Effects of Ce and F doping and reduction on the electronic structure of $Nd_{2-x}Ce_xCuO_4$ and $Nd_2CuO_{3.6}F_{0.4}$ as determined by x-ray-emission spectroscopy

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The Cu $L_{\alpha,\beta}$, O K_α, and F K_α x-ray spectra of $Nd_{2-x}Ce_xCuO_4$ and $Nd_2CuO_{3.6}F_{0.4}$ are presented. It is found that doping with Ce or F and reduction lead to the formation of Cu^+ ions. The O K_α difference spectra of $Nd_{2-x}Ce_xCuO_4$ ($x \neq 0$) and Nd_2CuO_4 exhibit a charge-density redistribution from Cu-O to Ce-O bonds. Fluorine ions are introduced into oxygen sites in Nd_2O_2 layers.

I. INTRODUCTION

The report[1] on the discovery of electron-doped superconductors $Nd_{2-x}Ce_xCuO_4$ has aroused a great deal of interest, since superconductivity in cuprate compounds was believed to be intrinsic in only hole-doped oxides. It has been found that the superconducting properties of the new superconductors (including the superconducting phase transition temperature T_c) are similar to those of $La_{2-x}Sr_xCuO_4$ compounds, regardless of the polarity of the charge carriers. Therefore, an investigation of these oxides provides further understanding of the superconductivity mechanism. In both types of superconductors, the crystal structure is dominated by CuO_2 layers, where each Cu atom is surrounded by four O atoms. However, in the $Nd_{2-x}Ce_xCuO_4$ system (the so-called T' structure), two apical oxygen atoms below or above the CuO_2 layer, which are found in $La_{2-x}Sr_xCuO_4$ (T structure), are absent.

Since the discovery of the $Nd_{2-x}Ce_xCuO_4$ system, many x-ray-spectroscopic studies of its electronic structure have been carried out. However, the results obtained are not consistent with each other.

It still remains to be ascertained which of the Cu $3d$ or Cu $4s$ states are occupied by the dopant electrons, and why the oxygen content is crucial in determining the superconducting and metallic properties of these materials. For unreduced samples, the authors of Refs. 2–6 have observed a linear increase of Cu^+ concentration on doping with Ce. On the other hand, Fujimori et al.[7] have found no evidence for the occupancy of Cu $3d$ orbitals n_d by dopant electrons up to $x \leq 0.15$. For reduced samples, several workers report a linear dependence of Cu^+ on Ce content,[5,6,8] however, Ishii et al.[3] point out that n_d is independent of Ce concentration for $0.1 \leq x \leq 0.2$. Thus, insofar as the character of the additional charge is concerned, there are several interpretations: (i) the electrons donated by Ce fill the Cu $3d$ holes, leading to formation

of $3d^{10}$ configurations in the ground state [see, in addition to the aforementioned references, the x-ray absorption spectroscopy (XAS),[9,10] electron-energy-loss spectroscopy (EELS),[11] photoelectron spectroscopy (PES),[12,13] and Auger electron spectroscopy (AES)[14] data]; (ii) the electrons are injected into a band rather than being localized on Cu sites[15,16]; (iii) the additional charge has a Cu $4s$-like nature.[7,17]

In turn, reduction of the sample, according to the authors of Ref. 18, involves adding electrons to the Cu-$4s$-O-$2p\sigma$ bond and enhances the Cu-O bond covalency; however, according to Refs. 2, 4, 5, 13, and 19, it leads to Cu^+ formation.

Another method of bringing about electronic superconductivity in the Nd_2CuO_4 cuprate is the replacement of part of the oxygen by fluorine.[20] In this case, an increase in Cu^+ concentration upon F doping has been found.[21] But so far, the Nd-Cu-O-F system has received little or no x-ray-spectroscopic study.

X-ray-emission spectroscopy is a much less surface-sensitive method than photoemission spectroscopy (for Nd_2CuO_4, the maximum escape depth of x rays for a 4-keV electron beam is ~ 2500 Å) and provides direct information about the occupancy of the energy levels and about the local densities of electronic states of each of the elements in the valence band of the compound.

