

# X-ray-absorption studies of the high- $T_c$ superconductors $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ and $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_4$

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X-ray-absorption studies of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  and  $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_4$  indicate that no structural transition that alters the valence or the near-neighbor environment by  $>0.01 \text{ \AA}$  occurs between 4 and 300 K. The doping with Sr and Ba primarily changes the Cu-O distance and width along the  $c$  axis. The larger width of the superconducting transition region observed in the Ba-doped material may result from its larger static disorder. Estimates of the Cu-O vibrational frequencies suggest that a phonon-coupling mechanism is just compatible with the observed  $T_c$ .

The newly discovered superconductivity<sup>1</sup> in layered perovskite structures with unprecedented high transition temperatures ( $T_c$ ) raises questions concerning their intrinsic superconducting properties and the underlying interactions responsible for the electron pairing. The structure and local atomic environment is likely to play a key role. In fact, all the previously known high- $T_c$  compounds ( $T_c \leq 23 \text{ K}$ ) contain Nb, indicating that a local, chemical effect is involved. In the new materials the Cu—O bond may play a similar role to that of Nb in the other superconductors. As a consequence, we have undertaken a structural investigation, using the x-ray-absorption spectrum, both near-edge and extended x-ray-absorption fine structure (EXAFS), of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  (LSCO) and  $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_4$  (LBCO) high- $T_c$  superconductors. Particular emphasis was placed on the Cu-O local environment.

The crystal structure is the tetragonal  $\text{K}_2\text{NiF}_4$  structure (Fig. 1, inset) which consists of two-dimensional layers of copper-oxygen octahedra elongated along the  $c$  axis and separated by layers of La which share the oxygen in a rocksaltlike arrangement.<sup>2,3</sup> The structure can be unstable with respect to small rotations and distortions of the octahedra. All models<sup>4</sup> proposed for the band structure agree that the conduction band is derived from the half-filled antibonding  $\text{Cu}(3d_{(x^2-y^2)})-\text{O}(2p_{x,y})$  band. The almost perfect nesting of the Fermi surface for pure  $\text{La}_2\text{CuO}_4$  is believed to result in a Peierls transition to an orthorhombic phase (below  $260^\circ\text{C}$ ) with consequent

semiconducting behavior. The shift in the Fermi surface, caused by doping with divalent Ba or Sr substituted for the trivalent La, is thought to reduce the Fermi surface nesting so that it becomes energetically unfavorable to distort, and the tetragonal phase, which is metallic, is stabilized. Electron-phonon coupling involving the Cu-O breathing mode is then estimated<sup>4</sup> to be of sufficient strength to give the observed  $T_c$ 's. In contrast to such conventional electron-phonon-coupling models stand theories based on electron-electron interactions. Depending on the screening length, it is possible to have the pairing occur within the unit cell or at interfaces. Some version of polarization pairing such as the Allender-Bray-Bardeen<sup>5</sup> formulation may be valid. An entirely different model has been suggested by Anderson<sup>6</sup> in which the pairing is between antiferromagnetically coupled near-neighbor spins which become charged superconducting pairs when the Sr or Ba dopes the Cu-O conduction band sufficiently.

Our EXAFS measurements indicate that the planar Cu—O(1) bonds are strong, while the Cu—O(2) bonds along the  $c$  axis are somewhat weaker. No structural phase transition, that results in a significant change in the near-neighbor distances or widths, occurs over the temperature range 4–300 K. Likewise, no change in valence of the ions is observed. The doping with Ba or Sr affects primarily the locations and distribution of the O(2) atoms. For LBCO the large value of the width of the O(2) peak likely indicates that static disorder is a contributing factor

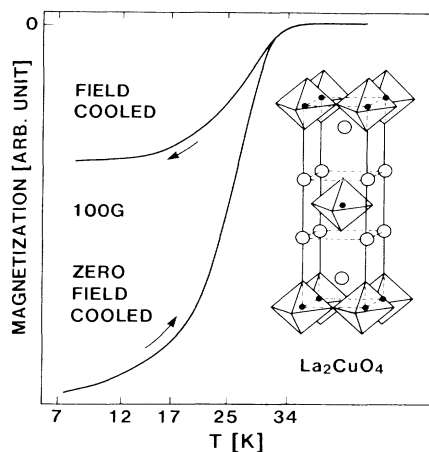


FIG. 1. Magnetization as a function of temperature for LSCO as measured with a SQUID magnetometer, both for the sample cooled in a 100-G field and for the sample cooled in zero field and then warmed in a 100-G field. Inset: tetragonal structure of  $\text{La}_2\text{CuO}_4$ ; the elongated octahedra consist of oxygen atoms about the Cu atoms (solid dots); the open circles are La.

to the large width in the superconducting transition when compared with LSCO. In addition, the values of the Einstein temperature obtained indicate that  $T_c$ 's in the range of 40–50 K are just compatible with a phonon-coupling model; significantly higher  $T_c$ 's may require another mechanism.

