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# Electronic structure of $LaBa_2Cu_2NbO_8$ and related candidates for high-$T_c$ superconductivity

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The nominally tetragonal, triple-perovskite compound $LaBa_2Cu_2NbO_8$ contains a pair of $CuO_2$ layers that are separated by an oxygen-free La layer as well as a BaO-$NbO_2$-BaO triple layer. The results of linear augmented-plane-wave band calculations for this (and a proposed isoelectronic Ti) compound exhibit electronic features near $E_F$ (i.e., a pair of nearly degenerate, half-filled Cu $d_{x^2-y^2}$-O $p_{x,y}$ $\sigma$-antibonding subbands) that are characteristic of known cuprate superconductor parent compounds. This suggests that high-$T_c$ superconductivity may be possible in appropriately doped $LaBa_2Cu_2NbO_8$-, $LaBa_2Cu_2TaO_8$-, or $BaLa_2Cu_2TiO_8$-type samples (or their chemical equivalents), although initial efforts have been unsuccessful thus far in the case of the group-V–type materials.

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Since the discovery of high-temperature superconductivity ($T_c \sim 30$ K) in the La-Ba-Cu-O system by Bednorz and Müller,[1] a wide variety of other cuprate superconductors has been synthesized, with $T_c$'s now extending above 100 K to the 110–125 K range.[2,3] Although the crystal structures for the known cuprate superconductors differ in many details, they all share a common structural element, namely, the presence of one or more $CuO_2$ layers within a quasitetragonal unit cell. Within these electronically active $CuO_2$ layers, neighboring $CuO_2$ square complexes are joined by oxygen-sharing vertices along the [100] and [010] axes, thereby providing the strong Cu $3d$–O $2p$ hybridization effects near $E_F$ which are an important feature of the cuprate superconductors.

In general terms, the crystal structures for these cuprates consist of one or more perovskite-type cells stacked along the $c$ axis. A systematic description of the various stacking constituents in terms of block layers has been provided by Tokura and Arima.[4] In most cases, the crucial $CuO_2$ subunits in neighboring primitive cells are structurally and chemically isolated by semiconducting rocksalt-type (or fluorite-type) bilayers (trilayers), which also introduce a body-centering translation. The rocksalt bilayers can be formed either by the outermost faces of the perovskite subunits (as in $La_2CuO_4$) or by the insertion of extra monoxide layers (e.g., TlO, BiO). Since these rocksalt or fluorite buffer layers consist of oxides with relatively large cations, the obvious choices for these constituents (i.e., Ca, Sr, Ba, Y, La, Tl, Pb, Bi, and rare earths) have been thoroughly explored by materials scientists.

In searching for new classes of cuprate superconductors, it is necessary to explore alternative schemes for joining the $CuO_2$ layers of neighboring units cells while preserving their structural and electronic isolation. One interesting possibility is suggested by the Aurivillius phases,[5] a series of tetragonal layer compounds (i.e., Bi-Ti-O, Bi-Nb-Ti-O, Bi-Ta-Ti-O, etc.) with Ti, Nb, and Ta constituents which have lattice parameters ($a \approx 3.84$ Å) and nearest-neighbor oxygen bond distances ($\sim a/2$) which are comparable to those of typical cuprate superconductors ($a \approx 3.80$–$3.85$ Å). Since the $d$ bands for these constituents fall 3.0–3.5 eV above the O $2p$ bands in related semiconducting perovskite compounds[6] (i.e., $SrTiO_3$, $KTaO_3$), it is reasonable to expect that one might form new high-$T_c$ candidate materials by interrupting the $c$-axis stacking of cuprate-type perovskite cells with structurally similar semiconducting perovskite layers. In contrast to the rocksalt or fluorite layers which are rotated by 45°, the present compounds would maintain the vertex-oxygen sharing feature in both the $CuO_2$ and semiconducting layers, thereby producing a simple-tetragonal structure.