In this study, measurements of the Cu $L_{\alpha,\beta}$, O K_α, and F K_α x-ray-emission spectra of unreduced and reduced $Nd_{2-x}Ce_xCuO_4$ ($x = 0$, 0.05, 0.1, 0.15, 0.20) and $Nd_2CuO_{3.6}F_{0.4}$ samples were carried out. As a result, we came to the conclusion that Ce or F doping and reduction lead to formation of monovalent copper and the additional charge has Cu $3d$ character.

II. EXPERIMENT

$Nd_{2-x}Ce_xCuO_4$ ($x = 0$, 0.05, 0.1, 0.15, 0.20) samples were prepared using high-quality Nd_2O_3, CeO_2, and CuO

as starting materials. Mixtures of nominal composition were sintered at 950 °C for 12 h and at 1100 °C for 24 h, with intermediate regrinding, pressing into pellets, and cooling together with the furnace. Some of the samples were reduced in a helium atmosphere at 900 °C for 12 h. As a result, the $x = 0.15$ sample showed bulk superconductivity with $T_c = 22$ K.

$Nd_2CuO_{3.6}F_{0.4}$ samples were obtained using NdF_3 as a fluorine-containing reagent. Stoichiometric mixtures of starting materials were ground, pressed into pellets, and annealed at 1050 °C for 12 h. After regrinding, the material was pressed into pellets and synthesized at the same temperature for 24 h. To obtain superconductivity, the samples were reduced in vacuum. For the final material, the T_c was found to be ~ 21 K.

The composition of the samples was checked by the x-ray phase analysis method (a DRON-3M diffractometer, Cu K radiation). $Nd_2CuO_{3.6}F_{0.4}$ samples exhibited a small impurity of NdOF.

Cu $L_{\alpha,\beta}$, O K_α, and F K_α x-ray-emission spectra were measured with an RSM-500 x-ray electron excitation spectrometer using a diffraction grating ($R = 6$ m, 600 lines mm^{-1}). The O K_α and F K_α radiation were recorded in the first reflection order (the instrumental broadening was ~ 0.7 and larger than 0.8 eV, respectively), and Cu $L_{\alpha,\beta}$ spectra were obtained in the first and second reflection order (the instrumental broadening was 1.1 and less than 0.6 eV, respectively) with the x-ray-tube operating parameters being $V = 4$ kV, $I = 0.2$–0.3 mA.

For detection of Cu L_α (the second reflection order), O K_α, and F K_α radiation, the spectrometer was calibrated using V L_l (446.5 eV), Cr L_l (500.3 eV), V L_α (511.3 eV), and Co L_l (677.8 eV) lines of pure metals,[22] respectively. The vacuum in the x-ray tube, better than 10^{-6} Torr, was produced by oilless pumping.

III. RESULTS AND DISCUSSION

A. Copper

$L_{\alpha,\beta}$ x-ray-emission spectra ($3d \rightarrow 2p_{3/2}$ and $3d \rightarrow 2p_{1/2}$ transitions, respectively) of $3d$ transition metals provide direct information about the occupancy of $3d$ orbitals, allowing one to estimate the chemical state of these metals in any compound.

Figure 1 shows the variation of the occupancy of Cu $3d$ orbitals in both unreduced and reduced $Nd_{2-x}Ce_xCuO_4$ ($x \neq 0$) samples upon Ce doping in comparison with that in Nd_2CuO_4. The difference occupancy was evaluated as

