Electronic Band Properties and Superconductivity in $La_{2-y}X_yCuO_4$

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The results of electronic-structure calculations for tetragonal La_2CuO_4 provide insight concerning the origin of high-temperature superconductivity in the $La_{2-y}X_yCuO_4$ alloys. A half-filled Cu(3*d*)-O(2*p*) band with two-dimensional character and a nearly square Fermi surface produces a Peierls instability for $y=0$ that opens a semiconductor gap over the Fermi surface. Alloying with divalent or tetravalent atoms should spoil the nesting features while maintaining the strong coupling of O phonons to the conduction electrons.

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The report of possible high-temperature ($T_c \sim 30$ K) superconductivity in the Ba-La-Cu-O system by Bednorz and Müller[1] has stimulated intensive studies of these materials by several groups.[2-5] While specific information is not yet generally available, the early studies by Uchida *et al.*[2] and Takagi *et al.*[3] have confirmed that superconductivity is a bulk property. Furthermore, Takagi *et al.*[3] have succeeded in identifying the structure (K_2NiF_4 type) of the superconducting phase.

The purpose of the present investigation is to calculate the electronic properties of these $La_{2-y}X_yCuO_4$ compounds in order to identify those features that are crucial for an understanding of the origin of high-temperature superconductivity. The results of this study show that the electronic and superconducting properties of $La_{2-y}X_yCuO_4$ are closely analogous to those of the $BaPb_{1-x}Bi_xO_3$ alloy series.[6,7] In particular, both systems are rather unique in that Fermi-surface electrons have substantial O 2*p* character. In addition, these orbitals form strong σ bonds with neighboring Cu or Pb/Bi atoms. The modulation of these bonds by breathing-type O vibrations couples very strongly with the conduction bands at E_F, leading to potentially large values for the electron-phonon interaction constant λ. Because of the light mass and high frequency of the vibrating O atoms, the prefactor in the standard McMillan[8] T_c equation is also enhanced, thereby resulting in higher transition temperatures for these materials. The calculations demonstrate the critical role of X substitutions in tuning of the superconducting properties of these compounds.

The present study has been carried out with the use of a self-consistent, scalar-relativistic version of the linear-augmented-plane-wave (LAPW) method.[9] The formulation and implementation of this scheme impose no shape approximations on either the charge density or the potential. The values of various computational parameters and cutoffs were set in a manner analogous to that applied in previous calculations[9] for $BaPb_{1-x}Bi_xO_3$. Exchange and correlation effects are included within the local-density-functional approximation by use of the Wigner interpolation formula.[10]

LAPW calculations have been carried out on the body-centered-tetragonal (bct) phase (space group D_{4h}^{17}) of La_2CuO_4 (which is observed[11] to be stable above 260 °C) as well as on a distorted phase with orthorhombic symmetry. Appropriate values of the lattice and internal position parameters [$a=3.79$ Å, $c=13.21$ Å, $z(\mathrm{La})=0.362$, $z(\mathrm{O})=0.182$] have been estimated from the available structural data.[1,11] The structure can be described[11] in terms of alternating layers of perovskite-type ($LaCuO_3$) and rocksalt-type (LaO) units along the c axis. The central CuO_6 octahedron, which is symmetric in the perovskite structure, is now stretched along the c axis, producing two long (2.40 Å) and four short (1.90 Å) Cu—O bond lengths.

The LAPW energy bands for bct La_2CuO_4 are plotted along symmetry lines in the Brillouin zone (BZ) in Fig. 1. Γ and X are in the central BZ plane, while Z and S are on the zone face along the c axis.[12] As shown in the inset, the central (ΓX) and top (ZS) BZ faces are coplanar in an extended-zone scheme. The seventeen-band complex that is centered at −3 eV below E_F consists primarily of O 2*p* and Cu 3*d* states. The unoccupied bands above 2 eV involve La orbitals, including the flat 4*f* bands at ∼4 eV.