Clearly, a basic problem with these proposed materials is that they must maintain an ordered layer structure despite the fact that the transition-metal constituents have similar ionic sizes. For example, recent studies[7] of the Y-Ba-Cu-W-O system reveal the formation of a three-dimensional superlattice with $YBa_2Cu_2WO_{9-\delta}$ composition and a fcc structure rather than the desired layer configuration. However, in studies involving the substitution of Ta for Cu (at the chain site) in the La analogue of the 1:2:3 phase, $LaBa_2Cu_{3-x}Ta_xO_{7+\delta}$, Murayama *et al.*[8] have succeeded in forming the ordered compound $LaBa_2Cu_2TaO_8$ in which the required layering of $CuO_2$ and $TaO_2$ planes is achieved, with no measurable intermixing. In particular, detailed structural studies have shown that $TaO_2$ replaces the chain CuO complex between the BaO layers of the 1:2:3 structure. Semiconducting properties and a simple-tetragonal structure have been determined from resistivity and powder x-ray-diffraction measurements.[8]

Subsequent neutron-diffraction studies[9] on a $LaBa_2Cu_2TaO_8$ as well as an analogous $LaBa_2Cu_2NbO_8$ sample have confirmed the $CuO_2$ and $TaO_2$ or $NbO_2$ layer ordering in both compounds. Efforts to observe superconductivity in appropriately doped samples (Ca,Sr→La, or Ti→Nb,Ta) have been unsuccessful thus far.[9] A recent high-resolution neutron-diffraction study[10] on $LaBa_2Cu_2NbO_8$ has revealed the presence of rotational distortions of the $NbO_6$ octahedra which are similar to those observed[11] below the 110 K cubic-to-tetragonal phase transition in $SrTiO_3$.

The purpose of the present investigation is to evaluate the potential of $LaBa_2Cu_2NbO_8$ and a proposed isoelectronic prototype compound, $BaLa_2Cu_2TiO_8$, as parent compounds for possible new high-$T_c$ cuprate superconductors. With this objective, self-consistent band-structure calculations have been carried out for $LaBa_2Cu_2NbO_8$ and $BaLa_2Cu_2TiO_8$ in the local-density approximation (LDA) with the use of a scalar-relativistic version of the linear augmented-plane-wave (LAPW) method.[12] These calculations neglect the rotational distortions that have been reported by Rey *et al.*[10] since these distortions are regarded as incidental to the occurrence of superconductivity. The calculations assume the undistorted simple-tetragonal $LaBa_2Cu_2NbO_8$ primitive unit cell that is shown in Fig. 1. The observed[9] lattice parameters and atom position parameters for this phase are summarized in Table I.

According to Fig. 1, this simple-tetragonal structure consists of a triple stacking of perovskite-type cells along the *c* axis with an oxygen vacancy at the origin in the central La plane. The neighboring $CuO_2$ and BaO planes produce pyramidal coordination at the Cu sites, with an apical-oxygen bond distance ($\sim$2.27 Å) which is about 14% greater than the corresponding planar ($\sim$2.00 Å) values. The octahedrally coordinated Nb site is more symmetric, with apical- and planar-oxygen bond distances of 1.95 and 1.99 Å, respectively. The measured $c/a$ ratio is 3.02. Assuming that Nb is 5+, a simple valence analysis suggests that the formal valence of Cu is 2+, the standard value for cuprate superconductor parent compounds.

A promising isoelectronic Ti compound would be obtained if the La and Ba constituents were interchanged and Ti is substituted for Nb. Because of differences in the ionic radii for $La^{3+}$ (1.15 Å), $Ba^{2+}$ (1.35 Å), $Ti^{4+}$ (0.68 Å), and $Nb^{5+}$ (0.70 Å), some modifications to the La-Ba-Cu-Nb-O structural parameters in Table I are expected for this proposed $BaLa_2Cu_2TiO_8$ phase. However, these variations have been neglected in the present study since they are expected to introduce only quantitative changes in the final electronic-structure results.

