Electronic structure studies on the n-type doped superconductors $R_{2-x}M_x\text{CuO}_{4-\delta}$ ($R=\text{Pr,Nd,Sm}$; $M=\text{Ce,Th}$) and $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$ by electron-energy-loss spectroscopy

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The electronic structure of the high-T_c superconductors $R_{2-x}M_x\text{CuO}_{4-\delta}$ ($R=$Pr, Nd, Sm; $M=$Ce, Th) and $\text{Nd}_2\text{CuO}_{3.8}\text{F}_{0.2}$ has been studied by high-energy electron-energy-loss spectroscopy in transmission. Core-level spectroscopy, particularly on O $1s$ and Cu $2p$ levels yields information on the partial unoccupied density of states near the Fermi level, while that on R and Ce $3d$ and $4d$ levels may serve as a valence monitor for these constituents. A pre-edge structure in the O $1s$ spectrum is polarized in the CuO_2 plane and assigned to transitions into a two-dimensional conduction band consisting of Cu $3d$ hybridized to O $2p$ states. In the Cu $3d^9$ configuration we found a slight admixture ($\sim 10\%$) of Cu $3d_{3z^2-r^2}$ to the Cu $3d_{x^2-y^2}$ hole states similar to the p-type doped superconductors. Upon doping we recognized a reduction ($\sim 14\%$) of the excitonic Cu $2p_{3/2}$ line, indicating that the introduced electrons go onto the Cu sites, thus producing charge carriers having predominantly Cu $3d$ character.

I. INTRODUCTION

Since their discovery[1] the n-type doped superconductors $R_{2-x}M_x\text{CuO}_{4-\delta}$ ($R=\text{Pr,Nd,Sm};M=\text{Ce,Th}$) have attracted a widespread interest among the high-T_c community. That the charge carriers are electrons and not holes as in p-type doped systems is based on chemical arguments; i.e., trivalent R is replaced by tetravalent M, on the observation of a negative Hall coefficient[2], and the measured sign of the Seebeck coefficient,[3,4] both opposite to p-type doped superconductors. Since both quantities strongly depend on the band structure and the Hall coefficient shows an anomalous temperature dependence, the determination of the nature of the charge carriers from these quantities is not straightforward.

For an understanding of the normal-state properties of high-T_c superconductors, the determination of the nature of the charge carriers is of particular importance. It is still controversial whether the additional charge has Cu $3d$, Cu $4s$, Cu $4p$, or O $2p$ character. By performing Cu K-edge x-ray-absorption (XAS) measurements, Tranquada et al.[5] concluded by comparing $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ with Cu_2O spectra that, upon Ce doping, Cu^+ is formed. Alp et al.,[6] from the same kind of experiment, conclude that no Cu^+ is formed upon doping, the extra electrons rather being transferred to a delocalized band. Perform-

ing x-ray-induced photoemission (XPS) measurements on the Cu $2p$ level, Ishii et al.[7] and Fujimori et al.[8] have determined the intensity ratio between the satellite structure and main peak. While for the unreduced samples this ratio decreases upon doping, this ratio is constant for well-prepared samples, and hence no change in the Cu valence upon doping is observed. On the other hand, Grassmann et al.,[9] using a simple cluster approach[10] for the evaluation of their XPS spectra, deduced a substantial increase of Cu^+ upon doping. Our own results on the Cu L_3 edge published previously[11] did not permit unambiguously to decide whether Cu^+ is formed or not.

Band-structure calculations by Massidda et al.[12] using the local-density approximation (LDA) were not able to reproduce a semiconducting Nd_2CuO_4 compound, but their work resulted in a metallic behavior similar to that from calculations on the parent compounds of p-type doped superconductors.[13–23] A rigid-band-like Fermi level upon Ce doping as suggested by band-structure calculations was observed by Reihl et al.[24] using ultraviolet photoemission spectroscopy (UPS). In their resonant photoemission measurements, Allen et al.[25] observed a filling of the gap upon doping, the Fermi level being at the same position for p- and n-type doped systems. Also, other authors[26,27] put forth a picture in which, upon doping, a midgap (or impurity) band is formed in the

charge-transfer gap.

In this paper we report on core-level electron-energy-loss spectroscopy (EELS) in transmission on O $1s$ and Cu $2p_{3/2}$ absorption edges of the superconducting compounds $R_{1.85}M_{0.15}CuO_{4-\delta}$ (R = Pr,Nd,Sm; M = Ce,Th) and $Nd_2CuO_{3.8}F_{0.2}$ and their semiconducting parent compounds R_2CuO_4. Information on the nature of unoccupied states and on the character of charge carriers is obtained. From measurements of R $3d_{5/2}$ and R $4d$ absorption edges, the valence of rare-earth ions was derived from a comparison to related rare-earth oxides. Parts of these results have been published previously.[11,28-30]

II. EXPERIMENT

We used high-energy EELS in transmission, which is a non-surface-sensitive method in contrast to XPS, bremsstrahlung isochromate spectroscopy (BIS), or XAS in the total yield mode. Bulk properties on a scale of ~ 1000 Å are measured. The energy and momentum resolution of the spectrometer[31] was chosen to be $\Delta E = 0.4$ eV and $\Delta q = 0.2$ Å^{-1}, respectively. The primary energy of the electrons was $E_0 = 170$ keV. The spectra were taken at small momentum transfer, where dipole selection rules apply. As the oxygen K and copper L_3 edges did not show any time-dependent changes during the measurements, radiation damage effects can be excluded.

The symmetry of empty states in Nd_2CuO_4 has been determined by measurements on a single-crystalline sample with momentum transfer parallel and perpendicular to the copper-oxygen planes as described in Ref. 32.

