PHYSICAL REVIEW B VOLUME 35, NUMBER 13 1 MAY 1987

Rapid Communications

The Rapid Communications section is intended for the accelerated publication of important new results. Since manuscripts submitted to this section are given priority treatment both in the editorial office and in production, authors should explain in their submittal letter why the work justifies this special handling. A Rapid Communication should be no longer than 3½ printed pages and must be accompanied by an abstract. Page proofs are sent to authors, but, because of the accelerated schedule, publication is not delayed for receipt of corrections unless requested by the author or noted by the editor.

X-ray absorption studies of $La_{2-x}(Ba,Sr)_xCuO_4$ superconductors

J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, and M. Suenaga
Brookhaven National Laboratory, Upton, New York 11973

(Received 18 February 1987)

X-ray absorption spectroscopy has been used to study superconducting compounds with the composition $La_{2-x}(Ba,Sr)_xCuO_4$ for $x=0$ to 0.3. X-ray absorption measurements at the Cu K edge indicate that the copper valence is 2+ for all dopant concentrations, and that the mean-square relative displacements for Cu-O nearest neighbors are approximately the same for all compositions, with an average characteristic temperature of 570 ± 30 K. Measurements at the La L_3 edge suggest that the number of empty states near the Fermi energy with O $2p$ character increases with dopant concentration.

Materials which are superconducting at temperatures above 35 K and have the general formula $La_{2-x}(Ba,Sr)_xCuO_4$ have recently been reported.[1,2] The compounds which show superconducting behavior at the highest temperatures have a Ba or Sr concentration x of ~0.15. The first evidence for such behavior in oxide systems was obtained in a study[3] of compounds of the form $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$, in which the samples were found to contain several different structural phases. Further work[4,5] revealed that the superconducting phase has the K_2NiF_4-type structure with composition $La_{2-x}Ba_xCuO_{4-y}$. The oxygen content of such materials is known to depend on the method of sample preparation and subsequent treatment;[6] however, a neutron-diffraction study[7] on a sample of $La_{1.85}Ba_{0.15}CuO_4$ found that the concentration of oxygen vacancies is 1% or less.

The observations of superconductivity at such high temperatures have generated a considerable amount of excitement and have led to numerous speculations about the superconducting mechanisms in these systems. For example, in a purely ionic model, one might expect that the substitution of some Ba^{2+} or Sr^{2+} for La^{3+} might be compensated by the conversion of some Cu^{2+} to Cu^{3+}.[5,6] Alternatively, the reduction in the number of valence electrons might result in an increase in oxygen vacancies. It has been suggested that the presence of mixed-valent copper might result in strong electron-phonon coupling, and indeed the expectation of finding polaronic effects appears to have motivated Bednorz and Müller's original study of the Ba-La-Cu-O system.[3] Possible similarities with the superconducting oxide $BaPb_{1-x}Bi_xO_3$ have also been suggested.[2,8] A theoretical study[9] of that system suggested that a "breathing"-type phonon mode involving the oxygen neighbors about a Bi atom could be responsible for strong electron-phonon coupling and a relatively high T_c. For $La_{2-x}Sr_xCuO_4$ it is speculated that a high-frequency breathing mode of the elongated octahedron of oxygen atoms about each copper could be important.

We have performed x-ray absorption measurements on samples with the nominal compositions $La_{2-x}Sr_xCuO_4$ with $x=0$, 0.1, 0.15, 0.2, and 0.3, and $La_{2-x}Ba_xCuO_4$ with $x=0.15$, 0.2, and 0.3. Studies of the x-ray absorption near-edge structure (XANES) of the Cu K edge show that Cu has a valence of 2+ which does not vary with increasing dopant concentration. On the other hand, measurements of the La L_3 edge reveal a systematic increase in the density of unoccupied states having d symmetry with respect to the site. The increase in d-symmetry holes is most likely due to a decrease in occupation of O $2p$ states caused by the reduction of valence-electron density through doping. From temperature-dependent measurements of the extended x-ray-absorption fine structure (EXAFS) at the Cu K edge, the mean-square relative displacements (MSRD's) between Cu and O nearest neighbors have been determined. We find that the Cu—O bond is quite strong, with no significant variations due to doping and no anomalous behavior as a function of temperature. Analogous measurements on the $A15$-structure superconductor Nb_3Sn show large anomalies in the MSRD's for Nb-Nb and Nb-Sn near neighbors at low temperature, indicative of the strong electron-phonon coupling existing in that system.[10,11]

The measurements were performed on beam line X-$11A$ at the National Synchrotron Light Source (NSLS) using a double-crystal monochromator with Si(111) crystals and a nominal energy resolution at 9 keV of ~1.3 eV for near-edge scans and ~2.4 eV for EXAFS scans.