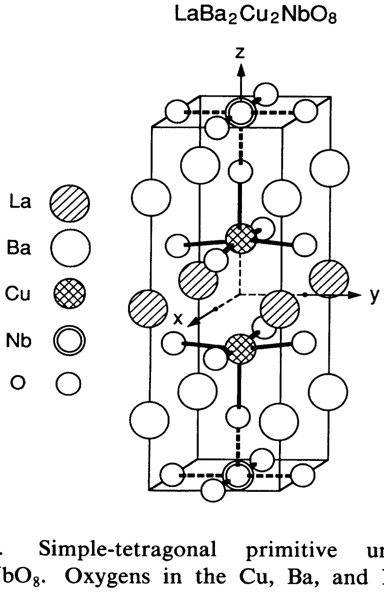

FIG. 1. Simple-tetragonal primitive unit cell for $LaBa_2Cu_2NbO_8$. Oxygens in the Cu, Ba, and Nb layers are denoted by O(1), O(2), and O(3), respectively.

TABLE I. Atom-position parameters for tetragonal $LaBa_2Cu_2NbO_8$ (space group $P4/mmm$), as determined from neutron-diffraction measurements by Greaves and Slater (Ref. 9), where $a = 3.970$ Å and $c = 11.989$ Å, respectively.

| Atom | Site | $x/a$ | $y/a$ | $z/c$ |
|---|---|---|---|---|
| La | 1*c* | 1/2 | 1/2 | 0 |
| Ba | 2*h* | 1/2 | 1/2 | 0.3082 |
| Cu | 2*g* | 0 | 0 | 0.1479 |
| Nb | 1*b* | 0 | 0 | 1/2 |
| O(1) | 4*i* | 1/2 | 0 | 0.1309 |
| O(2) | 2*g* | 0 | 0 | 0.3375 |
| O(3) | 2*e* | 1/2 | 0 | 1/2 |

The present LAPW calculations, which impose no shape approximations on either the charge density or the potential, treat exchange-correlation effects via the Wigner interpolation formula.[13] They include an LAPW basis involving plane waves with an 11.5-Ry cutoff ($\sim$840 LAPW's) and spherical-harmonic terms through $l=8$ ($l=6$) for the metal (oxygen) constituents. The charge density and potential are expanded using $\sim$9000 plane waves (55 Ry) in the interstitial region and by means of lattice-harmonic expansions with $l_{\max}=6$ ($l_{\max}=4$) within the metal-atom (oxygen) muffin-tin spheres. A ten-point **k** sample has been used for Brillouin-zone integrations. The electrons in the outermost shells of the atomic constituents (e.g., Ba $5p^6 6s^2$, La $5p^6 5d 6s^2$, Cu $3d^{10}4s$, Nb $4d^4 5s$, Ti $3d^3 4s$, and O $2s^2 2p^4$) are treated as valence electrons in these calculations. A rigid-core approximation is applied to treat the remaining inner-shell electrons.

The LAPW energy-band results for $BaLa_2Cu_2TiO_8$ and $LaBa_2Cu_2NbO_8$ are plotted along symmetry lines in the basal plane ($\Gamma X M \Gamma$) of the tetragonal Brillouin zone and along one *c*-axis direction ($\Gamma Z$) in Fig. 2. The nearly filled 34-band valence manifold evolves from the 10 Cu(3*d*) and the 24 O(2*p*) states. In both materials, these bands are occupied by a total of 66 valence electrons, leaving a pair of half-filled subbands. These valence bands are nearly two dimensional, exhibiting minimal ($\sim$0.2 eV) dispersion along *c*-axis directions. As expected, the Ti(3*d*) and Nb(4*d*) bands lie above $E_F$ in each compound. The lowest portions of these bands are labeled with triangle symbols in Fig. 2. In both materials, the lowest unoccupied Ti or Nb *d*-band state at $\Gamma$ has $d_{xy}$ orbital symmetry.