The polycrystalline samples of $R_{2-x}M_xCuO_{4-\delta}$ were prepared as described in Ref. 1. They were synthesized from a mixture of rare-earth (RE) metal oxides (CeO_2, ThO_2, Pr_6O_{11}, Nd_2O_3, and Sm_2O_3) and CuO. The mixed powders were first calcined at ~ 950 °C for 10 h in air. Then the samples were quenched to room temperature in air. To obtain superconductivity, procedures of annealing the Ce- or Th-doped samples under a reducing atmosphere were necessary. Without reduction no superconductivity could be obtained. The $Nd_2CuO_{3.8}F_{0.2}$ sample was prepared as described by James, Zahurak, and Murphy:[33] First, a stoichiometric mixture of CuO, Nd_2O_3, and freshly prepared NdF_3 was heated in air at 900 °C for 14 h, then pressed into pellets, and annealed at 890 °C for 14 h in flowing N_2. To make sure that we investigated only single-phase samples, the purity was checked by both x-ray and electron diffraction. Measurements of the resistivity of the samples $R_{2-x}M_xCuO_{4-\delta}$ ($x = 0.15$) showed that the M = Ce compounds had a slightly higher T_c value than those with M = Th. The T_c values ranged from about 16 K for $Nd_{1.85}Th_{0.15}CuO_{4-\delta}$ up to 23 K for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$.[34] The fluorinated sample showed bulk superconductivity with a T_c of about 27 K, but the superconducting transition was very broad.[33] The samples were cut with an ultramicrotome using a diamond knife and, as a liquid, alkaline water. The thickness of the films was about 1000 Å. By measurements with a superconducting quantum interference device (SQUID), it

was verified in some cases that the transition temperature of the superconducting samples did not change during the cutting process or during floating the films in alkaline water onto standard electron microscope grids. Furthermore, the lattice structure of the films was checked by elastic electron scattering.

III. RESULTS

Figure 1 shows the O $1s$ absorption edges of CuO, $Ca_{0.86}Sr_{0.14}CuO_2$, $R_{2-x}M_xCuO_{4-\delta}$ (R = Pr,Nd; M = Ce,Th; x = 0, 0.15), $Nd_2CuO_{3.8}F_{0.2}$, Sm_2CuO_4, and $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$. The background was subtracted and the spectra were normalized in the energy region 532-537 eV. The solid line in all figures is a guide to the eye. Clearly visible in all spectra is a pre-edge structure at about 529 eV. A similar feature has been observed in p-type doped systems.[35,36] As outlined in these previous papers, the O $1s$ absorption edges probe in a first approximation the local unoccupied density of states (DOS) with $2p$ symmetry at the oxygen sites. The interaction of the
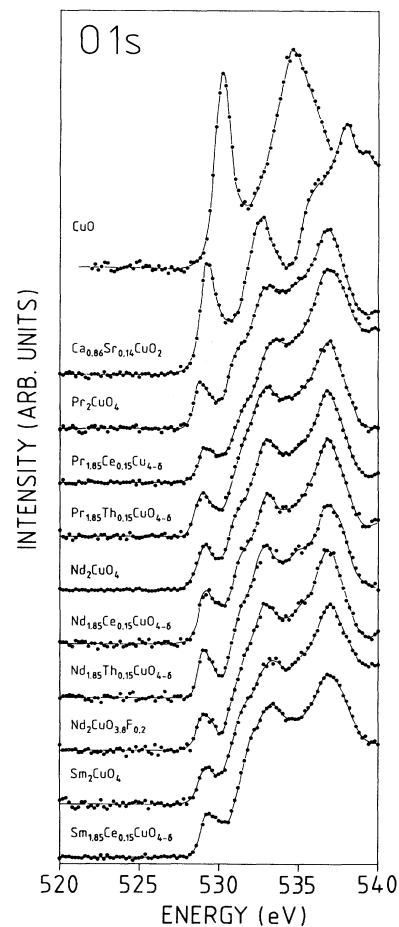

FIG. 1. O $1s$ absorption edges of CuO, $Ca_{0.86}Sr_{0.14}CuO_2$, Pr_2CuO_4, $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Pr_{1.85}Th_{0.15}CuO_{4-\delta}$, Nd_2CuO_4, $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Nd_{1.85}Th_{0.15}CuO_{4-\delta}$, $Nd_2CuO_{3.8}F_{0.2}$, Sm_2CuO_4, and $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$.

final states with the core hole is probably smaller than the width of the O $2p$ bands, and therefore excitonic effects are small. This is supported by core-level measurements on similar systems, such as transition-metal carbides and nitrides, where the measured absorption edges are very close to the calculated total DOS.[37] The threshold of the O $1s$ absorption edge in all undoped and n-type doped T'-phase cuprates is observed at 528.6 eV within 0.2 eV (see Fig. 1).

The shape, energetic position, and intensity of the prepeak for the different compounds show only small variations. There is even no systematic change between doped and undoped samples. The differences may be explained by the orientation dependence of the prepeak structure (see below) in possibly textured samples. The shape of the spectra for $E \geq 530$ eV, mainly consisting of R $5d$ and $4f$ as well as Cu $4s$ and $4p$ hybridized with O $2p$ states, seems to be almost unchanged upon n-type doping. The minor changes may be related again to a texture of the samples. There are two prominent peaks at about 533 and 537 eV.

The O $1s$ spectra of the antiferromagnetic insulators CuO and $Ca_{0.86}Sr_{0.14}CuO_2$ exhibit an intense prepeak structure at about 529.6 and 528.8 eV threshold energy, respectively. The higher-energy region of the O $1s$ edges of both compounds has no similarity with those of $R_{2-x}M_xCuO_{4-\delta}$ or $Nd_2CuO_{3.8}F_{0.2}$, because the spectral features resulting from the R_2O_2 layers are absent, and in addition new features due to Ca $4s$ and $3d$ as well as Sr $5s$ and $4d$ hybridized with O $2p$ states appear.

