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Electronic structure of $HgBa_2Ca_2Cu_3O_8$: The role of mercury

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Local-density-approximation calculations are used to elucidate the electronic structure of $HgBa_2Ca_2Cu_3O_8$. Unlike the case in the corresponding single-CuO_2-layer material, there is a Hg-derived band that dips below the Fermi energy, and this hole dopes the cuprate planes. This difference is related to apparent electronegativity differences of one-, two-, and three-layer stacks of CuO_2 planes.

I. INTRODUCTION

Putilin *et al.*[1] have recently reported the synthesis of a new cuprate phase, $HgBa_2CuO_{4+\delta}$ that is metallic and superconducting with a critical temperature of $T_c = 94$ K. Except for the presence of approximately 8% excess oxygen in the samples, the crystal structure is particularly simple. The primitive tetragonal unit cell contains a single CuO_2 layer, with apical oxygens above and below the Cu ions. Barium ions are present above and below the centers of the cuprate squares (here we take Cu at the corners of the squares and O on the edge centers), and as a rough approximation may be regarded as being in the same plane as the apical oxygens. This single CuO_2 plane with BaO planes above and below it may be regarded as the basic structural unit. These three-layer sheets are stacked with the "glue" provided by Hg ions lying directly between the apical oxygens (excess oxygen is also present in this plane).

Since then, Schilling *et al.*[2] have observed a record T_c of 133 K in multiphase samples containing analogous compounds with two and three CuO_2 layers per unit cell, in addition to ordered superstructures. Detailed structural information is, however, not available at present. Further, the highest-T_c superconducting phase has yet to be identified. Possibilities are the single-layer material with different stoichiometry (T_c can be strongly dependent on the doping level), the two-layer material, the three-layer material, or the ordered superstructure. If the Hg system follows the pattern of the Tl-based materials, $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ (N.B. *two* $Tl^{3+}O^{2-}$ layers have the same formal valence as a *single* Hg^{2+} layer), the highest T_c would be expected in the three-layer compound. In the present paper, the electronic structure of this compound is elucidated using local-density-approximation (LDA) calculations. Such electronic structure calculations have become increasingly important in the effort to formulate a theory of the normal and superconducting states in high-T_c compounds.[3] The electronic structure is found to be qualitatively different from that of single-layer $HgBa_2CuO_4$.

The LDA electronic structure of stoichiometric $HgBa_2CuO_4$ was reported shortly after the discovery of that single-CuO_2-layer material.[4] Remarkably, the band structure displayed only the Cu-O $pd\sigma^*$ antibonding band that is characteristic of the layered cuprates crossing the Fermi energy (E_F); a Hg-derived band approached from above, but did not touch E_F along the X-R line in the Brillouin zone. Accordingly, the Cu-O $pd\sigma^*$ band is predicted to be exactly half filled in the stoichiometric material, which should then display insulating behavior as do the other undoped layered cuprates (e.g., La_2CuO_4). This means that the metallic character and superconductivity observed in $HgBa_2CuO_{4+\delta}$ is due entirely to off-stoichiometry. In contrast, the present calculations show that the three-layer material $HgBa_2Ca_2Cu_3O_8$ is self-doped, i.e., in the *stoichiometric* material the CuO_2 layers are hole doped by the Hg layer.

II. COMPUTATIONAL METHODS

Underlying any electronic structure calculation is the crystal structure of the material. However, as mentioned, the crystal structure of $HgBa_2Ca_2Cu_3O_8$ has yet to be reported. Accordingly, a structural model was employed. In particular, the known structure of the analog, $TlBa_2Ca_2Cu_3O_9$ with the TlO plane replaced by a Hg plane was used.[5] One indication of the extent of the error in this model comes from the lattice parameters, which have been measured. The c- and a-lattice parameters are 1.3% and 2% smaller in $TlBa_2Ca_2Cu_3O_9$ than in $HgBa_2Ca_2Cu_3O_8$. In order to provide an assessment of the errors that might result from the use of this model, parallel calculations were performed with the lattice parameters increased to the measured values in $HgBa_2Ca_2Cu_3O_8$ but the other structural parameters held fixed.