Only two of the seventeen bands in the Cu(3*d*)-O(2*p*) manifold are important. These, labeled *A* and *B* in Fig. 1, arise from strong nearest-neighbor ($pd\sigma$) interactions between Cu 3*d* orbitals with x^2-y^2 symmetry (i.e., pointing towards the oxygens) and neighboring O 2*p* orbitals that are directed along the (short) Cu—O bond axes in the *xy* plane. The *A* (or antibonding) subband is half filled, representing a total carrier density of $\sim 10^{22}$ cm^{-3}. The fifteen intermediate bands correspond to more weakly bonding Cu(3*d*)-O(2*p*) states, including the weaker $pd\sigma$ bonds along the c axis where the Cu—O distance is longer.

The general features of this picture are illustrated by the density-of-states (DOS) results in Fig. 2. The total DOS is shown in the top panel. The value at E_F (1.32 states/eV·cell) is about 60% larger than that calculated[6] for cubic $BaBiO_3$. The lower panels represent the total DOS weighted by the integrated charge within spheres[9] surrounding the La ($R=2.81$ a.u.), Cu ($R=1.84$ a.u),

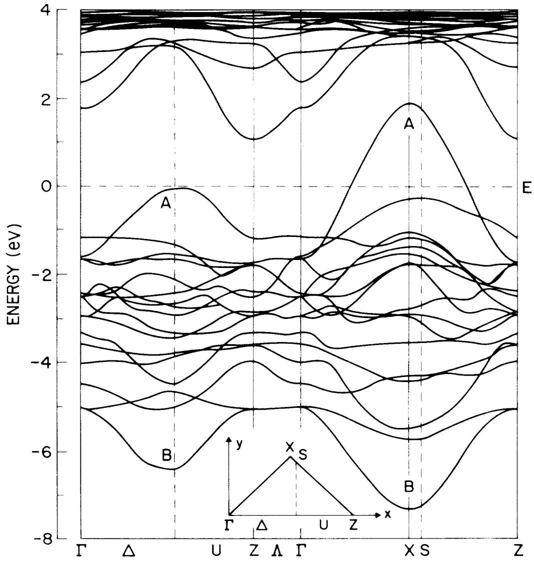

FIG. 1. LAPW energy bands for La_2CuO_4 along symmetry lines in the bct Brillouin zone (see inset and discussion in text).

and O ($R=1.62$ a.u.) sites. As expected, the La states have little weight below E_F. Also, the principal contribution from the $O_2(z)$ atoms (long Cu—O bond length) is below E_F. The predominant orbitals near E_F are the strongly antibonding $d(x^2-y^2)$ and $p(x,y)$ states described earlier.

The essential features of the bands labeled A and B in Fig. 1 can be understood in terms of a two-dimensional tight-binding model that includes $pd\sigma$ interactions between the Cu $d(x^2-y^2)$ orbitals and the neighboring O $p(x,y)$ orbitals that point along the (short) Cu—O bond axes. (One measure of the two-dimensional nature of the results in Fig. 1 is the limited band dispersion along Λ. A second is the symmetry of the results about X and near the Δ-U midpoint, which provides another measure of the c-axis dispersion.) With two parameters ($E_d=E_p=-3.2$ eV, $pd\sigma=-1.85$ eV), this model provides an accurate description of the bands labeled A and B in Fig. 1 while collapsing the fifteen intermediate bands to a degenerate level at -3.2 eV.

The two-dimensional Fermi surface that is obtained from this model consists of a square hole surface centered at X that nests perfectly with its electron counterpart at Γ. The size and orientation of the Γ-centered electron surface is shown by the dot-dashed lines in Fig. 3. The closed solid curves represent the calculated LAPW Fermi surface. The similarity of the LAPW results in the central (ΓX) and top (ZS) faces of the BZ again reflects the two-dimensional nature of these compounds.

