

Determination of valence of Cu in superconducting $\text{La}_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$

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The measurement of Cu *K*-edge x-ray absorption near-edge structure of monovalent, divalent, and trivalent copper oxides has been used to identify the presence of different valence of copper in the $\text{La}_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$ ($x = 0.0-0.3$) system. The results indicate the coexistence of CuII and CuIII states in these compounds. Theoretical calculations based on a cluster of $\text{CuO}_4\text{O}_2\text{La}_8\text{LaSr}$ predict the presence of nearly degenerate electronic ground states representing nominally CuII and CuIII configurations.

The observation of high superconducting transition temperatures in doped La_2CuO_4 (Refs. 1-5) has created new interest in the long disputed valency of Cu in these compounds.^{6,7} The compound La_2CuO_4 has an orthorhombic structure and exhibits semiconducting behavior at low temperatures. The substitution of trivalent La atoms by nominally divalent Ba or Sr atoms stabilizes the tetragonal K_2NiF_4 -type structure. These substituted compounds $\text{La}_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$ are superconducting for $x < 0.3$ with transition temperatures as high as 40 K. There are numerous speculations regarding the role of divalent atoms substituting for La. The charge neutrality in the lattice can be achieved through the formation of oxygen vacancies. However, careful neutron-diffraction studies have revealed that such vacancy concentrations are rather small,^{5,8} suggesting that the charge balance is established due to the presence of CuIII ions. The above discussion is strictly based on an ionic model of the compound, which is most unlikely to be true in view of the short Cu-O bond length in the basal plane. Theoretical models for superconductivity in these oxides suggest the existence of Peierls distortions involving the ambivalence of Cu atoms.⁹ The present Rapid Communication describes an attempt to observe the ambivalence of Cu atoms from the measurement of x-ray absorption near-edge structure (XANES) in this class of oxides.

The measurements of XANES has extensively been used in the past to study the valence fluctuation of rare-earth atoms in many systems.¹⁰ The measurement provides a signature of a particular charge state, which is stable over a period of 10^{-14} s or longer. The *K*-edge XANES of Cu primarily represents electric dipole transitions (*E*1) from the 1*s* core level to final states with nonzero *np* components, which are governed by the electronic structure of the material. Hence, the presence of suggested ambivalent Cu can be identified from a detailed

comparison of the XANES of the superconducting and semiconducting compound with those of stable Cu chemical configurations in standard oxides.

In the present work, we are reporting XANES measurements of a series of Ba- and Sr-doped La_2CuO_4 compounds. The standard oxides chosen for the study are Cu_2O , CuO , and KCuO_2 ,¹¹ in which copper atoms assume monovalent, divalent, and trivalent states. All the oxides were freshly synthesized, and were characterized using x-ray diffraction, as well as magnetic susceptibility and electrical resistivity measurements. In the case of Ba- or Sr-substituted La_2CuO_4 , the superconducting properties were in agreement with the literature.^{3-5,12}

The Cu *K*-edge x-ray absorption measurements were carried out using the X-18B beamline at the National Synchrotron Light Source. The energy resolution of the monochromator for this measurement was better than 0.005%. Figure 1 shows the results of these measurements on Cu_2O , CuO , KCuO_2 , and La_2CuO_4 . The spectrometer calibration is done with simultaneous measurements of the absorption edge of a copper metal foil. The Cu *K*-edge measurements were extended to 500 eV above the absorption edge to allow background subtraction by a polynomial spline method and normalization of the absorption jump.

In Fig. 1 we present the normalized spectra of Cu_2^{2+}O , Cu^{3+}O , La_2CuO_4 , and $\text{KCu}^{4+}\text{O}_2$. There is a set of features identified by labels *A*, *B*, *C*, and *D* in these spectra (see Table I). They correspond to an overlap of electric dipole transitions from the 1*s* state to various *np* final states. While the detailed assignment of these transitions will be discussed later in this Rapid Communication, it is adequate to point out that the peak *A* mainly represents a transition from the 1*s* state to the axial 4*p* states, and the feature *B* mainly to the planar 4*p* states. The general feature of the XANES measurement of standard chemi-

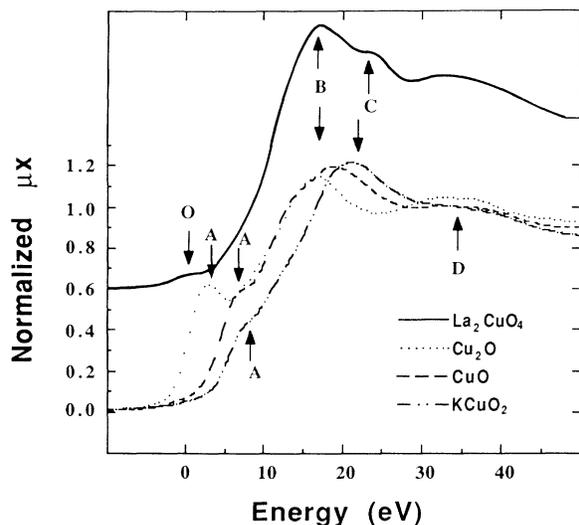


FIG. 1. Cu *K*-edge XANES of Cu_2O , CuO , KCuO_2 , and La_2CuO_4 . The valence of copper is I, II, III, and II/III, respectively.

cal compounds is that the entire spectrum moves to the higher energies with increasing valence on Cu. The measured shifts of the *A* and *B* peaks are roughly 2 eV per change in valence.

