ELSEVIER

Physica B 208&209 (1995) 487–490

PHYSICA B

Symmetry of hole states in $La_{2-x}Sr_xCuO_{4+\delta}$ and $La_{2-x}Sr_xNiO_{4+\delta}$

E. Pellegrin[a,*], C.T. Chen[b], J. Zaanen[c], J. Fink[d]

[a] *Kernforschungszentrum Karlsruhe, INFP, P.O. Box 3640, D-76021 Karlsruhe, Germany*
[b] *AT&T Bell Laboratories, Murray Hill, NJ 07974, USA*
[c] *Lorentz Institute for Theoretical Physics, Leiden University, NL-2300 RA Leiden, The Netherlands*
[d] *Institut für Festkörper- und Werkstofforschung Dresden e.V., Institut für Festkörperforschung, D-01171 Dresden, Germany*

Abstract

We present results from polarization-dependent X-ray absorption spectroscopy (XAS) of the O1s absorption edges of single-crystalline $La_{2-x}Sr_xCuO_{4+\delta}$ and $La_{2-x}Sr_xNiO_{4+\delta}$. From these measurements we derive the differences in the unoccupied electronic structure close to the Fermi level between the undoped cuprate and nickelate. In case of the doped nickelate, we present evidence for (a) the strongly bound Zhang–Rice character of the carriers and (b) their binding to crystal field excitons.

1. Introduction

The interest in the physics of transition metal oxides has been strongly increased by the discovery of high-temperature superconductivity in the cuprates. A lot of experimental and theoretical effort has been focussed on the cuprates, but it is now becoming increasingly clear that the nickelates are also systems which show rich physics and complex phenomena such as electron correlation and polaron localization. Nevertheless, the electronic structure of e.g. $La_{2-x}Sr_xNiO_{4+\delta}$ is still under debate and experimental work yielding information on that subject is strongly demanded.

2. Experimental

The XAS measurements were performed using the bulk-sensitive fluorescence-yield mode with synchrotron radiation from the AT&T Bell Laboratories Dragon beamline at the National Synchrotron Light Source. The monochromator energy resolution at the energy of the O1s absorption threshold was chosen to be about 100 meV for the nickelates.

3. Results and discussion

In Fig. 1, we show the polarization-dependent O1s absorption edges ($\boldsymbol{E}\perp\boldsymbol{c}$ and $\boldsymbol{E}\parallel\boldsymbol{c}$) of the undoped antiferromagnetic insulators $La_2NiO_{4+\delta}$ and $La_2CuO_{4+\delta}$. The cuprate data are taken from Ref. [1]. Fig. 1 also displays the O1s absorption spectrum for polycrystalline NiO. No anisotropy is expected for the latter compound, since it adopts the cubic NaCl crystal structure. The spectra are normalized in the energy interval between 590 and 610 eV.

Following both dipole selection rules and symmetry considerations, only $1s \rightarrow p_z$ transitions are allowed for $\boldsymbol{E}\parallel\boldsymbol{c}$ whereas for $\boldsymbol{E}\perp\boldsymbol{c}$ only $1s \rightarrow p_{x,y}$ transitions are

* Corresponding author.

0921-4526/95/$09.50
SSDI 0921-4526(94)00869-8

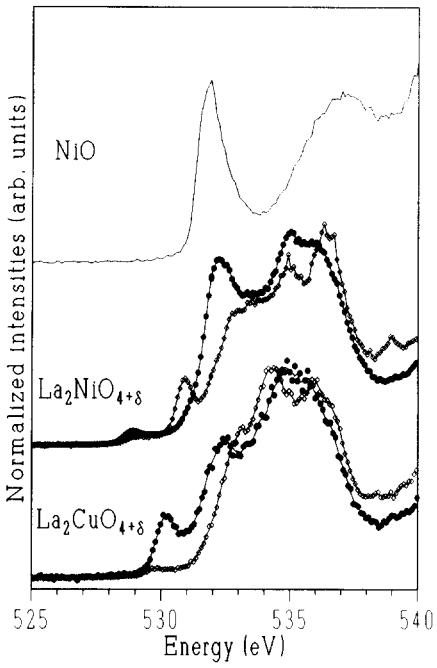

Fig. 1. Polarization-dependent O1s X-ray absorption spectra of single-crystalline $La_2NiO_{4+\delta}$ and single-crystalline $La_2CuO_{4+\delta}$. Closed circles: $E \perp c$, open diamonds $E \parallel c$. In addition, we show the O1s absorption edge of polycrystalline NiO (solid line).

