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Soft-x-ray absorption spectroscopy of electron-doped $(\text{Nd,Sm})_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ compounds

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The oxygen 1s and copper 2p x-ray absorption spectra of the semiconductor, superconductor, and metallic compounds $(\text{Nd,Sm})_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ have been measured. After cerium doping, the O 1s absorption edge does not give a change in the density of unoccupied O 2p–Cu 3d molecular-orbital states, but shows a decrease in the O 2p–Cu 4s molecular-orbital states with a_1 symmetry. The Cu 2p absorption spectra show a decrease in Cu 3d⁹, although a strong Cu 3d¹⁰ peak is not observed. As a result of the strong mixing between the O 2p and Cu 4s states of a_1 symmetry, a composite state of Cu 3d, Cu 4s, and O 2p orbitals can be formed in these compounds, as has been predicted by the cluster calculation of Tohyama, Ohta, and Maekawa [*Physica C* **158**, 525 (1989)].

I. INTRODUCTION

The recent discovery of “electron-doped” copper-oxide superconductors $L_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ with $L = \text{Pr, Nd, or Sm}$ by Tokura, Takagi, and Uchida^{1,2} has stimulated much discussion about the theories of high- T_c oxide superconductors.^{3–5} The “electron-doped” $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ was found to be superconducting with a T_c up to 24 K. One of the key questions to be answered is whether these materials are really electron doped or hole doped just as the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds. Transport measurements give evidence that the charge carriers are *electrons* donated by the substitution of Nd^{3+} ions with Ce^{4+} ions.² X-ray absorption spectroscopy (XAS) of the Cu 1s edge⁶ and Cu 2p x-ray photoemission spectroscopy (XPS) (Refs. 7 and 8) confirm that an electron fills the Cu 3d band and creates a Cu 3d¹⁰ configuration after Ce doping. On the other hand, Fujimori *et al.*,⁹ Takahashi *et al.*,¹⁰ and Alp *et al.*¹¹ claim that there is no evidence for the filling of Cu 3d orbitals by doping and Nücker *et al.*¹² concludes from O 1s electron energy loss spectroscopy (EELS) that there is evidence for holes at the oxygen sites after Ce doping.

The most direct probe of the local O 2p unoccupied density of states is O 1s absorption spectroscopy. The dipole selection rules and the local character of the optical-transition matrix elements involving a core state assure that only the local unoccupied states of O p character are probed. If the hole states at the Fermi level are of primarily O 2p character, a precontinuum edge peak should be visible in the O 1s with an intensity related to

the O 2p concentration. Similarly, the Cu 2p absorption probes the unoccupied Cu 3d density of states in the presence of a core hole.

II. EXPERIMENT

A. Preparation

Samples of the semiconductor compounds $\text{Nd}_2\text{CuO}_{4-\delta}$ and $\text{Sm}_2\text{CuO}_{4-\delta}$, the superconductor compounds $\text{Nd}_{1.86}\text{Ce}_{0.14}\text{CuO}_{4-\delta}$ and $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$, and the metallic compounds $\text{Nd}_{1.82}\text{Ce}_{0.18}\text{CuO}_{4-\delta}$ and $\text{Sm}_{1.83}\text{Ce}_{0.17}\text{CuO}_{4-\delta}$ are prepared by mixing the starting oxides thoroughly and then heating the components in air to react for 24 h at 900°C. After cooling, the sample is ground thoroughly and pressed into pellets which are heated in air for 24 h at 1150°C and then air quenched. This procedure is repeated several times in order to make uniform samples. The final heat treatment is done in a N_2 gas flow for 16 h at 925°C, after which the sample is slowly cooled to room temperature.

Superconductivity of the samples is checked by ac-susceptibility and ac-resistivity measurements. The size of the diamagnetic signal depends strongly on the heat treatment.

The phase is checked by x-ray powder diffraction to be single phase with the T' - $\text{Nd}_2\text{CuO}_{4-\delta}$ structure and to consist of CuO_2 planes with no apical oxygen.¹³ The single-phase sample can be prepared with increasing the Ce doping up to approximately $x = 0.2$. At higher Ce concentration a second phase appears in the diffraction

pattern. The lattice parameters are clearly corresponding to the doping rate: the c parameter decreases linearly with Ce concentration up to $x=0.2$, above which it is almost constant, indicating the solubility limit of Ce in the $\text{Nd}_2\text{CuO}_{4-\delta}$ structure. On the other hand, the a parameter does not change appreciably. It is interesting to note that the lattice parameters change smoothly across the superconducting phase region, which is between $x=0.15$ and 0.18 .