The spectrum of La_2CuO_4 has four main features. The strong peak at *B* is located roughly at the position of the analogous peak in the spectrum of CuO , corresponding to the divalent state of Cu. The peak *C* roughly coincides in energy with the peak *C* of KCuO_2 , corresponding to the trivalent state of Cu. Thus the measured spectra suggest that in La_2CuO_4 we observe the presence of both Cu II and Cu III states. This observation is contrary to the speculation that the Cu III state is introduced only by substitutional Sr or Ba doping.^{4,13} A comparison of the XANES for semiconducting orthorhombic La_4CuO_4 with that of superconducting ($T_c = 36$ K), which is tetragonal $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, displayed in Fig. 2, indicates that the electronic structure of Cu is remarkably similar in both compounds. The main effect of Sr doping is a slight enhancement of the Cu III peak (*C*) already present in the undoped La_2CuO_4 . The presence of both valence states has been measured down to 4.2 K. There are definite but small changes in the intensities of various XANES features for both these compounds at low temperatures. Such changes are also observed in the spectra of different

TABLE I. Observed peak positions in the Cu *K*-edge spectra of several copper oxides given in Fig. 1.

Compound	Nominal Valence	Peak positions			
		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
Cu_2O	I	2.8	16.9	...	35
CuO	II	6.3	18.6	...	35
KCuO_2	III	7.1	...	21.2	35
La_2CuO_2	II and III	~10	17.1	24	33

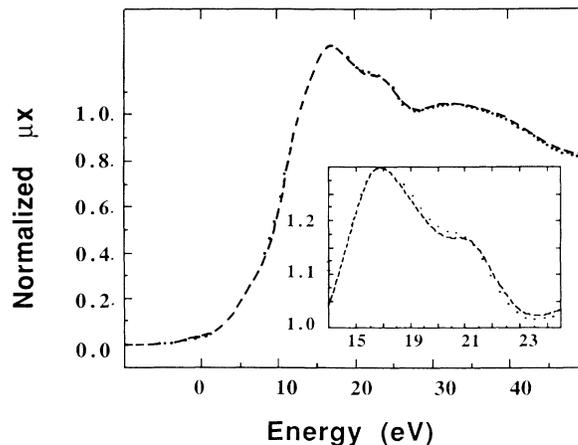


FIG. 2. Cu *K*-edge XANES of La_2CuO_4 (dotted line) and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ (dashed line). The inset shows the top portion of peaks *B* and *C* to indicate small changes as a function of Sr doping.

concentrations.

This interpretation of our experimental data is supported by theoretical calculations of the Cu *K*-edge XANES in La_2CuO_4 . In such studies it is necessary to approximate the real system with different model clusters. We have used the following procedure.

First, electronic structure calculations were made on molecular clusters representative of idealized tetragonal La_2CuO_4 and Sr-substituted compound, using the self-consistent-field local-density (LD) theory. The discrete variational method (DV- $X\alpha$) was used, with a basis set consisting of numerical LD free-ion orbitals.¹⁴ The clusters were embedded in the Coulomb and exchange fields generated by an infinite host crystal; lattice summations were carried out by an Ewald procedure.

The clusters considered were CuO_4O_2 , $\text{CuO}_4\text{O}_2\text{La}_2$, $\text{CuO}_4\text{O}_2\text{LaSr}$, $\text{CuO}_4\text{O}_2\text{La}_8\text{La}_2$, and $\text{CuO}_4\text{O}_2\text{La}_8\text{LaSr}$, where we have distinguished between planar (O_4) and axial (O_2) anion sites. Experimental distances determined for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ were used in all cases.⁵ The calculations lead to two nearly degenerate electronic ground states nominally representing the two valence states of Cu. The details of these states will be presented later. For the calculation of XANES, the nominally Cu II state was stabilized as the electronic ground state in the molecular cluster. The self-consistent DV- $X\alpha$ potential was projected onto muffin-tin form, and a charged spherical boundary was placed around the entire cluster to provide an asymptotic $1/r$ potential to generate continuum final states. The multiple-scattering (MS- $X\alpha$) procedure was used to generate these states, and the dipole approximation cross section was calculated in the manner described by Kutzler *et al.*¹⁵ Although the muffin-tin projection causes various distortions of energy-level positions, especially near the top of the valence band, this procedure is adequate for discussing major features of the absorption spectra, as shown by previous applications.

