Lattice Instability and High-T_c Superconductivity in $La_{2-x}Ba_xCuO_4$

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$La_{1.85}Ba_{0.15}CuO_4$ exhibits high-T_c superconductivity with an onset temperature near 33 K as measured by resistivity and magnetic susceptibility. The nonsuperconducting end-member compound, La_2CuO_4, which has an orthorhombic, *Cmca*, structure, exhibits semiconducting behavior. The orthorhombic distortion is proposed to result from a Peierls $2k_F$ instability or a soft zone-boundary phonon mode. The role of Ba is to suppress the instability and stabilize a higher-symmetry tetragonal, *I4/mmm*, structure which is metallic and superconducting.

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The discovery[1] and confirmation[2,3] of superconductivity with onset temperatures in the range of 30 K in the $La_{2-x}Ba_xCuO_4$ system has raised many questions about the role of Ba substitution, oxygen vacancies, and structural phase transitions in producing the high T_c. In this Letter we report the results of resistivity, magnetic susceptibility, and neutron powder diffraction measurements versus temperature on superconducting $La_{1.85}Ba_{0.15}CuO_4$ and the nonsuperconducting end-member compound La_2CuO_4. In particular, the first refined structural parameters of the superconducting phase are presented, and the nature of the phase transition which separates the two compounds and its relation to the observed high-T_c superconductivity are discussed.

The samples used in this study were synthesized by coprecipitation of La, Ba, and Cu oxalates with the proper stoichiometry and subsequent sintering in air at 1100°C for about 12 h. Neutron-diffraction data confirmed that the samples were well crystallized and over 95% single phase. Resistivity measurements were made by the four-point method on as-sintered lumps over the temperature range 295–5 K. dc magnetic susceptibility measurements were performed in a SHE Corp. SQUID magnetometer. The onset and width of the transition depend on sample preparation methods, as reported by the previous authors.[1-3] The best samples had onset temperatures near 35 K. The resistivity and magnetic susceptibility of the same sample of $La_{1.85}Ba_{0.15}CuO_4$ used in the neutron powder diffraction measurements are shown in Fig. 1. The onset of the drop in resistivity for this sample is at 33 K and the resistance is zero below 19 K. Diamagnetism also begins near 33 K. For the same sample cooled in a 100-G field, the flux exclusion at 20 K is about 20% of that observed for Nb, indicating bulk superconductivity.

The curve of resistivity versus temperature for the undoped compound, La_2CuO_4, is shown in Fig. 2. The slowly decreasing resistivity from room temperature to around 100 K, followed by a sharp rise in resistivity at lower temperatures, is characteristic of a typical doped semiconductor.

Neutron powder diffraction data were collected for $La_{1.85}Ba_{0.15}CuO_4$ and La_2CuO_4 for several temperatures in the range 295–10 K by use of the special-environment powder diffractometer at the Intense Pulsed Neutron Source and analyzed by the Rietveld structure-refinement technique. $La_{1.85}Ba_{0.15}CuO_4$ has the tetragonal, *I4/mmm*, structure (similar to K_2NiF_4) with two formula units per unit cell as proposed previously from indexing of powder x-ray data.[3] No phase transitions or other structural anomalies (e.g., unusual thermal expansion which could indicate an isostructural electronic transition) were observed as a function of temperature from 295 to 10 K. The structural parameters at 295 and 10 K

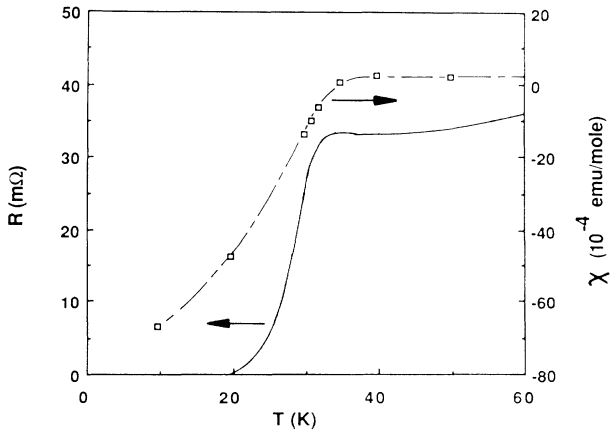

FIG. 1. Electrical resistance and dc magnetic susceptibility (for a sample cooled in a 2-kG field) vs temperature for $La_{1.85}Ba_{0.15}CuO_4$.

