Soft x-ray absorption studies on high- T_c superconducting oxides

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We report measurements of the Cu 2p, O 1s, and La 3d absorption edges in La₂CuO_{4-y} and a Sr-doped, superconducting sample of La_{1.8}Sr_{0.2}CuO_{4-y}. The Cu 2p absorption edge in the superconducting sample is considerably broader and exhibits additional structure compared to the normal La₂CuO_{4-y}. This additional structure is consistent with models for the superconductivity, which involve difference valence states of the Cu atoms or different spin configurations at the Cu sites. The oxygen edge exhibits fine structure which changes with sample preparation and is presumably due to oxygen defects in the samples.

La₂CuO_{4-y} with various substitutions has gained considerable interest in the past few months as the base material for superconductors having transition temperatures up to about 50 K.^{1,2} Even though experimentally the superconductivity at these temperatures is confirmed as a property of the bulk material in single phase or even single-crystalline samples, there is no definite theoretical model established for the mechanism. Explanations range from a basic BCS superconducting mechanism, in which the carriers are coupled via a very soft phonon mode,³ to new models involving spin pairs in resonating valence bonds.^{4,5} These new models involve static or dynamic charge or spin fluctuations at the Cu sites in the samples, whereas in a usual BCS superconductor one might expect only one type of Cu atom to be present.

We have measured the soft x-ray absorption of normal La_2CuO_{4-y} and Sr-doped $La_{1.8}Sr_{0.2}CuO_{4-y}$, having a superconducting transition temperature of about 35 K. In this energy range we can study the absorption of the Cu 2s and 2p electrons, the La 3d absorption and the O 1s absorption in the samples; i.e., we can probe all the main atomic constituents of the samples. Especially the Cu absorption edge can be expected to be a very sensitive probe of the chemical environment, charge, and spin state of the Cu atoms. Previous studies of the Cu 2p absorption edges have shown dramatic differences for different compounds like CuO, Cu₂O, and for Cu metal^{6,7}

The measurements were performed at the U1 beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.⁸ The basic wavelength resolution of the extended-range grasshopper monochromator in this energy range is approximately constant at 0.02 Å, which corresponds to 500 meV at the oxygen edge (540 eV) and 1.5 eV at the Cu 2p edges (930 and 950 eV). The same pellets⁹ were inserted into ultrahigh vacuum (UHV) by a sample transfer mechanism. The samples were cleaned *in situ* by scraping with a tungsten carbide file or alternatively by Ar- or O-ion bombardment. All these treatments resulted in samples free of any surface contaminants as checked by x-ray photoelectron spectroscopy (XPS). Samples which were scraped immediately prior to insertion also did not exhibit contamination detectable by XPS. The absorption spectra were taken by measuring the total electron emission from the sample by a Keithley 427 current amplifier directly connected to the sample. The total current is dominated by inelastically scattered secondary electrons, which originate within a region about 100-Å deep from the surface. Thus this technique maximizes the bulk absorption signal, such that the spectra are not very sensitive to the conditions at the sample surface. The spectra are normalized to the incoming photon flux, which is simultaneously measured by the photoemission of an Au grid placed into the incident photon beam. All spectra were taken with the samples at about 295 K.

Figure 1 shows an overview scan of the total electron yield signal for the photon energy range from 500 to 1000 eV. This spectrum is dominated by the rather strong spin-orbit doublet of the La 3d to 4f transitions observed



FIG. 1. Overview of the soft-x-ray absorption of $La_{1.8}Sr_{0.2}$ -CuO_{4-y} measured by the total electron yield of the sample. The total electron yield is proportional to the photon absorption in this energy range. The curve shows the absorption structures due to the transitions involving O 1s La 3d and Cu 2p electrons in the sample.

approximately at 835 and 851 eV. The unoccupied 4f states are located near the bottom of the conduction band, just as in La₂O₃.¹⁰ The O 1s absorption edge is visible at about 534 eV, whereas the Cu 2p absorption structures are observed at 932 and 950 eV. The Cu absorption is fairly weak, relative to the strong background of the La 3d continuum absorption.

A high resolution scan of the Cu $2p L_3$ absorption edge is shown in Fig. 2 for La₂CuO_{4-y} and Sr-doped La_{1.8}Sr_{0.2}CuO_{4-y}. Clearly, the absorption structure of the Sr-doped superconducting samples is broadened compared to the peak of the normal La₂CuO_{4-y} and exhibits a different substructure. The Cu L₃ absorption of La₂CuO_{4-y} can be readily decomposed into two Gaussians located at 931.5 and 933.5 eV with a full width at half maximum (FWHM) of 2 eV each. The absorption of the Sr-doped sample, on the other hand, has a substructure which is more complex.

The Cu L_3 absorption of the undoped La₂CuO_{4-y} is distinctly different from the absorption structure of either Cu metal or the oxides CuO or Cu₂O.^{6,7} Metallic Cu exhibits an edgelike absorption structure, whereas both CuO and Cu₂O show sharp white lines, attributed to core excitons. These exciton lines are about 2.5 eV wide (FWHM). In comparison to these lines the total width of the absorption structure in La₂CuO_{4-y} is about twice as large.

