Investigation of the Electronic Structure of High-Temperature Superconductors by Polarized X-Ray Absorption Spectroscopy

N. Nücker[1], *E. Pellegrin*[1], *G. Roth*[1], *C. Politis*[1], *J. Fink*[1], *M. Domke*[2], *M. Gutierez*[2], *Z.W. Hu*[2], *S. Molodsov*[2], *E. Navas*[2], *O. Strebel*[2], *G. Kaindl*[2], *A.Krol*[3], *J.L. Peng*[4], *Z.Y. Li*[4], *R.L. Greene*[4], *S. Uchida*[5], *H. Takagi*[5], *Y. Tokura*[5], *J. Markl*[6], *M. Klauda*[6], *G. Saemann-Ischenko*[6], *D. Hahn*[7], *T. Zetterer*[7], *H.H. Otto*[7], *and K.F. Renk*[7]

[1]Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, Postfach 3640, W-7500 Karlsruhe, Fed. Rep. of Germany
[2]Institut für Experimentalphysik, Freie Universität Berlin, W-1000 Berlin, Fed. Rep. of Germany
[3]Department of Physics, SUNY at Buffalo, NY 14260, USA
[4]Department of Physics, University of Maryland, College Parc, MD 20742, USA
[5]Engineering Research Institute, University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan
[6]Physikalisches Institut Universität Erlangen, W-8520 Erlangen, Fed. Rep. of Germany
[7]Universität Regensburg, W-8400 Regensburg, Fed. Rep. of Germany

Abstract. The electronic structure of high-temperature superconductors near the Fermi level which is of primary interest for the understanding of the mechanism of superconductivity, is not yet well understood. Most theoretical investigations deal with $Cu3d_{x\text{-}y}$ and $O2p_{x,y}$ orbitals at E_F, but whether or not $O2p_z$ and $Cu3d_{3z\text{-}r}$ orbitals contribute to states at E_F is still under discussion. The contribution of states with out-of-plane orbital character has been investigated by polarized x-ray absorption spectroscopy (XAS) on HTSC single crystals. For $La_{2-x}Sr_xCuO_4$ a small contribution from $O2p_z$ orbitals (8% of holes in O2p valence band states) was observed which increased to about 13% on 30% Sr doping. In n-type doped HTSC there is no clear evidence for $O2p_z$ orbitals at E_F, but states are observed slightly above E_F with $O2p_z$ character depending on the doping and annealing conditions. An observed admixture of Cu $3d_{3z\text{-}r}$ states to the predominant $3d_x$. hole states at E_F of a few percent did not significantly exceed the expermental error limits.

1. Indroduction

The commonly accepted picture for the electronic structure of CuOplanes in La_2CuO_4 as derived from cluster calculations gives a lower occupied Cu 3d band, the lower Hubbard band, and an occupied O2p band separated by

Springer Series in Solid-State Sciences, Vol. 113 Electronic Properties of High-T_c Superconductors
Editors: H. Kuzmany, M. Mehring, J. Fink

a charge transfer gap from the unoccupied upper Hubbard band. On p-type doping, states with $Cu3d_{x^2-y^2}$-$O2p_{x,y}$ symmetry having strong Zhang-Rice singlet [1] character form in the gap. These states may be related to superconductivity. This picture satisfactorly describes the observed O1s absorption edges for LaSrCuO. Upon Sr doping O2p hole states at the top of the valence band are formed and the transfer of spectroscopic weight from the upper Hubbard band to states at E are observed as measured by Romberg *et al.* [2] and Chen *et al.* [3]. According to Khomskii *et al.* [4], upon p-type doping the cuprates the energy of the $3d_{x^2-y^2}$ states are lowered, while states with $3d_{3z^2-r^2}$ orbital character crosses E_F. Maekawa *et al.* [5] point out that the increase of apical $O2p_z$ states to the in-plane holes may destabilize the Zhang-Rice singlets and thus may destroy superconductivity. On the other hand, electron-phonon Jahn-Teller interactions involving the apical oxygen was at the origin of the search for the cuprate superconductors [6]. In the d-d model of Weber [7] holes in the O2p band pair mainly via virtual excitations of d-d transitions on Cu sites. Kamimura *et al.* [8] have proposed a spin-polaron model with high-spin hybrides of $Cu3d_{3z^2-r^2}$ and $O2p_z$ orbitals for p-type doped cuprates and of $Cu3d_{x^2-y^2}$ and Cu4s orbitals for n-type doped cuprates. Experimental investigations of the symmetry and orbital character of the states near to the Fermi level are very valuable as they allow discrimination between different models.

