Electronically Driven Instabilities and Superconductivity in the Layered $La_{2-x}Ba_xCuO_4$ Perovskites

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Body-centered tetragonal La_2CuO_4 is shown to have its electronic structure and properties dominated by the layered in-plane Cu-3*d*–O-2*p* interactions. A strong Fermi-surface instability along [110] with $|\mathbf{q}| = 2k_F$ leads, via a soft-phonon mode, to the observed orthorhombic phase and accounts for its semiconducting properties. The addition of divalent metals, i.e., Ba, Sr, suppresses the instability and stabilizes the tetragonal phase where the same soft-phonon branch apparently contributes to a large electron-phonon interaction and a high T_c.

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The first report[1] of possible high-temperature superconductivity in the La-Ba-Cu-O system has been followed by detailed observations of ever increasing new records for superconducting transition temperatures.[2-4] In this early exciting phase, new observations on this system—now identified to be almost entirely the layered perovskite K_2NiF_4 phase—and a growing class of materials having this structure are occurring at a rapid pace. The obvious need to understand these observations has given rise to considerable speculation, especially as to the origin of the high-T_c superconductivity.

We here report, as a first step towards achieving this understanding, an investigation based on the electronic structure of the body-centered-tetragonal (bct) phase (*I*4/*mmm*) of La_2CuO_4 determined at the low-temperature lattice constants[4] for superconducting $La_{1.85}Ba_{0.15}CuO_4$ with a state-of-the-art all-electron local-density method.[5] We find that the electronic structure (energy-band structure, density of states, Fermi surface, charge density) and properties (including superconductivity) are dominated by the layered character of the crystal structure arising from the in-plane Cu-3*d* and O-$2p_\parallel$ electron interactions. Thus, the band structure is dispersionless in the *c* direction throughout the broad (9-eV) hybridized Cu-3*d*–O-2*p* bands. The single-sheet Fermi surface, arising from a single (essentially two-dimensional) parabolic *d*-*p* band's crossing E_F, is dominated by very strong nesting features (with a spanning vector $\mathbf{q} \| \Gamma X$ and $|\mathbf{q}| = 2k_F$) and gives rise to a strong peak in the generalized susceptibility,[6] $\chi(\mathbf{q})$. Thus it may lead, through strong electron-phonon coupling, to a soft-mode crystallographic phase transformation to the observed[7] orthorhombic (*Cmca*) phase and accounts for its semiconducting properties. The doping with Ba (or other divalent elements) lowers E_F, removes the $2k_F$ nesting, and hence suppresses the crystallographic phase transformation and stabilizes the bct structure. The same softening of the phonon branch is (apparently) still strong enough to contribute to a large electron-phonon interaction and a high T_c.

We use the full-potential linearized augmented-plane-wave (FLAPW) method[5] and Hedin-Lundqvist exchange correlation within the local-density approximation of the density-functional theory. The potential and density are expanded inside the spheres in lattice harmonics with $l \leq 6$ and in the interstitial space in 6633 plane waves. The number of basis functions used in the calculations is more than 440 for each *k* point. We have obtained self-consistent calculations using twenty and forty as well as sixty *k* points inside the $\frac{1}{16}$ IBZ (irreducible Brillouin zone) to check out the accuracy of our results (and, in particular, the delicate peak structure in the low density of states near E_F). The self-consistency obtained is up to $2.6\times10^{-4}e/(\text{a.u.})^3$ in the charge density.

La_2CuO_4 in the bct structure has the space group D_{4h}^{17} (*I*4/*mmm*) with atom positions (cf. Fig. 1) for a unit cell given by Cu, (0,0,0); La, $(0,0,\pm u_{La})$; O(1), $(0,\frac{1}{2},0)$, $(\frac{1}{2},0,0)$; and O(2), $(0,0,\pm u_O)$. We use the low-temperature (10-K) values of the lattice parameters, $a = 3.7817$ Å and $c = 13.2487$ Å, and position values $u_{La} = 0.3607$ and $u_0 = 0.1824$, determined recently with neutrons for a $La_{1.85}Ba_{0.15}CuO_4$ sample by Jorgensen.[4]

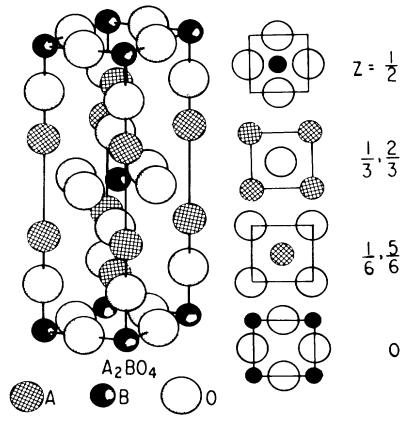

FIG. 1. Atom positions in the bct structure for a bimolecular cell; horizontal layer positions are shown for different *z* values.

