Photoelectron-spectroscopy study of superconductive $Nd_2CuO_{4-x}F_x$

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A photoelectron spectroscopic study was performed to investigate both the fluorine sites in and the electronic structure of superconductive $Nd_2CuO_{4-x}F_x$ ($x=0$, 0.1, 0.16, 0.2, and 0.3). The x-ray photoelectron spectroscopic (XPS) results for F $1s$ spectra showed that the doped fluorine ions were located on the oxygen sites in the tetragonal Nd_2CuO_4 lattice. Furthermore, comparison between the XPS spectra of $Nd_2CuO_{4-x}F_x$, CuF_2, NdF_3, and NdOF suggested that the fluorine ions were not located on the O(2) sites around the Nd^{3+} ion but rather on the O(1) sites in the CuO_2 planes. The XPS result for Cu $2p$ spectra indicated that the amount of Cu^{1+} ions increased as x increased. In addition, according to the ultraviolet photoelectron spectroscopic measurements, the density of states in the vicinity of the Fermi level seemed to increase as the F content increased.

I. INTRODUCTION

The superconductivity in $Nd_2CuO_{4-x}F_x$ (Ref. 1) was discovered just after the appearance of the "n-type" superconductor $Nd_{2-y}Ce_yCuO_4$.[2] It was found that the normal-state properties of $Nd_2CuO_{4-x}F_x$ were parallel to those of $Nd_{2-y}Ce_yCuO_4$ from the measurements of transport properties[3-5] and the observation of electronic structure using electron-energy-loss spectroscopy.[6] In contrast to the case of $Nd_{2-y}Ce_yCuO_4$, however, there have been only several reports available for $Nd_2CuO_{4-x}F_x$.

In particular, the determination of the sites for doped F ions has been an unresolved problem for $Nd_2CuO_{4-x}F_x$. In the Nd_2CuO_4-type tetragonal lattice,[7] there are two oxygen sites which are called O(1) and O(2) site, respectively: the O(1) site is in the CuO_2 plane (Cu-O bond) and the O(2) site is between two Nd planes (Nd-O bond). Previously, we suggested[3] that F ions were doped into the O(2) sites based on the lattice parameter measurement results; that is, the a axis increased in proportion to x for the samples with $x < 0.3$, in spite of the fact that the ionic radius of the F^- ion [$r=0.133$ nm (Ref. 8)] is smaller than that of the O^{2-} ion [$r=0.140$ nm (Ref. 8)]. However, the lattice parameters would be affected by not only the ionic radius but also the charge distribution, when F ions are doped into the sample. Thus, we may not simply conclude that F ions are doped into the O(2) sites.

Unfortunately, it seems impossible to assign sites for doped F ions by neutron diffraction analysis, because the neutron scattering cross section for fluorine is approximately the same as that for oxygen.[9] Furthermore, it was found[4] that the TEM observation gave no significant information on the sites for doped F ions.

On the other hand, photoelectron spectroscopic analysis of core levels can provide the information on the nature of bonding; hence, there is a possibility to identify the position of F ions, if the core-level binding energies in the case of the Cu-F bonding are apparently different

from those of the Nd-F bonding. In addition, a photoelectron-spectroscopic study of the valence band gives the information on the electronic structure; indeed, numerous photoelectron-spectroscopic studies of high-T_c superconductors indicate the existence of an edge structure at the Fermi level.[10] Although some photoelectron-spectroscopic studies[11,12] on $Nd_{2-y}Ce_yCuO_4$ were already reported, there are, to the authors' knowledge, no reports on the F-doped samples.

In this paper, we report on a photoelectron-spectroscopic study of $Nd_2CuO_{4-x}F_x$ in order to assign sites for the doped F ions and investigate the change in the electronic structure due to F doping.

II. EXPERIMENT

The polycrystalline samples of $Nd_2CuO_{4-x}F_x$ ($x=0$, 0.1, 0.16, 0.2, and 0.3) were synthesized by a solid-state reaction technique using reagent-grade Nd_2O_3, NdF_3, and CuO powders. Stoichiometric mixtures of the starting materials were thoroughly mixed by a planetary ball mill using ethanol as solvent. After drying, the mixtures were calcined at 860 °C for 10 h in 20% O_2-Ar gas mixture flow. After regrinding, the calcined powder was pressed into rectangular bars and sintered at 1100 °C for 14 h in 1% O_2-Ar gas mixture flow. Then, the samples were annealed at 910 °C for 14 h in nitrogen gas flow and furnace cooled to room temperature with a rate of ~4 °C/min.