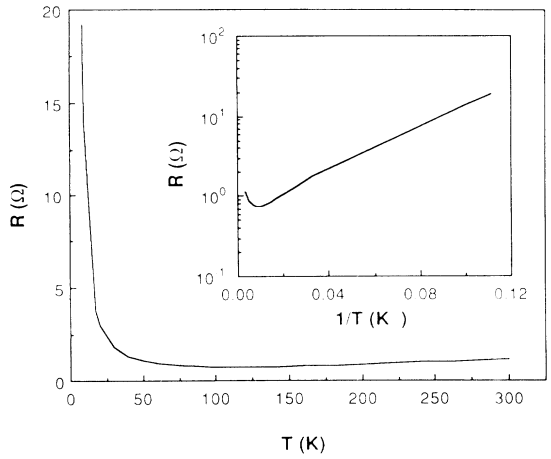

FIG. 2. Electrical resistance vs temperature for La_2CuO_4. Inset: Same data plotted on a logarithmic scale vs $1/T$.

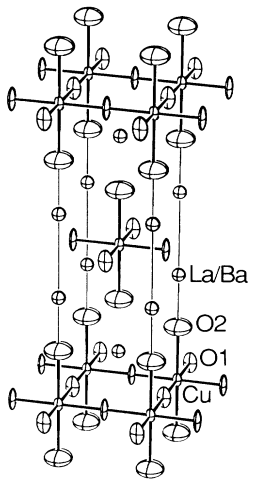

FIG. 3. Tetragonal structure of $La_{1.85}Ba_{0.15}CuO_4$. The atoms shown comprise one unit cell except that the full oxygen coordination around the copper atoms at the corners is shown for clarity. The anisotropic thermal ellipsoids are those obtained from the 295-K refinement.

are given in Table I. The refined site occupancies for the oxygen sites (O1 and O2) set a limit on the concentration of oxygen vacancies in this sample at 1% or less, with the O2 site showing full occupancy and the O1 site showing a small vacancy concentration which should be interpreted as being within the limits of accuracy of a powder diffraction measurement and, thus, may not be real. Therefore, the Ba^{2+} defects are not charge compensated by oxygen vacancies.

The structure of $La_{1.85}Ba_{0.15}CuO_4$ is shown in Fig. 3. Cu is in a site of tetragonal, $4/mmm$, symmetry with four strongly bonded oxygen neighbors (O1) in a square planar arrangement at a distance of 1.8936(1) Å, and two other oxygen neighbors (O2) much farther away along the $+z$ and $-z$ directions at a distance of 2.428(2) Å, thus forming an octahedron that is elongated in the z direction. O2 is actually closer to La [2.368(2) Å] than to Cu. Thus, the La (Ba) and O2 atoms form double-corrugated layers between the tightly bonded planar layers of Cu and O1 atoms.

Since conflicting reports of the structure of La_2CuO_4 appear in the literature,[4-6] the structure of La_2CuO_4 was solved directly from the neutron powder diffraction data to yield the orthorhombic, *Cmca*, space group with atom positions at 295 K that are virtually identical to those previously obtained from x-ray data by Grande, Müller-Buschbaum, and Schweizer.[4] (Structural data at other temperatures will be published later.) The orthorhombic cell is obtained from the tetragonal cell by a doubling of the basal plane in a $\sqrt{2}a\times\sqrt{2}a$ fashion. The new cell edges are $5.3562(1)\times5.3990(1)\times13.1669(2)$ Å^3 at 295 K. The symmetry of the Cu site is lowered to monoclinic, $2/m$, with the distances from Cu to O1 and O2 remaining essentially unchanged at 1.9035(1) and 2.432(2) Å, respectively. The largest atom displacements are those associated with a nearly rigid tilting (5° at 10 K) of the O_6 octahedra surrounding each Cu atom around one of the original [110] tetragonal axes. Since the O_6 octahedra share corners in the basal plane, neighboring octahedra tilt in opposite directions, resulting in the observed cell doubling and the lowering of symmetry from tetragonal to orthorhombic.

