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Electronic structure of $La_{2-x}Sr_xCuO_4$ studied by soft-x-ray-fluorescence spectroscopy with tunable excitation

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The O $K\alpha$ x-ray fluorescence of $La_{2-x}Sr_xCuO_4$ ($x=0.02$, 0.04, 0.07, 0.1, 0.15) has been recorded using tunable and high-resolution monochromatized synchrotron-radiation excitation. A strong variation in the shape of the O $K\alpha$ emission spectra depending on incidence photon energy is observed. This variation results from different in-plane and apical oxygen contributions to the emission line. The x-ray emission bands which reflect the partial density of $2p$ states pertaining to the two inequivalent oxygen sites are distinguished. The experimental results show that holes induced by the Sr doping are mainly located on in-plane oxygen atoms and suggest the existence, at least at $x \geq 0.07$, of doped holes which have Cu $3d_{xz,yz}$-O $2p_z\pi$ character.

INTRODUCTION

It is generally accepted that Sr doping of the insulator compound La_2CuO_4 leads to the formation of electronic holes on oxygen atoms.[1] The holes are presumed to be the charge carriers in the superconducting state. The existence of two inequivalent oxygen atoms in the crystal structure of this cuprate has stimulated a discussion on the contribution of these particular atoms to the high-T_c superconductivity. Most researchers assume that the induced holes have predominantly in-plane O $2p_{x,y}$ and Cu $3d_{x^2-y^2}$ orbital character (see, for example, Ref. 2, and references therein). At the same time, the importance of the apical oxygen is subject to discussion.[3]

This discussion is an incentive to perform spectroscopic measurements which can clarify the role of the different oxygen atoms and states of different symmetry. Recently, polarization resolved O $1s$ x-ray-absorption spectra of $La_{2-x}Sr_xCuO_4$ have been obtained by Chen *et al.*[4] and Pellegrin *et al.*[5] These data give evidence of both the in-plane and out-of-plane orbital character of doped holes. The authors assign the symmetry of the holes to Cu $3d_{x^2-y^2}$-O $2p_{x,y}$ and Cu $3d_{3z^2-r^2}$-O $2p_z$ σ bonds. However, there are a number of first-principle quantum-chemical calculations on CuO clusters which predict the occurrence of in-plane $\pi_{x,y}$ (Refs. 6 and 7) and out-of-plane π_z holes.[8] Also, a band-structure calculation by Mattheiss and Hamann,[9] taking the on-site correlation into consideration, shows some contribution of O $2p$ $\pi_{x,y}$ and π_z states at the Fermi level at high doping levels. Since the polarization resolved x-ray absorption spectroscopy (XAS) measurements cannot separate the O $2p$ $\sigma_{x,y(z)}$ and $\pi_{x,y(z)}$ holes, experimental information on the density of both unoccupied and occupied states of inequivalent oxygen atoms would be valuable.

The application of x-ray-fluorescence spectroscopy with selective excitation can provide information of this kind. Intense high-resolution monochromatized synchrotron radiation provides the possibility to do narrow-band-pass fluorescence spectroscopy. In this paper we present O $K\alpha$ x-ray-emission spectra of $La_{2-x}Sr_xCuO_4$, and demonstrate that soft-x-ray-fluorescence spectroscopy has a unique capability to provide information on both occupied and unoccupied states of the two inequivalent oxygen atoms. Exciting at the O K edge we have separated the in-plane and apical oxygen x-ray-emission bands which reflect the partial density of $2p$ states of the two inequivalent oxygen sites. The experimental results show good agreement with local-density approximation (LDA) band-structure calculations. By comparing our results with those of polarized XAS measurements, we conclude that doped holes can also have in-plane oxygen $2p_z$ π character at high doping levels.

EXPERIMENT

The experiments were performed at the undulator beamline X1B of the National Synchrotron Light Source, Brookhaven National Laboratory. The beamline, equipped with a 35 period undulator and a spherical grating monochromator, provides intense high-resolution soft-x-ray radiation.[10] The samples were high-density ceramic $La_{2-x}Sr_xCuO_4$ samples with different doping of Sr (Refs. 11,12) and $LaCuO_3$.