The pellets were powdered in a dry nitrogen atmosphere and the powder was pressed into an Al plate which had been plated with a thin layer of carbon. The sample plates were immediately introduced under nitrogen atmosphere into the experimental chamber on beamline 3.4 at the Synchrotron Radiation Source (SRS) in Daresbury and pumped down. After a pumping-down period of ~ 1 h, measurements were done in a final pressure of 10^{-7} torr. Samples prepared in this way were also measured on beam line 1.1 where the sample plate was first introduced in a mini-preparation chamber which was pumped down for 6 h without bakeout, then introduced into the main experimental chamber where a final pressure of 10^{-9} torr was obtained. We checked if there were any changes in the spectra as a function of time by measuring the samples immediately after the final pressure was obtained and 20 minutes later. We could not detect any change in the Cu $2p$ as well as the O $1s$ x-ray absorption spectra.

B. X-ray absorption

The x-ray absorption measurements were performed in total electron yield mode. The Cu $2p$ and Nd, Sm, and Ce $3d$ absorption spectra were measured on beamline 3.4 using a double crystal monochromator equipped with beryl (10 $\bar{1}$ 0) crystals which gives an energy resolution of ~ 400 meV at the Cu $2p$ edge.¹⁴ The spectra have been corrected for the incident flux which is simultaneously measured by total electron yield from a $0.75\text{-}\mu\text{m}$ Al foil in front of the sample. The O $1s$ absorption spectra were measured using the monochromator of beamline 1.1 with a 1050 lines/mm spherical grating, which gives an energy resolution of ~ 350 meV at the O $1s$ edge.¹⁵ The monochromator gives a second-order contribution of $\sim 20\%$. No oxygen edge is observed from the Pt-coated optics.

III. RESULTS AND DISCUSSION

A. Rare-earth $3d$ absorption edges

Figure 1 shows the energy region of the oxygen $1s$ absorption spectra of the semiconductor compound $\text{Sm}_2\text{CuO}_{4-\delta}$ and the superconductor compound $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$. The structure above the dashed demarcation line, with maxima at 537.3 and 539.5 eV is the Sm $3d_{5/2}$ edge, which arises from the second-order contribution of the monochromator. Exactly the same spectral structure is found in first order using the double crystal monochromator, and we have checked that there is no other structure which can interfere in higher order with the O $1s$ region. Since the Sm $3d$ position is accu-

rately known,¹⁶ it can be used for the energy calibration of the O $1s$ region. From the $3d$ absorption spectra of the samples it would be found that Nd and Sm have a valence of $3+$, and that Ce has a valence of ~ 3.4 as in CeO_2 . The spectra of these edges are not displayed since they are identical to earlier published spectra of rare-earth elements with the same electronic configuration.¹⁶

B. O $1s$ absorption spectra

1. O $1s$ pre-edge

Figure 1 shows a pre-edge feature at 529.4 eV which has a width of about 1 eV. This feature, but much more intense, is also found in CuO.¹⁷⁻¹⁹ The peak can be attributed to oxygen $2p$ states which are covalent mixed with metal $3d$ states.^{19,20} In the XAS spectra of the Sm cuprates the pre-edge is independent of the Ce doping