Each of the samples measured was ground to a fine powder and rubbed onto Kapton or Scotch Magic tape. The energy scale of the Cu K-edge spectrum for each sample was referenced to a simultaneous Cu foil measurement, giving an accuracy in the relative energy scale of ± 0.1 eV. For the temperature-dependent measurements, the powder-on-tape samples were mounted on a copper sample holder and cooled with an Air Products Displex refrigerator. Temperatures were monitored with a gold-chromel thermocouple attached to the sample holder.

The starting materials for sample synthesis were La_2O_3, CuO, and $BaCO_3$ or $SrCO_3$, all of reagant grade or better. Components were mixed in the appropriate proportions, ground together, and fired in air at 1000-1100 °C. After a second grinding, pellets were formed and fired in air at 1100 °C. Some of the samples were fired a third time at 900-1100 °C in air or oxygen. The superconducting properties were characterized by measuring the change in ac magnetic susceptibility with temperature. For the samples doped with Sr, $x=0.1$, 0.15, and 0.2, and Ba, $x=0.15$, the signal strength indicated essentially bulk superconductivity, with onsets of superconducting behavior at 29, 36, 28, and 26 K, respectively. X-ray diffraction measurements indicate that the content of impurity phases is generally less than 5%, with no observable impurities above ~2% in some cases.

By doping La_2CuO_4 with Sr or Ba one obtained a crystal with a tetragonal structure[6,7] in which each Cu atom is coordinated by four oxygen atoms in the a-a plane at a distance of 1.89 Å, with two more along the c axis at 2.43 Å, forming an elongated octahedron. The La ions are ninefold coordinated by oxygen atoms at several different distances. In the "pure" material, the octahedra are tilted by a few degrees with respect to the tetragonal c axis, with neighboring octahedra tilted in opposite directions, resulting in a lower-symmetry, orthorhombic structure.[7] The tetragonal-to-orthorhombic distortion causes only very small changes in distances between near-neighbor atoms, and the Cu environment remains relatively unchanged.

Cu K-edges for samples with a Sr doping of $x=0$, 0.15 and 0.3 are compared with Cu^{1+} and Cu^{2+} standards in Fig. 1. All three edges line up quite well with the 2+ standard. Since a good reference material containing Cu^{3+} was not available, atomic calculations were performed to estimate the expected edge shift.[12] In both the ionic and fully screened cases the edge shift in going from Cu^{2+} to Cu^{3+} was comparable to the shift between Cu^{1+} and Cu^{2+}, which experimentally is about 10 eV. In a purely ionic model with no oxygen vacancies, for each Sr^{2+} atom which replaces a La^{3+} atom, a copper atom would go from 2+ to 3+. This is clearly not consistent with the Cu K-edge results, as the main edge is almost unaffected by doping and no new absorption features appear at higher energies. A small constant shift in the main peak does occur on going from $x=0$ to $x>0$, probably corresponding to the change in crystal symmetry previously mentioned. For Sr doping the shift is 0.6 ± 0.1 eV and for Ba doping it is 0.8 ± 0.2 eV. The small feature near -3 eV is due primarily to quadrupolar transitions to Cu $3d$ states.[13] Again it is found that this feature is strengthened in going from $x=0$ to $x>0$, but is independent of doping levels.