The O $K\alpha$ emission spectra were recorded using a high-resolution (1.2 eV) grazing incidence grating spectrometer with a two-dimensional detector.[13,14] The incidence angle of the excitation photon beam was about 20° to the sample plane. The x-ray fluorescence was detected in the horizontal plane and normal to the incident photon beam. The resolution of the monochromator was set to 0.3 eV for the photon energy of 530 eV. Zn $L_{2,3}$ emission lines were recorded in second order for energy calibration. The O $K\alpha$ emission spectra presented here were smoothed with a Gaussian line shape [full width at half-maximum (FWHM) = 0.3 eV].

RESULTS

The soft-x-ray-absorption spectra of $La_{2-x}Sr_xCuO_4$ recorded near the O *K* edge using fluorescence yield detection are shown in Fig. 1. The results are similar to those obtained by Chen *et al.*[15] Upon Sr doping, a low-energy peak *A*, associated with the unoccupied O 2*p* states in the charge-transfer gap, grows up at ~528.5 eV. Also, one observes a decrease of the prepeak *B* at ~530.4 eV, which already exists in the insulating compound La_2CuO_4,[5] and corresponds to an O 2*p* admixture to the vacant Cu 3*d* states (upper Hubbard band). The prepeak disappears at $x \geq 0.3$, when the compound becomes a normal metal. The strong absorption above 531.5 eV, largely invariant upon doping by Sr, is attributed to O *p* states hybridized with La *d* and *f* states. The arrows indicate the different excitation energies used for the O $K\alpha$ x-ray-emission spectra of $La_{2-x}Sr_xCuO_4$ and $LaCuO_3$.

The prepeak *A* also exists in the O *K*-edge absorption spectrum of $LaCuO_3$ indicating its metallic character. This prepeak is more pronounced for $LaCuO_3$ than $La_{2-x}Sr_xCuO_4$. It is interesting that the prepeak *B* is not observed in the compound.

Figure 2 shows the O $K\alpha$ x-ray-emission spectra of $La_{2-x}Sr_xCuO_4$ ($x = 0.07$) recorded at selected excitation energies (see the arrows in Fig. 1). As one can see, there are large variations in the shape of the spectra with increase of the excitation energy. When the energy of the exciting photon beam is set at 528.5 eV, the O $K\alpha$ spectrum exhibits a double-peak shape. The main peak E_1 and a low-energy shoulder E_2 are located at ~526.4 and ~523.8 eV, respectively. Increasing the excitation energy by ~1.9 eV leads to an enhancement of the O $K\alpha$ intensity in the 524–526 eV range, which eliminates the dip between E_1 and E_2. In turn, the 532.8-eV excited O $K\alpha$ spectrum shows a much narrower and nearly symmetrical band with a maximum at 525.5 eV. This spectrum is much different from those two obtained at lower excitation energies. Further increase of the excitation energy causes only some broadening of the band and a small shift toward higher energy. Eventually, the O $K\alpha$ spectrum recorded at a photon energy of 556.5 eV is very similar to that of previous measurements using electron-beam excitation.[16–18] Similar changes in the O $K\alpha$ shape with excitation energy were observed also for samples with other Sr concentrations (see, e.g., Fig. 3).

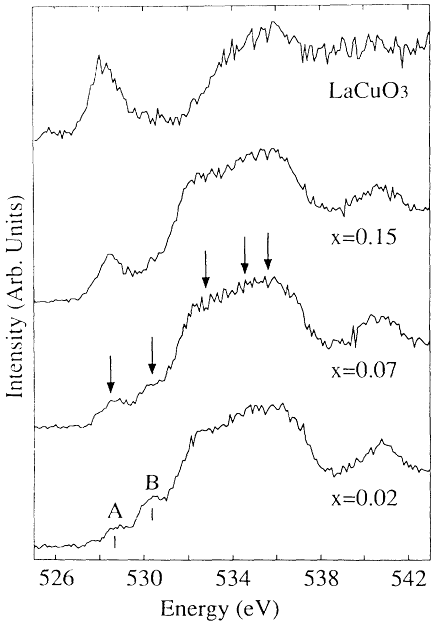

FIG. 1. The x-ray-absorption spectra of $LaCuO_3$ and $La_{2-x}Sr_xCuO_4$ ($x = 0.02, 0.07, 0.15$) near the O *K* edge.

