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# Electronic structure of $La_4BaCu_5O_{13-x}$

Frank Herman
*IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099*

Robert V. Kasowski and William Y. Hsu
*Central Research and Development Department, E.I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898*

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Although $La_4BaCu_5O_{13-x}$ is metallic and chemically and structurally similar to known high-$T_c$ copper-oxide superconductors, it is not superconducting above 5 K, at least for the observed values of $x$ slightly above and below 0. In order to explore possible reasons why this material is not a high-$T_c$ superconductor, we carried out detailed energy-band calculations. Even though the Cu-O network of $La_4BaCu_5O_{13-x}$ may be regarded as an array of one-dimensional (1D) strands, we find that the interstrand coupling is actually sufficiently strong to make the band structure more nearly 3D than 1D in the neighborhood of the Fermi level. Since the band structures of known high-$T_c$ copper-oxide superconductors have features which are distinctly 1D and/or 2D, the absence of superconductivity in $La_4BaCu_5O_{13-x}$ might be due to the predominantly 3D band structure of samples studied so far, for which $x \neq 0$. Our studies suggest that nested 1D bands separated by a reduced wave vector can be introduced on the Fermi surface by using samples with $x = 0$. If low dimensionality is indeed a significant factor, there is a chance that stoichiometric $La_4BaCu_5O_{13}$ could also be a high-$T_c$ superconductor.

## I. INTRODUCTION

It is widely believed that the 30–40 K values of $T_c$ in the $La_2CuO_4$-type copper-oxide superconductors are associated with two-dimensional (2D) Cu-O networks, and that the 90–100 K values of $T_c$ in the $YBa_2Cu_3O_{7-x}$-type materials are associated with the combined presence of 2D Cu-O networks and 1D Cu-O ribbons.[1] Many theoretical models have already been proposed to account for the high values of $T_c$ in these ceramics,[2] but our understanding of the fundamental nature of the superconducting mechanisms in these materials is still rudimentary. In order to be able to test the adequacy of such models, it is important to study nonsuperconducting counterexamples which are structurally and chemically closely related to the high-$T_c$ copper oxides. Correct theories of high-$T_c$ superconductors should be able to explain not only why (suitably doped and processed) $La_2CuO_4$ and $YBa_2Cu_3O_{7-x}$ are high-$T_c$ superconductors, but also why the counterexamples are not.

In the present paper, we will consider just such a counterexample, the oxygen-deficient perovskite $La_4BaCu_5O_{13-x}$, whose crystal structure has recently been determined by neutron diffraction by Michel *et al.*[3,4] Recent measurements by Torrance, Tokura, Nazzal, and Parkin[5] have shown this material to be metallic, but not superconducting down to 5 K. According to Torrance *et al.*, the conductivity of $La_4BaCu_5O_{13-x}$ is comparable in magnitude to that of the high-$T_c$ copper oxides in their normal state; moreover, the magnetic susceptibilities of $La_4BaCu_5O_{13-x}$ and $La_2CuO_4$- and $YBa_2Cu_3O_7$- type superconductors are all very similar to one another. In the samples studied by Michel *et al.*[3,4] and by Torrance *et al.*,[5] the reported values of $x$ were slightly negative and slightly positive, respectively.

With a view to discovering possible reasons why $La_4BaCu_5O_{13-x}$ is not a high-$T_c$ superconductor, in spite of its close chemical and structural resemblance to known high-$T_c$ copper-oxide superconductors, we calculated the electronic band structure of stoichiometric $La_4BaCu_5O_{13}$ and compared the results with those obtained earlier by ourselves and others for $La_2CuO_4$[6–8] and $YBa_2Cu_3O_7$.[1,9–11]