In Fig. 2 the O $1s$ spectra of single-crystalline Nd_2CuO_4 and polycrystalline Nd_2O_3 are shown. The spectra were measured with momentum transfer parallel to the (a,b) plane and parallel to the c axis, respectively,
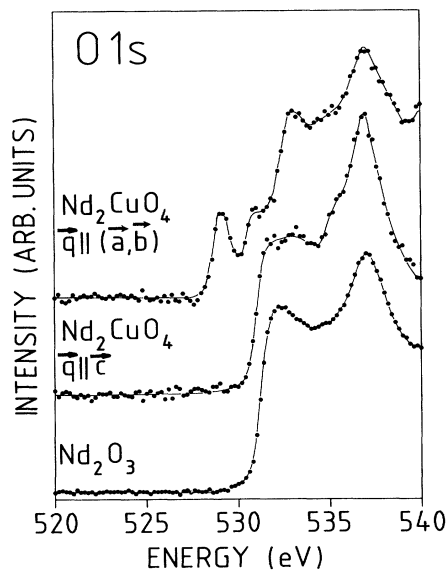
and were corrected for finite momentum resolution. Clearly, the prepeak is polarized in the (a,b) plane. In the spectrum for $q\|(a,b)$, there are a shoulder at 531 eV and two peaks at ~533 and 537 eV. In the spectrum for $q\|c$ a threshold at 531 eV followed by a strong peak at 537 eV is observed. There is a close similarity between the $q\|c$ spectrum of the Nd_2CuO_4 and of the unpolarized Nd_2O_3 spectrum. This indicates that the main features above 531 eV in the Nd_2CuO_4 spectra are related to the Nd_2O_2 planes. The small difference may be due to the fact that the environment of the O ions is not the same in both compounds.

In Fig. 3 the Cu $2p_{3/2}$ absorption edges of the compounds Nd_2CuO_4, $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Nd_{1.85}Th_{0.15}CuO_{4-\delta}$, $Nd_2CuO_{3.8}F_{0.2}$, Sm_2CuO_4, and $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$ are shown. No Cu $2p_{3/2}$ spectra could be evaluated for the Pr compounds because the very strong Pr $3d_{5/2} \rightarrow 4f$ transition occurs at ~930 eV, thus overlying the relatively weak Cu $2p_{3/2}$ structure. According to dipole selection rules, Cu $2p$ electrons may be excited into empty states either with $3d$ or $4s$ symmetry. The transitions $2p \rightarrow 3d$ are about 30 times stronger
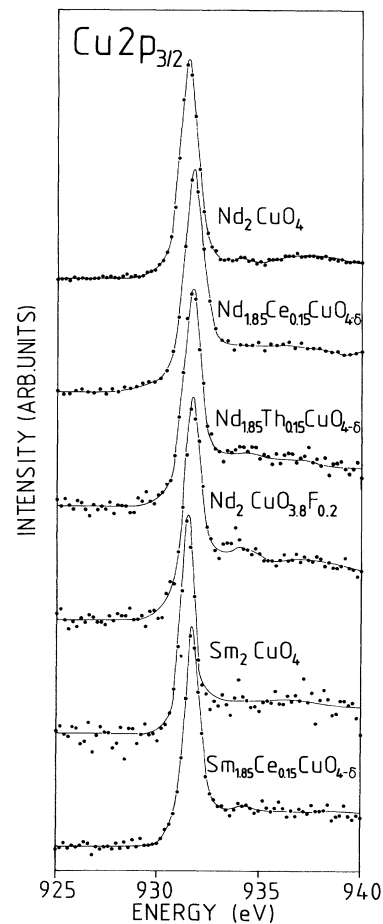

FIG. 2. O $1s$ absorption edges of a single crystal of Nd_2CuO_4 with momentum transfer q parallel ($\|$a,b) and perpendicular ($\|$c) to the CuO_2 plane. For comparison the O $1s$ absorption edge of polycrystalline Nd_2O_3 is shown.

FIG. 3. Cu $2p_{3/2}$ absorption edges of Nd_2CuO_4, $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Nd_{1.85}Th_{0.15}CuO_{4-\delta}$, $Nd_2CuO_{3.8}F_{0.2}$, Sm_2CuO_4, and $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$.

in intensity than the $2p \rightarrow 4s$ transitions.[38] This is due to the large overlap of the $3d$ wave functions with the $2p$ ones. The resonancelike (excitonic) absorption due to this large overlap does not represent the details of unoccupied $3d$ states, but the intensity of this line is a measure of the total amount of unoccupied $3d$ states.[39,40] For the undoped samples Nd_2CuO_4 and Sm_2CuO_4, we detected a strong absorption line at about 931.5 eV. For the doped compounds $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Nd_2CuO_{3.8}F_{0.2}$, $Nd_{1.85}Th_{0.15}CuO_{4-\delta}$, and $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$, this line is observed at 931.7 eV. A slightly increased intensity in the energy range above 933 eV is apparent for the doped compounds. This enhancement is more pronounced in the Nd than in the Sm samples. There is no pronounced structure at $\sim$934 eV, indicating formally Cu^+ as detected in $YBa_2Cu_3O_6$ (see Ref. 32) and other monovalent copper compounds.[41] To investigate the change of the effective charge on copper sites upon doping, we measured the relative intensities of the Cu $2p_{3/2}$ absorption line normalized to the intensity of the Nd $3d_{5/2}$ line at $\sim$979 eV. For the doped compounds the reduction of the Nd content in the samples was corrected for. In contrast to previous experiments[11] where a reduction of $6\pm5\%$ upon doping was measured, a systematic study on 20 films from 4 different samples resulted in a reduction of $14\pm4\%$ (see Fig. 4). Spectra taken for three orthogonal q directions were added in order to exclude texture effects. In contrast to the p-type doped superconductors such as $YBa_2Cu_3O_7$ or $La_{1.85}Sr_{0.15}CuO_4$, the Cu $2p_{3/2}$ line has a symmetric shape in all semi- or superconducting n-type doped superconductors. The full width at half maximum (FWHM) is about 0.9 eV, in contrast to $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$ with a FWHM of $\sim$1.3 eV.[32] In La_2CuO_4 and $YBa_2Cu_3O_6$, we measured[32] a

symmetric line with a FWHM of about 0.9 eV, comparable to the value in $R_{2-x}M_xCuO_{4-\delta}$.