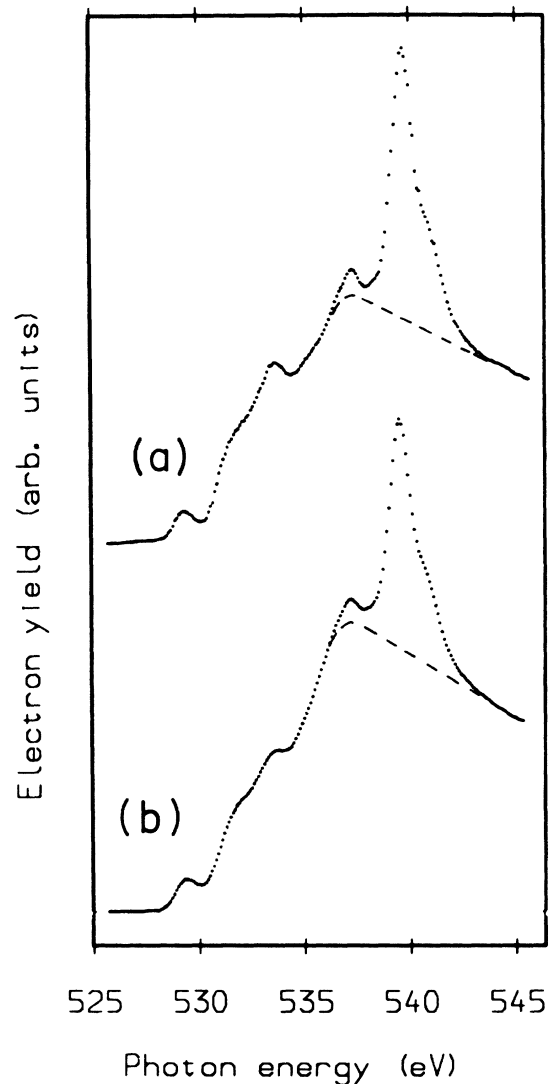


FIG. 1. The O $1s$ absorption spectra: (a) $\text{Sm}_2\text{CuO}_{4-\delta}$ and (b) $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$. The dashed line gives the demarcation with the Sm $3d_{5/2}$ absorption structure, which comes from the second-order contribution of the monochromator.

within 5%, which is different from the EELS spectra of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ measured by Nücker *et al.*¹² and Fink *et al.*²¹ They reported that the pre-edge contribution is increased after Ce doping. An increase of this prepeak would not necessarily be an indication for hole doping, but merely an indication for an increase in the covalent mixing. The same feature was found in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ where it is independent of Li doping,²⁰ and in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where it is independent of the hole concentration.¹⁸ These two compounds show an additional prepeak at lower energy (~ 528 eV) that *does* have an intensity related to the amount of oxygen holes.

2. O 1s main structure

The structure above 531 eV is due to O 2p states which are covalent mixed with Cu 4s and 4p states. From an augmented-localized-spherical wave calculation for a CuO_4^{6-} cluster, the peaks at 534 and 537.5 eV can be ascribed to a $2a_{1g}$ and $3e_u$ molecular orbital, respectively.¹⁹ The spectra in Fig. 1 have slightly better energy resolution than the O 1s EELS spectra of the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ compounds,¹² which also show two peaks with a separation of 3.5 eV and a low-energy shoulder. In contrast to the EELS spectra of the Nd compounds where the structure remains unaltered after doping, the Sm superconductor shows a decrease in the $2a_{1g}$ peak compared to the $3e_u$ peak. This indicates a decrease in the unoccupied density of states for the $2a_{1g}$ molecular orbital with O 2p and Cu 4s p character in the superconductor.

C. Cu 2p absorption spectra

1. Cu 2p main structure

Figure 2 shows the Cu $2p_{3/2}$ absorption edge of the model compound CuO. The absolute energy scale was calibrated to the Cu $2p_{3/2}$ peak in CuO at 931.2 eV. The ground state in CuO is a mixture of $\sim 60\%$ $3d^9$ and $\sim 40\%$ $3d^{10}\underline{L}$ character, which makes the formal valency equal to $2+$.²² In XAS the main peak and the satellite can be ascribed to $2p3d^{10}$ and $2p3d^9 4s$ final states, respectively, where $2p$ refers to a $2p_{3/2}$ hole.²³ It is important to note that the assignments for the configurations used here and in the following discussion refer to the main character of the states and that these states are not pure, but can be hybridized with other states.²²

The main peak in the spectra of the semiconductor, superconductor, and metallic rare-earth cuprate compounds is similar to the one in CuO—only slightly shifted in energy. This line attributed to a $2p3d^{10}$ final state implies a predominantly Cu^{2+} ($3d^9$) ground state in all compounds. Table I gives the intensities of the main absorption line relative to the continuum. It is clear that the contribution of the $2p3d^{10}$ final state peak at ~ 931 eV is reduced in the superconductor phase compared with the semiconductor. In the metallic compound the main peak is even more reduced. This indicates that the

$3d^9$ character decreases with doping. The small energy shift (Table I) can be a result of the larger hybridization energy in the ground state.

