Unconventional Oxygen Doping Behavior in $HgBa_2Ca_2Cu_3O_{8+\delta}$

David J. Singh and Warren E. Pickett
Complex Systems Theory Branch, Naval Research Laboratory, Washington, DC 20375

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Local density approximation supercell calculations for $(HgBa_2Ca_2Cu_3O_8)_2O$ are used to elucidate the effects of oxygen doping on $HgBa_2Ca_2Cu_3O_8$. The CuO_2 planes are found to be hole doped by the addition of O in the O(4) site. The doping level is considerably lower than would be predicted assuming that O enters as O^{2-} ions. Rather, strong covalency is found between the dopant O(4) and Hg atoms. States associated with the neighboring Hg atoms are pushed up in energy by occupation of the O(4) site to the extent that some antibonding O(4)-*p* Hg-*d* states occur above the Fermi energy. Thus the hole doping of the CuO_2 layers is reduced by nearly half from that expected from ionic considerations, and this is accompanied by a coalescence of the three plane derived Fermi surfaces.

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The discovery of record high superconducting critical temperatures (T_c) [1–3] combined with favorable properties for applications [4–6] in layered Hg-Ba-Ca-Cu-O compounds has stimulated intense activity aimed at understanding the properties and underlying mechanisms in these materials. Bulk samples of one, two, and three CuO_2 layer containing phases (denoted Hg-1201, Hg-1212, and Hg-1223) have been synthesized [1,3,7] and detailed structural refinements performed [8–12]. The observation of superconductivity at 150 K and above in the Hg-1223 system under pressure [13,14] has caused a further increase in interest in these materials, since it raises the hope that suitable chemical modifications may also increase T_c into the 150 K and above range. It has been suggested [13,14] that the strong increase in T_c under pressure implies that the CuO_2 planes in the Hg-1223 system are underdoped, making it crucial to improve our understanding of doping in the Hg containing cuprates.

The compounds, whose chemical formulas may be written as $HgBa_2Ca_{n-1}Cu_nO_{2+2n+\delta}$ where n is the number of Cu-O layers, contain stacks of square planar CuO_2 sheets separated by Ca ions, analogous to the Tl and Bi containing homologous series. Above and below each stack is a BaO plane with the O in the apical position directly above (below) the neighboring plane Cu ion. These units stack in the *c*-axis direction with intervening Hg ions twofold coordinated by the apical O atoms. This structure leaves a rather large open space surrounded by positive ions (Hg and Ba) in the plane of the Hg ion. This site [denoted O(4) in Hg-1223] is partially filled with O and accounts for the δ in the chemical formulas. Substantial variations in superconducting properties are observed when δ is varied by annealing or high pressure synthesis [9,12,15]. Measured values of δ in high-T_c samples are approximately 0.06 in Hg-1201, 0.22 in Hg-1212, and 0.4 in Hg-1223. Lowered values yield lower T_c; increasing δ to 0.35 in Hg-1212 also results in lower T_c [12]. Assuming fixed Ba, Ca, and Hg valences of +2 and apical and Hg layer O valences of −2, a doping level of the CuO_2 planes of $2\delta/n$ holes per Cu ion is obtained. This corresponds to 0.12, 0.22, and 0.27 holes per Cu atom for Hg-1201, Hg-1212, and Hg-1223, respectively. These values for Hg-1212 and Hg-1223 are considerably higher than the optimum doping levels found in other high-T_c cuprates and would seem at odds with the observed decrease in T_c in reduced samples and the strong increases in T_c found under pressure. Clearly, an understanding of the role of the Hg layer O and related effects are crucial for optimizing superconductivity in these compounds.

Density functional calculations within the local density approximation (LDA) have become an important tool in understanding the high-T_c cuprates. A number of studies have shown that it accurately describes the Fermiology and properties related to the charge distribution among the various ions including, for example, phonon frequencies and structural parameters [16].

Several theoretical studies reporting LDA electronic structures for the stoichiometric ($\delta = 0$) compounds have been carried out [17–21]. These show that the CuO_2 plane in Hg-1201 is undoped, while slight self-doping is present in Hg-1212 and Hg-1223. They also find a large sensitivity of the positioning in energy of the Hg derived electronic states to the number of CuO_2 layers as compared to the corresponding TlO derived structure in the Tl series. Here supercell calculations for O doped Hg-1223 are used to elucidate the effects on the electronic structure of partial occupation of the O(4) site. Strong covalency between O(4) and Hg atoms is found along with incomplete occupation of the O *p* states. The implication is that the doping level of the CuO_2 planes is considerably lower than expected from formal ionic considerations.