The Cu $2p_{3/2}$ edges of the Nd_2CuO_4 single crystal with momentum transfer parallel to the (a, b) plane and parallel to the c axis are shown in Fig. 5. The main line at $\sim$931.5 eV exhibits a strong orientation-dependent intensity. For q$\|$c the intensity is reduced to about 10% of that for q$\|$(a, b). No shift in energy was observed within an accuracy of 100 meV, and the main line is symmetric for both orientations. Similar results were obtained for the p-type doped superconductors.[32,42]

To investigate the valence of the RE ions Pr, Nd, Sm, and Ce, we measured their $3d$ and $4d$ absorption edges. These spectra are related to the transitions into $4f$ states and show mainly the multiplet splitting caused by a hole in the $3d$ level and the partially filled $4f$ state. In Fig. 6 we compare the Pr $3d_{5/2}$ edges of several Pr compounds. The PrO_2 spectrum with a double line at $\sim$931 eV and a shoulder at 937 eV is representative for tetravalent Pr. In principle, the Pr_2O_3 spectrum should be representative for trivalent Pr. Comparing our spectrum with previous XAS measurements,[43,44] there is an indication of some PrO_2 contamination leading to the small shoulders at 931 and 937 eV. The Pr_6O_{11} spectrum indicates a mixture between trivalent and tetravalent Pr oxide. The Pr cuprates show spectra similar to trivalent Pr compounds, e.g., to Pr_2O_3. In Fig. 7 we compare the Nd $3d_{5/2}$ absorption edges of various Nd compounds. No chemical shift is visible as the top of the main absorption line is at the same energy (978.5 eV) in all compounds. The main line has an asymmetric shape, and at 974 eV we observe a small peak. There is a perfect overall agreement of all the Nd $3d_{5/2}$ spectra irrespective of doping. In Fig. 8 the Sm $3d_{5/2}$ absorption edges of Sm_2CuO_4,
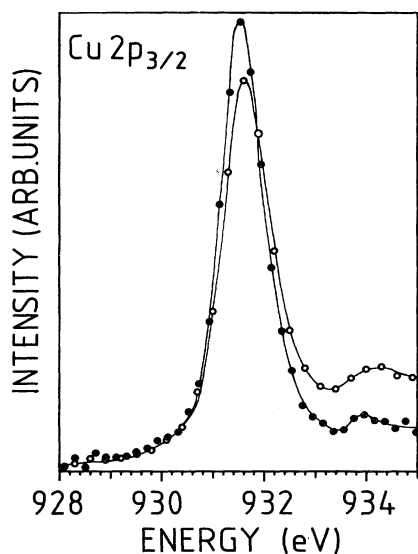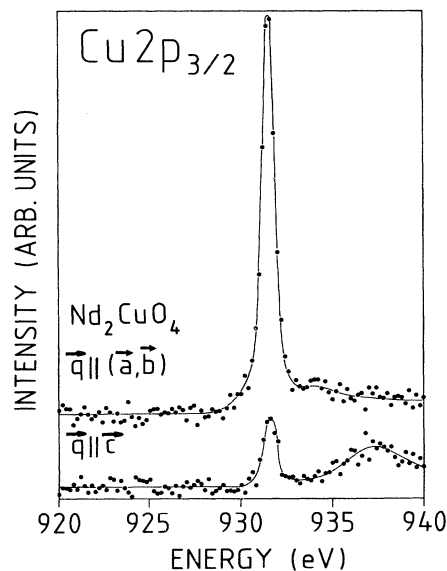

FIG. 4. Comparison of the Cu $2p_{3/2}$ absorption edges of Nd_2CuO_4 (solid circles) and $Nd_{1.85}Th_{0.15}CuO_{4-\delta}$ (open circles) normalized to the Nd $3d_{5/2}$ absorption edge.

FIG. 5. Cu $2p_{3/2}$ absorption edges of a single crystal of Nd_2CuO_4 with q parallel ($\|$a,b) and perpendicular ($\|$c) to the CuO_2 plane.
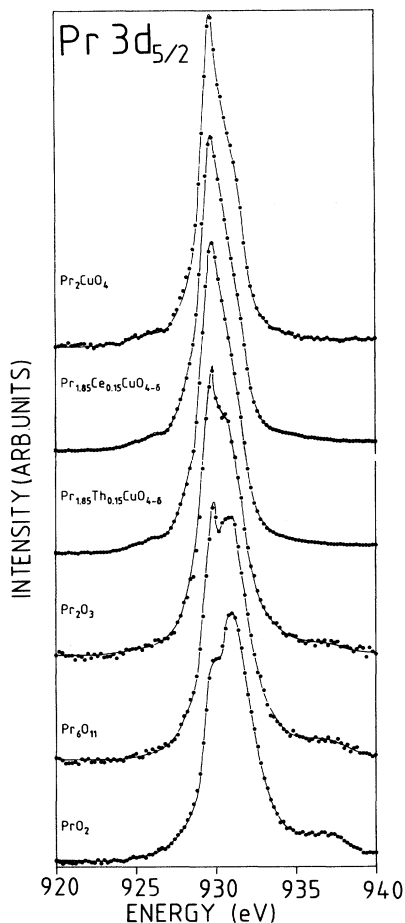
FIG. 6. Pr $3d_{5/2}$ absorption edges of Pr_2CuO_4, $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Pr_{1.85}Th_{0.15}CuO_{4-\delta}$, Pr_2O_3, Pr_6O_{11}, and PrO_2.
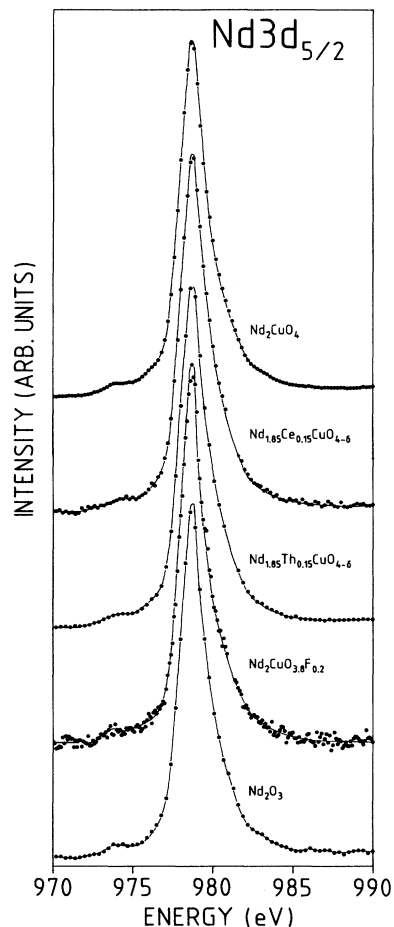
FIG. 7. Nd $3d_{5/2}$ absorption edges of Nd_2CuO_4, $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Nd_{1.85}Th_{0.15}CuO_{4-\delta}$, $Nd_2CuO_{3.8}F_{0.2}$, and Nd_2O_3.

$Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$, and Sm_2O_3 are shown. The spectra of all measured compounds, including trivalent Sm in Sm_2O_3, are nearly identical. The main absorption line is seen at an energy of about 1080 eV. A peak at about 1075 eV and a high-energy shoulder at about 1082 eV are realized. The FWHM of the main peak is about 2 eV. Finally, we investigated the Ce $3d_{5/2}$ edge (see Fig. 9). The spectra of $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, and $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$ are in good agreement with the reference spectrum of CeO_2. There is a small difference in spectral shape between $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$ and the other compounds on the low-energy side of the main line (~ 881.2 eV), where a shoulder appears. A slight overall shift (~ 0.2 eV) toward lower energies is apparent, too.

The measured R $4d$ absorption edges are shown in Figs. 10–12. The overall agreement of the multiplet structure of the $4d$ absorption edges within each particular group of RE compounds is very good. The difference in the peak positions is less than ~ 0.1 eV. In the Pr compounds there is an increased broadening of the lines

going from Pr_2CuO_4 via $Pr_{1.85}Th_{0.15}CuO_{4-\delta}$ and Pr_2O_3 to Pr_6O_{11}. The shoulder in the $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$ spectrum at ~ 125 eV may be due to the giant resonance of the Ce $4d$ excitation.

IV. DISCUSSION

The appearance of the prepeak structure at about 529 eV in the O $1s$ absorption edges seemed very astonishing since, for p-type doped superconductors, this feature was explained in terms of holes on oxygen sites in the CuO_2 planes. There are various interpretations of the prepeak structure: (i) The prepeak is, as in p-type doped systems, related to holes in the valence band.[11] (ii) There may be holes in the R_2O_2 layers. (iii) The prepeak may be caused by O $2p$ states hybridized with R $4f$ states. (iv) The prepeak is related to transitions into the O $2p$ admixture to the conduction band having predominantly Cu $3d$ character. Interpretation (i) of the prepeak in the n-type doped cuprates is related, at least in the semiconducting
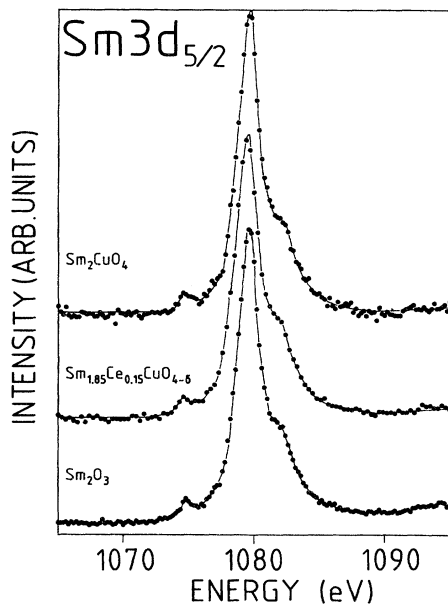
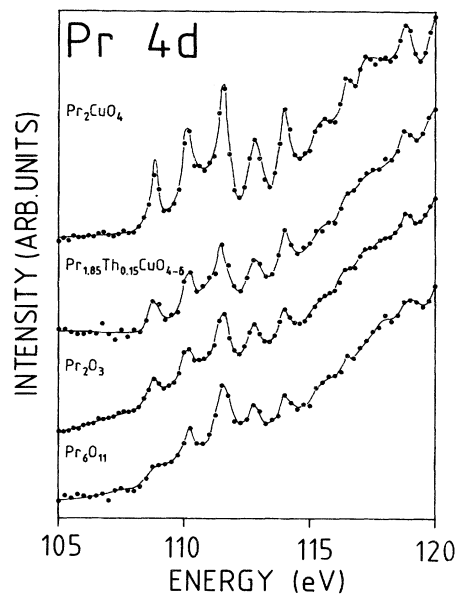FIG. 8. Sm $3d_{5/2}$ absorption edges of Sm_2CuO_4, $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$, and Sm_2O_3.

FIG. 10. Pr $4d$ absorption edges of Pr_2CuO_4, $Pr_{1.85}Th_{0.15}CuO_{4-\delta}$, Pr_2O_3, and Pr_6O_{11}.

compounds, to the existence of localized holes on oxygen sites. In this picture we would expect, upon doping, a shift of the threshold of the prepeak towards higher energies and a reduction of its total intensity by about 15%, both not observed experimentally. Even a small increase of intensity was observed in most of the doped compounds.

In interpretation (ii) holes are supposed to be in the

R_2O_2 layers. As the single-crystal results show that the prepeak structure is polarized parallel to the (a, b) plane, these holes may only be in O $2p_{x,y}$ orbitals. We have estimated the crystal field produced by the R^{3+} ions acting upon the $2p$ states of the O atoms in the O_2 plane. Each oxygen atom is surrounded by four R ions in a quasi-tetrahedral arrangement. It is well known that the states