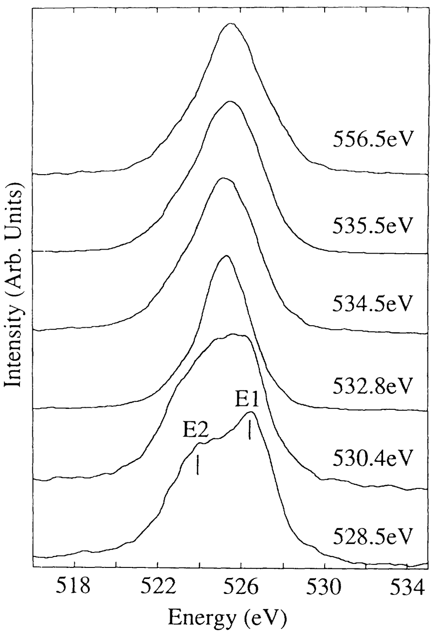

FIG. 2. The O $K\alpha$ x-ray-emission spectra of $La_{2-x}Sr_xCuO_4$ ($x = 0.07$) at different excitation energies.

The origin of the sensitivity of the O $K\alpha$ emission spectra to the excitation energy is to be found in the

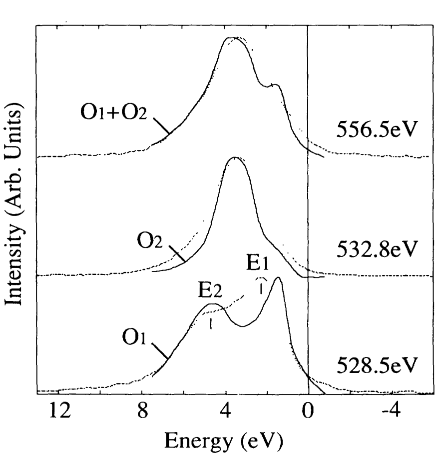

FIG. 3. The experimental O $K\alpha$ x-ray-emission spectra (dotted lines) of $La_{2-x}Sr_xCuO_4$ ($x = 0.15$) with different excitation energies; and the LDA band-structure calculated O $K\alpha$ emission spectra (solid lines) for in-Cu_2O-plane oxygen (O_1), apical oxygen (O_2) and superposition of both ($O_1 + O_2$) (Ref. 19).

significant difference of the O 2*p* density of states (DOS) between in-plane [O(1)] and apical [O(2)] oxygen atoms. According to the results from LDA band-structure calculations[19–21] (see Fig. 3), the distribution of O(1) 2*p* states has an extended two-band structure, while the maximum of O(2) 2*p* states is located between these two bands. The distance between Cu and in-plane oxygen atoms, 1.89 Å,[22] is much shorter than that between Cu and apical oxygen 2.42 Å; the strong chemical bonding in the CuO_2 plane leads to appreciable splitting between Cu 3*d*-O(1) 2*p* bonding and antibonding states.

In Fig. 3 the experimental O $K\alpha$ x-ray-emission spectra of $La_{2-x}Sr_xCuO_4$ ($x=0.15$), plotted on a binding-energy scale by using the binding energy of the O 1*s* core level (528.5 eV), are compared with the calculated O $K\alpha$ emission spectra of Redinger, *et al.*[19] As one can see, the experimental O $K\alpha$ spectrum obtained at 528.5-eV excitation energy is very similar to the calculated contribution of O(1) atoms in the emission band. Some difference may be caused by relaxation effects.[23] Also a small contribution of O(2) atoms may lead to the enhancement of the intensity observed in the dip between E_1 and E_2.[4,5] The O $K\alpha$ spectrum excited by 532.8-eV photons shows symmetrical single-band shape and noticeably narrower width, and it is attributed mostly to O(2) 2*p* states. The experimental O $K\alpha$ emission line recorded at 556.5-eV excitation energy is in good agreement with the calculated superposition of O(1) and O(2) emission bands, except for a shoulder at low-binding energy in the calculated spectrum.