Both LBCO and LSCO were prepared by the solid-state reaction of  $\text{La}_2\text{O}_3$ , CuO, and either  $\text{BaCO}_3$  (Ref. 7) or  $\text{SrCO}_3$ .<sup>8</sup> X-ray diffraction measurements indicate that the materials are single phase and have the tetragonal  $\text{K}_2\text{NiF}_4$  structure. A relatively sharp superconducting transition was noted for LSCO with a midpoint of 32 K and a width of about 3 K in the resistivity measurements.<sup>8</sup> The transition for LBCO was much wider with an onset of about 27 K.<sup>7</sup> Figure 1 displays the magnetization results for LSCO, where the field-cooled Meissner signal is seen to be 40% of the signal due to the persistent currents induced by the same field. This 40% signal is a conservative lower limit of the fraction of superconducting material in our sample since trapped flux will reduce the observed signal. The EXAFS samples were prepared by grinding the sintered pellets into fine powder. We verified that this powdering procedure has a negligible effect on  $T_c$ .

The x-ray-absorption measurements were performed for x-ray energies in the vicinity of the Cu and Sr  $K$  edges and the Ba and La  $L$  edges as a function of temperature from 4 to 300 K. Both the near-edge and EXAFS regions were investigated. The near-edge structure, which is sensitive to the electronic structure and the bonding configuration, shows no change with temperature. This indicates that no electronic transition, such as a valence change, occurs on going from well above to well below  $T_c$ .

A thorough analysis was made of the EXAFS data on the Cu  $K$  edge and La  $L_{\text{III}}$  edge in each sample. The data were reduced in the usual manner.<sup>9</sup> A typical spectrum, i.e., the Fourier transform of the EXAFS,  $k\chi(k)$ , is shown in Fig. 2 for the EXAFS on the Cu  $K$  edge in LSCO at 4.2

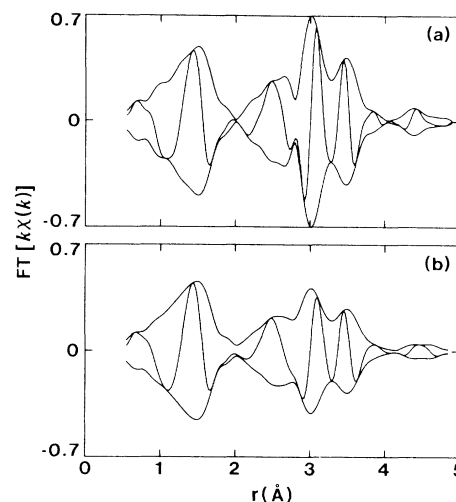


FIG. 2. The magnitude (envelope) and real part of the Fourier transform of the EXAFS,  $k\chi(k)$ , on the Cu  $K$  edge for LSCO at (a) 4.2 K and (b) 300 K. The transform range is  $k = 2.9\text{--}17.2 \text{ \AA}^{-1}$  broadened by a Gaussian of half-width  $0.5 \text{ \AA}^{-1}$ . The first peak is due to the six oxygen neighbors to the Cu, and the second set of peaks is due to the (La,Sr) and Cu second neighbors.

and 300 K. The first peak is due to the six oxygens forming the distorted octahedra about the Cu ions. Two distances exist,  $r_1$  for the four nearby oxygens [O(1)] in the basal plane ( $\approx 1.9 \text{ \AA}$ ) and  $r_2$  for the two oxygens [O(2)] further away along the  $c$  axis ( $\approx 2.3 \text{ \AA}$ ).  $r_1$  and  $r_2$  are not resolved in this figure but are readily apparent in the shape of the peak and confirmed by a detailed analysis. The next set of three peaks is the second-neighbor environment, consisting of (La,Sr) and Cu atoms. The only significant change in these spectra from 4.2 to 300 K is a slight broadening of the peaks with a resultant reduction in peak height. This is due to the increase in the amplitude of thermal vibration of the atoms that has a stronger effect on the second neighbors than on the first neighbors which are more tightly bound. Without any detailed analysis, this figure shows that no phase transitions that would significantly modify the near-neighbor distances occur. An orthorhombic distortion such as that in pure  $\text{La}_2\text{CuO}_4$  (Ref. 2) would, however, not be observed since the distortion consists of a small orthorhombic strain and a rotation of the  $\text{CuO}_6$  octahedra with little or no change in the near-neighbor distances. In addition, no structural anomaly, such as phonon softening, or any unusual thermal expansion that may signal an isostructural electronic transition is observed.