Self-consistent LDA calculations were performed using a local orbital extension of the general potential linear augmented plane wave (LAPW) method [22,23] for undoped Hg-1223 using the neutron refined structure of Chmaissem *et al.* [10] with the exception that the O(4) sites were kept vacant. In order to take account of the partial occupancy of the O(4) site a parallel calculation was performed for a doubled $c(2 \times 2)$ tetragonal $P4/mmm$ unit cell in which every second O(4) site was occupied (Fig. 1), corresponding to $\delta = 0.5$ as compared to the experimentally determined value $\delta = 0.41$. These scalar relativistic [24] calculations were performed using a well converged basis set consisting of approximately 3100 LAPW's [25]. Additional local orbitals were used to relax the linearization of the Hg $5d$ and Cu $3d$ bands as well as to include the upper lying extended core states associated with the Ca and Ba ions. Self-consistency was obtained using a set of three special **k** points in the irreducible $\frac{1}{16}$ of the Brillouin zone. The electronic density of states (DOS) was determined using a 30 **k** points in the wedge.

The band structure and corresponding DOS and projections [26] are given in Figs. 2 and 3, respectively. As may be expected the Hg layer derived electronic structure is strongly affected by partial occupation of the O(4) site. The Hg $5d$ bands are raised by approximately 2 eV relative to the Fermi energy (E_F) and are broadened. Moreover, the Hg derived band that dips below E_F in the stoichiometric material, leading to a small level of self-doping is pushed well above E_F and no longer contributes to the doping. Also, the occupation of the O(4) site does hole dope the CuO_2 planes. This is evident, for example, from examining the position of the plane derived electronic structure relative to E_F. Interestingly, the doping level is such that E_F falls almost exactly on a peak in the plane derived density of states [27], which is related to a van Hove singularity that has been discussed in the context of high T_c in these materials [21].

There are remarkable unexpected effects visible in the electronic structure as well. First of all, strong hybridization involving the Hg and O(4) atoms is evident in the DOS. Second, there is considerable Hg layer O p derived weight in the DOS at and above E_F. This is from antibonding combinations primarily of Hg($5d$)-O(p) orbitals, with a smaller but significant admixture of apical O p_z states. The dispersion of these flat bands near E_F can be reproduced with a simple tight binding model with $|t(pd\sigma)| = 1$ eV and $\varepsilon(p) - \varepsilon(d) \approx 5$ eV. While the details of the bands giving rise to this weight will no doubt be sensitive to the disorder that is present, the covalency and the incomplete ionicity of the O(4) atom revealed in the present calculation are expected to persist.

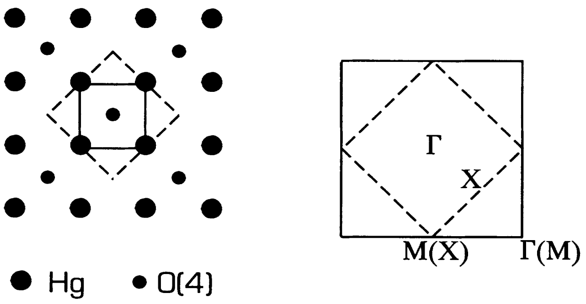

FIG. 1. Structure of the $c(2 \times 2)$ $(HgBa_2Ca_2Cu_3O_8)_2O$ supercell in the Hg-O(4) plane (left) and the Brillouin zone in the $k_z = 0$ plane (right). The symmetry points of the folded zone (dashed lines) are in parenthesis while those of the original 1×1 zone (solid lines) are not.

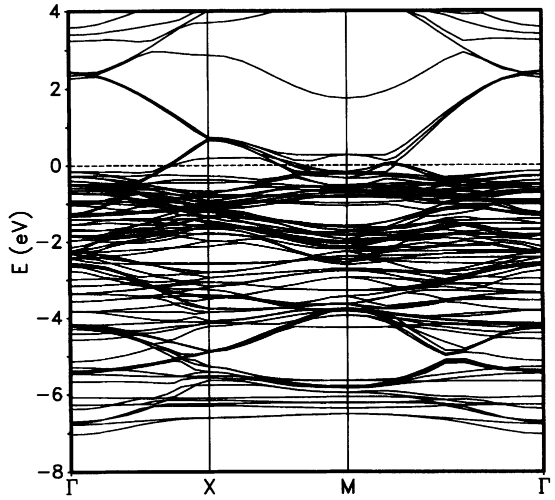

FIG. 2. Calculated band structure in the $k_z = 0$ plane of the doubled $(HgBa_2Ca_2Cu_3O_8)_2O$ supercell. The dashed horizontal line denotes the Fermi energy. Note that the M point corresponds to the X point in unfolded zone, while the original M point is folded back to Γ. Thus the point labeled X is the midpoint of the Γ-M line in the unfolded zone.