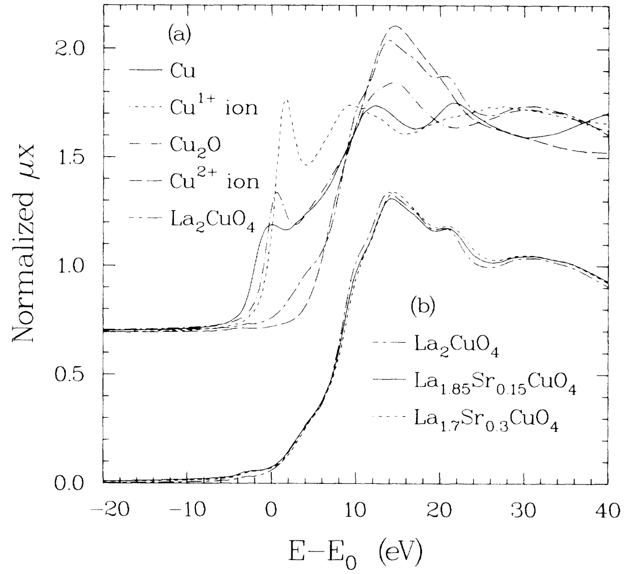

FIG. 1. XANES measured at the Cu K edge ($E_0=8980$ eV), normalized to the edge step. (a) Comparison of edges for several valences of Cu. The Cu^{1+} was obtained by electrochemically dissolving a Cu electrode in an HCl solution, and the Cu^{2+} was produced by dissolving $CuCl_2$ in water. (b) Comparison of edges in $La_{2-x}Sr_xCuO_4$.

The area under the "white line" observed at an L_3 edge is proportional to the number of empty states near the Fermi energy with d symmetry relative to the absorption site.[14] Because of spin-orbit coupling, the d-symmetry final states will have total angular momentum quantum numbers $j=\frac{3}{2}$ or $\frac{5}{2}$. It has been shown[15] that the white line intensity at an L_3 edge, with an initial state of $2p_{3/2}$, should be proportional to $(5h_{5/2}+h_{3/2})/6$, where h_j is the number of d-symmetry holes with angular momentum j. For a complete characterization of the density of d-symmetry empty states, one should also look at the L_2 edge, which we have not yet done. Nevertheless, Fig. 2 shows normalized L_3 edge absorption measurements in $La_{2-x}Sr_xCuO_4$ for $x=0$ to 0.3. The height of the white line and the area beneath it clearly increase with Sr concentration, although the increase is not strictly monotonic. Similar results have been obtained for Ba doping. In both cases the increase in area of the La white line is ≃8%-10% at higher doping levels. Measurements at the Ba L_3 edge in $La_{2-x}Ba_xCuO_4$ are shown in Fig. 3. The density of empty d states about a Ba ion, in contrast to that about La, decreases with Ba concentration.

The L_3 edge results indicate that the number of d-symmetry empty states about the La site increases with Sr or Ba concentration. This observation is consistent with a decrease in the number of valence electrons due to the doping. The fact that this change is observed at the La edge suggests that electron energy bands crossing the Fermi level must involve either La $5d$ or, more probably, O $2p$ states. (An appropriate combination of O $2p$ states can form a state of d symmetry with respect to a La site.)

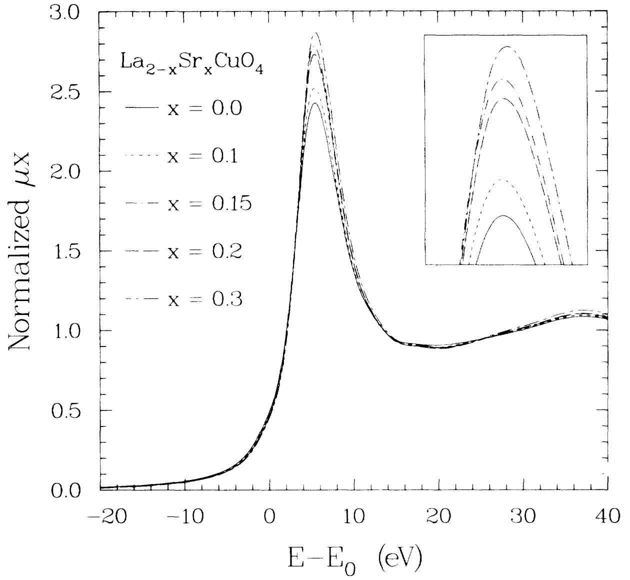

FIG. 2. Normalized XANES measured at the La L_3 edge ($E_0 = 5483$ eV) in $La_{2-x}Sr_xCuO_4$. The inset gives an expanded view of the white line peaks.