$$\Delta n_d = \frac{I_x - I_o}{I_e} ,$$

where I_x, I_o, and I_e denote the integral intensities of Cu $L_{\alpha,\beta}$ lines normalized to the intensity of the core Cu L_l line ($3s \rightarrow 2p_{3/2}$ transition) for $Nd_{2-x}Ce_xCuO_4$ ($x \neq 0$), Nd_2CuO_4, and Cu_2O oxides, respectively (we postulated that I_e corresponds to $n_d = 10$). The Cu $3s$ electrons do not take part in the chemical bonds; therefore, the intensity of Cu L_l spectra is not sensitive to a change in the chemical state of copper. Indeed, a model self-consistent
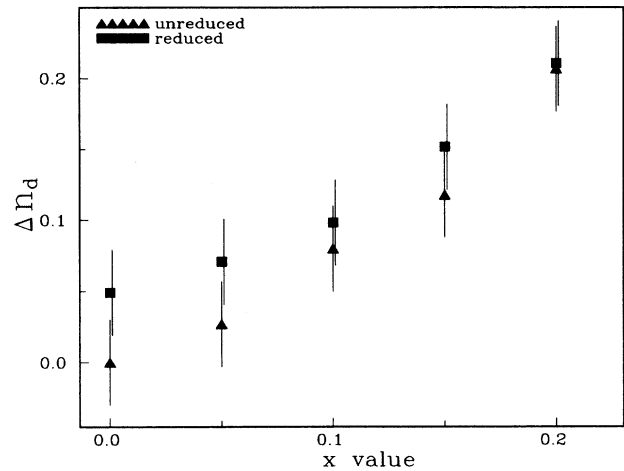

FIG. 1. The change of the occupancy of Cu $3d$ orbitals (Δn_d) in $Nd_{2-x}Ce_xCuO_4$ ($x \neq 0$) samples upon Ce doping in comparison with that in Nd_2CuO_4.

calculation (Dirac-Hartree-Fock-Slater approximation) of the matrix elements of the transition probabilities corresponding to Cu L_l spectra for Cu^0 and Cu^{2+} ($Cu3d^9$) ions has shown that they differ by a small amount (0.5%).[23]

Inspection of Fig. 1 shows that upon Ce doping, the n_d value increases in both unreduced and reduced $Nd_{2-x}Ce_xCuO_4$, being higher in reduced samples in comparison with that in unreduced samples although the difference between samples of both types with equal x values is within the measurement error.

On the strength of these data, we evaluated oxygen losses during reduction. The δ values obtained vary from ~ 0.03 in $Nd_2CuO_{4-\delta}$ to ~ 0.002 in $Nd_{1.8}Ce_{0.2}CuO_{4-\delta}$. This is in good agreement with results of thermogravimetric analysis (TGA)[24] and electron paramagnetic resonance (EPR)[25] investigations.

The increase of the occupancy of Cu $3d$ orbitals when the Nd-Ce-Cu-O system is doped with Ce can be a result of both Cu^+ formation and the increase of the contribution by the $3d^{10}\underline{L}$ configuration ($\underline{L}$ denotes a hole on a ligand) to the ground state of divalent copper.

Earlier, we pointed out the dependence of the ratio of the integral intensities of Cu L_β and Cu L_α lines [$I(L_\beta)/I(L_\alpha)$] on the chemical state of Cu atoms.[26] For monovalent copper, this ratio is appreciably lower than that for Cu^{2+}. The $I(L_\beta)/I(L_\alpha)$ values for both unreduced and reduced samples of Nd-Ce-Cu-O and Nd-Cu-O-F systems are presented in Table I. As the dopant concentration is increased the $I(L_\beta)/I(L_\alpha)$ ratio decreases; its diminution, for example, in $Nd_{1.8}Ce_{0.2}CuO_4$ compared to that in Nd_2CuO_4, being equivalent to the appearance of 15% of the monovalent copper [for Cu_2O the $I(L_\beta)/I(L_\alpha)$ ratio is 0.182].

Cu L_α x-ray-emission spectra of $Nd_{2-x}Ce_xCuO_4$ oxides are depicted in Fig. 2. For unreduced samples, no change is observed in the energy of the L_α peak, while the full width at half maximum (FWHM) of this line increases by 0.3 eV as $x = 0.15$ is doped with Ce (see Table

TABLE I. The ratios of the integral intensities of Cu L_β and Cu L_α lines $[I(L_\beta)/I(L_\alpha)]$ of $Nd_{2-x}Ce_xCuO_4$ and $Nd_2CuO_{3.6}F_{0.4}$ compounds.