The calculated spectrum shown in Fig. 3 represents a powder average. The analysis of the final states in the

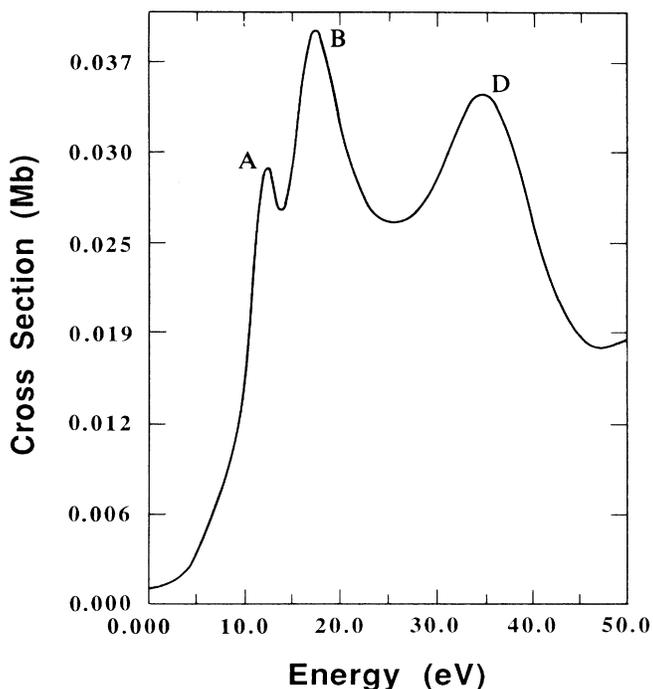


FIG. 3. Calculated Cu K-edge XANES for the cluster of $\text{CuO}(4)\text{O}(1)\text{SrLa}(8)$. The transitions corresponding to A–D are discussed in the text.

scattered wave scheme permits us to identify the main features of the spectrum which resemble the measured spectrum of Fig. 1(c) and Fig. 2. The feature A is due to transition to the final states made up of Cu II axial $4p$ states with weak scattering from the oxygen neighbors. The feature B is from the transitions to the planar $4p$ states with moderate scattering from the planar oxygen neighbors. The peak D is totally due to multiple scattering. The peak C identified to represent the Cu III peak in the experimental data is absent in these calculations. This is no surprise, since the calculations were forced to stabilize the Cu II state.

These XANES calculations thus support the conclusions arrived at earlier, regarding the presence of both Cu II and Cu III valence states in both the semiconducting and the superconducting systems. It is of some interest to point out that the weak feature labeled as 0 in the XANES spectrum of La_2CuO_4 is traditionally associated with a quadrupolar transition.^{16,17} However, it is possible to account for this transition in the framework of the present calculation as a dipolar transition to $2p$ states of the planar and axial oxygen coupled to the $4p$ states of Cu. This peak position is arbitrarily set to be the zero of energy.

Analysis of the energy levels and charge distribution for the “unperturbed” $\text{CuO}_4\text{O}_2\text{La}_8\text{La}_2$ cluster shows an effective configuration $\text{Cu II } 3d(9.39)4s(0.06)4p(0.07)$ with a net magnetic moment of $0.59\mu_B$. Mixed ionic-covalent bonding between Cu d and O-anion $2p$ levels is seen in a band of states spanning several electron volts around the Fermi level. The most interesting feature is a near twofold degeneracy at E_F , with an occupied $d_{x^2-y^2}$ planar O level lying only ~ 0.03 eV below an unoccupied $d_{3z^2-r^2}$ axial O level. The configuration for this nominally Cu III state shows a loss of $0.3e$ in the $3d$ shell, compared to the “divalent” state and a consequent reduction in its magnetic moment. Very small perturbations on the system, or even refinements in calculational procedure could easily invert this level order. We also note that the axial level contains small but significant amounts of La $5d$ character. Since the Cu d populations of the two levels differ (planar 86% and axial 57%), any mechanism (static or dynamic) which alters their occupancy will change the effective valency of the Cu site. We have referred to the above Cu valence states to be Cu II and Cu III in our earlier discussion. This analysis is also consistent with the small paramagnetic moment of Cu in La_2CuO_4 .⁶

Examination of the perturbed $\text{CuO}_4\text{O}_2\text{La}_8\text{LaSr}$ cluster shows that substitution of La^{3+} by Sr^{2+} provides a sufficient change in the self-consistent potential to invert the level ordering. Here we find the $d_{3z^2-r^2}$ axial O level to be occupied lying 0.04 eV below the planar state. The required electron withdrawal takes place mainly on the axial oxygen adjacent to the Sr site; however, the Cu site also loses $\sim 0.2e$, and planar oxygens each contribute a small amount of charge. The changes in the electronic structure of Cu due to doping are small and are reflected accordingly in the Cu XANES of these compounds (Fig. 2).

It has recently been suggested^{9,18} that the presence of a Peierls $2k_F$ distortion may play an important role in the superconducting properties of the doped La_2CuO_4 system. The concomitant modulation of the electronic charge density could provide a possible mechanism for stabilizing the two different charge states of Cu in La_2CuO_4 and in the doped compound. Such an essentially static picture of the Cu II and Cu III states is consistent with our experimental observation. However, our experiments do not rule out the possibility of dynamic charge fluctuations at the Cu site, driven either by phonons or Coulomb interactions.

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