## II. CRYSTAL STRUCTURE

According to Michel *et al.*,[3,4] $La_4BaCu_5O_{13-x}$ is an oxygen-deficient perovskite composed of groups of $CuO_5$ pyramids linked together through $CuO_6$ octahedra, as indicated in Fig. 1. Each octahedron shares four corners with four pyramids, and the two remaining corners with two other octahedra. Moreover, each pyramid is connected to four other pyramids and one octahedron. There are oxygen vacancies between pairs of $CuO_5$ pyramids, and these vacancies form 1D channels along the $z$ axis. There are two sets of symmetrically inequivalent channels, corresponding to the two oxygen vacancies per unit cell. The La and Ba atoms are not shown in Fig. 1, but they are ordered, lying on crystallographically inequivalent sites. The atomic coordinates obtained by neutron diffraction[4] are listed in Table I for reference.

Since the 2D Cu-O networks in $La_2CuO_4$-and $YBa_2Cu_3O_{7-x}$-type materials and the 1D Cu-O networks in the latter appear to play a crucial role in the high-$T_c$ superconductors,[1,2] it is important to understand the nature of the Cu-O networks in $La_4BaCu_5O_{13-x}$, particularly their dimensionality. This involves knowing not only the crystal geometry shown in Fig. 1, but also the relative

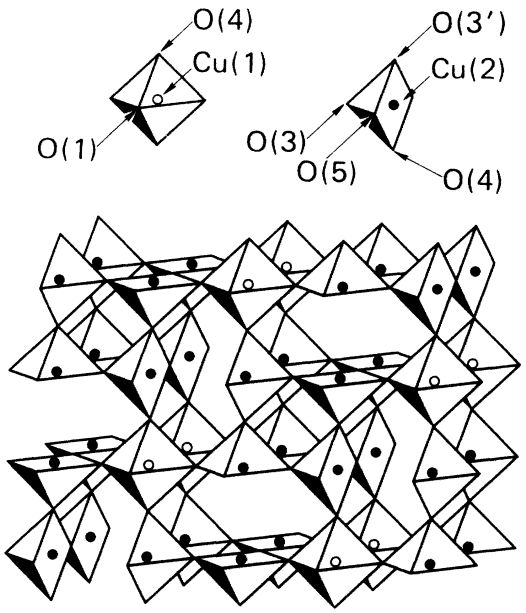


FIG. 1. Crystal structure of $La_4BaCu_5O_{13}$ The $z$ axis points out of the plane of the paper. Cu atoms belonging to the $CuO_5$ pyramids and the $CuO_6$ octahedra are represented by full and open circles, respectively. La and Ba atoms are not shown. Cu and O sites are labeled in the notation of Table I.

strength of the various Cu-O interactions, which can be inferred from the Cu-O interatomic distances (cf. Table I). We may disregard the La and Ba atoms since these are not coupled to the Cu-O network.

Turning first to the $CuO_5$ pyramids, we see from Table I that the distance between the Cu(2) atom in the base and the apex O at O(3) is 0.34 to 0.40 Å larger than the distances between Cu(2) and the four O atoms in the (nearly) square base. It follows that Cu(2) is more strongly coupled to the four base O atoms than to the apex O atom. Based on our experience with the high-$T_c$ copper-oxide superconductors, where similar asymmetries in Cu-O distances occur, we will assume, provisionally, that the Cu(2)-O(3) apex coupling is very weak, so that it can be disregarded or at best treated as a small perturbation. So far as the $CuO_5$ pyramids are concerned, their Cu-O bases are coupled to one another through their common vertices, and these bases form 1D Cu-O ribbons along the $z$ axis. Moreover, adjacent 1D Cu-O ribbons are coupled only weakly to one another because the attachment between adjacent $CuO_5$ pyramids in the $x$ and $y$ directions is via the weak Cu(2)-O(3) apex link.