Material	$I(L_\beta)/I(L_\alpha)$, ± 0.004	
	Unreduced	Reduced
Nd_2CuO_4	0.301	0.298
$Nd_{1.95}Ce_{0.05}CuO_4$	0.297	0.290
$Nd_{1.9}Ce_{0.1}CuO_4$	0.289	0.295
$Nd_{1.85}Ce_{0.15}CuO_4$	0.294	0.285
$Nd_{1.8}Ce_{0.2}CuO_4$	0.283	0.283
$Nd_2CuO_{3.6}F_{0.4}$	0.284	0.282

II). One might have accounted for this broadening only by the contraction of the unit cell volume of doped Nd_2CuO_4 (see, for example, Ref. 27), leading to larger overlapping on valence electron wave functions. But the similar effect exists in Nd-Cu-O-F oxide, where such a contraction has not been found (see below). On the other hand, the Cu L_α line of a reduced, superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ sample is narrower in comparison with that of nonsuperconducting $Nd_{1.85}Ce_{0.15}CuO_4$.

In addition, Fig. 2 shows Cu L_α spectra of the $Nd_2CuO_{3.6}F_{0.4}$ system, and one can see that F doping of unreduced Nd_2CuO_4 also leads to an increase in the Cu $3d$ bandwidth, while the reduction of $Nd_2CuO_{3.6}F_{0.4}$ gives rise to a decrease in the FWHM of the Cu L_α line. Such changes of the spectra are similar to those observed for the $Nd_{2-x}Ce_xCuO_4$ system. However, although the lattice parameters for Nd_2CuO_4 reveal similar behavior (the a axis expands and the c axis contracts) as Ce and F are substituted, no contraction of the unit cell volume with increasing F content is observed.[28]
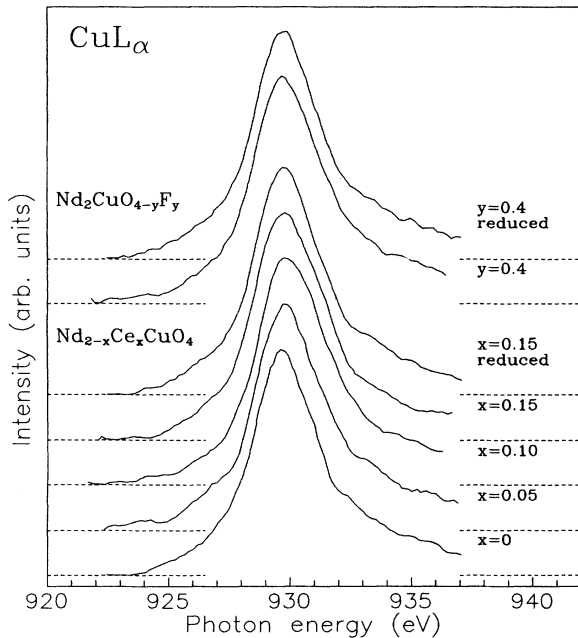

FIG. 2. Cu L_α x-ray-emission spectra of $Nd_{2-x}Ce_xCuO_4$ and $Nd_2CuO_{4-y}F_y$.

The cause for the variation of the FWHM of Cu L_α emission bands is probably the presence of excess oxygen atoms in the compound studied,[29,30] atoms which can be reversibly introduced or removed by oxygen or vacuum annealing. Such excess oxygen atoms may be located on apical oxygen sites, which are normally empty in the ideal T' structure. Tanaka, Okada, and Kotani[31] have calculated the Cu L_α spectra of CuO and La_2CuO_4 using the Anderson impurity model. According to that calculation, the hybridization enhancement for the a_{1g} symmetry states (i.e., Cu-$3d_{z^2-r^2}$-O-$2p\sigma$ hybridization) in La_2CuO_4 owing to the existence of the apical oxygen leads to broadening of the Cu L_α band as a result of a redistribution of the $^3B_{1g}$ spectral component. Thus, in oxygen-rich Nd_2CuO_4, Ce and F substitution, resulting in c-axis contraction, gives rise to a decrease in the Cu-apical-O distance and, hence, to the enhancement of the a_{1g} hybridization.