Powder x-ray-diffraction studies and electron-probe microanalysis indicated that the samples with $x \leq 0.2$ were nearly single phase of the Nd_2CuO_4-type tetragonal structure. In contrast, the sample with $x=0.3$ included small amounts of NdOF and CuO phases besides the $Nd_2CuO_{4-x}F_x$ phase. The electrical resistivity and magnetic susceptibility measurements showed that the values of $T_{c,on}$ were ~27 K for the samples with $x > 0.1$, though the zero-resistance states were observed only for the samples with $x=0.2$ and 0.3 at 20 and 19 K, respectively. The characterization and physical properties of the sam-

ples are reported in detail elsewhere.[3−5]

The photoelectron-spectroscopic measurements were carried out in an ultrahigh-vacuum system equipped with an Al x-ray source (1486.6 eV) for x-ray photoelectron spectroscopy (XPS) and a noble-gas discharge lamp for ultraviolet photoelectron spectroscopy (UPS). The energy distribution of the photoelectron was determined by an electron-energy analyzer, the resolution of which was set at 0.8 and 0.15 eV for XPS and UPS measurements, respectively. Core-level binding energies were referenced to the adventitious C $1s$ peak at 285.0 eV. For the UPS measurement, the Fermi energy was determined directly from the zero binding energy of the analyzer, because no charge-up was observed and the accuracy was better than 0.15 eV. The typical pressure during the measurements was $\sim 2\times10^{-10}$ torr. The sample was scraped in vacuum by a diamond file before each measurement. In this study, all of the spectra were taken at room temperature.

III. RESULTS AND DISCUSSION

A. Core-level spectra

The F $1s$ core-level XPS spectra from $Nd_2CuO_{4-x}F_x$ ($x=0$, 0.1, 0.16, 0.2, and 0.3) are shown in Fig. 1. The peak observed in the spectrum for each of the F-doped samples indicates that the binding energy of F $1s$ in $Nd_2CuO_{4-x}F_x$ is about 684 eV. Since the peak intensity (at ~684 eV) increases with x, the F content in $Nd_2CuO_{4-x}F_x$ rises with x, as expected. Furthermore, this increase in the peak intensity at the same binding energy of ~684 eV suggests that the F ions are doped into a certain site in the Nd_2CuO_4-type tetragonal unit cell; this is also supported by the fact that the observed binding energy is different from that of F in NdOF, which was the only impurity phase including F ions in the samples, as will be mentioned later.

Figure 2 shows the F $1s$ XPS spectra from $Nd_2CuO_{3.8}F_{0.2}$, CuF_2, NdF_3, and NdOF. There is a marked difference between the top two spectra and the bottom two spectra. The binding energies of F $1s$ are estimated to be about 683.9, 684.6, and 684.6 eV in CuF_2,

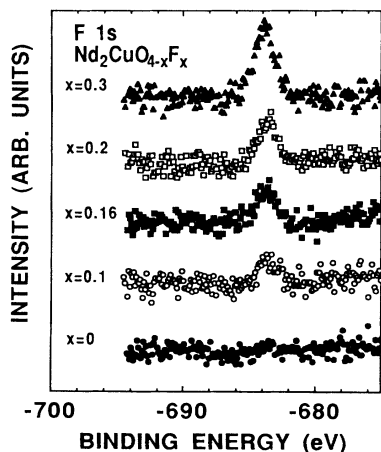FIG. 2. XPS core spectra of F $1s$ from $Nd_2CuO_{3.8}F_{0.2}$, CuF_2, NdF_3, and NdOF.

NdF_3, and NdOF, respectively. The binding energy of F in $Nd_2CuO_{4-x}F_x$ (~684 eV) is close to that in CuF_2 rather than to those in NdF_3 and NdOF. This suggests the possibility of the existence of Cu-F bonds in the sample. While it is difficult, based only on the XPS results at this moment, to assign sites for the doped F ions, the similarity of the spectra for F $1s$ from CuF_2 and $Nd_2CuO_{4-x}F_x$ suggests that the F ions are doped into O(1) sites in the CuO_2 planes. This seems to be against the result of the lattice parameter measurements.[3] However, as described above, it is difficult to assign sites for the doped F ions only from the changes in the lattice parameters.

The XPS spectra for other inner core levels of Nd, Cu, and O are shown in Figs. 3–5. The Nd $3d$ core-level spectra show no special changes caused by the F doping. Thus, the valence of the Nd ions in $Nd_2CuO_{4-x}F_x$ is considered to be trivalent. This situation is similar to the case of $Nd_{2-y}Ce_yCuO_4$.[10] Additionally, this seems to indicate that the Nd-F bond does not exist in the F-doped samples.