2. Experimental

$La_{2-x}Sr_xCuO_4$ crystals used in this investigations were large enough to cut a,c-oriented surfaces. The other cuprate samples studied were thin single crystalline platelets with a,b oriented surfaces. The crystals were glued to Pt-covered sample holders and clean, flat and mirror-like surface were produced using an ultramicrotome with a diamond knife. Finally, they were mounted on a manipulator which can be rotated around the horizontal and the vertical axes to adjust the crystal axis under investigation so as to be parallel to the electrical field vector of the incident light. Bulk sensitive, polarized XAS measurements were performed at the SX700/II monochromator at BESSY using a Germanium fluorescence detector. The energy calibration and resolution were monitored with the help of a low-pressure Ne gas cell. The energy resolution used was 340 meV (780 meV) for most O1s (Cu2p) investigations. The O1s absorption measurements were corrected for the intensity variation of the photon beam as a function of energy with the help of a normalizing spectrum derived from total electron yield measurements of a clean Au surface. Self absorption corrections had to be applied to the Cu2p absorption data considering the different experimental geometries.

3. Results

Fig.1 shows the fluorescence yield spectra of $La_{2-x}Sr_xCuO_4$ for x = 0, 0.1 ± 0.01, 0.15 ± 0.01, and 0.3 ± 0.02 for the polarization vector **E** of the incident synchrotron light perpendicular and parallel to the crystallographic c-axis. For **E**⊥**c** and x = 0 there is a peak at 530.2 eV assigned to transitions to $O2p_{x,y}$ states hybridized with $Cu3d_{x-y}$ states in the conduction band (i.e., the upper Hubbard band). This is followed by a steep rise at 531 eV due to transitions into unoccupied $O2p_{x,y}$ states hybridized to La4f and 5d states. For x > 0 a new peak due to hole states in the valence band (E ~ 529 eV) and a transfer of spectral weight from the conduction band to valence band states is observed. These results agree with previous investigations on polycrystalline samples [2,3] and with theoretical investigations [9,10]. For **E** ∥ **c** the spectral weight below 531 eV is strongly reduced, but shows a similar x-dependence. A chemical shift of 0.3 eV is observed for the absorption threshold energies between the **E** ∥ **c** and **E** ⊥ **c** spectra. This indicates that the absorption edges originate from different O sites, that for **E** ⊥ **c** from the in-plane O sites and that for **E** ∥ **c** from the apical oxygen sites. From an analysis of the pre-peak at 529 eV we infer an O2p character relative to the total number of O2p holes induced by doping of 9%, 7%, and 13% for samples with x = 0.1, 0.15, and 0.3, respectively. The absence of Op_z holes in $Bi_2Sr_2CaCu_2O_8$ (T_c = 85 K) [11] and the lower T_c < 40 K for $La_{2-x}Sr_xCuO_4$ samples with about 8% of apex holes may be taken as an argument for the destabilization of the Zhang-Rice singlet due to holes on the apical oxygen.

In contrast to the O1s spectra of $La_{2-x}Sr_xCuO_4$, those of the n-type doped $(Nd, Sm)_{2-x}Ce_xCuO_{4-\delta}$ show no unoccupied states in the valence