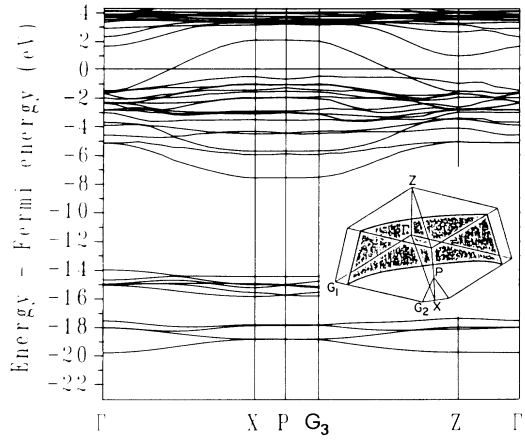

FIG. 2. Energy-band structure along some high-symmetry directions in the BZ (cf. Fig. 3). Inset: Fermi surface in a $\frac{1}{8}$ section of the BZ.

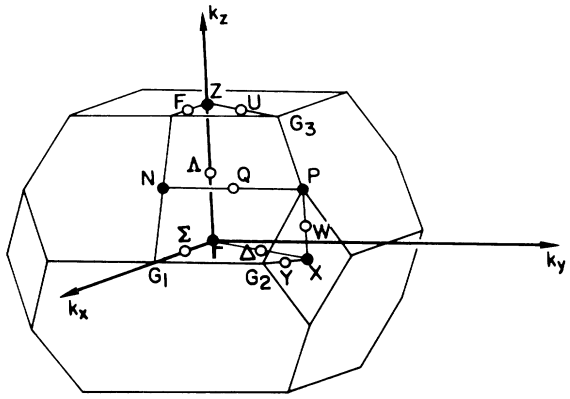

FIG. 3. Brillouin zone for the bct structure using the Bradley and Cracknell notation (to which general point labels, G_i, have been added).

These data also show that the distance between Cu and O(1), 1.89 Å, is much shorter than that between Cu and O(2), 2.42 Å. These values emphasize the layered nature of the system and that possible strong anisotropic (layer-dependent) properties are expected—and found. For example, a plot of the valence charge density shows that the Cu and O(1) atoms interact very strongly within their layers, whereas along the c axis, there is little overlap of the atomic charges. This fact is also reflected in the band structure shown in Fig. 2 along high-symmetry directions in the Brillouin zone (Fig. 3). One sees only flat bands, i.e., almost no dispersion, along the c axis; this demonstrates that the interactions between the Cu, O(2), and La atoms are quite weak. In sharp contrast, along basal-plane directions there are very strong interactions between the Cu and O(1) atoms leading to large dispersions and a very wide bandwidth ($\sim$9 eV), the bulk of which falls well below E_F. The bottom of the La-5d, seen at $\sim$1 eV above E_F, merges into the La-4f band (about 3 eV above E_F). The O-2s and La-5p bands are well below ($\sim$20 and 14 eV, respectively). Thus, there is, as expected from a crude chemical description, significant charge transfer from the La atoms but little contribution to the occupied conduction bands. The density of states at E_F, which falls above a relatively weak (but sensitive) peak, has a low value, 15 states/Ry·cell.

The remarkable feature of the band structure which dominates the Fermi surface is the strongly dispersed single Cu-3d–O(1)-2p free-electron-like band. This band crosses E_F at the midpoint of the Γ-X and Z-G_3 lines in the BZ and gives rise to a Fermi surface strongly nested along the [110] direction. As seen from Fig. 2, the FS is a cylinder flattened perpendicular to the [110] direction with a large part of its surface area participating in the nesting. As a result there is a very strong peak in the calculated generalized susceptibility,[6] $\chi(\mathbf{q})$, that may well drive a phonon branch soft. It is thus apparent that this $\mathbf{q}=[110]$ $2k_F$ instability correlates well with the crystallographic phase transformation from the body-centered tetragonal to the observed orthorhombic structure of La_2CuO_4 in a mode consistent (from symmetry arguments and a phenomenological Landau-theory description) with the picture of Grande, Müller-Buschbaum, and Schweizer.[7] This transformation introduces new BZ planes at which energy gaps are opened, thereby explaining the observed[4] semiconducting behavior at low T. In Fig. 4, a plot of the charge density for the state at E_F crossing along Γ-X is given both in the $z=0$ plane and in a vertical face of the cell. The 2D confinement to the Cu-O(1) planes is clear as is the Cu:3$d_{(x^2-y^2)}$-O(1):2p bonding which is so important to the driving of the instability. Figure 4 demonstrates dramatically the 2D (i.e., highly anisotropic) properties expected for the Ba- (or Sr-) stabilized systems we now discuss.