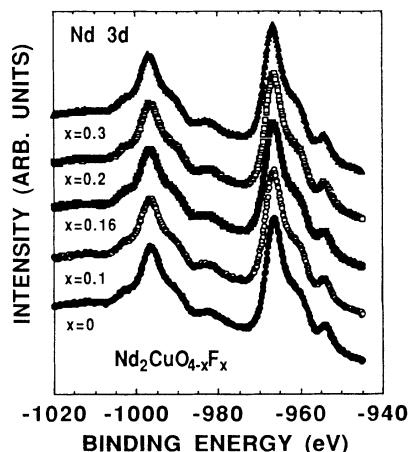The Cu $2p$ core-level spectra for $Nd_2CuO_{4-x}F_x$ are shown in Fig. 4(a). Each spectrum consists of a main

FIG. 1. XPS core spectra of F $1s$ from $Nd_2CuO_{4-x}F_x$ with $x=0$, 0.1, 0.16, 0.2, and 0.3.

FIG. 3. XPS core spectra of Nd $3d$ from $Nd_2CuO_{4-x}F_x$.

peak at 932.4 eV and a broad satellite peak at ~ 942.5 eV; usually,[12] the former is assigned to the charge-transfer-screened $2p3d^{10}L$ final state and the latter is assigned to the unscreened $2p3d^9$ final state. Since F^- ion is considered to be a hard base,[13] the substitution of O by F in Nd_2CuO_4 should provide electrons in the CuO_2 planes; as
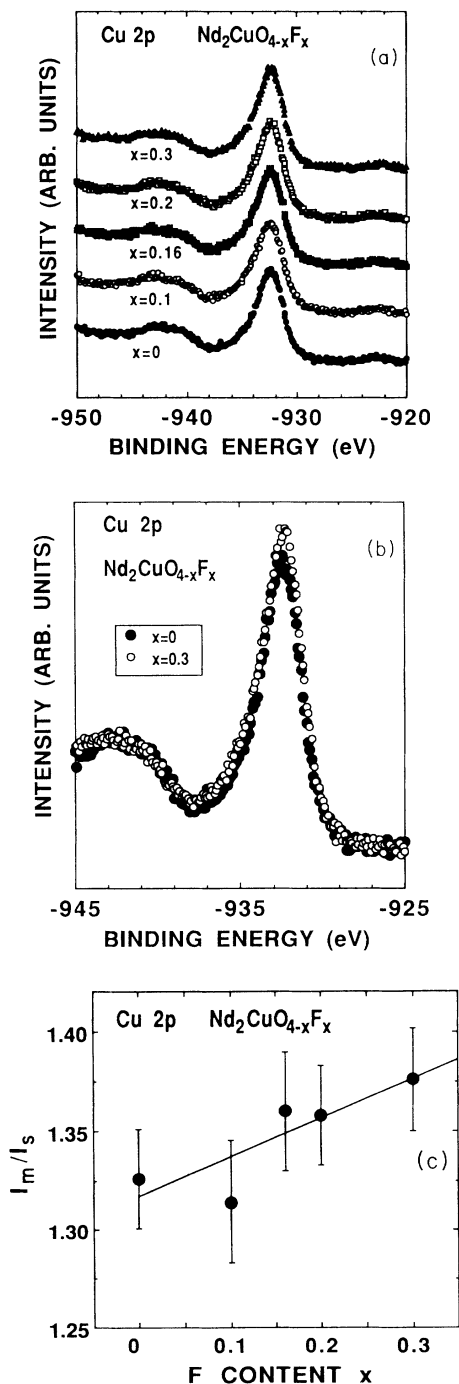

FIG. 4. (a) XPS core spectra of Cu $2p$ from $Nd_2CuO_{4-x}F_x$ with $x=0, 0.1, 0.16, 0.2,$ and 0.3; (b) the comparison of two XPS spectra of Cu $2p$ from Nd_2CuO_4 and $Nd_2CuO_{3.7}F_{0.3}$; (c) the relationship between I_m/I_s and x, where I_m and I_s are the intensity of the main and satellite peak, respectively.
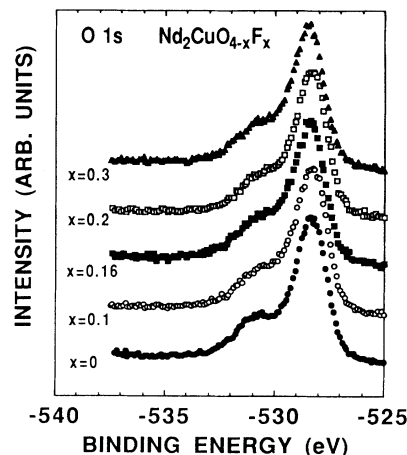