The difference in binding energy between calculated and experimental O $K\alpha$ emission spectra may be caused by two reasons. First, the calculation has been made for the tetragonal phase of La_2CuO_4 with low-temperature lattice constants for the superconductor $La_{2-x}Ba_xCuO_4$. However, when part of the La atoms is replaced by Sr atoms in the supercell used for band-structure calculation, a strong redistribution of the spectral weight of the O(2) atoms close to Sr sites is obtained.[20] The DOS of $O(2)_{Sr}$ atoms, which experience a less attractive electrostatic potential than $O(2)_{La}$ atoms, due to the difference in ionic charge between Sr^{2+} and La^{3+}, is closer to the Fermi level. Thus, the doping with Sr leads to a shift of the O(2) states to E_F, while the O(1) states are less affected. Second, the calculated O $K\alpha$ emission spectrum of O(2) is moved by 0.66 eV away from E_F to take into account the chemical shift between O(1) 1*s* and O(2) 1*s* core levels.[19] This shift has, however, been estimated to be only ~ 0.3 eV from more recent O 1*s* XAS measurements.[4,5]

The assertion that the origin of the O $K\alpha$ sensitivity in $La_{2-x}Sr_xCuO_4$ to the variation of the excitation energy is the inequivalence of O(1) and O(2) sites is supported by O $K\alpha$ measurements for perovskite $LaCuO_3$ (see Fig. 4), where oxygen atoms are on nearly equivalent positions.[24] All spectra are similar to each other and show almost no change with the increase of excitation energy, except for a prolonged low-energy tail and slight broadening. The asymmetrical shape seen is in accordance with the band-structure calculations[21] due to, essentially, the Cu-O chemical bond [Cu-O bond distance is 1.91 Å (Ref. 24)].

Finally, in Figs. 5–7 the O $K\alpha$ x-ray-emission spectra of $La_{2-x}Sr_xCuO_4$ with different Sr concentrations recorded at the same excitation energy are presented in order to consider the changes in the spectra as a function of *x*. In Fig. 5 the O $K\alpha$ spectra obtained (which have been normalized to the background in the 547.3–554.5 eV energy region) at an excitation energy of 528.5 eV exhibit a more prominent 526.5-eV peak and as a consequence, a more pronounced double-peak structure with increasing *x* (see, the difference spectra a and b in Fig. 5). This behavior is evidence of an enhancement of the relative O(1) contribution to the emission spectra. In Fig. 6, some decrease of the relative O(1) fraction is noticed when the excitation energy is set at 530.4 eV. It follows from the analysis of the shape of the difference curve be-

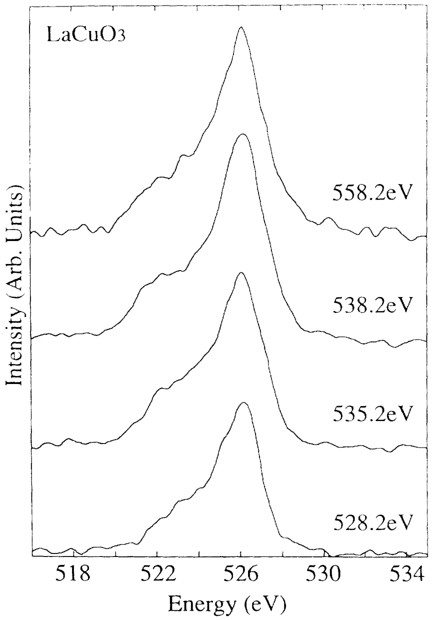

FIG. 4. The O $K\alpha$ x-ray-emission spectra of $LaCuO_3$ at different excitation energies.

