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Electronic band properties of $Ba_2Tl_2CuO_6$

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The electronic structure of body-centered-tetragonal $Ba_2Tl_2CuO_6$, the simplest member of a new family of high-T_c superconducting cuprates, has been calculated with the use of the linear augmented-plane-wave method. The overall results exhibit features that are similar to those of the earlier cuprate superconductors. A unique feature is a pair of slightly filled antibonding Tl(6*s*)-O(2*p*) subbands that decrease the effective valence of the oxygen atoms in the Ba and Tl planes.

High-temperature superconductivity has been reported in the Ba-Tl-Cu-O system.[1] These results have been confirmed and extended to the Ca-Ba-Tl-Cu-O system,[2-4] where onsets as high as ~140 K have been observed. This family of Tl-based superconductors is related chemically and structurally to the recently discovered superconductors in the Ca-Sr-Bi-Cu-O system, which have T_c's in the 80–110 K range.[5,6] The new Tl materials are reported[2] to have body-centered-tetragonal (bct) structures with the *I*4/*mmm* space group. A sequence of related Tl compounds with compositions $Ba_2Tl_2CuO_6$, $CaBa_2Tl_2Cu_2O_8$, and $Ca_2Ba_2Tl_2Cu_3O_{10}$ has been identified.[2,3]

The structure of the simplest member of the new family, which we study here, is shown in Fig. 1. It is seen to consist of a single central CuO_2 layer of the sort present in all the cuprate superconductors, bounded by a pair of BaO layers, which are in turn bounded by a pair of TlO layers. Oxygen atoms in the Cu, Tl, and Ba planes are denoted O(1), O(2), and O(3), respectively. The $(a/2,a/2)$ basal-plane shift accompanying the *c*-axis translation in the bct structure joins the two TlO layers such that each Tl is octahedrally coordinated by O. The more complex members of this family form related structures with added CuO_2 and Ca planes.[2] In common with the isostructural Bi materials, the Tl compounds lack the one-dimensional CuO chains present in the well-studied $YBa_2Cu_3O_7$-type superconductors. They also apparently lack[2,3] the orthorhombic distortions that are present in all the other cuprate superconductors. While T_c increases as the number of CuO_2 sheets increases from 1 to 3, the single-Cu structure is unique in that it produces a T_c as high as ~85 K without multiple sheets. This is to be compared with a maximum of 40 K in $La_{2-x}Sr_xCuO_4$, which also contains a single CuO_2 layer.

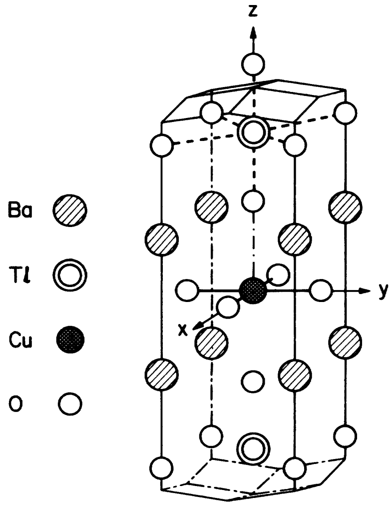

FIG. 1. Structural model for the primitive bct cell of $Ba_2Tl_2CuO_6$.

The main objective of the present investigation is to identify unique aspects of the electronic structure, possibly associated with the TlO double layers, which may enhance the superconductivity of $Ba_2Tl_2CuO_6$ and the related compounds. One expects to find $Cu(d_{x^2-y^2})$-$O(p_{x,y})$ bands that are nearly half-filled, as in La_2CuO_4, $YBa_2Cu_3O_7$, and $CaSr_2Bi_2Cu_2O_8$, since these are generally believed to provide the superconducting carriers in these materials.[7-9] In $CaSr_2Bi_2Cu_2O_8$, a pair of antibonding Bi(6*p*)-O(2*p*) bands also cross E_F.[9] In $Ba_2Tl_2CuO_6$, the O coordination octahedron of the Tl is compressed, with *c*-axis Tl—O bondlengths of 1.98 Å and basal plane Tl—O bondlengths of 2.73 Å,[2] compared to ionic radii sums of 2.80 Å for Tl^{1+}-O^{2-} and 2.35 Å for Tl^{3+}-O^{2-}. Therefore, we might expect some mixed-valent character in the Tl-O complex, manifested as partially filled bands at E_F.