In Nd_2CuO_4, the Madelung energy acting on an electron at a Cu site has been shown to be 3.0 eV (Ref. 32) lower than that in La_2CuO_4. Hence, the presence of apical oxygen atoms is unfavorable for electron doping of the CuO_2 planes due to the repulsive Coulomb interaction. In turn, a sample reduction, removing the excess oxygen atoms, results in an increase of the occupancy of Cu $3d$ orbitals owing to the introduction of an additional charge into CuO_2 planes and in Cu L_α narrowing as a consequence of the weakening of the a_{1g} hybridization. However, according to Wang et al.[30] in the reduced $Nd_{2-x}Ce_xCuO_4$ compounds with $x \geq 0.15$ the oxygen content becomes lower than 4. Therefore, another cause for decreasing the Cu L_α bandwidth may be removal of oxygen from CuO_2 planes, as found in Ref. 33, and, hence, the formation of Cu^+ ions. A more drastic narrowing of the Cu L_α line owing to oxygen depletion and the appearance of monovalent copper has been observed by Mariot et al.[34] for the $YBa_2Cu_3O_x$ system.

Anyway, we can see that the additional charge introduced by Ce or F doping of Nd_2CuO_4 and by the reducing procedure has a Cu $3d$ character.

B. Oxygen

In Fig. 3 we show O K_α x-ray-emission spectra of $Nd_{2-x}Ce_xCuO_4$ and $Nd_2CuO_{3.6}F_{0.4}$ compounds. The energies and FWHM of these spectra are presented in Table II. Comparing the O K_α bands of Nd_2CuO_4 (T structure) and La_2CuO_4 (T' structure) [Fig. 4(a)], which are parent compounds for n- and p-type superconductors, one can see that the centers of gravity of these bands almost coincide with each other; however, there are some differences on the low-energy side of the emission lines. The O K_α spectrum of Nd_2CuO_4 reveals an enhanced intensity in the vicinity of ~ 524 eV and a decreased intensity near ~ 522 eV as compared with the O K_α spectrum of La_2CuO_4. Such differences are observed owing to the different distribution of the valence O $2p$ states in these compounds, since the O $1s$ binding energies in the samples studied are much the same (529.1 eV for Nd_2CuO_4 and 529.0 eV for La_2CuO_4). According to LMTO-ASA
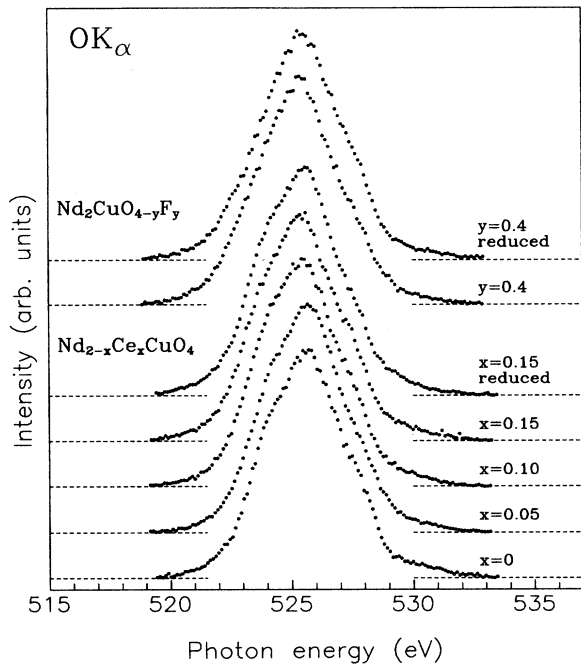
FIG. 3. O K_α x-ray-emission spectra of $Nd_{2-x}Ce_xCuO_4$ and $Nd_2CuO_{4-y}F_y$.

calculation of Szotek, Guo, and Temmerman,[35] $2p$ states of oxygen atoms located in Nd_2O_2 layers reveal a shift by ~ 2 eV towards higher binding energies in comparison with those of apical oxygen atoms in La_2CuO_4 (for the latter compound, the $2p$ states of apical oxygen make a fundamental contribution to the main peak of the O K_α band). Hence, O $2p$ states hybridized with Nd $5d$ states induce the enhanced intensity of the O K_α spectrum of Nd_2CuO_4 at ~ 524 eV, while the higher intensity in the vicinity of ~ 522 eV in La_2CuO_4 arises owing to the higher contribution by the $2p$ states of oxygen atoms located in CuO_2 planes in going from the T' to the T structure. Note that Szotek, Guo, and Temmerman consider Nd $4f$ states as well-localized and inner states in their calculation. Actually, there is an Nd-$4f$–O-$2p$ hybridization.[12,36] Quite probably, the O $2p$ states hybridized with