For added clarity, the important bands within the valence-band manifold have been labeled with square symbols. These identify the $\sigma$-type bonding, nonbonding, and antibonding ($\sigma^*$) combinations of Cu $d_{x^2-y^2}$ and O $p_{x,y}$ orbitals which are a distinctive characteristic of all cuprate superconductors. In particular, the upper pair of $\sigma^*$ bands at $E_F$, which have their maxima at $M$, contains exactly two electrons in perfectly stoichiometric samples; thus, each is half filled. The small splittings between

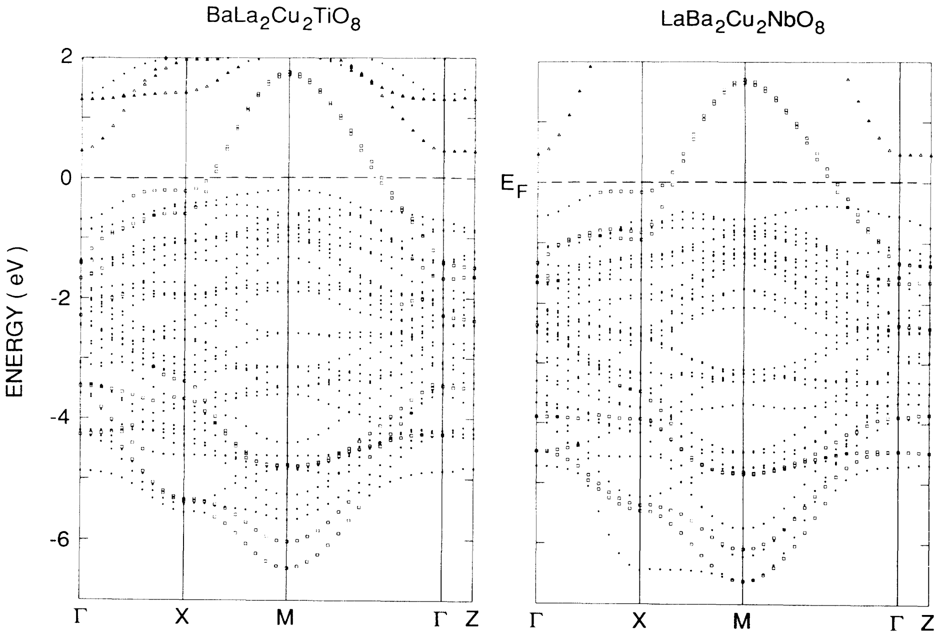

FIG. 2. LAPW energy-band results for $BaLa_2Cu_2TiO_8$ and $LaBa_2Cu_2NbO_8$ along symmetry lines in the tetragonal Brillouin zone. The square (triangle) symbols identify band states that have at least 30% Cu $d_{x^2-y^2}$–O(1)$p_{x,y}$ (Ti 3*d* or Nb 4*d*) orbital weight within the corresponding muffin-tin spheres.

these nearly degenerate $\sigma^*$ subbands reflect interactions between neighboring $CuO_2$ planes. These splittings vary from about 0.05 eV at $M$ to $\sim 0.10$ eV near $E_F$.

In typical parent compounds such as $La_2CuO_4$, the half-filled $\sigma^*$ band produces an antiferromagnet with insulating properties. Metallic behavior and superconductivity are observed when the band filling is varied so that extra carriers (holes or possibly electrons) are added to the $CuO_2$ planes. Efforts to introduce holes into La-Ba-Cu-Nb-O and La-Ba-Cu-Ta-O samples via chemical substitution (i.e., Ca,Sr→La, or Ti→Nb,Ta) have been unsuccessful thus far,[9] producing impurity phases. The present results suggest that further attempts to dope these compounds should be pursued.