Turning next to the $CuO_6$ octahedra, we note that these are slightly contracted in the $z$ direction: The Cu(1)-O(1) distance along the $z$ axis is 0.11 Å less than the Cu(1)-O(4) distance in the transverse direction. This asymmetry of 0.11 Å is much less than the corresponding asymmetry in $La_2CuO_4$, where it is 0.25 Å and of opposite sign. In view of the small $CuO_6$ asymmetry in $La_4BaCu_5O_{13-x}$, the Cu(1) atom at the center of the octahedron is coupled nearly as strongly to the four O atoms at the O(4) sites in the $x$-$y$ plane, as it is to the two O atoms at the O(1) sites along the $z$ axis. Thus, the $CuO_6$ octahedra are coupled to one another along the $z$ axis, forming 1D Cu-O chains. Moreover, each $CuO_6$ octahedron is also coupled to the four adjacent bases of the $CuO_5$ pyramids in the $x$-$y$ planes.

In contrast with the $La_2CuO_4$- and $YBa_2Cu_3O_{7-x}$-type materials, where the Cu-O networks form electronically distinct 1D and 2D networks, the Cu-O network in $La_4BaCu_5O_{13-x}$ consists of a periodic array of thick 1D strands, as depicted in Fig. 2. Each of these strands is composed of a central chain of $CuO_6$ octahedra, surrounded by four ribbons formed from the bases of $CuO_5$ pyramids. The diameter of each strand is approximately three $CuO_5$ base diagonals. Adjacent strands are coupled only weakly to one another via the Cu(2)-O(3) and Cu(2)-

TABLE I. Atomic coordinates and selected interatomic distances for $La_4BaCu_5O_{13}$, based on Ref. 4. The space group is $P4/m$. The lattice constants are $a = 8.6475$ Å and $c = 3.8594$ Å. The O vacancy site is O(2). In Ref. 4, O(2) is actually a partially filled site with an occupancy equal to $0.06 \pm 0.02$. Cu-O interatomic distances are listed at the right (in Å units).

| Atom | Site | $x/a$ | $y/a$ | $z/c$ | Cu(1)-O( ) | Cu(2)-O( ) |
|---|---|---|---|---|---|---|
| Ba | 1($d$) | 0.5 | 0.5 | 0.5 | | |
| La | 4($k$) | 0.1262 | 0.2789 | 0.5 | | |
| Cu(1) | 1($a$) | 0 | 0 | 0 | | |
| Cu(2) | 4($j$) | 0.4154 | 0.1718 | 0 | | |
| O(1) | 1($b$) | 0 | 0 | 0.5 | 1.930 | |
| O(2) | 2($e$) | 0 | 0.5 | 0 | | 1.656 |
| O(3) | 4($j$) | 0.2697 | 0.3905 | 0 | | 2.272 |
| O(3') | | | | | | 1.880 |
| O(4) | 4($j$) | 0.2267 | 0.0650 | 0 | 2.039 | 1.875 |
| O(5) | 4($k$) | 0.4157 | 0.1559 | 0.5 | | 1.935 |

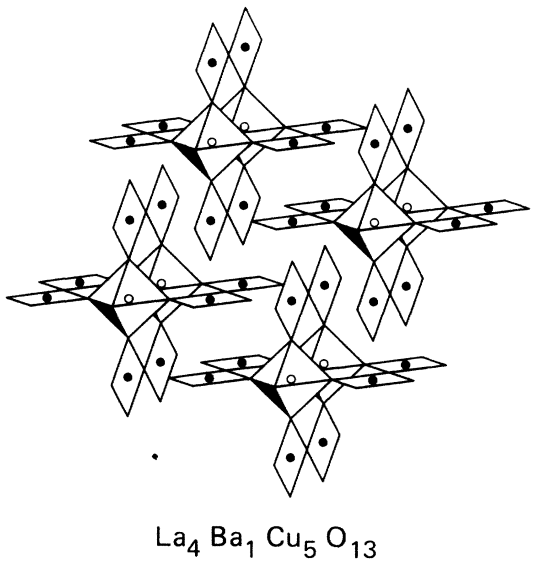


FIG. 2. Cu-O networks in $La_4BaCu_5O_{13}$. The 1D strands are emphasized by retaining only the $CuO_6$ octahedra and the bases of the $CuO_5$ pyramids.