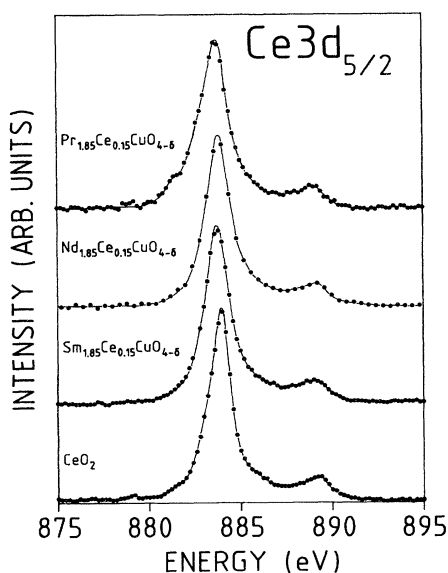FIG. 9. Ce $3d_{5/2}$ absorption edges of $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$, and CeO_2.
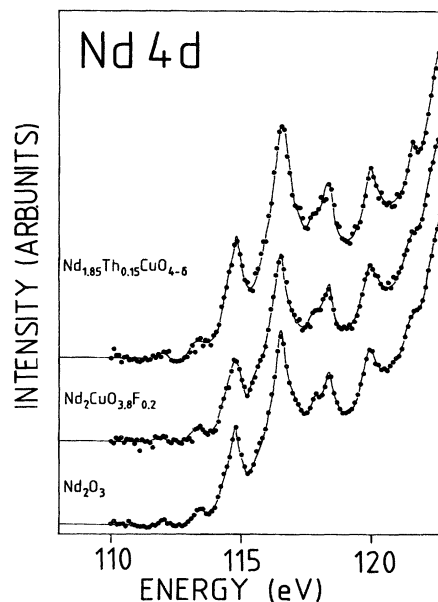
FIG. 11. Nd $4d$ absorption edges of $Nd_2CuO_{3.8}F_{0.2}$, $Nd_{1.85}Th_{0.15}CuO_{4-\delta}$, and Nd_2O_3.
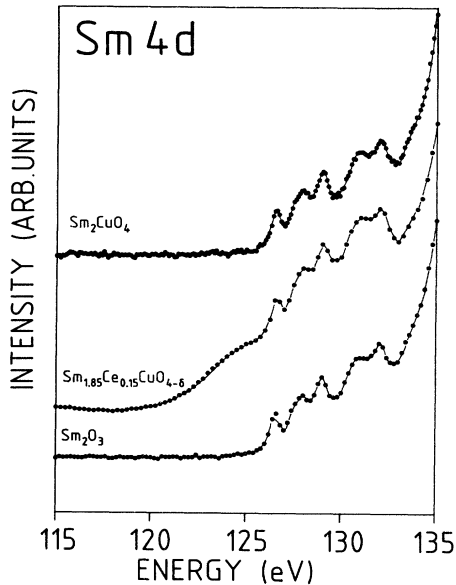
FIG. 12. Sm 4d absorption edges of Sm_2CuO_4, $Sm_{1.85}Ce_{0.15}CuO_{4-\delta}$, and Sm_2O_3.
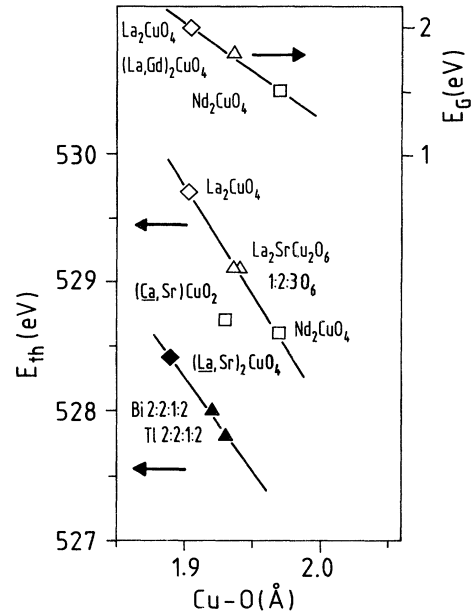

FIG. 13. Plot of the gap energy E_g and the O 1s threshold energy E_{th} for various undoped (open symbols) and doped (solid symbols) cuprates: diamonds, compounds with two apex O atoms; triangles, compounds with one apex O atom; squares, compounds with no apex O atom.

p_x, p_y, and p_z are degenerate in a tetrahedral environment. In the T' structure the R ions are closer to the O_2 plane, thus favoring the p_z orbital for a hole, in contradiction to the experimental results. Even the inclusion of hybridization should not be able to reverse this result totally.

The possibility (iii) for the prepeak to be caused by the R 4f hybridized with O 2p states may be ruled out. Allen *et al.*[25] derived from their resonant photoemission spectra that there are no 4f states near the Fermi level. Further on, we found no such prepeak structure in the O 1s spectrum of Nd_2O_3. Finally, it is expected that the 4f levels shift toward lower energies, when going from Pr via Nd to Sm, while the prepeak remains at the same energy.

In interpretation (iv) the prepeak is caused by transitions into the two-dimensional conduction band. This band is often called the upper Hubbard band.[45] This explanation is supported by the observation of a prepeak in the O 1s spectra of CuO and $Ca_{0.86}Sr_{0.14}CuO_2$ (see Fig. 1) at threshold energies (E_{th}) of 529.6 and 528.8 eV, respectively. In the latter compound and in $R_{2-x}M_xCuO_{4-\delta}$ (R = Pr,Nd,Sm; M = Ce,Th) (E_{th} = 528.6 eV), there are no apex oxygen atoms, and it is remarkable that the threshold energies are almost the same. In the related insulating compounds with one or two apex oxygen atoms, the threshold of the corresponding prepeak appears at about 529.4 and 529.9 eV, respectively.[46] Systematic measurements of the O 1s threshold energies for various undoped and p-type doped cuprates are plotted in Fig. 13 versus the Cu—O distance in the CuO_2 planes. In addition, the gap energy for various insulating cuprates as derived from optical measurements[47] is plotted. In particular, we note that also for undoped La_2CuO_4 a well-pronounced

prepeak appears at 529.7 eV, and upon doping this peak disappears, whereas another one due to hole states in the valence band increases at 528.4 eV (see Refs. 36 and 46). The shift in threshold energy for the insulating compounds is due to both a change in the gap energy and a chemical shift of the O 1s level. There is a linear relationship between E_{th} and the Cu—O distance for the undoped systems, indicating that in all the insulating compounds the threshold is caused by transitions into the same conduction band. At present it is unclear why the insulating $(Ca,Sr)CuO_2$ compound is not found on that line. The decrease of E_{th} with increasing Cu—O distance can be explained by the fact that at larger Cu—O distances (weaker covalency) there are more O 2p electrons at the O sites. This leads to a better shielding of the nuclear charge and thus reduces the binding energy of the O 1s level. Also, the reduced gap widths with increasing Cu—O distance may be explained by weaker covalency. For the p-type doped systems, the appearance of a threshold about 1.5 eV (~the gap energy) below the threshold for the insulating compounds indicates that in these systems the Fermi level is close to the top of the valence band.