The effect of doping of La_2CuO_4 with divalent atoms (M=Ba, Sr, ...) to stabilize the bct structure of $La_{2-x}M_xCuO_4$ can be readily understood on the basis of our results. As substitutional replacements for the La atoms, they serve to change mainly the c parameter and the number of conduction electrons in the cell which lowers E_F. Clearly, lowering E_F serves to remove the strong Fermi-surface nesting instability which drives the phase transformation to the orthorhombic structure in pure ($x=0$) La_2CuO_4 and hence stabilizes the bct phase. The resulting phonon softening is still strong enough to drive the superconducting transition. The strength of the instability is seen from the fact that the orthorhombic structure persists[8] with Ba, Sr concentrations up to at least $x=0.07$ (below which concentration it is not superconducting).

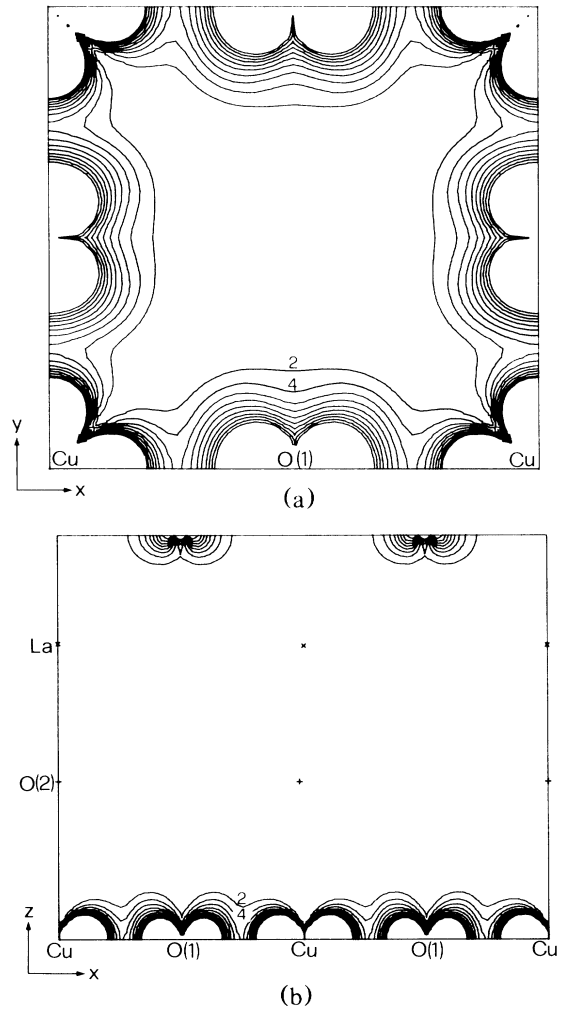

FIG. 4. Charge-density contours (on a linear scale) for the state crossing E_F along Γ-X: (a) $z=0$ basal plane and (b) xz vertical plane [units $10^{-3}e/(\text{a.u.})^3$].

Consider now the origin of superconductivity in $La_{2-x}M_xCuO_4$. In the absence of knowledge of the electron-phonon spectral function $\alpha^2F(\omega)$, a general solution of the Eliashberg equation is not possible. A first-principles frozen-phonon approach to calculate phonon-dispersion curves is now possible[9] and is being undertaken. In the meantime, a qualitative picture of superconductivity and its driving mechanism has emerged from our electronic-structure results.

The low density of states at E_F and the electronically driven instability from the bct to orthorhombic structure found here indicate strong similarities to the previously studied tungsten bronzes,[10] A_xWO_3, and the $BaPb_{1-x}Bi_xO_3$ alloys[11] where a rich interplay of superconductivity, structural changes, and metal-insulator transitions has been reported. These observations are part of generally accepted[10] empirical correlations between the existence of phonon anomalies, lattice instabilities, and high T_c. Soft modes in these materials and in other perovskites are a general and well studied occurrence. (As emphasized in this work, the major difference between $La_{2-x}M_xCuO_4$ and these materials lies in the layered nature of their perovskite structure, and their strongly tetragonally distorted Cu-O octahedra.) Thus, phonon-softening anomalies, like the one demonstrated here, can contribute to a large electron-phonon interaction and a high T_c in these materials.

Finally, the 2D character of the electronic structure (charge density, band structure, Fermi surface, etc.) for the La-M-Cu-O system will have, as some of its important consequences, strongly anisotropic (transport, magnetic, etc.) properties which we are calculating. There is thus an added urgent reason for synthesis and measurements on single crystals.

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