The present self-consistent calculations were performed within the LDA with the Hedin-Lundqvist exchange-correlation function.[6] A local-orbital extension[7] of the general potential linearized-augmented-plane-wave (LAPW) method[8,9] was employed. This method imposes no shape approximations to either the potential or charge density, making it well suited to materials with low site symmetry. A well-converged basis of approximately 2000 LAPW's plus 84 local orbitals was used.[10]

The use of the local-orbital extension of the LAPW method allowed the inclusion of high-lying extended core states as valence states. The states included in this way were the Cu 3s and 3p, O 2s, Ba 5s and 5p, Ca 3s and 3p, and the Hg 5p and 5d. (Additional local orbitals were used to relax the linearization of the Cu 3*d* states.) These upper core states and the valence states were treated in a scalar relativistic approximation. Calculations on one-layer $HgBa_2CuO_4$ have shown that spin-orbit effects do not significantly modify the band structure near the Fermi energy.[4] The lower-lying core states were treated fully relativistically in a self-consistent spherical approximation.

The iteration to self-consistency was performed using a sampling of 20 special points[11] in the irreducible $\frac{1}{16}$ of the Brillouin zone. The electronic density of states (DOS) was obtained from eigenvalues at 84 uniformly distributed *ab initio* **k**-points in the wedge.

III. RESULTS

The principal result of this calculation is the band structure, which is displayed along symmetry directions in Fig. 1. Although it has similarities to that of $HgBa_2CuO_4$, there are also important qualitative differences. The electronic density of states (DOS) and projections onto the various LAPW spheres are displayed in Fig. 2. Fermi surfaces in the $k_z=0$ and $k_z=\frac{1}{2}$ (in reciprocal lattice units) planes are displayed in Fig. 3.

The band structure near E_F is dominated by the three CuO_2 derived $pd\sigma^*$ antibonding bands that are characteristic of the layered cuprates (each layer contributes one; the actual bands are linear combinations). These bands lead to three large barrel sections of Fermi surface, flattened along the *X*-*M* and equivalent directions. There is one additional band that crosses E_F; this largely unoccupied band has substantial Hg *p*-like character and dips below E_F around the *X*-*R* line in the Brillouin zone. The band minimum is at *R* and is 0.19 eV below E_F; the dispersion from *R* to *X* is extremely small (0.7 meV). This results in a small electronlike Fermi surface, con-

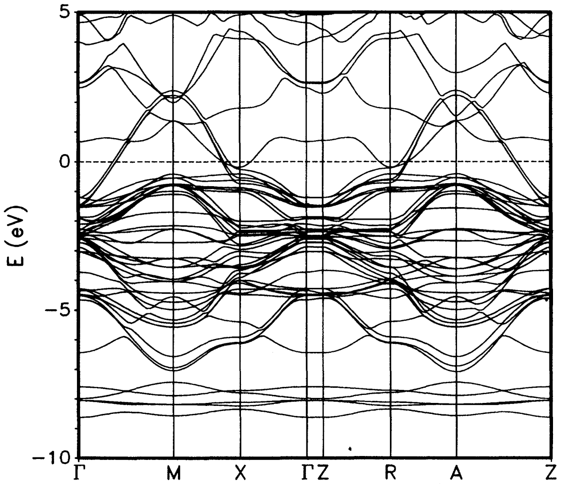

FIG. 1. Electronic band structure of $HgBa_2Ca_2Cu_3O_8$ along symmetry directions. The plot is such that the small *c*-axis dispersion is reflected in the lack of symmetry with respect to the midpoint of the Γ-*Z* line. The horizontal dashed line denotes the position of the Fermi energy. The lowest-energy five bands shown are the Hg 5*d* manifold.

