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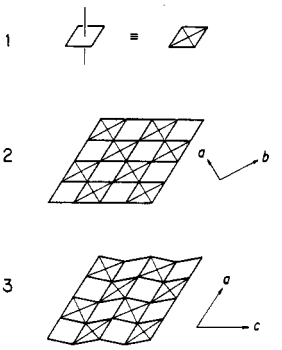
Band Electronic Structure Study of La_2CuO_4 and the High-Temperature Superconductor $La_{2-x}M_xCuO_4$: Non-Peierls Nature of the Tetragonal to Orthorhombic Distortion of La_2CuO_4 and Its Implications

Sir:

The report by Bednorz and Müller[1] of possible high-critical-temperature (T_c) superconductivity in the Ba–La–Cu–O system touched off intensive studies of the $La_{2-x}M_xCuO_{4-y}$ phases (M = Ba, Ca, Sr; $x \lesssim 0.2$; $y \simeq 0$),[2-14] eventually leading to the discovery by Wu et al.[15] of the first ambient-pressure superconductor with $T_c \simeq 94$–98 K, well above liquid-nitrogen temperature (77 K). The structure of the parent compound in this series, La_2CuO_4, is orthorhombic at room temperature[16] but becomes tetragonal above 533 K.[16b] The orthorhombic structure of La_2CuO_4 at room temperature was confirmed in a recent powder neutron diffraction study.[8] Doping La_2CuO_4 with an alkaline-earth metal, M, makes the resulting phase $La_{2-x}M_xCuO_4$ tetragonal in structure at room temperature, as also shown by the powder neutron diffraction study of $La_{1.85}Ba_{0.15}CuO_4$[8] and the single-crystal X-ray diffraction study of $La_{2-x}Sr_xCuO_4$ ($x \simeq 0.05$–0.07).[17] Both the pristine and the doped phases contain layers composed of interlinked CuO_4 moieties, which are constructed from distorted CuO_6 octahedra **1** (with four short and



two long Cu–O distances) upon sharing their "equatorial" oxygen atoms. The CuO_4 layers of $La_{2-x}M_xCuO_4$ and orthorhombic La_2CuO_4 are flat and bent as depicted in **2** and **3**, respectively, and the La^{3+} and M^{2+} cations are located between the CuO_4 layers. To examine how the dopant M causes high-T_c superconductivity in $La_{2-x}M_xCuO_4$, we have carried out tight-binding band calculations[18] on La_2CuO_4 and on a single CuO_4 layer of $La_{2-x}M_xCuO_4$. Our one-electron band electronic structure calculations complement the recent self-consistent-field (SCF) band studies[19,20] on tetragonal La_2CuO_4.

As expected from the formal oxidation $(La^{3+})_2Cu^{2+}(O^{2-})_4$ and the copper coordination of **1**, both the SCF band [19,20] and our one-electron band calculations show the $x^2 - y^2$ band of tetragonal La_2CuO_4 to be half-filled and do not support the suggestion[21] that the z^2 band of La_2CuO_4 crosses the Fermi level. As far as the d-block bands are concerned, results of three-dimensional (3D) band calculations on La_2CuO_4 are essentially identical with those

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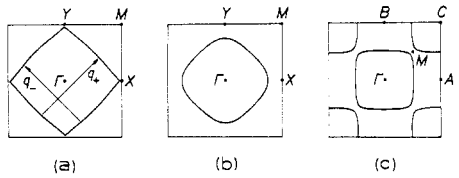
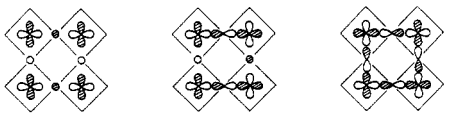


Figure 1. Two-dimensional Fermi surfaces associated with $x^2 - y^2$ bands of the $CuO_4^{(6-x)-}$ layers present in La_2CuO_4 and $La_{2-x}M_xCuO_4$: (a) the flat CuO_4^{6-} layer of tetragonal La_2CuO_4; (b) the flat $CuO_4^{5.85-}$ layer of tetragonal $La_{1.85}M_{0.15}CuO_4$; (c) the bent CuO_4^{6-} layer of orthorhombic La_2CuO_4. In (a) and (b), **X** and **M** refer to $(a^*/2, 0)$ and $(a^*/2, b^*/2)$, respectively. Due to the "folded-back" nature of the $x^2 - y^2$ band in orthorhombic La_2CuO_4, which occurs when the unit cell size is doubled, the two Fermi surfaces for the lower and the upper parts of this $x^2 - y^2$ band are combined into one in the extended Brillouin zone in (c), where **M**, **A**, **B**, and **C** refer to $(a^*/2, c^*/2)$, $(a^*, 0)$, $(0, c^*)$, and (a^*, c^*), respectively.

