Cu-O bonds. The small rounded rectangular electron pockets midway between Γ and Z arise from Bi-O states.

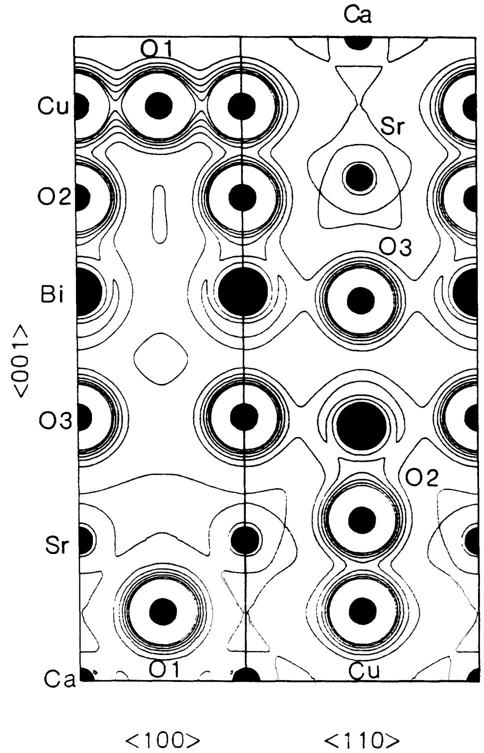

FIG. 4. Contours of the constant valence charge density in two high-symmetry planes. Note the very small density between the two Bi-O3 planes at the center of the figure. Contour values run from 0.005 to 0.105 in steps of 0.02 e/a.u.^{3}.

high-temperature treatment.

Instabilities (charge- or spin-density wave) of the material may be related to the Fermi surface, which is shown in Fig. 3. A pair of large, nearly degenerate surfaces centered at the zone corner (only one of which is shown, for clarity) arise from the bonding and antibonding combinations of Cu d and O p states. These are similar to the corresponding bands in the other cuprates; however, E_F does not fall at half-filling because of the Bi-O band which crosses E_F. The Bi-O band contributes a pair of symmetry-related electron surfaces of rounded rectangular shape, with the major axes lying along the (100) and (010) axes. This Bi-O surface, which has dimensions of $0.30(2\pi/a)\times 0.16(2\pi/a)$, could drive a charge-density-wave formation in the Bi-O subsystem, but these calipers are not related in any obvious way to the charge-density wave which is seen in structural studies.[1-5] The extreme two-dimensionality can be seen from Fig. 3 as well, since the Fermi surfaces look the same from the point of view of the Γ and Z points. This occurs only with vanishing k_z dispersion, and these surfaces are much more two dimensional than the 2-1-4 surface.[9]

The valence charge density in the (100) and (110) planes is pictured in Fig. 4. There is a quite appreciable density around the Bi ion, and it is bonded both to the in-plane O3 ion and with the O2 ion which bridges the Bi and Cu atoms. A remarkable feature is the charge separation between the two Bi-O planes as well as the (expected) similar separation between the two Cu-O planes. This decoupling of the structure into rather isolated CuO1-O2-BiO3 separated on the CuO side by Ca atoms accounts for the extreme lack of dispersion in the band structure, as well as the lamellar, micaceous character[4] of the material.

In conclusion, although there are aspects in common with the previous high-T_c cuprates, the Bi-based material displays important new features related directly to the Bi. It is expected that these differences will lead to quite different bonding character and transport behavior, as well as providing new insights into the mechanism of high-T_c superconductivity.

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