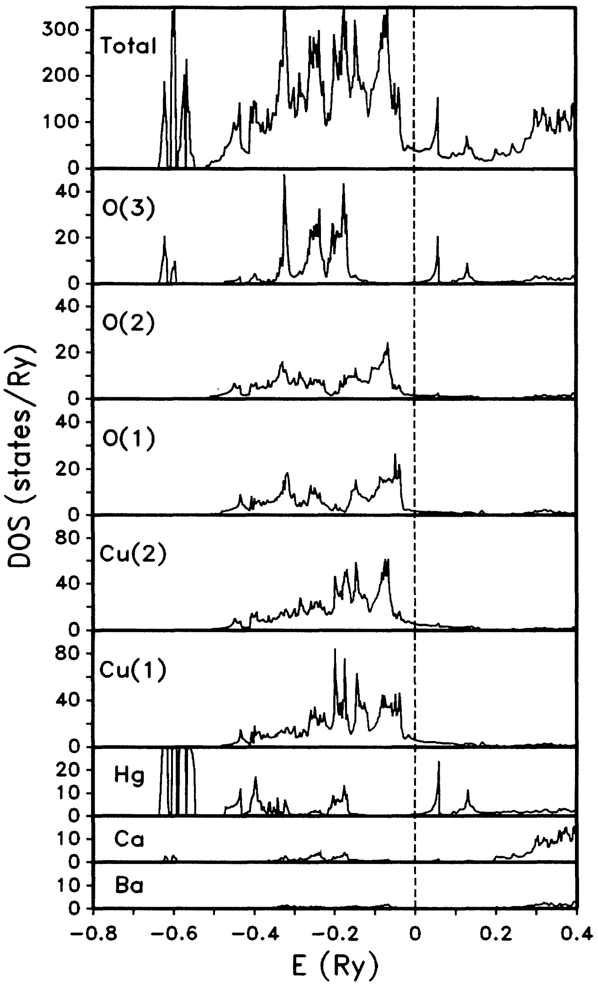

FIG. 2. Total DOS (top panel) for $HgBa_2Ca_2Cu_3O_8$ and local site DOS on a per atom basis for each of the independent sites. O(1) is in the central Cu(1) layer, O(2) is in the Cu(2) layer, and O(3) is the apical oxygen. The local site DOS are from projections of the charge in each state onto the LAPW spheres.

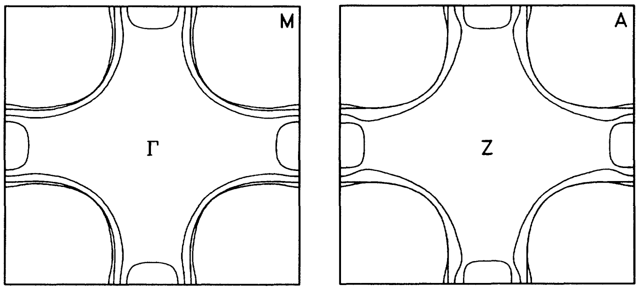

FIG. 3. Fermi surface cross sections in the basal plane $k_z=0$ (left), and in the $k_z=\frac{1}{2}$ plane (right), showing the large Cu-O $pd\sigma^*$ derived barrel surfaces centered on the *M*-*A* line and the smaller Hg related cylinder around *X*-*R*. The *X*(*R*) points are at the edge centers of the figure.

taining approximately 0.1 electrons. The band leading to this Fermi surface hybridizes with the CuO_2 band leading to the outer barrel section, most strongly in the $k_z=\frac{1}{2}$ plane; the small Fermi surface in this plane has mixed CuO_2 and Hg character, and the character changes significantly over the Fermi surface. This is reminiscent of the behavior seen in calculations for stoichiometric $Bi_2Sr_2CaCu_2O_8$.[12–15]