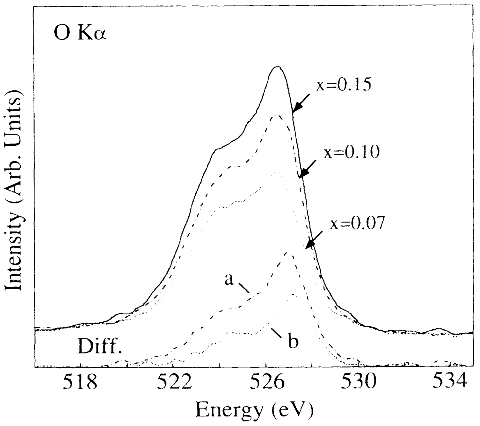

FIG. 5. The O $K\alpha$ x-ray-emission spectra of $La_{2-x}Sr_xCuO_4$ ($x=0.07$, 0.10, 0.15) at an excitation energy of 528.5 eV (top three curves). The spectra a and b correspond to differences between spectra of $x=0.15$ and $x=0.07$, respectively, $x=0.10$ and $x=0.07$.

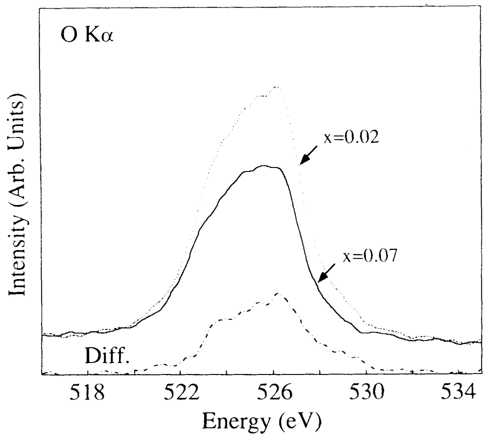

FIG. 6. The O $K\alpha$ x-ray-emission spectra of $La_{2-x}Sr_xCuO_4$ ($x=0.02$, 0.07) at an excitation energy of 530.1 eV. The spectrum (at the bottom) corresponds to difference between spectra of $x=0.02$ and $x=0.07$.

tween the O $K\alpha$ spectra of the $x=0.02$ and 0.07 samples. The difference curve shows more pronounced E_1- and E_2-like features in comparison with the parent spectra. An inspection of Fig. 7 shows a small high-energy shift of 532.8-eV excited O $K\alpha$ spectra at high x, which is discussed above.

DISCUSSION

The tuning of the energy of synchrotron radiation on the energy of the prepeaks A and B in the O 1s XAS spectra (Fig. 1) leads to the O 1s core excitation into unoccupied 2p states hybridized with the Cu 3d states. Since the 2p orbitals of each oxygen atom overlaps with Cu 3d orbitals, the excited state can decay with radiate transition of an electron from practically any point of the 2p valence band into the 1s inner vacancy. As a result, the O $K\alpha$ x-ray-emission spectrum reflects nearly the 2p DOS of these atoms. This is supported by the measurements for the simple copper oxides Cu_2O and CuO,[25] where the O $K\alpha$ obtained at the lowest excitation energy (O 1s core excitation into unoccupied 2p states hybridized with the Cu 3d states) are similar to those excited with electron beam[26] or white light of synchrotron radiation. Thus, the changes of the O $K\alpha$ shape of $La_{2-x}Sr_xCuO_4$ as a function of the incidence photon energy is caused by the variation of the relative number of the excited oxygen atoms in two inequivalent sites.

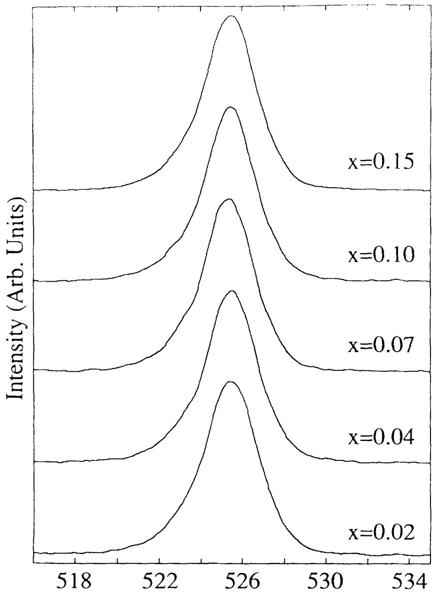

FIG. 7. The O $K\alpha$ x-ray-emission spectra of $La_{2-x}Sr_xCuO_4$ ($x=0.02$, 0.04, 0.07, 0.10, 0.15) at excitation energy of 532.8 eV).