Nd $4f$ states make a certain contribution to the main peak of the O K_α band. On the binding energy scale, this peak lies ~ 3.4 eV lower the Fermi level, and hybridized Nd $4f$ states measured by resonant photoemission spectroscopy[12] reveal the same binding energy, although, according to Ref. 37, $4f$ states manifest themselves weakly in the p band of light elements.

For superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ and $La_{1.83}Sr_{0.17}CuO_4$ samples, the differences in O K_α spectra are more considerable [Fig. 4(b)]. The gravity center of the O K_α line of a p-type superconductor moves to higher energies with respect to that of an n-type superconductor. This is caused by the energy rise of $2p$ states of apical oxygen atoms due to the Sr doping of La_2CuO_4.[38] On the other hand, according to one calculation,[35] Ce doping of Nd_2CuO_4 leads to lowering of $2p$ states of oxygen atoms close to the rare-earth element atoms, as a result of the metal-$5d$–oxygen-$2p$ hybridization in the $Nd_{2-x}Ce_xO_2$ layers. Indeed, the feature observed in emission O K_α spectra at ~ 524 eV is more pronounced in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ as compared with that in Nd_2CuO_4. It is interesting that this feature disappears in O K_α spectra of the $Nd_2CuO_{3.6}F_{0.4}$ system. This disappearance seems to be evidence of the introduction of F ions into oxygen sites in Nd_2O_2 layers.

In Fig. 5, we show on the binding energy scale the O K_α difference spectra between unreduced samples with different Ce content, and Nd_2CuO_4 and the partial densities of $2p$ states of oxygen atoms located in inequivalent crystallochemical positions as were calculated by Szotek, Guo, and Temmerman[35] for $Nd_7CeCu_4O_{16}$. To realize the subtraction procedure, the O K_α spectra were normalized to the intenity of the Cu L_l line of the respective sample. The partial densities of states are combined with experimental data so that the gravity centers of the total density of O $2p$ states and the O K_α spectrum of Nd_2CuO_4 should coincide. Note that according to calculation, the occupied Ce $5d$ states are located deeper than those of Nd. The origin of this is the strengthening of the "rare-earth-element–oxygen" chemical bond due to the higher overlapping of the valence electron wave functions, since the radius of the Ce ion is larger than that of the Nd ion.

Inspection of the figure shows that upon Ce doping the intensity of the O K_α emission band increases in the bind-

TABLE II. The energies (E) and full widths at half maximum (FWHM) of emission lines (eV).

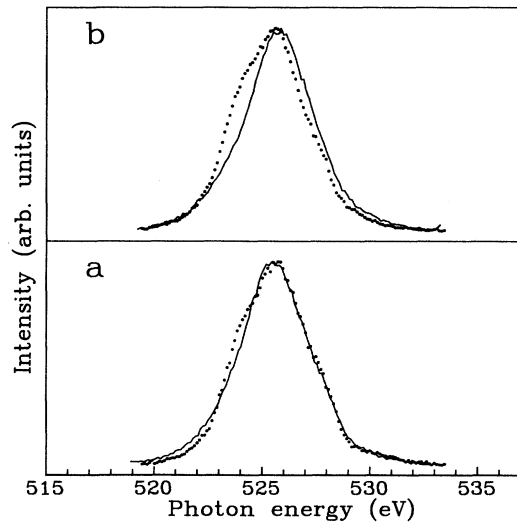| Material	Cu L_α		O K_α		F K_α	
	$E \pm 0.2$	FWHM	$E \pm 0.1$	FWHM	$E \pm 0.2$	FWHM
Nd_2CuO_4	929.7	3.3	525.7	4.1		
$Nd_{1.95}Ce_{0.05}CuO_4$	929.8	3.5	525.7	4.0		
$Nd_{1.9}Ce_{0.1}CuO_4$	929.8	3.6	525.5	4.2		
$Nd_{1.85}Ce_{0.15}CuO_4$	929.7	3.6	525.5	4.3		
$Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$	929.7	3.4	525.6	4.1		
$Nd_2CuO_{3.6}F_{0.4}$	929.7	3.6	525.5	3.9	676.9	2.4
$Nd_2CuO_{3.6-\delta}F_{0.4}$	929.7	3.4	525.5	4.0	677.0	2.5
NdF_3					677.2	2.8
CuF_2					677.2	4.6