Summarizing the above given arguments, we conclude that the observed prepeak in the O 1s spectra of $R_{2-x}M_xCuO_{4-\delta}$ is caused by an excitation into the O 2p states of the conduction band having predominantly Cu 3d character. In a similar way Grioni *et al.*[48] and de Groot *et al.*[49] attributed the first peak in the O 1s spectrum of CuO to an excitation into a conduction band with mainly 3d character. This interpretation for the prepeak is also supported by Takahashi, Katayama-

Yoshida, and Matsuyama.[50] The interpretation of their XAS O $1s$ measurements on $Bi_2Sr_2CaCu_2O_8$ and $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ is based on O $1s$ XPS data from Fujimori *et al.*[8,51] on these systems. The XPS measurements indicated the same O $1s$ binding energy for both compounds. From this they concluded that the XAS threshold energy is related in $Bi_2Sr_2CaCu_2O_8$ to a Fermi level in the valence band, while the threshold in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ about 1 eV higher is caused by an excitation into the upper Hubbard band. In their interpretation the Fermi level for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ is not in the upper Hubbard band. They concluded that $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ is indeed an n-type superconductor, but the character of the doped electrons remained unclear. To align their XPS and XAS data, they assumed an equal excitonic shift in both systems. However, we believe that there are at least two arguments against their evaluation of the experimental results. First, the uncertainty in the determination of the binding energies by XPS is very high (~ 1 eV), and energies quoted in the literature differ from group to group.[51–54] A comparison of XPS binding and EELS threshold energies for various cuprates has been given previously.[30] Moreover, the O $1s$ XPS line is expected to be composed of several lines related to different oxygen sites. Within experimental resolution these lines cannot be separated even if the energies differ by 1 eV. Furthermore, it is not clear why in an insulator such as Nd_2CuO_4 and in metals such as $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ or $Bi_2Sr_2CaCu_2O_8$ the excitonic effect should be the same. In addition, as outlined in Sec. III, excitonic effects in the O $1s$ spectra are expected to be small.

It is interesting to note that the intensity of the O $1s$ prepeak normalized to the intensity of the Cu $2p_{3/2}$ line is almost the same for all compounds shown in Fig. 1. This indicates a similar amount of oxygen $2p$ admixture to the Cu $3d$ conduction band. A comparison with $La_{2-x}Sr_xCuO_4$ yields an admixture $\geq 10\%$,[46] in fair agreement with recent calculations by Schlüter.[55]

Allen *et al.*[25] suggested that upon doping, states originating from the valence and conduction bands arise in the band gap. They concluded that the Fermi level is at the same energy in both Nd and La compounds. A similar picture has been developed by Matsuyama *et al.*[26] and Takahashi,[27] who propose the formation of an "impurity" band in the gap upon doping. These ideas are not compatible with our O $1s$ absorption edges. When interpreting the prepeak in R_2CuO_4 in terms of excitations into the upper Hubbard band, a partially filled impurity band should be observable in n-type doped systems as an additional peak at lower energies. This is clearly not observed in the present experiments. Therefore, we suggest that for n-type doped systems the Fermi level is close to the bottom of the conduction band. On the other hand, for p-type doped systems we have deduced from O $1s$ absorption edges[46] that the Fermi level is close to the top of the valence bands. These results are in contradiction to the results of Allen *et al.*,[25] but in agreement with recent theoretical calculations.[56–58]

We now turn to the Cu $2p_{3/2}$ spectra as shown in Fig.

3. The intensity in the energy region beginning at about 933.2 eV is enhanced for the n-type doped superconductors when compared to the undoped compounds. This enhancement must be assigned to Cu $3d$ states because, as mentioned above, the $2p_{3/2} \rightarrow 4s$ transitions are a factor of 30 less intense than $2p_{3/2} \rightarrow 3d$ transitions. This additional unoccupied Cu $3d$ DOS may be caused by a mixing of Cu $3d$-$4s$,$4p$ states[48,59–61] due to the potential of dopant atoms. An influence of the Ce $3d_{3/2} \rightarrow 4f$ line with a maximum at about 901.5 eV can be excluded because the same spectral weight above ~ 933 eV appears in the Th- and F-doped compounds, and Th, as well as F, has no strong absorption lines in the neighborhood of the investigated Cu $2p_{3/2}$ edge. As reported by Grioni *et al.*[41] many nominally monovlanet Cu compounds exhibit a similar spectral structure as do the n-type doped superconductors at an energy above ~ 933 eV. Therefore, it may be an indication for the existence of monovalent Cu or Cu atoms with a higher number of $3d$ electrons (closer to $3d^{10}$) in the doped compounds. Another much stronger indication for either the local formation of Cu^+ or the filling of a band with predominantly Cu $3d$ character is given by the reduction of the excitonic Cu $2p_{3/2}$ line upon doping as shown in Fig. 4. Since the spectral weight of this line is a measure of the number of empty states with Cu $3d$ character, a reduction indicates the filling of empty Cu $3d$ states. For a doping concentration of $x = 0.15$, the line is found to be reduced by an amount of $\sim 14\%$ with an uncertainty of $\sim 4\%$. From this reduction we conclude that the introduced electrons go onto the Cu sites and have predominantly $3d$ character. This is in agreement with several previous high-energy spectroscopy investigations.[5,7,9]

The widths and shapes of the Cu $2p_{3/2}$ line give a further indication of the nonexistence of holes on oxygen sites. In all known p-type doped superconductors, a slight broadening of the Cu line or an additional shoulder at higher energy is observed when compared to the undoped compounds. This broadening as well as the asymmetry of the Cu line is ascribed to the influence of holes on oxygen sites.[62] Thus the lacking of asymmetry in the n-type doped superconductors and their parent compounds is a strong hint against the formation of holes on oxygen sites.