The CuO_2 layers are widely believed to display strong correlation effects in all the high-T_c materials, leaving the applicability of the local-density-functional approximation employed here open to question. Indeed, in the limit that the uppermost band of the CuO_2 layer is exactly half filled (as in stoichiometric La_2CuO_4), the material is an antiferromagnetic insulator, and a Mott-Hubbard description is undoubtedly necessary. Nevertheless, the overall charge distribution and the interlayer electrostatic potentials should be given properly by the local-density method. In particular, the bands of the Tl-O layers should not be influenced by strong correlation effects, and their position and filling should be properly described by this scheme.

Appropriate values of the lattice and internal position parameters for $Ba_2Tl_2CuO_6$ have been estimated from available experimental data,[2] and are given in Table I. We neglect the small displacements of O(2) off symmetry sites in random directions which were found in the x-ray analysis.[2] The self-consistent band structure has been calculated in the local-density approximation with the use of a scalar-relativistic version of the linear augmented-plane-wave (LAPW) method.[10] The implementation imposes no shape approximations on either the charge density or the potential. The LAPW basis has included plane waves with energies up to 11.25 Ry (~750 LAPW's) and spherical-harmonic cutoffs of $l=8$ (Ba, Tl), $l=7$ (Cu), or $l=5$ (O), depending on the muffin-tin radii. The charge density and potential are expanded using ~8000 plane waves (55 Ry) in the interstitial region and by means of lattice-harmonic expansions ($l=6$ for Ba, Tl, and Cu and $l=4$ for O) within the muffin-tin spheres. A ten-point k sample in the $\frac{1}{16}$ irreducible wedge was used to carry out the Brillouin-zone integrations. Exchange and correlation effects have been included with the use of the Wigner interpolation formula.[11] The atomic Ba($5p^6 6s^2$), Tl($5d^{10} 6s^2 6p^1$), Cu($3d^{10} 4s^1$), and O($2s^2 2p^4$) states are treated as valence-band electrons, whereas the more tightly bound core like states are handled using a frozen-core approximation.[10]

The present LAPW results for bct $Ba_2Tl_2CuO_6$ are plotted along symmetry lines in the basal plane of the Brillouin zone and along one c-axis symmetry line (Γ-Z) in Fig. 2. The 25-band complex situated between -7.5 and +2 eV evolves from the atomic Tl($6s$), Cu($3d$), and O($2p$) levels and contains 45 electrons. The "background" nonbonding or π-bonding bands in this complex are identified by points. Certain bands of special interest have been marked by other symbols.

The bands we consider first have predominant Tl(s)-O(2), O(3)(p_z) character, and are denoted by triangles. Note that because of the body-centering translation, Tl is vertically aligned with O(3) in its own unit cell and O(2) in the neighboring cell, and that these bondlengths are short and nearly equal. The upper (0 to +2 eV) and lower (-8.5 to -7.5 eV) pairs of subbands in this set are formally bonding and antibonding combinations of these orbitals.[12] However, the lower pair is in fact dominantly Tl(s) and the upper pair dominantly O(2), O(3)(p_z) in character. From normal valence considerations, we would take all the O atoms as O^{2-}, Cu atoms as Cu^{2+} (as in the other cuprate superconductors), and Ba atoms as Ba^{2+}, which would imply Tl^{3+}. From the calculated bands, however, it is clear that the valence of Tl is closer to 1+, and that of O(2) and O(3) to 1 −, which is certainly an unanticipated result. To complete the discussion of these bands, we note that the third one just crosses the Fermi level at Γ, resulting in a very small electron ellipsoid of Fermi surface. Above E_F, these bands overlap at D with the lower portion of the Tl($p_{x,y}$) bands, denoted by ×'s. The "triangle" bands are predominantly two dimensional, but the upper pair have a few tenths of an eV of c-axis dispersion.