O(3') pyramidal apex links.

The array of 1D strands is clearly anisotropic, but is the effective dimensionality of the crystal 1D or 3D? We will investigate this question quantitatively by calculating the energy-band structure. If the interstrand coupling is sufficiently weak, as suggested by the qualitative arguments given earlier, the energy bands in $k_z$ =const planes in the reduced zone will be flat, and the crystal can be regarded as 1D from an electronic point of view.

Turning finally to the O vacancies, we see from Table I that the distance between Cu(2) and the O vacancy site O(2) is considerably smaller than the remaining Cu-O distances. The presence of vacancies results in a distortion of the lattice which leaves less room for O atoms at the empty O sites than at the occupied O sites. Thus, the interchange of O atoms between occupied and vacant sites is not energetically favorable, so one should not expect to find oxygen-vacancy rearrangements and as wide a range of oxygen content as in $YBa_2Cu_3O_{7-x}$. However, we should make allowance for the variation of the band structure and related physical properties with changing oxygen content.

## III. ELECTRONIC BAND STRUCTURE

We have calculated the electronic structure of stoichiometric $La_4BaCu_5O_{13}$ using the first-principles pseudofunction method[12] and the atomic coordinates listed in Table I. The numerical results confirm simple estimates indicating that there are 3.5 empty Cu $3d$/O $2p$ bands,[13] so this material is clearly a metal within the framework of one-electron theory. As expected, we find that the Ba and La orbitals do not contribute importantly to the occupied bands, nor do the Cu $4s$ orbitals. The energy-band profiles along various directions in the tetragonal reduced zone are shown in Fig. 3. As can be seen from this figure, there are four broad bands approximately 2.8 eV wide that cross the Fermi level $E_F$ and lie mostly above it.

These four anisotropic bands arise from strong antibonding combinations of Cu and O orbitals associated primarily with the four $CuO_5$ pyramids per unit cell. There is also a narrower anisotropic band, about 1.1 eV wide, that crosses $E_F$. This band arises from antibonding combinations of Cu and O orbitals associated primarily with the single $CuO_6$ octahedron in the unit cell. Note that in the right-hand part of the drawing, which corresponds to the top and sides of the reduced zone, $E_F$ lies below roughly five bands, one of which is doubly degenerate. In the left-hand part, corresponding to the $k_z$ =0 plane, $E_F$ lies below only two of these bands. Allowing for the anisotropy of these bands, we confirm that there are 3.5 empty bands, as stated earlier.

In the equatorial plane of the reduced zone ($k_z$ =0), the band structure in the vicinity of $E_F$ is clearly not flat, suggesting that the interstrand coupling [through the Cu(2)-O(3) and Cu(2)-O(3') links] cannot in fact be totally neglected. As one moves upward in the reduced zone (from $k_z$ =0 to 1.12), the five highest bands move to higher energies, as would be the case for a 1D band structure, but these bands are never exactly flat in any $k_z$ =constant plane. The general conclusion, then, is that the structure of the five highest bands in the neighborhood of $E_F$ is more nearly 3D than 1D. This is primarily a consequence of the fact that the Cu-O hybrid orbitals for these bands are oriented perpendicular to the strands, and hence are most subject to interstrand coupling. The band dispersions are also influenced by the thickness of the individual strands, or more precisely, by the intrastrand interactions.

This result should be contrasted with the band structures of $La_2CuO_4$ and $YBa_2Cu_3O_{7-x}$ whose top-most bands contain well-defined 1D and 2D features.[1,6-11] If band-structure dimensionality is important for high-$T_c$ superconductivity, then the absence of prominent 1D and 2D features in the top-most bands of $La_4BaCu_5O_{13}$ might account for the absence of high-$T_c$ superconductivity.