The shift (~ 0.2 eV) of the Cu $2p_{3/2} \rightarrow 3d$ line toward higher energies as observed in the doped compounds in comparison to the undoped ones may be caused by at least three different reasons. First, it is possible that the free charge carriers with mainly Cu $3d$ character in the doped compounds are able to screen the core hole potential on the Cu atom, and therefore the excitonic effect may be reduced, thus resulting in a slightly higher excitation energy. Second, the bands with $3d$ character may be shifted toward higher energies due to the potential of Th, Ce, or F ions. Third, the charge of the Ce, Th, or F ions may change the Madelung potential on the Cu ions, thus shifting the Cu $2p$ level.

The orientation-dependent measurements of the Cu $2p_{3/2}$ edge of the single-crystalline Nd_2CuO_4 compound indicate that there is, as in all of the high-T_c materials, a

slight admixture of unoccupied Cu $3d_{3z^2-r^2}$ states ($\sim 10\%$) to the dominant $3d_{x^2-y^2}$ ones.[30] The slightly enhanced intensity above the white line may again be explained by the existence of Cu $3d$-$4s$ or Cu $3d$-$4p$ hybridization.

The spectral feature of the $3d$ edges in the trivalent RE compounds is mainly influenced by pure atomic processes,[43] and therefore, with the exception of Pr^{4+} and Ce^{4+} compounds,[44] the shape is independent of the environment the ions are embedded in. Thus we can compare the $3d$ edges of the RE's in the n-type doped superconductors and their parent compounds with those of the RE oxides to get information on their valence. In the case of Ce^{4+} and Pr^{4+}, there are, in addition to the pure atomic transitions, multielectron effects causing at least one additional peak at higher energies compared to the position of the main peak. This peak is always similar to that calculated for the RE element with a nuclear charge Ze, decreased by $1e$ with respect to the investigated one, but the spectral width is increased by about 40–50 %.[44] Therefore, it is also possible to decide whether Ce or Pr are in the formally tetravalent or trivalent state by using a theory of $4f$ states first introduced by Gunnarson and Schönhammer[63] for intermetallic compounds and further developed for the case of insulating systems by Kotani, Jo, and Parlebas.[64]

In the case of the $4d$ absorption edges, in general it is not so easy to determine the charge of the investigated RE ions because hybridization has an effect on line strength, line position, and linewidth in the pre-edge region of the $4d \rightarrow 4f$ transition. Nevertheless, a description within a free-ion model with slightly reduced Slater integrals is possible.[65] The spectral shape of the lines caused by autoionization cannot be described by a free-ion model and varies from solid to solid.[66,67] Thus a comparison between the multiplet structure of the $4d$ transitions of $R_{2-x}M_x CuO_{4-\delta}$ compounds and those related to the R oxides is meaningful only due to the fact that the R ions are embedded in a comparable environment. We think that it is meaningful to compare the multiplet structure of doped and undoped samples as well as those of the related oxides because the dopant concentration is small enough not to disturb the environment of the RE ions. We could get information on the question if the additional electron possibly changes the charge structure of the RE ions. The only exception to the statements mentioned above would be Ce because the pre-edge structure of the Ce $4d$ transitions of formally tetravalent Ce (in CeO_2) has a very different spectral shape in comparison to the trivalent compounds.[68,69] Thus a measurement of the $4d \rightarrow 4f$ pre-edge structure gives an additional possibility to determine the valence state of the Ce ion. Unfortunately, because of the low Ce concentration, the Ce $4d$ absorption could not be measured.

From Figs. 6–8 and using the theory of the $3d$ edges of RE's,[43] we readily conclude that the RE ions Pr, Nd, and Sm are in the trivalent state. The overall agreement between the $3d$ edges of the RE's in $R_{2-x}M_x CuO_{4-\delta}$ and those of the related oxides R_2O_3 is very good, and thus no change in the charge structure of the RE's Pr, Nd, and Sm upon doping with Ce, Th, or F can be observed. The agreement of the Pr, Nd, and Sm $4d$ edges between the $R_{2-x}M_x CuO_{4-\delta}$ and the related R_2O_3 compounds confirmed the trivalency of the R ions.

The $3d_{5/2}$ edge of Ce (Fig. 9) reveals by application of the theory of Kotani, Jo, and Parlebas[64] the formal tetravalency of Ce as is the case in CeO_2. The $4f$ count $\langle n_{4f} \rangle$ of the Ce ion is ~ 0.5. The only exception is detected in the Ce $3d$ edge of the Pr compound, which shows a shoulder at the low-energy side of the main peak. This shoulder is usually assigned to Ce^{3+}.[70] Therefore, there may be a small difference in the Ce $4f$ count between the compounds with $R = Pr$ and those with $R = Nd,Sm$.

V. SUMMARY

We investigated the n-type doped superconductors $R_{2-x}M_x CuO_{4-\delta}$ ($R = Pr,Nd,Sm$; $M = Ce,Th$), $Nd_2CuO_{3.8}F_{0.2}$, and their semiconducting parent compounds. The observed prepeak in the O $1s$ absorption edges is interpreted in terms of transitions into the conduction band having predominantly Cu $3d$ character and an admixture of O $2p$ states. In contrast to p-type doped cuprate superconductors, there are only minor changes in the occupation of O $2p$ states upon doping and annealing in a reducing atmosphere. Upon doping the Fermi level appears at the bottom of the conduction band. We observed a clear decrease of unoccupied Cu $3d$ density of states when going from the semi- to the superconducting compound by an amount of 14 ± 4 %. Therefore, the conduction electrons have mainly Cu $3d$ character. Because of the low cross section of a Cu $2p \rightarrow 4s$ transition, an additional $4s$ character of the charge carriers, if present, is not easily detected in high-energy spectroscopies. As in all p-type doped superconductors and their parent compounds, the holes on Cu in Nd_2CuO_4 have again predominantly $3d_{x^2-y^2}$ character and $\sim 10\%$ admixture of $3d_{3z^2-r^2}$ states. The valence of the rare-earth ions Pr, Nd, and Sm is found to be $+3$. The $4f$ count of Ce is about 0.5, comparable to that of formally tetravalent Ce in CeO_2 for the Nd and Sm compounds, but possibly with a small admixture of formally trivalent Ce in $Pr_{1.85}Ce_{0.15}CuO_{4-\delta}$.

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