A comprehensive overview of the $BaLa_2Cu_2TiO_8$ electronic properties is provided by the density-of-states (DOS) results in Fig. 3. These have been calculated using tetrahedral interpolation based on LAPW results at 42

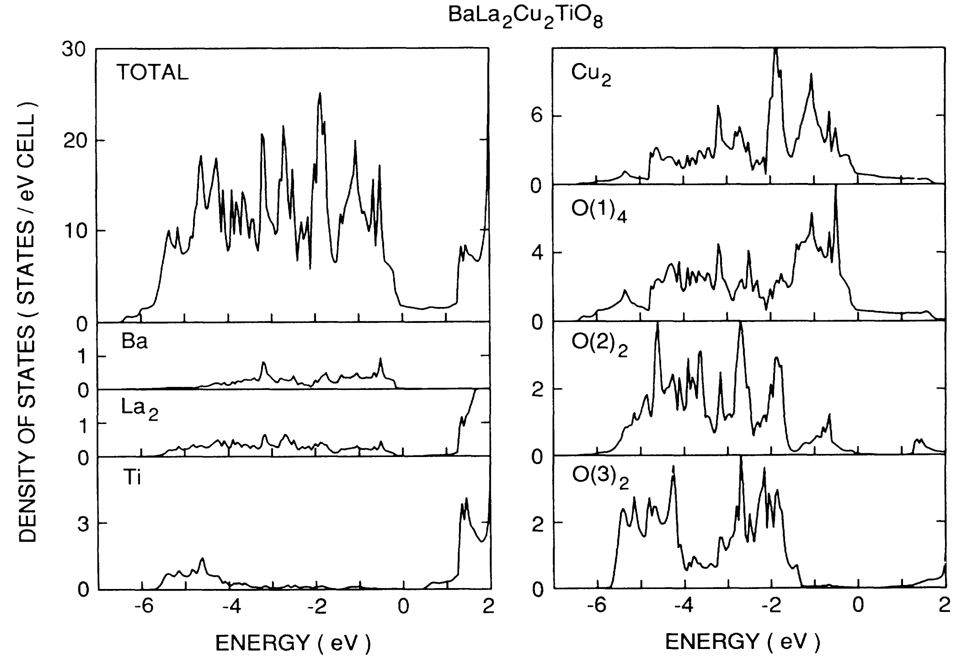

FIG. 3. Total and muffin-tin projected density-of-states results for $BaLa_2Cu_2TiO_8$.

uniformly distributed **k** points in the $\frac{1}{16}$ irreducible Brillouin-zone wedge. As expected, the Ba, La, and Ti constituents are electronically and chemically inactive, contributing minimal weight to the projected DOS in the valence-band energy range. The same is true for the oxygens in the Ba and Ti layers [i.e., O(2) and O(3), respectively]. The main contribution to the DOS near $E_F$ originates from the $CuO_2$ planes. Above $E_F$, the La(5$d$) and Ti(3$d$) components become increasingly important.

From a band-structure point of view, it is clear that the prototype compounds $BaLa_2Cu_2TiO_8$ and $LaBa_2Cu_2NbO_8$ both exhibit the characteristic band properties of a cuprate superconductor parent compound. However, these properties probably should be considered as a necessary but not sufficient requirement for the occurrence of cuprate superconductivity. For example, it has been shown[14] that the halo-oxocuprate compounds $Ca_2CuO_2X_2$ ($X$ =Cl,Br) exhibit the requisite band features, though superconductivity has not yet been observed in these materials or their $Sr_2CuO_2X_2$ counterparts.