possible. As can be expected, the intensity above 531.5 eV, which is mainly due to O2p orbitals hybridized with La(4f, 5d) states within the (La, Sr)O planes is almost the same for $La_2NiO_{4+\delta}$ and $La_2CuO_{4+\delta}$, whereas that of NiO is quite different. Comparing the spectrum of NiO with those for $E \perp c$ of undoped $La_2NiO_{4+\delta}$ and $La_2CuO_{4+\delta}$ in Fig. 1, it can be seen that the first strong peak is at 531.8, 532.2 and 530.2 eV, respectively (the occurrence of the low-intensity features between 528 and 530 eV in the reduced $La_2NiO_{4+\delta}$ sample is attributed to remaining excess-O). This first strong pre-edge is due to transitions into the unoccupied in-plane upper Hubbard band (UHB) states consisting of mainly planar Cu(Ni)$3d_{x^2-y^2}$ orbitals with some admixture of $O2p_{x,y}$ orbitals which is a consequence of the $d^{10}\underline{L}$ ($d^9\underline{L}$) component in the respective ground states, where $\underline{L}$ denotes an O2p ligand hole. The analogous peaks for the transitions into empty apex-O$2p_z$ orbitals hybridized with Cu(Ni)$3d_{3z^2-r^2}$ orbitals are at 531.8 eV in NiO and at 531 and 529.8 eV in the $E \parallel c$ spectra of $La_2NiO_{4+\delta}$ and $La_2CuO_{4+\delta}$, respectively. From this, it can be directly concluded that the separation in energy between the in-plane UHB and the out-of-plane states is vanishing in the case of NiO and close to ~ 1 eV in $La_2NiO_{4+\delta}$, taking into account that the O1s binding energy of the the apical O sites is about 0.3 eV lower than that for the planar O sites. In $La_2CuO_{4+\delta}$, the majority of the out-of-plane states seem to be situated below E_F, so that only a very small tail of the related density of states appears in the O1s and Cu2p XAS spectra [1]. Thus, the separation between the main part of the in-plane and of the out-of-plane states in $La_2CuO_{4+\delta}$ is about 1.8–2 eV, which corresponds to the size of the charge transfer gap. The reason for the different splittings between the e_g orbitals ($3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$) hybridized with O2p orbitals of appropriate symmetry is the different size of the tetragonal Jahn–Teller distortion of the Cu(Ni)O_6 octahedra and the related changes in the symmetry of the crystal field at the site of the metal atom. The tetragonal distortion of the Cu(Ni)O_6 octahedron is strongest for $La_2CuO_{4+\delta}$ and intermediate for $La_2NiO_{4+\delta}$, whereas in NiO the octahedron is undistorted. Accordingly, our measurements show that the tetragonal crystal field splitting between in- and out-of-plane states decreases when going from $La_2CuO_{4+\delta}$ to $La_2NiO_{4+\delta}$ and finally vanishes for NiO. Another important aspect is the Hund's rule stabilization of the high-spin ground state in the nickelates which will be discussed below.

In Fig. 2 we present the pre-edge features of $La_{2-x}Sr_xCuO_{4+\delta}$ as a function of the doping level x and of the polarization direction $E \perp c$ and $E \parallel c$ [1]. For in-plane polarization, the pre-edge peak at 530 eV decreases in intensity and shifts to higher energies with increasing x. A new single peak, roughly proportional to