This open shell nature has important implications for the doping of the CuO_2 layers and for the superconductivity. In particular, in previous estimates of the doping level of the CuO_2 planes and ionic model has been assumed. However, the present calculations show that such a model is clearly inappropriate and that the doping level is considerably lower than two holes per occupied O(4) site. In fact the DOS implies a doping level close to 1 electron per occupied site. This partial occupation leads to the unusually high O(4) p contribution to the DOS near E_F. We have analyzed the charge density in terms of overlapping atomic charges [28]. Although such decompositions are not unique, they are often useful in understanding bonding in nearly ionic materials. A reasonable [0.06e deviation for the charge in the O(4) sphere and 0.08e in the Hg sphere charge] fit is found using an O(4) charge of -1 (model I). An alternate ionic model, II, with the same cation charges but an O(4) charge equal to the other oxygen charges as was found reasonable for the chain, plane, and apical O in $YBa_2Cu_3O_7$ [28] yielded deviations 3 times larger, while an O(4) charge of 2− yielded a still larger deviation. Calculations of the band energies at Γ for these ionic densities support this. The main O(4)-$2p$–HG-$5d$ energy difference is approximately 5 eV for the self-consistent potential. The compares to 5 eV for I but 8 eV for II; assuming near O^{2-} puts much O(4) $2p$ weight above E_F, inconsistent with the assumption.

The estimate of the doping level may be made more quantitative by considering the Fermi surfaces (Fig. 4).

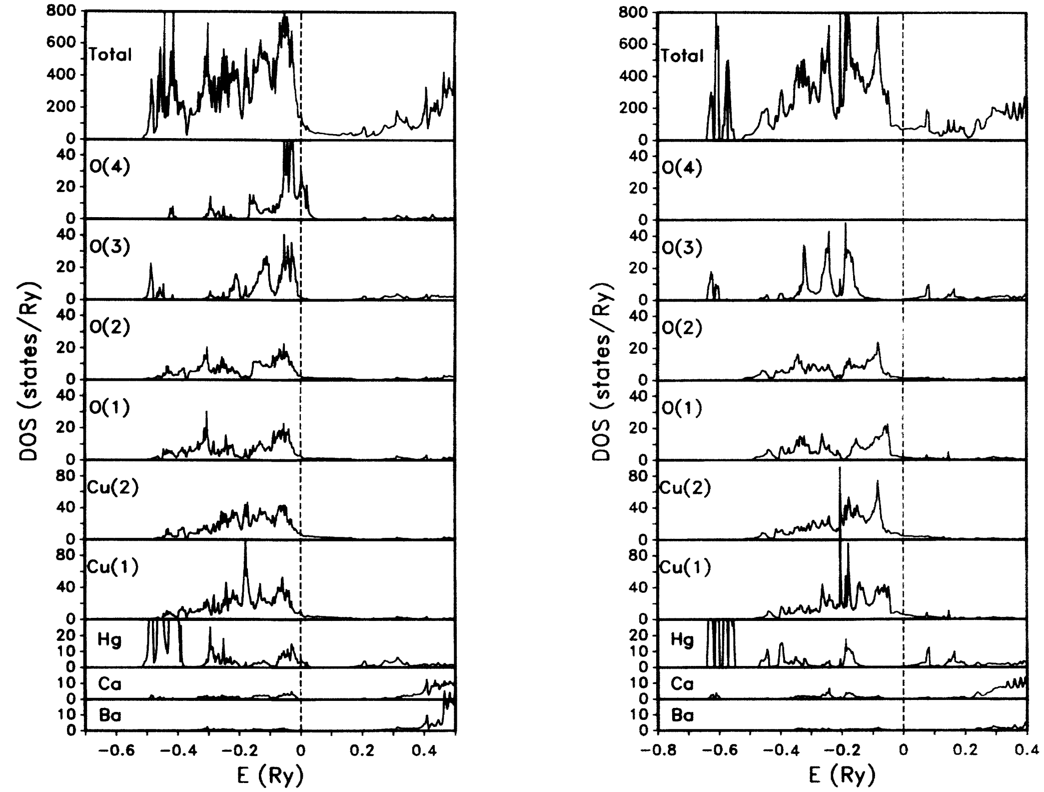

FIG. 3. Electronic DOS and its projections onto LAPW spheres for the $(HgBa_2Ca_2Cu_3O_8)_2O$ (left) supercell and for undoped Hg-1223 (right). The projections are on a per atom basis, while the total DOS is for the doubled unit cell (i.e., Hg-1223 formula units). The dashed lines denote the Fermi energy.