The initial failure[9] to form doped La-Ba-Cu-Nb-O and La-Ba-Cu-Ta-O samples which are homogeneous and superconducting could reflect the fact that these materials may be especially sensitive to preparation conditions. As in the case of the $La_{2-x}Sr_xCaCu_2O_6$ phase,[15] one can anticipate that the successful synthesis of appropriately doped $BaLa_2Cu_2TiO_8$- and $LaBa_2Cu_2NbO_8$-type samples may require carefully selected preparation and annealing conditions. The details of the annealing process may be particularly important for these compounds in order to minimize the intermixing of constituents within the $CuO_2$ and $TiO_2$ or $NbO_2$ planes. Undoubtedly, such intermixing would be detrimental to the occurrence of superconductivity in these materials.

Because of the required layer configuration of these proposed high-$T_c$ candidate materials, these compounds may be ideally suited for thin-film growth using molecular-beam-epitaxy procedures. Recent studies of high-$T_c$ superconductors have shown that two-dimensional growth occurs in unit-cell-sized layers when all the constituents are supplied simultaneously.[16,17] However, layer-by-layer growth can also be achieved by successively controlling the supply of the appropriate atomic constituents for each monolayer.[17] Such procedures might be important for the present compounds if standard bulk-synthesis techniques are unsuccessful.

It should be emphasized that the constituents of the prototype compounds $BaLa_2Cu_2TiO_8$ and $LaBa_2Cu_2NbO_8$ are to be regarded as illustrative rather than definitive. Clearly, it is important to investigate alternative combinations of trivalent (La,Y, rare earths), divalent (Ca, Sr, Ba), transition-element (Ti, Zr, Hf, V, Nb, Ta) constituents and dopants in the search for possible new superconducting phases. Analogous phases containing group-VI constituents (i.e., Cr, Mo, W) may also be possible high-$T_c$ candidates, including materials of the type $CaBa_2Cu_2WO_8$, etc. Here, the expected lowering of the group-VI $d$-band energies could lead to partial $d$-band occupancy. This could produce self-doping effects analogous to those calculated[18] for the Ca-Sr-Bi-Cu-O system.

Similarly, these triple-perovskite $BaLa_2Cu_2TiO_8$ and $LaBa_2Cu_2NbO_8$ phases should be regarded only as structural prototypes. It may be possible to form materials with fewer or greater numbers of $CuO_2$ layers. Using the Ba-La-Cu-Ti-O system as an example, one can regard the $BaLa_2Cu_2TiO_8$ compound as the $n=2$ member of the $La_2Ba_{n-1}Cu_nTiO_{2n+4}$ homologous series. The corresponding $n=1$ phase, $La_2CuTiO_6$, is simply a two-layer perovskite. Properly doped, it should also possess electronic properties that are favorable for high-$T_c$ superconductivity.

To summarize, the results of band calculations for two prototype cuprate compounds $BaLa_2Cu_2TiO_8$ and $LaBa_2Cu_2NbO_8$ show that the Ti and Nb constituents are 4+ and 5+, respectively. For the observed layer geometry of the Nb compound, both phases exhibit LDA band properties which are similar to those of typical cuprate superconductor parent compounds. These results suggest that appropriately doped samples of these (or chemically equivalent) phases should be explored as possible candidates for high-$T_c$ superconductivity.

*Note added in proof.* Bulk superconductivity ($T_c \sim 28$ K) has been discovered recently by Cava *et al.*[19] in cuprate compounds, which are similar to those discussed here in that they contain a $NbO_2$ or $TaO_2$ layer to separate the pair of $CuO_2$ planes in each primitive cell. These phases, with overall composition $Nd_{2-x}Ce_xSr_2Cu_2NbO_{10}$ or $Nd_{2-x}Ce_xSr_2Cu_2TaO_{10}$, are closely related to the simple-tetragonal structure that is shown in Fig. 1. The main difference is that the La monolayer in Fig. 1 is replaced by a fluorite-type $Nd_{2-x}Ce_xO_2$ trilayer. This introduces a body-centering translation and changes the space-group symmetry from $P4/mmm$ to $I4/mmm$.

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