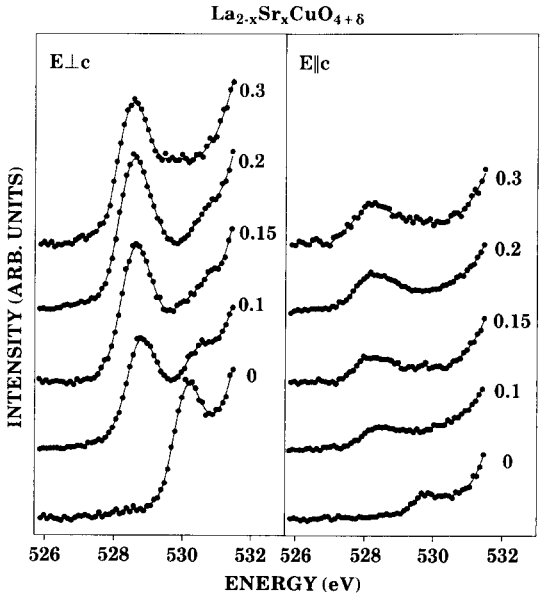

Fig. 2. Polarization- and doping-dependent O1s X-ray absorption spectra for the pre-edge region of $La_{2-x}Sr_xCuO_{4+\delta}$ for $E \perp c$ and $E \parallel c$. The spectra are labeled by the Sr concentration x.

x, appears at 528.7 eV upon doping. For $\boldsymbol{E} \parallel \boldsymbol{c}$ the spectral weight of the pre-edge features is strongly reduced but shows a similar dependence on doping concentration as for $\boldsymbol{E} \perp \boldsymbol{c}$.

The low-energy pre-edge at about 528.7 eV in the $\boldsymbol{E} \perp \boldsymbol{c}$ spectrum of $La_{2-x}Sr_xCuO_{4+\delta}$ can be explained on the basis of the charge-transfer model by transitions into hole states with predominantly O2p character doped into the valence band. This clearly demonstrates that due to strong correlation effects on the Cu sites, the charge carriers in p-type doped high-temperature superconductors have mainly O2p character. It can be seen from Fig. 2 that there is a transfer of spectral weight from the peak related to the UHB to the low-energy valence band peak for $\boldsymbol{E} \perp \boldsymbol{c}$ with increasing dopant concentration. This is a key signature for charge-transfer systems whose electronic structure can be described in the framework of an effective single-band Hubbard model [2, 3]. The holes are then doped into a Zhang–Rice singlet band pushed out from the valence band by the exchange interaction between the intrinsic hole on the Cu site and the doped hole delocalized over the neighbouring O sites.

The doping- and polarization-dependent O1s pre-edges of $La_{2-x}Sr_xNiO_{4+\delta}$ shown in Fig. 3 are quite different from those of the cuprate shown in Fig. 2. With increasing dopant concentration, a strong peak (A) with a shoulder (B) is observed for $\boldsymbol{E} \perp \boldsymbol{c}$ and the $\boldsymbol{E} \parallel \boldsymbol{c}$ spectrum exhibits a strong doping-induced peak (C). Similar to the results from $La_{2-x}Sr_xCuO_{4+\delta}$, the transfer of spectral weight between the UHB peak (labeled D, E for $\boldsymbol{E} \parallel \boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$, respectively) and the doping-induced features A, B, and C can be observed for both polarization directions, giving evidence for the charge-transfer insulator characteristics of this system.

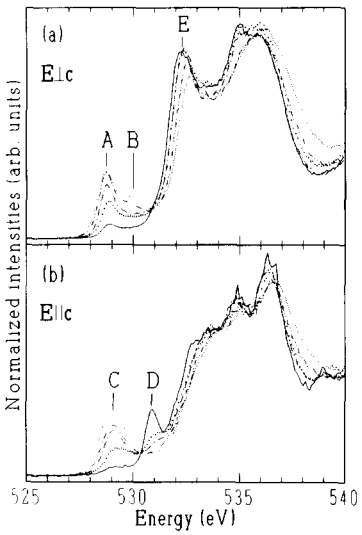

Fig. 3. Polarization- and doping-dependent O1s X-ray absorption edges of single-crystalline $La_{2-x}Sr_xNiO_{4+\delta}$: (a) $\boldsymbol{E} \perp \boldsymbol{c}$; (b) $\boldsymbol{E} \parallel \boldsymbol{c}$. Solid: $x = 0$; dotted: $x = 0.1$; dot-dashed: $x = 0.2$; dot-dot-dashed: $x = 0.4$; dashed: $x = 0.6$.