When the excitation energy is set at 528.5 eV, only the oxygen atoms which have induced holes are excited. As one can see, the O $K\alpha$ spectra (Figs. 2, 3, and 5), have a double structure characteristic for O(1) 2p DOS. This means that the induced holes mainly belong to in-CuO_2-plane oxygen atoms. Upon Sr doping, the O $K\alpha$ spectra exhibit the larger relative O(1) 2p fraction (Fig. 5) and give evidence of an increase of charge-carrier concentration on O(1) sites with respect to the total number of these carriers donated by the dopant. Also, polarized O 1s XAS measurements for $La_{2-x}Sr_xCuO_4$ (Ref. 4) show an increase of the ratio O $2p_z$/O $2p_{x,y}$ for unoccupied O 2p states in the energy gap as a function of x. Taking into account these findings, we conclude that the induced holes may occupy the O(1) $2p_z$ orbitals, at least at $x \geq 0.07$, and have a Cu $3d_{xz}$, $3d_{yx}$-O $2p_z\pi$ character. This is in agreement with the prediction of Mattheiss and Hamann[9] that the O $p_z\pi$ states give some contribution at E_F at higher doping levels. The existence of these holes explains the much slower growing of the $E\|c$ and $E\perp c$ intensity ratios for Cu $2p_{3/2}$ x-ray-absorption spectrum with Sr doping in comparison with that for the first prepeak in the O K edge absorption.[4,5] In this case the doped holes manifest themselves in both $E\|c$ and $E\perp c$ Cu $2p_{3/2}$ components through Cu $3d_{xz}$, $3d_{yz}$-O $2p_z\pi$ hybridization.

However, it is unclear whether O $2p_z\pi$ holes are relevant to the high-T_c superconductivity. Thus Johnson argues that O $2p_z\pi^*$ orbitals are formed at E_F under the influence of Cu $3d_{xz}$, $3d_{yz}\pi^*$ antibonding hybridization O-O "resonant π bonds," which are "Fermi-liquid" basis for Cooper pairing via dynamic Jahn-Teller coupling.[8] On the other hand, no empty $2p_z\pi$ states of in-CuO_2-plane oxygen atoms have been found in $Tl_2Ba_2CaCu_2O_8$ revealing $T_c=101$ K.[27] Therefore, more detailed investigations of this problem are necessary.

As to intrinsic holes in the Cu-O bonds of $La_{2-x}Sr_xCuO_4$, an analysis of the shape of the O $K\alpha$ spectra recorded at the excitation energy of 530.4 eV shows an appreciable number of these holes on the O(2) sites. The relative O(2) 2p states contribution in the O $K\alpha$ spectrum is largest at the excitation energy of 532.8 eV as a result of stronger La d, f O(2) p chemical bonding. Further raising the excitation energy cause also the O 1s transitions into O p states hybridized with Cu 4s, 4p

states. Therefore, some broadening of the O $K\alpha$ emission spectrum may be accounted for as an increase of relative spectral weight of O(1) atoms due to Cu 4s, 4p-O p hybridization.

CONCLUSION

We have recorded the soft-x-ray O $K\alpha$ emission spectra of $La_{2-x}Sr_xCuO_4$ and $LaCuO_3$ using monochromatized synchrotron-radiation excitation, and demonstrate the advantages of this experimental technique which provides us with the possibility to obtain information of both occupied and unoccupied states as to the contribution of inequivalent oxygen sites. The variation in the shape of the O $K\alpha$ spectra observed is connected with the change of the character of unoccupied states into which the O 1s electrons are excited. We have distinguished the in-plane and apical oxygen O $K\alpha$ emission bands which are in an agreement with LDA band-structure calculations. The results obtained show that most of the induced holes are located at oxygen sites in the CuO_2 plane. From comparison of our findings with those of polarized XAS measurements, we conclude that some induced holes can have in-plane oxygen $2p_z\pi$ character, at least for $x > 0.07$.

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