We cannot exclude the possibility that Cu 3*d* states contribute to the bands near the Fermi energy whose occupation varies with dopant concentration; however, the Cu *K*-edge measurements indicate that the number of atomically localized 3*d* states does not vary appreciably.

Next we turn to the analysis of the EXAFS data. Measurements were made at the Cu *K* edge at temperatures from 10 to 300 K for the samples La_2CuO_4, $La_{1.85}Sr_{0.15}$, $La_{1.7}Sr_{0.3}CuO_4$, and $La_{1.7}Ba_{0.3}CuO_4$ (hereafter to be referred to as pure, $Sr_{0.15}$, $Sr_{0.3}$, and $Ba_{0.3}$, respectively).

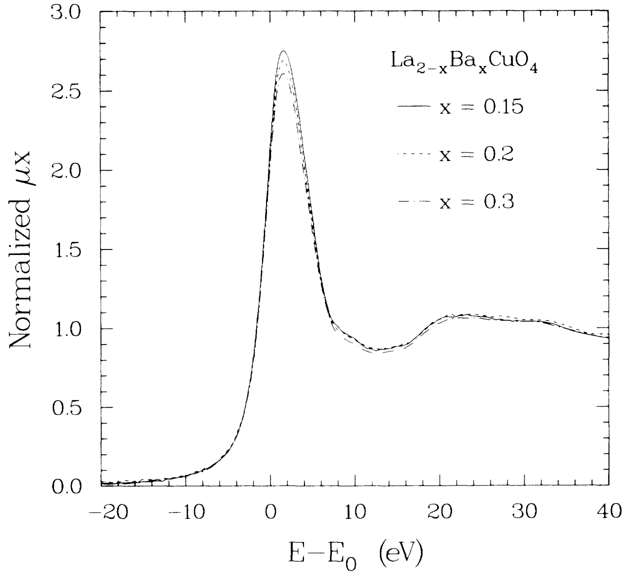

FIG. 3. Normalized XANES measured at the Ba L_3 edge ($E_0 = 5247$ eV) in $La_{2-x}Ba_xCuO_4$.

EXAFS interference function $\chi(k)$ was extracted from the measured absorption data using standard techniques.[16] Figure 4 shows Fourier transforms of $k^2\chi(k)$ for the pure and $Sr_{0.15}$ samples at 10 K. (The *k* range for the transforms is 2.0–17.7 $Å^{-1}$.) The differences between the transformed data for the two compounds occur mainly as small variations in peaks corresponding to distant metal atom coordination shells. The oxygen peak shows negligible changes due to doping.

The oxygen nearest-neighbor EXAFS contribution has been isolated by Fourier filtering the peak between 0.8 and 2.0 Å in *r* space. The resulting single shell data were analyzed using the ratio method.[17] Simulations indicate that the signal due to the two more distant O neighbors along the *c* axis should be quite small compared to that from the four neighbors in the basal plane. Indeed, comparing the 10-K data with the Cu-O shell in Cu_2O (in which Cu is doubly coordinated by O) we find oxygen coordinations of 3.9, 3.9, 4.0, and 4.1 for pure, $Sr_{0.15}$, $Sr_{0.3}$, and $Ba_{0.3}$, respectively, with an uncertainty of ± 0.1. If the reduction in the number of valence electrons with dopant concentration were exactly compensated by oxygen vacancies, all assumed to be located in the basal plane,[6] we should expect to observe a coordination varying from 4.0 to 3.7 as *x* varies from 0 to 0.3. Our observation of a roughly constant coordination, though not conclusive, is inconsistent with complete compensation by oxygen vacancies.

The thermal damping of the EXAFS from a single coordination shell depends on the MSRD σ^2 for the relevant atom pair.[18] The change in σ^2 with temperature for Cu-O nearest neighbors has been determined for each of the four samples. The temperature dependence can be parametrized with an Einstein model.[19] Very good fits to the data are obtained, indicating that any deviations from harmonic behavior are small. The Einstein temperature Θ_E, determined from a fit, corresponds to a characteristic frequency for the Cu–O bond length fluctuations, which include the breathing mode suggested to be important to