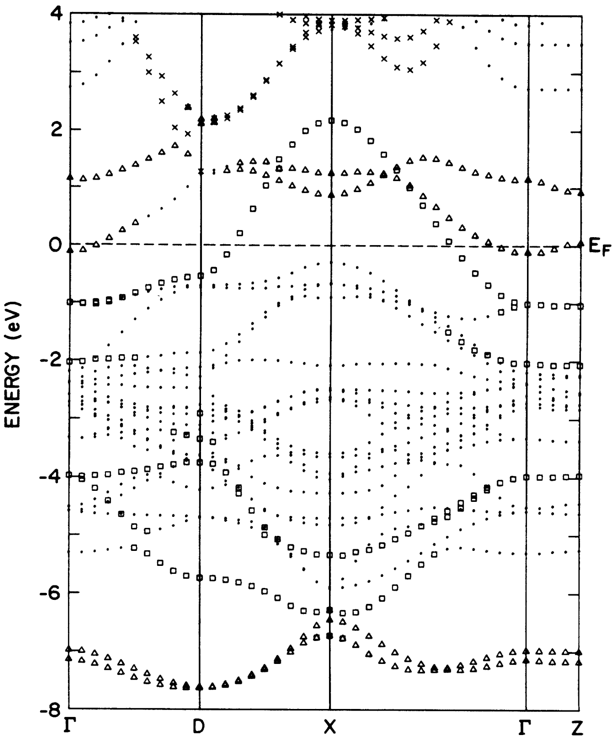

FIG. 2. Energy-band results for $Ba_2Tl_2CuO_6$ along symmetry lines of the bct Brillouin zone, where $D=(\pi/a,0,0)$, $X=(\pi/a,\pi/a,0)$, and $Z=(0,0,2\pi/c)$. Different symbols identify bands of specific orbital character as explained in the text.

TABLE I. Atomic position parameters for bct $Ba_2Tl_2CuO_6$ (space group $I4/mmm$) which have been estimated from the structural results of Subramanian *et al.* (Ref. 2) for $CaBa_2Tl_2Cu_2O_8$, with $a=3.855$ Å and $c=23.0$ Å

Atom	Site	x/a	y/a	z/c
Cu	$2a$	0	0	0.0
Ba	$4e$	$\frac{1}{2}$	$\frac{1}{2}$	0.0870
Tl	$4e$	0	0	0.2040
O(1)	$4c$	$\frac{1}{2}$	0	0.0
O(2)	$4e$	$\frac{1}{2}$	$\frac{1}{2}$	0.2103
O(3)	$4e$	0	0	0.1180

The bands usually considered as active in the cuprate superconductors are the Cu($d_{x^2-y^2}$)-O(1)($p_{x,y}$) subbands.[7-9] These bands are denoted by squares in Fig. 2. They are highly two dimensional as in the other materials, with negligible c-axis dispersion. The σ-antibonding band has its maximum at X and is almost exactly half filled at ideal stoichiometry, as in the other materials. The corresponding bonding band has its minimum at X at -5.3 eV. The "squares" band which lies lowest is in fact the "nonbonding" combination of the O(1)($p_{x,y}$) orbitals. In the simple tight-binding model proposed[7] for these materials, this band is completely dispersionless and sits symmetrically between the bonding and antibonding bands. What is omitted from this simplified picture is the fact that the O(1) ($p_{x,y}$) combination, which is nonbonding relative to Cu($d_{x^2-y^2}$), is bonding relative to Cu(s), and is lowered substantially as a result of this mixing. Another significant departure of the LAPW bands from this model[7] is a lowering of the antibonding band near D which is apparently caused by interaction with the upper "triangle" bands. At half filling, this model band intersects the Fermi level at D and exactly halfway along the Γ-X line. The calculated band intersects E_F 0.23 of the way from D to X and 0.38 of the way from Γ to X. Thus, the perfect Fermi-surface nesting of the model band, which is closely reproduced by calculations[7] for La_2CuO_4, is not even approximately achieved in $Ba_2Tl_2CuO_6$.

The LAPW valence charge density for $Ba_2Tl_2CuO_6$ is illustrated by means of the contour plots in Fig. 3. The strongest bonding occurs along the nearest-neighbor Cu-O(1) directions, as shown in Fig. 3(a). The coupling between the Cu and the O(3)'s along the c axis is seen to be weaker. The c axis O(2) and O(3) bonds to Tl are almost as strong as the Cu−O(1) bond, based on bond-center charge density. Note that the Tl−O(2) bond contours at the top center of Fig. 3(a) join to those in the lower left and right corners in Fig. 3(b) because of the body-centering translation. Figure 3(c) shows that the basal-plane bonding of Tl to O(2) is considerably weaker than the c-axis bonding because of the larger bondlengths. Figures 3(b) and 3(c) show moderate Ba bonding to both O(1) and O(3). By comparison with our calculated charge densities for $CaSr_2Bi_2Cu_2O_8$, the overall interplanar bonding is somewhat stronger, which accounts for the observation[2] that while the Bi materials cleave in micalike sheets, the Tl materials do not.

The density-of-states (DOS) results that are obtained from the present LAPW calculations are shown in Fig. 4. As in the case of the La_2CuO_4, (Ref. 7), $YBa_2Cu_3O_7$ (Ref. 8), and $CaSr_2Bi_2Cu_2O_8$,[9] the total DOS at E_F is relatively low (~1.24 states/eV cell). The near degeneracy of the Cu(3d) and O(1)(2p) orbital energies (~ −2 eV) is apparent visually from the center of gravity of the Cu and $O(1)_2$ projected DOS results. The Tl(s)-O(2), O(3)(p_z) bands discussed above are seen as distinct peaks above and below the Cu-O(1) bands in the Tl_2 and $O(2)_2$ projected DOS results. The intermediate $O(2)_2$ weight involves weaker bonding $p_{x,y}$ bands. The $O(3)_2$ results are similar to those for $O(2)_2$ and are not shown.