As may be seen from Figs. 1 and 3, the electronic structure is quite two-dimensional, particularly near E_F. The small deviations from two-dimensionality are shown in the form of a deviation from mirror symmetry with respect to the midpoint of the Γ-*Z* line in the band structure as plotted in Fig. 1 and in differences between the $k_z=0$ and $k_z=\frac{1}{2}$ Fermi surfaces. Thus the *c*-axis dispersion may be seen by folding the band structure of Fig. 1 relative to the midpoint of the Γ-*Z* line. The largest dispersions near E_F are for the small electron section and the outer barrel section; the maximum is 0.05 eV, but *c*-axis dispersions approaching this occur only in a small region where these two Fermi surfaces approach each other.

The distribution of the O 1*s* core levels contains useful information reflecting the different site potentials in the material. In general, core eigenvalues calculated within the LDA are underbound. Nonetheless, the variations between them are reproduced because the site potentials are well described. The calculated core eigenvalues for $HgBa_2Ca_2Cu_3O_8$ are −36.816, −36.830, and −36.914 Ry relative to E_F for the central layer [O(1)], the outer layer [O(2)], and the apical [O(3)] oxygens, respectively. The difference of approximately 1.3 eV reflects a larger difference in site potential between the plane and apical oxygens in this material as compared to $HgBa_2CuO_4$ (where the difference is 0.94 eV).[4] The central and outer layer Cu core levels follow the same pattern, in that the outer layer core levels are deeper. Cu 2*s* eigenvalues relative to E_F are −77.735 and 77.742 Ry for the Cu(1) and Cu(2) sites, respectively.

As mentioned, the accuracy of an electronic structure calculation depends on that of the crystal structure underlying it. Therefore, an additional calculation with different lattice parameters (see Sec. II, above) was performed, in order to quantify the errors that may have resulted from the use of a model crystal structure. Although the increased lattice parameters do alter the band structure, the changes near E_F are not large, and in particular the result that the Hg-derived band dips below E_F along the *X*-*R* line is unchanged (the minimum is shifted 0.05 eV closer to E_F leading to an approximately 25% reduction in the number of electrons contained in the small Fermi surface). A precise calculation using the actual crystal structure would be highly desirable when this structure is determined.

IV. DISCUSSION

The principal result of this study is that the CuO_2-derived bands in stoichiometric $HgBa_2Ca_2Cu_3O_8$ are hole doped away from half filling by the Hg layer. This is analogous to the situation in, e.g., the Tl-based series,[16–18] but with an interesting difference. That is, in the entire Tl-based series ($Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$, $n=1,2,3$) the Tl-O–derived "dopant" band dips below E_F, whereas in the Hg series ($HgBa_2Ca_{n-1}Cu_nO_{2+2n}$, $n=1,3$) this is not the case. Stoichiometric $HgBa_2Ca_2Cu_3O_8$ is predicted to be self-doped but $HgBa_2CuO_4$ is not.[4]

This can be partially understood based on the electronegativity of stacks of CuO_2 layers; two- and three-(more so) layer stacks seem to be less electronegative than a single layer. This may be seen by comparing the band structures of analogous one-, two-, and three-layer compounds for which band structures have been reported. Although the "dopant" band does dip below E_F in single-layer $Tl_2Ba_2CuO_6$, it does so by only 0.14 eV.[17,18] In contrast, the corresponding band dips 0.20 eV below E_F in the two-layer material and 0.25 eV below in the three-layer compound.[16] This variation of about 0.1 eV is to be compared to the larger variation of about 0.3 eV in the Hg-based materials. This no doubt has to do with chemical differences between the Hg vs double TlO layers. I speculate that the significant difference is the absence of O^{2-} ions in the Hg layer; these ions are large and highly polarizable and therefore may screen the changes in potential arising from differing numbers of CuO_2 layers in the Tl-based series.

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