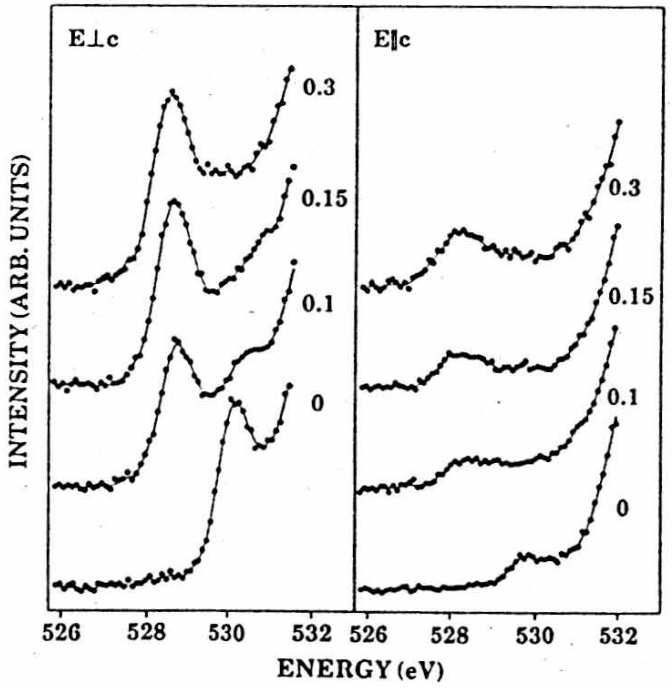

Fig.1: O1s x-ray absorption spectra of $La_{2-x}Sr_xCuO_4$ for x = 0, 0.1, 0.15, and 0.3 measured for polarizations **E** ⊥ **c** and **E** ∥ **c**.

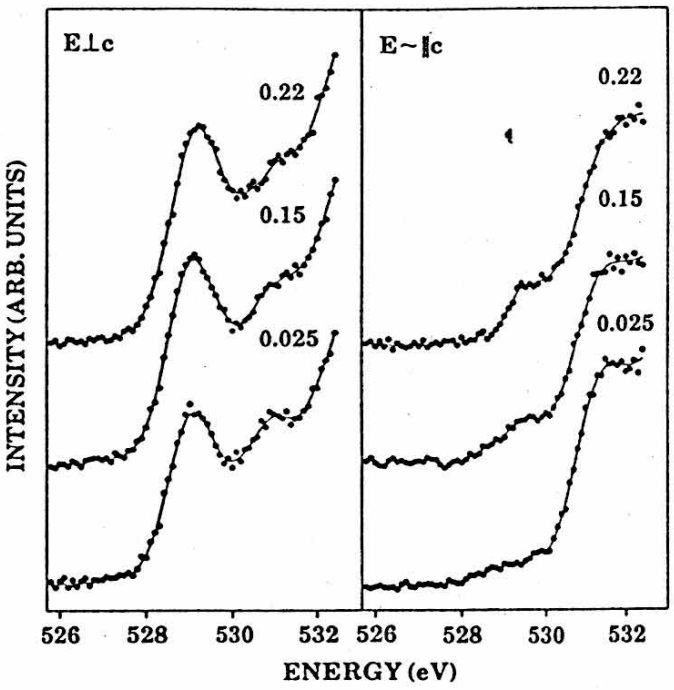

Fig.2: O1s x-ray absorption spectra of $Nd_{2-x}Ce_xCuO_{4-\delta}$ for x = 0.025, 0.15 and 0.3 measured for polarizations E ⊥ c and E ∥ c.

band. The relative intensity of the conduction band states for in plane (E⊥c) excitations does not change significantly with Ce doping. Despite the absence of apical oxygen sites there is some absorption observed for E ∥ c in the energy range of the conduction band (528-530.5 eV) even for the undoped samples. In $Nd_{2-x}Ce_xCuO_4$ (Fig.2), the absorption for E ∥ c seems to increase proportional to the doping concentration x. Hence, the observed $O2p_z$ states could be assigned to hybridization of O2p states with Ce4f and Ce5d states. Ce5d states are predicted by band structure calculations [12] to be close to the Fermi level. On the other hand, investigations on $Sm_2CuO_{4-\delta}$ (Fig.3) show that a similar increase in the E ∥ c absorption can be observed on reducing an undoped crystal. The similarity of the spectra for undoped, annealed and for x = 0.15 doped $Sm_{2-x}Ce_xCuO_4$ indicate that similar defect states at ~529.5 eV can be induced by oxygen defect states produced in a reducing atmosphere.