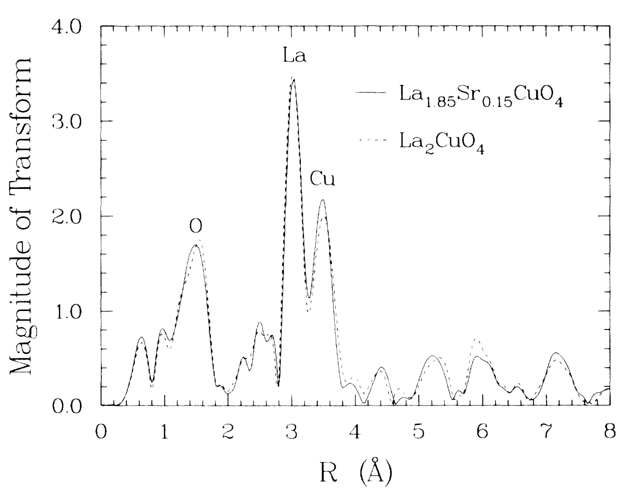

FIG. 4. Magnitudes of the Fourier transforms of $k^2\chi(k)$ obtained from Cu *K*-edge measurements in La_2CuO_4 and $La_{1.85}Sr_{0.15}CuO_4$ at 10 K.

the electron-phonon coupling.[8] The observed Einstein temperatures are 580 ± 30, 595 ± 50, 565 ± 30, and 550 ± 40 K for pure, $Sr_{0.15}$, $Sr_{0.3}$, and $Ba_{0.3}$, respectively. The uncertainties are large for two reasons. The first reason is that oxygen is a weak backscatterer, and the second is that because Θ_E is so high, the change in σ^2 is small over the temperature range studied. No statistically significant variation in the Cu–O bond strength is observed due to doping. Although Θ_E is high, the low mass of the oxygen atom results in an rms bond-length fluctuation of 0.06 Å at $T=0$, increasing only to 0.07 Å at room temperature. This fluctuation length is considerably larger than the difference of 0.01 Å in Cu-O distances observed between La_2CuO_4 and $La_{1.85}Ba_{0.15}CuO_4$ with neutron diffraction.[7]

This work was performed at beam line X-11 at the National Synchrotron Light Source and is supported by the U.S. Department of Energy under Contracts No. DE-AC02-76CH00016 and No. DE-AS05-80-ER10742.

---

[1] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[2] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietmann, Phys. Rev. Lett. **58**, 408 (1987).

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

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

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

[6] C. Michel and B. Raveau, Rev. Chim. Miner. **21**, 407 (1984).

[7] J. D. Jorgensen, H.-B. Shüttler, D. G. Hinks, D. W. Capone II, K. Zhang, M. B. Brodsky, and D. Scalapino, Phys. Rev. Lett. **58**, 1024 (1987).

[8] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[9] L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **28**, 4227 (1983).

[10] J. M. Tranquada and S. M. Heald, Bull. Am. Phys. Soc. **30**, 608 (1985).

[11] S. M. Heald and J. M. Tranquada, Adv. Cryog. Eng. **32**, 417 (1986).

[12] Relativistic calculations of the total energy of an atom in different configurations were performed using a computer program kindly provided by J. W. Davenport. Exchange and correlation were included within the local density approximation of Hedin and Lundquist. For details, see J. W. Davenport, M. Weinert, and R. E. Watson, Phys. Rev. B **32**, 4876 (1985); L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[13] J. E. Hahn, R. A. Scott, K. O. Hodgson, S. Doniach, S. R. Desjardins, and E. I. Solomon, Chem. Phys. Lett. **88**, 595 (1982).

[14] M. Brown, R. E. Peierls, and E. A. Stern, Phys. Rev. B **15**, 738 (1977).

[15] L. F. Mattheiss and R. E. Dietz, Phys. Rev. B **22**, 1663 (1980).

[16] E. A. Stern and S. M. Heald, in *Handbook on Synchrotron Radiation,* edited by E. E. Koch (North-Holland, Amsterdam, 1983), Vol. 1.

[17] E. A. Stern, D. E. Sayers, and F. W. Lytle, Phys. Rev. B **11**, 4386 (1975).

[18] G. Beni and P. M. Platzman, Phys. Rev. B **14**, 1514 (1976).

[19] E. Sevillano, H. Meuth, and J. J. Rehr, Phys. Rev. B **20**, 4908 (1979).