From these results it is clear that the role of Ba in the compound $La_{1.85}Ba_{0.15}CuO_4$ is to stabilize the higher-symmetry tetragonal, $I4/mmm$, phase which is metallic and superconducting. The amount of Ba needed to stabilize the tetragonal phase has not been determined, but must be below 0.1 atom per formula unit according to the report of Takagi *et al.*, that $La_{1.90}Ba_{0.10}CuO_4$ is also superconducting.[3] The mechanism of the phase transition separating the superconducting/metallic and nonmetallic phases is of particular interest. A soft zone-boundary phonon mode or a Peierls $2k_F$ instability are both possible mechanisms that could drive the structural

TABLE I. Structural parameters (with standard deviations in parentheses) for $La_{1.85}Ba_{0.15}CuO_4$ at 295 and 10 K. Space group $I4/mmm$; La (0,0,z), Cu (0,0,0), O1 (0,$\frac{1}{2}$,0), O2 (0,0,z).

	295 K	10 K
a (Å)	3.7873(1)	3.7817(1)
c (Å)	13.2883(3)	13.2487(3)
v (Å^3)	190.598(4)	189.478(5)
z(La)	0.36063(9)	0.36075(9)
z(O2)	0.1828(2)	0.1824(2)
n(O1)	1.97(2)	1.94(2)
n(O2)	2.04(2)	2.00(2)
R_{wp} (%)	7.54	8.43
R_{expt} (%)	4.38	3.03

instability. However, independent of the detailed nature of the driving mechanism, we believe that it is possible to describe qualitatively the effect of the observed structural distortions on the electronic properties in terms of a simple model.

Starting from a purely ionic picture of tetragonal La_2CuO_4 (with oxidation numbers La^{3+}, Cu^{2+}, and O^{2-}), we note that the tetragonal crystal field due to the elongated O_6 octahedra removes the orbital degeneracy of the Cu^{2+} $3d^9$ configuration, leaving the Cu-$d_{x^2-y^2}$ orbital as the only partially occupied atomic orbital.[7] The $d_{x^2-y^2}$ orbital overlaps strongly with the four surrounding O1 oxygen $p_\parallel$ orbitals (i.e., p_x and p_y orbitals that are oriented towards nearest-neighbor Cu atoms). All other atomic orbitals (because of their orientation) exhibit smaller overlaps with the Cu-$d_{x^2-y^2}$ orbitals. We propose, therefore, that the band structure near the Fermi energy ε_F can be approximately described by a simple tight-binding model which, for the undistorted (tetragonal) lattice, takes into account the direct nearest-neighbor $d_{x^2-y^2}$-$p_\parallel$ overlap integral t and the $d_{x^2-y^2}$ on-site energy ε_d, measured relative to the $p_\parallel$ on-site energy.[8] One then obtains three bands, $\varepsilon_k^{(0)}$, $\varepsilon_k^{(-)}$, and $\varepsilon_k^{(+)}$, that are (by construction) two-dimensional (2D) with $\varepsilon_k^{(0)} \equiv 0$ and $\varepsilon_k^{(\pm)} = \varepsilon_d/2 \pm [\varepsilon_d^2/4 + t_k^2]^{1/2}$ where

$$t_k^2 \equiv 4t^2[\cos^2(ak_x/2) + \cos^2(ak_y/2)].$$

Assuming that the d-p bond has partially ionic character, we take $\varepsilon_d > 0$ which puts the Fermi level into the $\varepsilon_k^{(+)}$ band with all $\varepsilon_k^{(0)}$ and $\varepsilon_k^{(-)}$ states fully occupied. As shown in Fig. 4, the 2D Fermi "surface" for the half-filled $\varepsilon_k^{(+)}$ band (corresponding to undoped La_2CuO_4) in this simple model has the shape of a square,[8,9] limited by the conditions $|k_x| + |k_y| = \pi/a$. It exhibits perfect nesting in the [110] and [−110] directions. The crucial observation here is that the static displacements associated with the octahedral tilting (which results in unit-cell doubling) can be written as a superposition of two modes with equal amplitudes, and wave vectors $\mathbf{Q}_1$ and $\mathbf{Q}_2$ of length $\sqrt{2}\pi/a$, pointing, respectively, in the same [110] and [−110] directions. The nesting wave vectors spanning opposite faces of the square Fermi surface are identical with the superlattice vectors $\mathbf{Q}_1$ and $\mathbf{Q}_2$ that are observed experimentally in the orthorhombic tilting distortion. Thus, in the presence of an electron-phonon coupling, the observed distortion manifests itself by opening a gap, Δ, at the Fermi surface and, hence, leads to semiconducting behavior. Because of the crystal symmetry ($I4/mmm$), the tilting modes do not give rise to a direct modulation of the overlaps or on-site energies of the $d_{x^2-y^2}$ and the $p_\parallel$ orbitals. However, the conduction electrons will couple to these modes indirectly via their overlaps with the O2 and La sites (where the tilting mode *does* introduce bond alternation).