The doublet structure and the width of the Cu L_3 absorption in La₂CuO_{4-y} can be explained by the presence of two different inequivalent oxygen neighbors in the distorted octahedral environment around the Cu atoms, consistent with the known crystal structure.¹¹ This conclusion is derived from a comparison with the oxygen 1s absorption edge, shown in Fig. 3, which also exhibits a 2-eV splitting into two components at 534.5 and 536.5 eV. The small peak at 529.5 eV is attributed to oxygen-defect structures. This peak grows in intensity upon heating the



FIG. 2. High-resolution scan of the Cu L_3 absorption of La₂CuO_{4-y} (dashed curve) and of a Sr-doped superconducting La_{1.8}Sr_{0.2}CuO_{4-y} sample (dotted curve).

sample to $400 \,^{\circ}$ C or sputtering it with Ar ions. It is important to note here that we did not observe any significant differences in the oxygen absorption edges between the undoped and the Sr-doped samples.

In the interpretation of these absorption spectra we encounter the usual problem, that either the initial states, which are the various core levels at the different atomic centers in the samples, or the final states of the transition, which are the unoccupied valence states of a particular symmetry just above the Fermi level, could be responsible for any observed shifts or splittings. However, the fact that the splittings in the oxygen edge and the Cu edge are identical indicates that these absorption edges are due to two different O 2p derived final-state bands, most likely associated with the two types of oxygen atoms which are located in the Cu and La planes of the samples, respectively. The oxygen p-like orbitals will form linear combinations which have d-like symmetry around the sites of the Cu atoms. Therefore, the same final states can be observed for transitions from the O 1s orbital into O 2p-like final states and from the Cu 2p orbital into final states of d-symmetry, which are formed from linear combinations of oxygen 2p wave functions. Actually, some bandstructure models agree that the conduction band is derived from linear combinations of Cu $3d(x^2-y^2)$ and O 2p states.¹²⁻¹⁴ This explains the doublet structure in the Cu 2p absorption in La₂CuO_{4-y}, in contrast to the much narrower lines in CuO and Cu₂O.^{6,7}

Another possibility for the doublet structure in the Cu L_3 absorption is the coupling to local magnetic moments associated with the Cu atoms. If there is a local spin associated with the Cu valence electrons, then we expect to observe a splitting in the excitonic white line, depending upon whether the spin of the excited core electron is parallel or antiparallel to the spin of the valence electron at the Cu site. The predominant energy splitting would be derived from the spin coupling of the two valence electrons, which would couple more weakly to the remaining core electron. The two valence electrons would be in a singlet or a triplet configuration, whereas the total state would al-



FIG. 3. Absorption (total electron yield) of $La_{1.8}Sr_{0.2}CuO_{4-y}$ in the region of the O K edge. The absorption structure is due to transitions from the O 1s orbital into unoccupied states of *p*-symmetry at the oxygen sites.

The existence of local magnetic moments and antiferromagnetic ordering at temperatures between 220 and 290 K in La₂CuO_{4-y} have been demonstrated by neutron scattering recently, ^{15,16} but only for samples having oxygen defects. Stoichiometric La₂CuO₄ does not appear to exhibit the antiferromagnetism.¹⁷ Our sample was from the same batch as measured in Refs. 15 and 17, and has a small number of oxygen defects (y = 0.02); the Néel temperature is 220 K and the ordered moment is $0.5\mu_B$ per Cu ion.¹⁵

The superconducting sample exhibits an additional broadening of the Cu L_3 edge and also a noticeable edge jump (rise in the background level compared above and below the energy of the peak). This is an indication of the metallic character of the sample. Undoped La₂CuO_{4-y} is an insulator at low temperatures, whereas Sr doping will create some density of states at the Fermi level such that the sample becomes metallic. The broadening of the edge can be explained by charge fluctuations at the Cu sites introduced by the substitution of trivalent La by divalent Sr. In a static ionic picture, this charge imbalance would be compensated for by the presence of divalent and trivalent

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Cu atoms in the sample, and the sample would remain insulating. Alternately, in a Mott-Hubbard model, valence-band holes would be introduced, and the material becomes metallic. The absolute energy of the peaks is larger than Cu_2O , where Cu is monovalent. Unfortunately, there is some discrepancy in the values for the white lines given for the Cu oxide standards⁷ and also there is about a 1 eV uncertainty at this photon energy in the calibration of our monochromator. Therefore, we cannot use the shift of the peak centroid to determine the exact ionization state of the Cu atoms.

In summary, soft x-ray absorption spectra of Sr-doped, superconducting $La_{1.8}Sr_{0.2}CuO_{4-y}$ reveal that the Cu 2p absorption structure exhibits an additional broadening mechanism beyond the splitting observed in the nonsuperconducting La_2CuO_{4-y} . This additional broadening is taken as evidence for the existence for charge and/or spin fluctuations as the Cu sites.

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3985