2. Cu 2p satellite structure

Figure 3 shows the Cu 2p satellite structure on an enlarged intensity scale. The large satellite, which is at 937 eV in the cuprates and at 939 eV in CuO is too high in energy to be due to a $2p3d^{10}\underline{L}$ or a $2p3d^{10}4s$ state and must be due to a $2p3d^9 4s$ state. The latter state has a higher energy because of the large 2p-3d Coulomb energy interaction.^{22,24} For example, in the x-ray photoemission spectrum of CuO, the $2p3d^9$ final state is approximately 9 eV above the $2p3d^{10}\underline{L}$ state and in $\text{Nd}_{1.86}\text{Ce}_{0.14}\text{CuO}_4$ this separation is comparable.^{7,8} In XAS the satellite separation is 7.5 eV in CuO and 5.5 eV in the rare-earth cu-

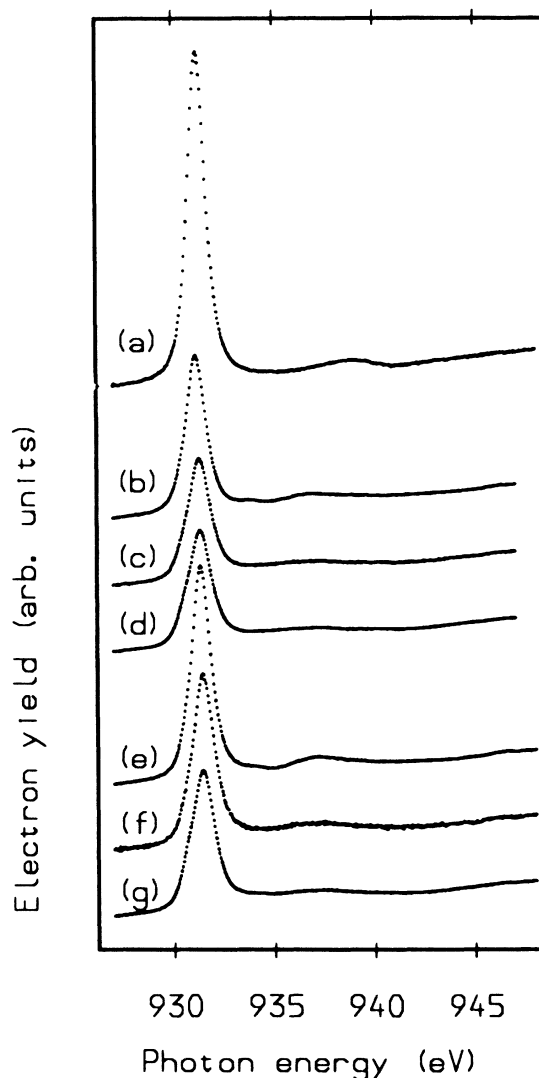


FIG. 2. The Cu $2p_{3/2}$ absorption structure: (a) CuO, (b) $\text{Nd}_2\text{CuO}_{4-\delta}$, (c) $\text{Nd}_{1.86}\text{Ce}_{0.14}\text{CuO}_{4-\delta}$, (d) $\text{Nd}_{1.82}\text{Ce}_{0.18}\text{CuO}_{4-\delta}$, (e) $\text{Sm}_2\text{CuO}_{4-\delta}$, (f) $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$, and (g) $\text{Sm}_{1.83}\text{Ce}_{0.17}\text{CuO}_{4-\delta}$.

TABLE I. Energy position and intensity (relative to the continuum) of the main line in the Cu $2p$ absorption spectrum.

	Compound	Energy (eV)	Intensity
(a)	CuO	931.20	12.8
(b)	Nd ₂ CuO _{4-δ}	931.17	6.4
(c)	Nd _{1.86} Ce _{0.14} CuO _{4-δ}	931.31	5.1
(d)	Nd _{1.82} Ce _{0.18} CuO _{4-δ}	931.34	5.0
(e)	Sm ₂ CuO _{4-δ}	931.35	8.4
(f)	Sm _{1.85} Ce _{0.15} CuO _{4-δ}	931.46	7.3
(g)	Sm _{1.83} Ce _{0.17} CuO _{4-δ}	931.44	6.2

prates. This reduction of the separation may be due to the more effective screening of the $3d$ hole.

The multiplet structure of the $2p3d^94s$ state in XAS is not the same as for the $2p3d^9+e^-$ final state in XPS. In XPS the emitted electron is not coupled to the $2p3d^9$ final state (sudden approximation) and the intensi-

ties can be calculated using fractional parentage.²² In XAS the intensities are governed by the dipole transition from the ground state to the accessible final states $2p3d^94s$, which results in a different structure than in XPS.