As pointed out recently by Zaanen and Olés [4], the doped carriers are bound to d–d crystal-field excitons as long as the Hund's rule interaction, J_H, exceeds the tetragonal crystal field splitting, E_Z. In the case of the intrinsic holes in $La_2NiO_{4+\delta}$, assuming the absence of the Hund's rule coupling, the d^8 ground state would be low-spin $|x\downarrow x\uparrow\rangle$ (x, z denote hole states with $x^2 - y^2$ and $3z^2 - r^2$ symmetry, respectively). However, if the two-particle potential J_H exceeds E_Z, the former forces the intrinsic holes to form the high-spin ground state $|x\uparrow z\uparrow\rangle$, as is the case in $La_2NiO_{4+\delta}$ as evident from the polarization dependence of the O1s edges shown in Fig. 1. For the doped compound, the carrier will be low spin $|x\uparrow x\downarrow z\sigma\rangle$ which is not affected by Hund's rule coupling. Therefore, the additional hole has the effect of 'unbinding' the crystal-field exciton. Spectroscopically, we expect the following exciton statellites starting from the low-spin ground state of the doped carrier $|x\downarrow x\uparrow z\sigma\rangle$:

$$|x\downarrow x\uparrow z\sigma\rangle \rightarrow |x\uparrow z\uparrow(\mathrm{T})\rangle + e^+(x) \quad \text{(A)}$$

$$|x\uparrow z\downarrow(\mathrm{S})\rangle + e^+(x) \quad \text{(B)}$$

$$|x\uparrow x\downarrow(\mathrm{S})\rangle + e^+(z), \quad \text{(C)}$$

where e^+ indicates an O1s core hole with x or z symmetry, while S and T refer to singlet or triplet character, respectively. Thus we find that the hole is binding to two crystal field excitons with a local spin-state different from the ground state and mutually different by their orbital occupancy. This explains the observed O1s pre-edge features in the nickelate and gives evidence for the Zhang–Rice nature of the doped holes.

What is the situation in $La_{2-x}Sr_xCuO_4$? Here J_H is possibly screened by the enhanced O2p character of the doped carriers, so that the crystal field splitting dominates. This results in a low-spin $|x\downarrow x\uparrow\rangle$ singlet configuration for the holes in the doped system. Evidence for this can be deduced from the absence of significant intensity for $\boldsymbol{E} \parallel \boldsymbol{c}$ polarization for $La_{2-x}Sr_xCuO_4$ in both the O1s edges presented in Fig. 2 and the Cu2p edges in Ref. [1], thus illustrating the reluctance of the doped cuprate to form high-spin holes.

4. Summary

We have performed polarization-dependent X-ray absorption measurements on the O1s edges of $La_{2-x}Sr_xNiO_{4+\delta}$ single crystals. From a comparison with the same kind of data on $La_{2-x}Sr_xCuO_{4+\delta}$ and NiO, we

get direct evidence for the differences in the energetic ordering of states with different orbital symmetry close to the E_F between the undoped above compounds due to the different size of the Jahn–Teller distortion of the $Cu(Ni)O_6$ octahedra. In the case of Sr doped $La_2NiO_{4+\delta}$, we find direct evidence for the Zhang-Rice character of the carriers which are bound to crystal field excitations.

Acknowledgements

E.P. gratefully acknowledges financial support through the HSP II program of the German Academic Exchange Service (DAAD).

References

[1] E. Pellegrin, N. Nücker, J. Fink, S.L. Molodtsov, A. Gutiérez, E. Navas, O. Strebel, Z. Hu, M. Domke, G. Kaindl, S. Uchida, Y. Nakamura, J. Markl, M. Klauda, G. Saemann-Ischenko, A. Krol, J.L. Peng, Z.Y. Li and R.L. Greene, Phys. Rev. B 47 (1993) 3354; C.T. Chen, L.H. Tjeng, J. Kwo, H.L. Kao, P. Rudolf, F. Sette and R.M. Fleming, Phys. Rev. Lett. 68 (1992) 2543.

[2] M.B.J. Meinders, H. Eskes and G.A. Sawatzky, Phys. Rev. B 48 (1993) 3916.

[3] H. Eskes, M.B.J. Meinders and G.A. Sawatzky, Phys. Rev. Lett. 67 (1991) 1035.

[4] J. Zaanen and A.M. Olés, Phys. Rev. B 48 (1993) 7197.