In Fig.4 we show the Cu2p absorption edges of SmCeCuO for E ⊥ c and E ∥ c. For E ⊥ c the transition into empty $Cu3d_{x^2-y^2}$ states is observed and assigned to the upper Hubbard band. For E ∥ c a strongly reduced peak is obseved at the same energy. This transition is commonly assigned to $Cu3d_{3z^2-r^2}$ states. In Table I the ratio of $Cu3d_{3z^2-r^2}$ to Cu3d (total) holes are given for cuprates from the present XAS investigations. These values represent upper limits, since systematic errors as misorientation of the whole crystal or local misorientation and non-perfect polarization of the photon beam will result in the inclusion of part of the $3d_{x^2-y^2}$ spectrum in the E ∥ c-spectrum.

In Fig.4, above 932 eV, a clear edge is observed for E ∥ c. In the undoped as prepared sample the edge appears at ~935.2 eV, while it is

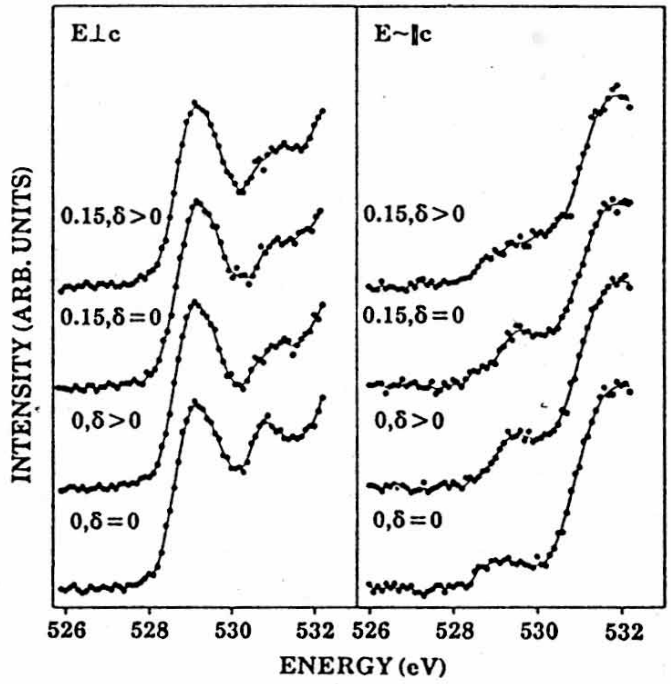

Fig.3: Polarized O1s x-ray absorption spectra of $Sm_{2-x}Ce_xCuO_{4-\delta}$ for x=0 and x=0.15. Samples with $\delta>0$ were annealed in argon.

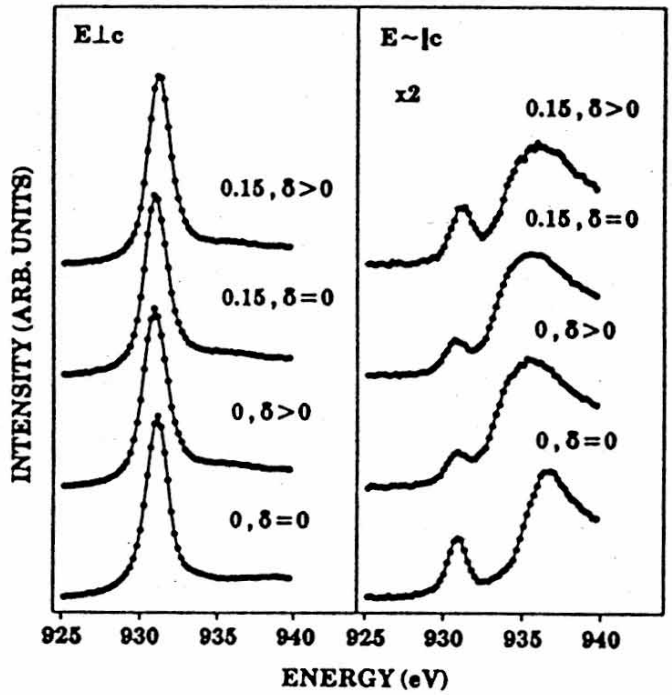

Fig.4: Cu2p absorption spectra of $Sm_{2-x}Ce_xCuO_{4-\delta}$ with x=0 and x=0.15, samples with $\delta>0$ were annealed in argon. The spectra are not corrected for self-absorption, which would enhance the $E \perp c$ spectrum by a factor of 2.8 in the maximum.