In YBa₂Cu₃O_{7-δ} compounds the main absorption peak at 931.1 eV has a high-energy shoulder at ~933 eV, which intensity increases with hole doping (defects).^{18,24} Since this shoulder is also present in doped La_{2-x}Sr_xCuO₄ compounds, it is believed to be characteristic of the additional ground-state holes present in the metallic regime. The energy of this shoulder coincide with the main line in XPS, which suggests that both features result from a similar $2p3d^{10}\underline{L}$ final states. The presence of a shoulder at 933 eV in XAS indicates $3d^9\underline{L}$ initial states (defect states). In the spectra of Fig. 3 they are clearly absent.

If Ce is inducing electron doping, one would expect a peak attributed to a $d^{10} \rightarrow 2p3d^{10}4s$ transition, which in Cu₂O is at 934 eV.²⁵ A small peak at 934 eV is sometimes found in CuO, which is significant for Cu⁺ contamination.²⁶ Figure 3 shows a small contribution at 934 eV for the cuprates. It is more pronounced in the semiconductor than in the superconductor compounds although this might be due to broadening effects or even to a small Cu₂O contamination. Kaindl *et al.*²⁵ attributed the peak at 934 eV in YBa₂Cu₃O_{7-δ} with $0.5 < \delta < 1$ ("electron doping") to a Cu $3d^{10}$ configuration. In this doping region, $0.5 < \delta < 1$, Chaillout *et al.*²⁷ have shown that the most likely oxygen atoms which are removed from the structure are those in the O(4) position. This results in a unit cell in which one Cu atom is linear coordinated by oxygen atoms. So it seems reasonable to attribute the 934-eV peak to Cu⁺ because of the similarity with the linear oxygen coordination of the Cu atom in Cu₂O. In our spectra the peak at 934 eV is not present, so there is no indication of Cu⁺ formation with Ce doping.

Fujimori *et al.*⁹ disputes the interpretation of Tranquada *et al.*⁶ for the Cu $1s$ absorption spectra of Nd_{2-x}Ce_xCuO_{4-δ}. Tranquada *et al.* claimed that the Cu d^{10} configuration is created by electron doping. However, this is based on the assumption that the $1s \rightarrow 4p_\pi$ absorption peak near the threshold of Cu₂O is characteristic of the Cu⁺ valence state, but the high intensity of this peak in Cu₂O is due to linear oxygen coordination of Cu—hence strong $4p_\pi$ character in this material.

Figure 3 shows a reduction in the relative intensity of the $2p3d^94s$ peak at ~937 eV. When the $3d^9$ character