The nearly perfect nesting of the LAPW Fermi surface suggests the likelihood of a charge-density-wave distortion in La_2CuO_4 with $\mathbf{q}_{\mathrm{CDW}}=2\mathbf{k}_F=(\frac{1}{2},\frac{1}{2},0)$ which would open a semiconductor gap at E_F, thereby stabilizing the distorted phase and spoiling potential superconductivity. The LAPW bands near E_F suggest two likely displacement patterns. One involves a planar breathing-type displacement of O atoms away from the central Cu site. The second has quadrupolar symmetry where one O pair moves in, the other out. A tight-binding analysis shows that only the breathing-type displacement opens a gap at E_F. This has been confirmed by LAPW calculations for $La_4Cu_2O_8$ with a frozen-in planar breathing-type O displacement $\delta=0.064$ Å, a value similar to that

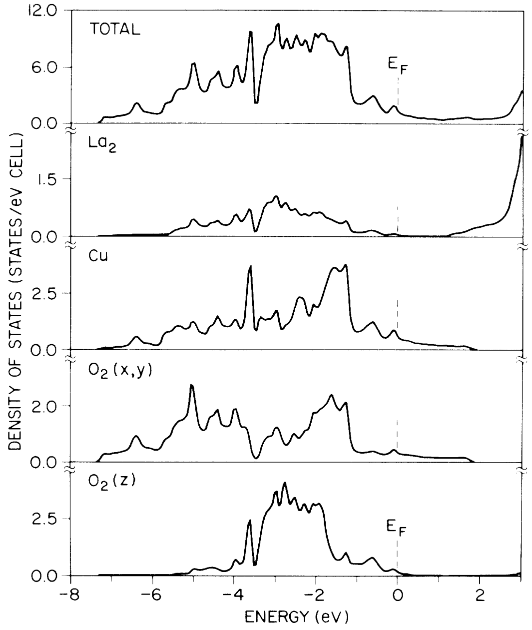

FIG. 2. Total and projected density-of-states results for bct La_2CuO_4 (smoothed with a Gaussian, FWHM $=0.1$ eV).

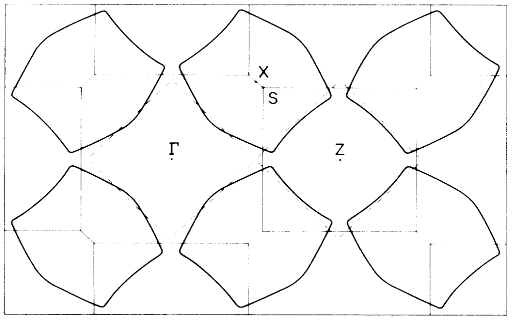

FIG. 3. Calculated La_2CuO_4 Fermi surface in the central (ΓX) and top (ZS) faces of the Brillouin zone which are coplanar in an extended-zone scheme. The closed solid curves surround unoccupied states. The dot-dashed lines indicate the perfectly nested surfaces derived from the tight-binding model described in the text.

in $BaBiO_3$. The calculated gap at the new zone boundary varies from ~0.2 to 0.5 eV, which leads to deformation potentials ~1.6–3.9 eV/Å. It is interesting to note that this distorted structure has orthorhombic symmetry. However, the space group is different from that proposed[11] for La_2CuO_4 at room temperature.

Thus, the present results make clear that the essential role of X is to suppress the charge-density-wave distortion, thereby allowing high-T_c superconductivity in the $La_{2-y}X_yCuO_4$ alloys. Substitutional alloying for La with either a divalent (X=Sr,Ba) or tetravalent element will lower or raise E_F, thereby spoiling the commensurate Fermi-surface nesting geometry. Further, the alloying will also affect the lattice parameter a to which our calculations suggest that the planar electron-phonon coupling, and hence T_c, will be sensitive. Incommensurate charge-density-wave distortions could still be possible, but these are not expected to open complete gaps over the Fermi surface. The alloy-induced Fermi-level shift must be large enough to eliminate the Peierls distortion but still provide states near the La_2CuO_4 Fermi surface where the deformation potentials (~1.6–3.9 eV/Å) are a maximum. This combination of strong deformation potentials and the high vibrational frequency of the oxygen bond-stretching modes provides the key ingredients for achieving high T_c in both the $La_{2-y}X_yCuO_4$ and $BaPb_{1-x}Bi_xO_3$ alloy systems.

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