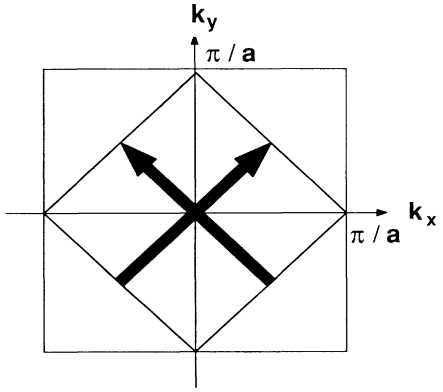

FIG. 4. 2D Brillouin zone and proposed Fermi surface (shaded) in the tetragonal phase of La_2CuO_4. The nesting wave vectors $\mathbf{Q}_1$ and $\mathbf{Q}_2$ are shown as arrows. The k_x and k_y axes in reciprocal space are along the a and b axes of the tetragonal real-space lattice, respectively.

In a simple rigid-band picture, substitutional Ba^{2+} doping will lower the Fermi energy and, in the 2D model, reduce the degree of Fermi-surface nesting. To the extent that the structural transition is driven by the electron-phonon interaction (i.e., a Peierls instability), divalent doping will tend to stabilize the high-symmetry tetragonal phase. In this "almost unstable" system, the two tilting modes (with wave vectors $\mathbf{Q}_1$ and $\mathbf{Q}_2$) have a finite, but still very low frequency.

A further important feature of our 2D model is that the electronic density of states exhibits a logarithmic Van Hove singularity[8-10] $\rho(\varepsilon) \propto \ln|\varepsilon - \varepsilon_F(\frac{1}{2})|$ at the Fermi energy $\varepsilon_F(\frac{1}{2})$ of the half-filled ($\varepsilon_k^{(+)}$) 2D conduction band.[11] Under conditions where the lattice instability is prevented by Ba^{2+} doping, the Van Hove–enhanced density of states[9] as well as the soft-phonon modes offer the possibility of an enhanced superconducting T_c.

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[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2]S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (to be published).

[3]H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (to be published).

[4]V. B. Grande, Hk. Müller-Buschbaum, and M. Schweizer, Z. Anorg. Allg. Chem. **428**, 120 (1977).

[5]K. K. Singh, P. Ganguly, and J. B. Goodenough, J. Solid State Chem. **52**, 254 (1984).

[6]J. M. Longo and P. M. Raccah, J. Solid State Chem. **6**, 529 (1973).

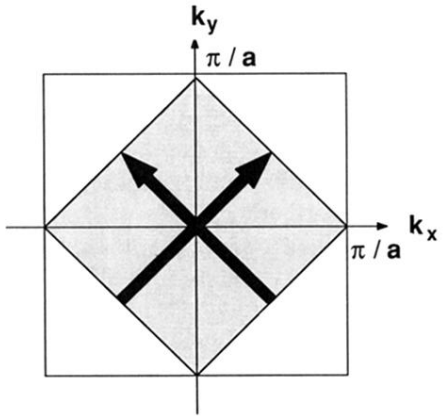
[7]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[8]S. Ellialtioglu and T. Wolfram, Phys. Rev. B **15**, 5909 (1977).

[9]J. E. Hirsch and D. F. Scalapino, Phys. Rev. Lett. **56**, 2732 (1986).

[10]T. M. Rice and C. K. Scott, Phys. Rev. Lett. **35**, 120 (1975).

[11]The effect of a small 3D interlayer overlap is to smooth out this singularity into a peak of finite height.



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