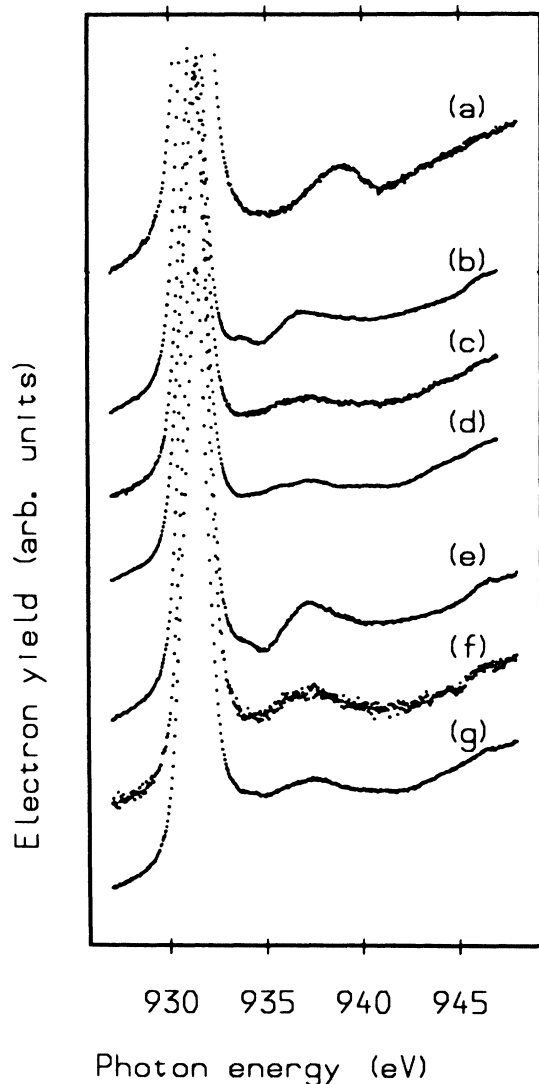


FIG. 3. Enlarged Cu $2p_{3/2}$ satellite structure from Fig. 2: (a) CuO, (b) Nd₂CuO_{4-δ}, (c) Nd_{1.86}Ce_{0.14}CuO_{4-δ}, (d) Nd_{1.82}Ce_{0.18}CuO_{4-δ}, (e) Sm₂CuO_{4-δ}, (f) Sm_{1.85}Ce_{0.15}CuO_{4-δ}, and (g) Sm_{1.83}Ce_{0.17}CuO_{4-δ}.

in the initial state decreases, both the $2p3d^{10}$ (main line) and the $2p3d^94s$ peak are expected to decrease in intensity, assuming that the mixing (hybridization) between the metal and the oxygen valence states does not change in the presence of the core hole.^{22,23,28} If this mixing is changing, the spectral intensities are no longer proportional to the initial state characters.

D. Comparison with cluster calculations

Tohyama *et al.*²⁹ have analyzed the electronic states in electron-doped superconductors such as $\text{Nd}(\text{Sm})_{2-x}\text{Ce}_x\text{CuO}_4$ by using a cluster model calculation. The T' crystal structure of these compounds consist of CuO_2 planes and have no apical oxygen. The calculated Madelung energy for an electron at the Cu site in the T' structure is 4.66 eV lower than in hole-doped oxides with a La_2CuO_4 -type T structure, although the Madelung energy at the O sites is not much different between the oxides when Cu^{2+} , O^{2-} , La^{3+} , and Nd^{3+} configurations are assumed.³⁰ Therefore, we may expect that there exists a strong hybridization between the Cu 4s and O 2p orbitals. Tohyama *et al.*²⁹ have found that the Cu 4s orbital plays an important role in the electron-doped oxides in contrast with the hole-doped oxides. With the doping, the electron density increases in the Cu $3d(x^2-y^2)$ and O 2p orbitals with b_1 symmetry but decreases in the Cu $3d(3z^2-r^2)$ since the Cu 4s and Cu $3d(3z^2-r^2)$ orbital have the same symmetry and hybridize with each other via O 2p states in the T' structure. Therefore, the total number of electrons in the Cu 3d orbitals increases with Ce doping by about 0.5. Assuming a maximum overlap between the Cu 4s and O 2p bands, they found that a spin-singlet composite state was formed involving Cu $3d(3z^2-r^2)$, Cu 4s and O 2p orbitals in the doped state. The change of the hole occupation numbers of the different orbitals due to electron doping shows an

increase in the Cu $3d(3z^2-r^2)$, a decrease in the Cu 4s, and a smaller decrease in the O 2p orbitals, all of a_1 symmetry.

A number of our experimental results support these calculations. The main point is an incomplete filling of the Cu 3d band so that a strong line at ~ 931 eV is expected instead of a band at ~ 934 eV (Cu^{1+}). The decrease in intensity of the Cu 2p absorption main line at ~ 931 eV and the satellite at ~ 937 eV is in agreement with a decrease in the $3d^9$ contribution with Ce doping resulting from the calculation. The calculated hole occupation of O 2p (a_1 symmetry) decreases after Ce doping. The O 1s absorption spectrum of $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ compared to Sm_2CuO_4 shows a decrease in intensity for the unoccupied density of states of the $2a_{1g}$ molecular orbital, which mixes the O 2p and Cu 4s p states. However, we do not observe a change in the number of holes in the O 2p-Cu 3d mixed state after doping.

IV. CONCLUSIONS

The Cu 2p absorption spectra indicate that the ground state of the rare-earth cuprate semiconductor is a mixture of $3d^9$ and $3d^{10}\underline{L}$ states with small amounts of $3d^{10}4s$ states present. The $3d^9$ character in the ground state is lower than in CuO. In the superconductor the $3d^9$ character is further reduced but the filling of the Cu 3d band is incomplete. The O 1s spectra indicate that after Ce doping the number of holes in the O 2p-Cu 3d molecular orbital is unchanged and the hole concentration in the $2a_{1g}$ molecular orbital, which mixes the O 2p and Cu 4s p states, is decreased.

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