These conclusions were quantified in a detailed analysis of the data. For the EXAFS data at each of the edges, one-Gaussian comparisons to the 4.2-K data were made for the first-neighbor environment. For the Cu  $K$ -edge data, we also compared the second-neighbor peak. In each case the fit was excellent, with a small shift ( $\Delta r < 0.01 \text{ \AA}$ ) in the near-neighbor peak position and a peak width that gradually increased for  $T$  above 77 K. Basically, the one-Gaussian comparisons indicate that

structural changes, if present, are very small. The change in width squared ( $\Delta\sigma^2$ ) increases slowly with  $T$ ; the temperature dependence for the Cu nearest neighbors is somewhat smaller than observed for the La and Sr near-neighbor environment.

To determine the distances to the two inequivalent oxygens about the Cu atoms, we performed two-Gaussian fits using  $\text{Cu}_2\text{O}$  as a structural standard. Although the ionic size of Sr is slightly less than La and the size of Ba considerably larger than La ( $r_{\text{Sr}}=1.13$  Å,  $r_{\text{La}}=1.15$  Å,  $r_{\text{Ba}}=1.35$  Å), both doped samples have a slightly increased value for the  $c$  axis lattice constant [ $c(\text{La}_2\text{CuO}_4)=13.15$  Å,  $c(\text{LSCO})=13.24$  Å, and  $c(\text{LBCO})=13.32$  Å].<sup>3</sup> The  $a$  axis lattice parameter changes very little, i.e., only about 0.01 Å. Consequently, we expect a larger variation in  $r_2$  with composition. In Fig. 3, we plot the temperature dependence of the two Cu-O distances for each sample. Our data clearly show a difference between  $r_1$  and  $r_2$  and hint at a slight increase with temperature that is consistent with the thermal expansion data<sup>2</sup> (dashed line).

The Cu-O distances in LBCO are in good agreement with those obtained by neutron diffraction.<sup>10</sup> The value for  $r_2$  is unexpectedly shorter for LSCO (2.3 Å) than for LBCO (2.45 Å) or the pure material (2.42 Å). This shorter Cu-O distance may give rise to a slight transfer of charge to the Cu-O plane perpendicular to the  $c$  axis, thereby resulting in a higher density of states at the Fermi surface. This distance is given by  $u(\text{O}(2))c$ , since the Cu atoms are at (000) and the O(2) atoms are at (00 $u$ ). These measured distances yield  $u(\text{O}(2),\text{Ba})=0.180$  and  $u(\text{O}(2),\text{Sr})=0.174$ . The value for LBCO agrees well with the neutron results of  $u(\text{O}(2))=0.183$  for  $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$ .

The squares of the widths of the Cu-O pair distribution functions  $\sigma^2$  are shown in Fig. 4. These values are actually

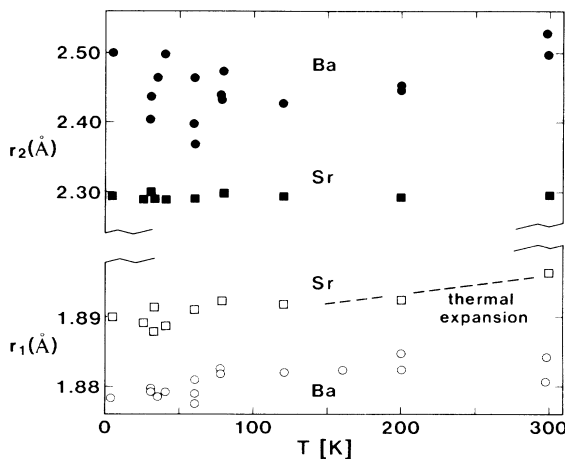


FIG. 3. The Cu-O first-neighbor distances as a function of temperature for LSCO and LBCO.  $r_1$  is for the four O(1) atoms in the basal plane and  $r_2$  is for the two O(2) atoms along the  $c$  axis. The dotted line shows the slope of the thermal expansion for  $\text{La}_2\text{CuO}_4$ .<sup>2</sup> Note the factor of 10 scale change between  $r_1$  and  $r_2$ .