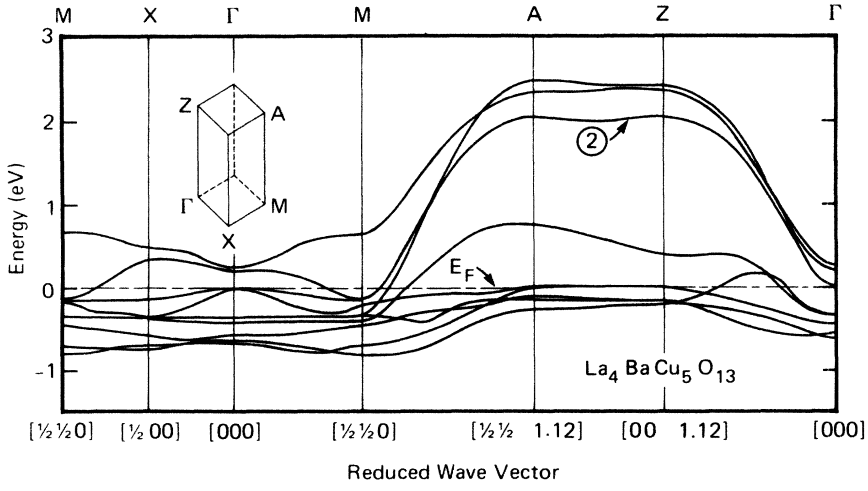


FIG. 3. Energy band structure of $La_4BaCu_5O_{13}$ showing the top-most 10 bands. One of the doubly degenerate band profiles is indicated by a circled 2 for clarity. Reduced wave vectors are expressed in units of $2\pi/a$. The reduced zone is shown in the insert.

Of course, the role of dimensionality might be more subtle. For example, the key might be that $La_2CuO_4$ and $YBa_2Cu_3O_{7-x}$ can support certain antiferromagnetic spin arrangements that are conducive to high-$T_c$ superconductivity, while $La_4BaCu_5O_{13-x}$ does not. In any event, we expect the present band-structure picture to be useful in further studies of $La_4BaCu_5O_{13-x}$.

## IV. DISCUSSION

Finally, let us consider the sixth and seventh highest bands, which also arise from Cu $3d$/O $2p$ hybrids, but ones that point along the strands. Since such orbitals on adjacent strands do not overlap one another as strongly as transverse orbitals do, these and other analogous bands are narrower than the five top-most bands previously considered. As can be seen from Fig. 3, these two bands remain below $E_F$ except on the top and bottom faces of the reduced zone, where they become very flat and touch one another. For stoichiometric $La_4BaCu_5O_{13}$, then, these bands form a prototypic 1D nested pair on the Fermi surface at the zone faces. It is not likely that this unique 1D feature occurs in samples studied to date by Michel *et al.*,[3,4] or by Torrance *et al.*,[5] since their respective samples had oxygen contents that were reported to be slightly larger and slightly smaller than 13. In these samples the Fermi level would either lie above these two bands, in which case they would not breach the Fermi surface, or these two bands would lie above the Fermi level, in which case they would be less perfectly nested, and their separation in the reduced zone would be less than a reduced wave vector.

Although this isolated 1D band-structure feature might well be overwhelmed by the overall 3D character under all conditions, the present study opens up the intriguing possibility that this 1D feature could be optimized and placed exactly on the Fermi surface by suitably changing the oxygen stoichimetry, possibly to exactly 13, or by changing the La and Ba stoichimetries slightly. It would then be interesting to see whether such fine tuning of the band structure leading to a 1D feature on the Fermi surface on the zone faces would lead to high-$T_c$ superconductivity. Whatever the outcome, the result would be a challenge to evolving theories of high-$T_c$ superconductivity.

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