of two-dimensional (2D) calculations on a single CuO_4 layer in our one-electron study. Therefore, the d-block bands of $La_{2-x}M_xCuO_4$ can be approximated by those of its CuO_4 layer, which will be referred to as the $CuO_4^{(6-x)-}$ layer to indicate the number of electrons in the $x^2 - y^2$ band (i.e., $1 - x$). Shown in **4a–c** are the $x^2 - y^2$ band orbitals of a flat CuO_4^{6-} layer **2** for the



wave vectors $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, and $M = (a^*/2, b^*/2)$, respectively. The orbitals of the "axial" oxygen of **1** do not have the correct symmetry to mix into the $x^2 - y^2$ band, which is therefore dispersionless along the interlayer direction. The p orbitals of the equatorial oxygen atoms make a more effective antibonding interaction with the copper $x^2 - y^2$ orbital than do the s orbitals of the equatorial oxygen atoms. It is clear from **4** that the $x^2 - y^2$ band dispersion along $\Gamma \rightarrow M$ would be about twice as strong as that along $\Gamma \rightarrow X$. This dispersion characteristic governs the shape of the Fermi surface (FS)[22] associated with the $x^2 - y^2$ band.

Shown in Figure 1a is the FS for the half-filled $x^2 - y^2$ band of a flat CuO_4^{6-} layer **2**. The four pieces of this FS are reasonably well-nested[23] by two wave vectors $\mathbf{q}_\pm = (a^*/2, \pm b^*/2)$. This nesting is destroyed when electrons are removed from the $x^2 - y^2$ band as illustrated by the FS of a flat $CuO_4^{5.85-}$ layer in Figure 1b. Such observations led to the suggestion[8,19,20] that the tetragonal → orthorhombic distortion of La_2CuO_4 that occurs at ~533 K[16b] is a Peierls distortion[24] associated with the nesting vector $\mathbf{q}_\pm$, and an important role of the dopant M is to suppress the Peierls distortion by destroying the FS nesting.

The measured electrical resistivity of orthorhombic La_2CuO_4 slowly decreases from room temperature to ~100 K, then slowly increases from ~100 to ~50 K, and sharply increases at lower temperatures.[8] This resistivity behavior may be interpreted as characteristic of a doped semiconductor.[8] However, the layer bending **2** → **3**, and the tetragonal → orthorhombic distortion of La_2CuO_4 as well, cannot open a band gap at the Fermi level due to the presence of twofold screw rotation symmetry along the c axis. As anticipated, our calculations show that orthorhombic La_2CuO_4 is a 2D metal, the FS of which, shown in Figure 1c, is reasonably well nested as in the case of tetragonal La_2CuO_4. As suggested earlier,[21,25] therefore, orthorhombic La_2CuO_4 behaves as a metal at least above ~100 K, and thus the tetragonal → orthorhombic distortion is not a Peierls distortion. In fact, our calculations show that the energy of a single $CuO_4^{(6-x)-}$ layer increases with bending (**2** → **3**), although the potential energy curve is very shallow for small bending. Therefore, the driving force for the tetragonal → orthorhombic distortion of La_2CuO_4, and that for the layer bending **2** → **3**, must originate from interactions between La^{3+} and O^{2-} ions (from CuO_6 octahedra). Each La^{3+} (or a combination of La^{3+} and M^{2+} in the doped material) is located in a pocket made by four equatorial and four axial oxygen atoms of one CuO_4^{6-} layer and by one axial oxygen of another CuO_4^{6-} layer, in which the last axial oxygen is closer to La^{3+} than to Cu^{2+}. The interactions between the La^{3+} and O^{2-} ions might lead to a soft phonon mode[8,26] responsible for the tetragonal → orthorhombic distortion.

When the tendency for the metal–insulator (MI) transition of a metal is reduced in magnitude, the remnant structural instability may help produce unusually strong electron–phonon coupling[27] and hence high-T_c superconductivity. Consequently, it is crucial to know what causes the "MI" transition of La_2CuO_4 that occurs below ~100 K in understanding how the dopant, M, suppresses it and induces high-T_c superconductivity in $La_{2-x}M_xCuO_4$. Provided that the MI transition is not a Mott transition[24c,28] arising from electron–electron repulsion, the structural distortion appropriate for a band gap opening at the Fermi level of orthorhombic La_2CuO_4 is one that creates two nonequivalent copper atoms (in other words, possible "mixed-valence" formation). One such distortion is the breathing mode displacement of the equatorial oxygen atoms around each copper atom.[19,27c] Further experimental studies on La_2CuO_4 are necessary to uncover the origin of its MI transition and to help unravel the structural and electronic factors governing the high-T_c superconductivity in $La_{2-x}M_xCuO_4$.

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