While some distortion may be noted, the CuO_2 barrel sections are essentially intact [29] and comprise the mouth shaped sections around the X points and the square sections around the M points. The prominent square sections around Γ are primarily Hg-O(4) derived, as determined by the wave function character of the band that gives rise to them. These surfaces contain an area equal to almost exactly half the zone. This Fermi surface may be strongly smeared by disorder that exists in the Hg-O layers. Nonetheless its area can be used to estimate the doping level. Thus a doping level, in the CuO_2 bands, of one additional hole per occupied O(4) site is obtained.

It is instructive to compare to the doping in the Tl materials, $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$, where n is the number of CuO_2 planes. Assuming ideal Tl^{3+} and O^{2-} ions no doping is obtained for the stoichiometric materials, as in the Hg series assuming Hg^{2+}. In the Tl based compounds, covalent interactions in the Tl-O layer modify this ideal behavior, contributing holes to the CuO_2 planes. For the $n = 2$ compound there are approximately 0.06 hole per Tl layer O, corresponding to a deviation from ideal ionic behavior of 0.06 electron per TlO unit [30]. This small difference is divided among the Tl and O ions. Similar results are found for the other members of the series [30–32]. In $HgBa_2Ca_2Cu_3O_{8.5}$ we find a deviation of 1 electron per Hg layer O from ideal ionic behavior. This is closer to the behavior of the chain O in $YBa_2Cu_3O_{7-\delta}$, although the deviation from ionic behavior is greater for the O(4) site in the Hg system.

Taking these results into account we estimate a doping level for $\delta = 0.41$ samples of 0.14 hole per Cu atom. This is equal to or slightly lower than the optimum doping levels estimated for other high-T_c cuprates. For $\delta = 0.5$, corresponding to our calculation, a doping level of 0.17 hole per Cu atom is estimated. Considering models in which proximity of E_F to van Hove singularities is important, the present calculations suggest that $\delta = 0.5$ is near the optimum doping level and may lead to higher

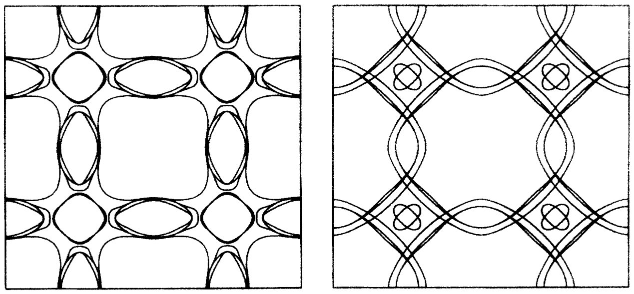

FIG. 4. Repeating zone $k_z = 0$ Fermi surfaces of the $(HgBa_2Ca_2Cu_3O_8)_2O$ supercell (left) and of undoped Hg-1223 folded into the same zone (right). The Γ point is at the corners, edge centers, and center of the plot.

critical temperatures. This is also consistent with the observed pressure dependence of T_c. Because of the disorder in the Hg-O layers, the local atomic structure will differ somewhat from that assumed in the present calculation, which could have a small quantitative effect on our estimate. It is noteworthy that the CuO_2 plane derived Fermi surfaces in the doped material (Fig. 4) are nearly coincident, reflecting an equal distribution of the holes among the CuO_2 barrel bands. This is in contrast to the behavior in the undoped material, and cannot be reproduced by a rigid band lowering of the Fermi energy. Rather, this effect is likely due to a rapidly rising energy cost as the doping level increases, leading to a tendency for all three planes to have the same doping level. Accordingly, we expect a similar effect to occur generally in three CuO_2 layer high-T_c materials with increasing doping. The energy cost may, however, be too large to achieve uniform doping in compounds with four or more layers due to the additional Coulomb repulsion of doped layers, accounting for their drop in T_c. The coincidence of the three barrel bands will enhance the effects of any features like nesting, saddle points, or the like since these would occur for the same energy and crystal momentum for all three bands.

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[24] The core states were treated fully relativistically in a spherical approximation.
[25] LAPW sphere radii of 2.1, 2.5, 1.9, 1.9, and 1.55 a.u. were used for the Hg, Ba, Ca, Cu, and O atoms, respectively.
[26] Projections are obtained by weighting each state φ by its contribution $\int \varphi^* \varphi$ over the LAPW sphere in question.
[27] There is a strong Hg-O(4) derived peak also at this energy. This is expected to be smeared by disorder in the Hg-O(4) layer. The CuO_2 related peak is not, however, caused by the occupation of the O(4) site as is evident from the fact that it also occurs in the DOS for undoped Hg-1223.
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