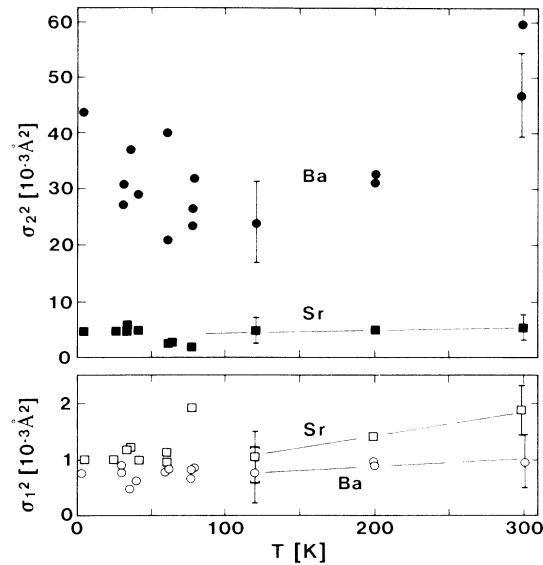


FIG. 4. The square of the width of the Cu-O pair distribution function for LSCO and LBCO for O(1) [ $\sigma_1^2$ ] and O(2) [ $\sigma_2^2$ ] as a function of temperature. Note the factor of 10 scale change between  $\sigma_1^2$  and  $\sigma_2^2$ .

the change in the widths relative to the  $\text{Cu}_2\text{O}$  structural standard at 4.2 K; however, an estimate of  $\sigma^2$  for the structural standard, using theoretical amplitudes and phases,<sup>11</sup> indicates that it is smaller than those indicated in Fig. 4. The plotted results are therefore close to the actual widths. It is seen that  $\sigma_1^2$  for the oxygen atoms in the plane is small and increases only slightly with temperature. This indicates that the Cu—O(1) bond is strong and is relatively unaffected by the alloying and thermal disorder. However,  $\sigma_2^2$  for the oxygen atoms perpendicular to the plane is an order of magnitude larger than  $\sigma_1^2$ , even at low temperatures. This indicates that static disorder due to alloying (and possible inhomogeneities) dominates, particularly in LBCO. The O(2) atom is also bonded to the (La,Ba) or (La,Sr) atoms and so is more affected by alloying than is O(1). That  $\sigma_2^2$  is larger for LBCO than for LSCO is consistent with the larger Ba ion size and correspondingly larger internal strains. Since these materials have a very large pressure dependence<sup>7</sup> for  $T_c$ , a broad distribution of strains can lead to a large distribution of  $T_c$ 's on a microscopic scale and result in the large transition width for LBCO in contrast to the narrow 3-K width for LSCO.

From the temperature variation of the Debye-Waller-type broadening of the pair distribution function and the assumption that the Cu—O bonds can be treated as Einstein oscillators, we can estimate<sup>9</sup> the characteristic frequencies  $\omega_E$  in the crystal using  $\sigma^2(T) \approx \hbar/(2M\omega_E) \times \coth(\hbar\omega_E/2k_B T)$ , with the reduced mass  $M \approx M_{\text{oxygen}}$ . For LSCO, we obtain an Einstein temperature  $\Theta_{E1}$  of the Cu—O(1) vibration of about  $610 \pm 80$  K. For the Cu—O(2) bond, we estimate  $\Theta_{E2} \approx 500 \pm 100$  K. The selective vibrations of La to O and to the other neighbors are estimated to be in the range 250–400 K. For LBCO, the temperature dependence of  $\sigma_1^2$  seems to be consider-

ably smaller than for LSCO, and  $\Theta_{E1}$  correspondingly larger,  $1000 \pm 200$  K. Conversely,  $\sigma_2^2(T)$  for LBCO appears much larger than for LSCO. Because of the large scatter in the low- $T$  data and the hint of a minimum, an estimate for  $\Theta_{E2}$  is difficult, an upper limit being 300 K. These values compare favorably with the results of infrared transmittance experiments which give frequencies corresponding to about 530, 720, and 980 K for  $\text{La}_2\text{CuO}_4$  (orthorhombic phase).<sup>12</sup> They also indicate that  $T_C/\Theta_D \sim 0.1$ , a strong coupling value. These values of  $\Theta_E$ , although high, are still compatible with an electron-phonon-coupling mechanism if one assumes that strong coupling is present in these materials. Some infrared measurements<sup>13</sup> indicate that the coupling may not be strong, but other infrared results<sup>14</sup> leave the question open. If other types of measurements indicate that the coupling is weak, then other mechanisms may have to be considered.

It would be particularly interesting, if samples of the Y-Ba-Cu-O multiphase superconductors with  $T_c \sim 100$  K (Ref. 15) can be made pure enough, to continue the work reported here in order to compare the bond lengths and temperature-dependent broadening with the present study.

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