shifted by ~2eV to lower energy upon reduction and/or doping. These edges may be assigned to $Cu3d_{r}2$ character probably hybridized with a broad Cu4s band. This would indicate that the Cu4s band would be shifted towards the Fermi level upon reducing and/or doping. The additional intensity formed upon doping or annealing as observed in the O1s

Table I: Experimental radio R = holes $3d_{3z^2-r^2}$/holes in 3d
(a = annealed in argon; g.a.: c in grazing angle; a,c: a,c-plane)

sample	x	R(%)	geom.
$Ca_{1-x}Sr_xCuO_2$	0.14	1	g.a.
$La_{2-x}Sr_xCuO_4$	0.0 0.1 0.15 0.3	1 4 2 4	a,c a,c a,c a,c
$Tl_2Ba_2CaCu_2O_8$		1	g.a.
$Sm_{2-x}Ce_xCuO_{4-\delta}$	0 0, a 0.15 0.15, a	3 1 2 3	g.a. g.a. g.a. g.a.
$Nd_{2-x}Ce_xCuO_{4-\delta}$	0 0.15, a 0.22, a	1 1 1	g.a. g.a. g.a.

absorption edges for **E ∥ c** (Figs.2 and 3) may be related to this shift of the Cu4s band to lower energies.

4. Conclusions

Common to most actual models for the high temperature superconductors, the states near E_F have dominant in-plane character. The contribution of $Cu3d_{3z^2-r^2}$ to 3d states in the upper Hubbard band is small or zero. In $La_{2-x}Sr_xCuO_4$, about 8% of holes on oxygen sites have O2p character. At x = 0.3 this number is slightly increased to 13%. These results are in qualitative agreement with those reported by Chen *et al.* [13]. For the n-type doped T' phase cuprates there are O2p states in the energy range of the upper Hubbard band close to E independent of doping. At slightly higher energy additional O2p states are formed upon doping.

References

[1] F.C. Zhang and T.M. Rice, *Phys. Rev.* B 37 (1988) 3759
[2] H. Romberg, M. Alexander, N. Nücker, P. Adelmann, and J. Fink, *Phys. Rev.* B 42 (1990) 8768

[3] C.T. Chen, F. Sette, Y. Ma, M.S. Hybertsen, E.B. Stechel, W.M.C. Foulkes, M. Schlüter, S.-W. Cheong, A.S. Cooper, L.W. Rupp, jr., B. Batlogg, Y.L. Soo, Z.H. Ming, A. Krol, and Y.H. Kao, *Phys. Rev. Lett*, **66** (1991) 104
[4] D.I. Khomskii and E.I. Neimark, *Physica* C **173** (1991) 342
[5] S. Maekawa, Y. Ohta, and T. Tohyama, *Springer Series in Solid-State Sciences*, **106** (1992) 29
[6] J.G. Bednortz and K.A. Müller, *Z. Phys.* B **64** (1986) 189
[7] W. Weber, *Z. Phys.* B **70** (1988) 323
[8] H. Kamimura, M. Eto, S. Matsumo, and H. Ushio, *Comments on Condensed Matter Phys.* **15** (1992)
[9] M.S. Hybertsen and M. Schlüter, to be published in: *New Horizons in Low Dimensional Electron Systems*, ed. H. Aoki et al., Kluwer Academic Publ.
[10] H. Eskes, M.B.J. Meinders, and G.A. Sawatzky, *Phys. Rev. Lett.* **67** (1991) 1035
[11] N. Nücker, H.Romberg, X.X.Xi, J.Fink, B.Gegenheimer, and Z.X. Zhao,*Phys.Rev.* **B** 39 (1989) 6619
[12] Z. Szoetk, G.Y. Guo, and W.M. Temmerman, *Physica* C **175** (1991) 1
[13] C.T. Chen, L.H. Tjeng, J. Kwo, H.L. Kao, P. Rudolf, F. Sette, and R.M. Fleming, *Phys. Rev. Lett.* **86** (1992) 2543