FIG. 4. O K_α x-ray-emission spectra: (a) La_2CuO_4 (—) (Ref. 38) and Nd_2CuO_4 (●●●); (b) $La_{1.83}Sr_{0.17}CuO_4$ (—) (Ref. 38) and $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ (●●●).

ing energy range from ∼3.5 to 8 eV and decreases in the ∼0–3.5 eV range, leading to a high binding energy shift of the band gravity center. The appearance of the features at ∼6 and ∼4.5 eV in the difference spectra is a consequence of the hybridization of O $2p$ states with Ce $5d$ and Ce $4f$ states, respectively (Szotek, Guo, and Temmerman[35] have not taken into account the Ce $4f$ states; however, according to an analogous calculation for $Nd_3CeCu_2O_8$,[39] the Ce $4f$ states occupied owing to the chemical bond are ∼1.5 eV closer to the Fermi level than Ce $5d$ states). It is clear that the Ce doping process
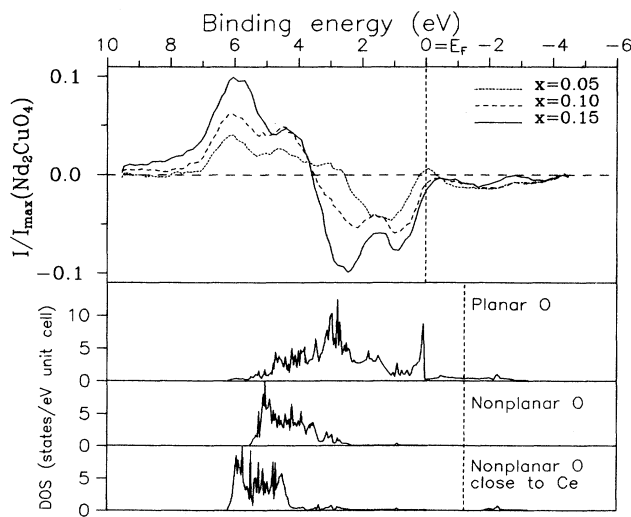

FIG. 5. The O K_α difference spectra between $Nd_{2-x}Ce_xCuO_4$ ($x\neq0$) and Nd_2CuO_4 in the binding energy scale (the top of figure) and partial densities of $2p$ states of oxygen atoms into inequivalent crystallochemical positions for $Nd_7CeCu_4O_{16}$ (see Ref. 35).

of Nd_2CuO_4 must stimulate the growth of the intensities of these features. Simultaneously, the intensity of the high binding energy side of the O K_α band is also formed by the contribution of the O $2p$ states hybridized with Nd $5d$ states. However, the decrease of Nd content in the samples studied as a result of Ce substitution weakly affects the firm growth of the peaks at ∼4.5 and ∼6 eV. This indicates a stronger Ce-O chemical bond compared with the Nd-O bond in the parent compound.

The lowering of the intensity of the O K_α band at low binding energies with increasing x is caused mainly by the weakening of Cu-$3d$–O-$2p$ hybridization due to Cu^+ formation and also by a decrease in the fraction of O $2p$ states hybridized with Nd $4f$ states. The negative difference spectrum, exhibiting a "U shape" upon small Ce concentration, later reveals itself on two minima at ∼1 and ∼2.5eV owing to the appearance of a distinct salient feature at ∼1.5 eV. This salient feature may be a manifestation of hybridized Ce $4f$ states, which, as emphasized by Namatame et al.,[36] are distributed predominantly near the top of the O $2p$ band. The enhancement of the hybridization of the valence O $2p$ and Cu $3d$ states along the c axis owing to the existence of excess oxygen atoms on apical oxygen sites may be another cause for the appearance of this salient feature. As a whole, the figure gives evidence of the redistribution of charge density from Cu-O to Ce-O bonds.