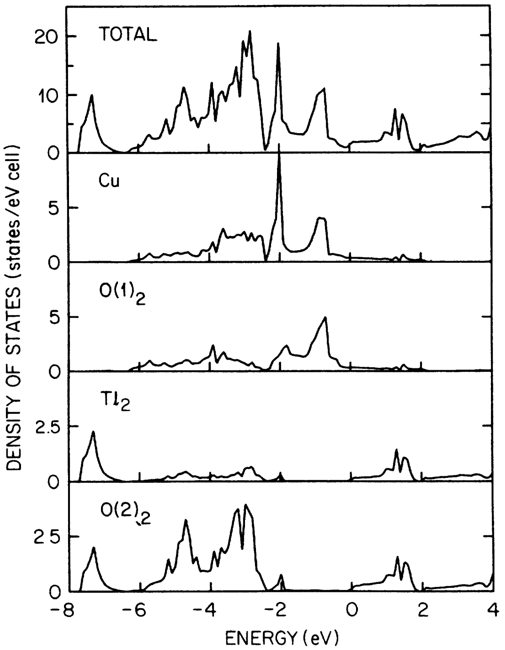

FIG. 4. Total and muffin-tin projected density-of-states results for $Ba_2Tl_2CuO_6$.

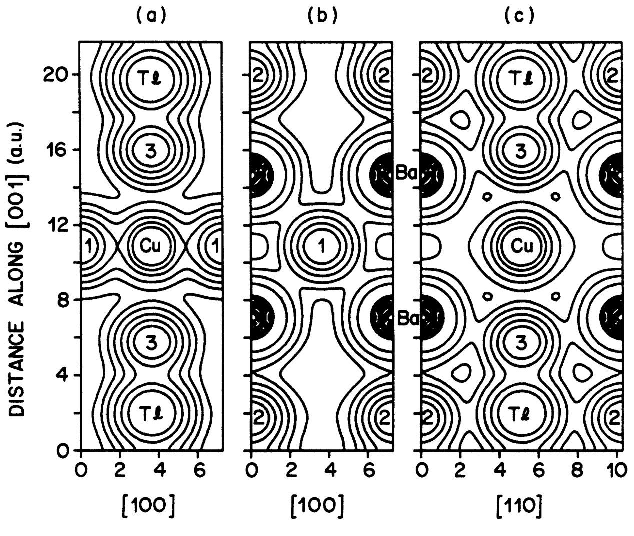

FIG. 3. Charge-density contours on the (a) central (100) plane, (b) noncentral (100) face, and (c) central (110) plane of the primitive bct $Ba_2Tl_2CuO_6$ structure. The oxygens O(1), O(2), and O(3) are labeled 1, 2, and 3, respectively. The innermost Cu and O contour values are 0.46 electrons/a_0^3. The contour increments are spaced lgoarithmically, 3 to the decade (0.46, 0.22, 0.1, etc.).

Since the mechanism of high-T_c superconductivity in the cuprates is not yet established, we can only speculate on the relationship between the special features of the calculated electronic structure of $Ba_2Tl_2CuO_6$ and this phenomenon. It is generally believed that the active superconducting carriers correspond to extra holes in the antibonding Cu-O band that reduce the filling below a half. It has been proposed[13] that these holes will be primarily on the oxygens in the Cu planes [represented by O(1) in the present structure]. In previously studied materials, the remaining O's were found to have essentially filled 2p shells.[7-9] The present results show that O(2) and O(3) have substantial hole concentrations in $Ba_2Tl_2CuO_6$, and presumably in the other members of this family with 2 and 3 Cu layers. The modest filling of these triangle subbands in Fig. 2 depends critically on the vertical Tl−O(2) and Tl−O(3) bondlengths in Fig. 1. Larger bondlengths would increase the filling of these subbands and provide semimetallic behavior in the Tl-O layers similar to that in $CaSr_2Bi_2Cu_2O_8$. In the present case, these bands are essentially insulating, so it is not clear how these limited carriers could contribute significantly to superconductivity in these materials. At a minimum, however, they provide a new source of final states for low-energy excitations, which could play a role in an excitonic-coupling mechanism.[14]

Note added: After this work was completed, we obtained measured structural parameters[15] for $Ba_2Tl_2CuO_6$ which proved to be extremely close to our estimates. An 0.06 Å increase of the Cu—O(3) bondlength over our assumed value could slightly lower the triangle band at E_F and increase its metallic character.

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