C. Fluorine

In F K_α x-ray emission spectra, a group of α', α_3, α_4, α_5, and α_6 satellites are observed on the high-energy side of the main $\alpha_{1,2}$ line (the initial state is $1s^{-1}$).[40] According to the energy calculations of the initial states for α', α_3, and α_4 satellites, the latter have $1s^{-1}(2s2p)^{-1}$ electron vacancy configuration (later on the K^1L^1 satellite), while configuration for α_5 and α_6 is $1s^{-1}(2s2p)^{-2}$ (K^1L^2 satellite).[41] As known, the intensity of the K^1L^1 satellite is affected by the chemical environment of F atoms (see, for example, Ref. 42). Part of the research groups em-
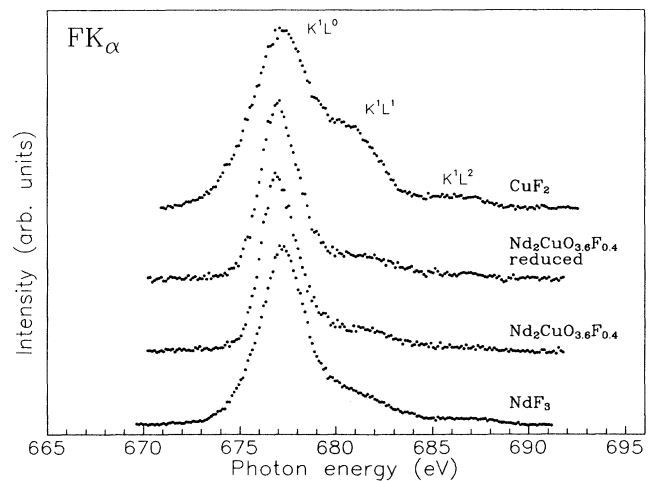

FIG. 6. F K_α x-ray-emission spectra of $Nd_2CuO_{3.6}F_{0.4}$, NdF_3, and CuF_2 compounds.

phasize such influence on the energy and FWHM of the main K^1L^0 line.[43]

Figure 6 shows F K_α spectra of unreduced and reduced $Nd_2CuO_{3.6}F_{0.4}$ samples, and also NdF_3 and CuF_2 compounds. One can see that the spectra of NdF_3 and CuF_2 are appreciably different in the energy range of the K^1L^1 satellite (~ 681 eV). Note that the high-energy shoulder formation in the F K_α spectrum of CuF_2 can also be caused by the Cu-$3d$–F-$2p$ hybridization. The K^1L^1 satellite intensity and FWHM of F K_α spectra of both $Nd_2CuO_{3.6}F_{0.4}$ samples are similar to those of the F K_α spectrum of NdF_3 (see Table II). Therefore, in spite of the existence of some impurity of NdOF in the $Nd_2CuO_{3.6}F_{0.4}$ samples, we concluded that F ions are introduced into the oxygen sites in Nd-O layers. This conclusion is in agreement with data of both x-ray diffraction[28] and nuclear magnetic resonance (NMR) investigations.[44]

IV. CONCLUSION

Cu $L_{\alpha,\beta}$ and O K_α x-ray-emission spectra of unreduced and reduced $Nd_{2-x}Ce_xCuO_4$ and $Nd_2CuO_{3.6}F_{0.4}$ give evidence of Cu^+ ion formation in these compounds as a result of Ce or F doping and the reducing process; the fluorine ions, as one can conclude from analysis of F K_α spectra, being introduced into oxygen sites located in Nd_2O_2 layers. The O K_α difference spectra between $Nd_{2-x}Ce_xCuO_4$ and Nd_2CuO_4 show the charge density redistribution from Cu-O to Ce-O bonds.

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