FIG. 5. XPS core spectra of O $1s$ from $Nd_2CuO_{4-x}F_x$ with $x=0, 0.1, 0.16, 0.2,$ and 0.3.

a result, the amount of Cu^+ ions in the sample would increase with x. Hence, as x increases, the intensities of the main and satellite peaks are expected to enlarge and reduce, respectively. Indeed, as shown in Fig. 4(b), apparent growth of the main peak is observed, making a comparison between the two spectra for Nd_2CuO_4 and $Nd_2CuO_{3.7}F_{0.3}$. To understand the changes in the intensities of the two peaks due to the F doping, Fig. 4(c) shows the main-to-satellite peak intensity ratio I_m/I_s as a function of x. It is clearly observed that the magnitude of I_m/I_s rises in proportion to x, indicating a linear increase in the amount of Cu^+ ions.

As shown in Fig. 5, the O $1s$ core-level spectra for $Nd_2CuO_{4-x}F_x$ consist of the sharp peak at 528.8 eV and the shoulders at ~ 531 eV. It is worth noting that the position of the main peak exhibits no systematic shifts due to F doping. In contrast, for $Nd_{2-y}Ce_yCuO_4$, it was observed that the sharp peak at 528.6 eV shifted slightly toward a higher binding energy due to Ce coping.[11] To explain the shift for $Nd_{2-y}Ce_yCuO_4$, it was supposed that the oxygen valence increased with y, such as $O^{2-}\rightarrow O^{(2-p)-}$. However, our result implies that the
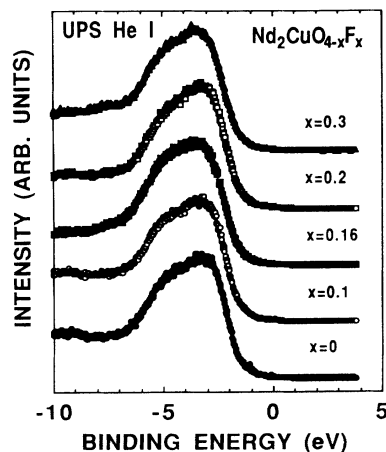

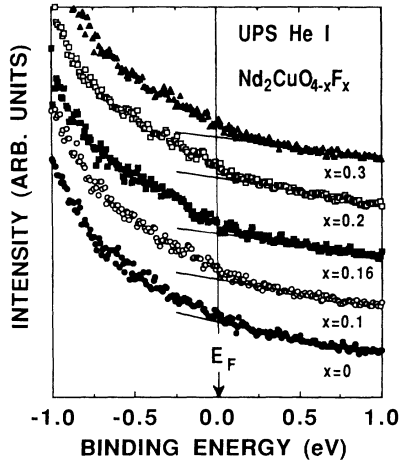FIG. 6. Valence-band UPS spectra (He I, $h\nu=21.2$ eV) from $Nd_2CuO_{4-x}F_x$ with $x=0, 0.1, 0.16, 0.2,$ and 0.3.

FIG. 7. Enlargement of the UPS spectra of Fig. 6 in the Fermi-level region.

FIG. 8. Valence-band UPS spectra (He I, $h\nu=21.2$ eV) from Nd_2CuO_4, $Nd_2CuO_{3.8}F_{0.2}$ and $Nd_{1.85}Ce_{0.15}CuO_4$.

valence of oxygen is not affected by the substitution for O by F. Only the valence of Cu seems to reduce due to F doping. On the other hand, the broad peak at ~ 531 eV is considered to be from the oxide impurities, probably CuO and Nd_2O_3, which are segregated at the voids and/or the grain boundaries. Therefore, although the intensity of the shoulder varies slightly with x, this change is not an essential feature.

B. Valence-band spectra

Figure 6 shows the UPS valence-band spectra for $Nd_2CuO_{4-x}F_x$. The fact that the shapes of the spectra do not change with x indicates a stable electronic structure to the F doping. In order to understand the detailed electronic structure at the Fermi level (E_F), the UPS spectra in the vicinity of E_F are shown in Fig. 7. For each of the samples with $x \geq 0.1$, a finite density of states can be observed at E_F. Furthermore, as x increases, the density of states at E_F, $N(E_F)$, seems to grow. Previously, we reported[3-5] that all of the resistivity, Hall coefficient and thermoelectric-power coefficient reduced in magnitude with x. This indicated an increase in the charge-carrier density due to F doping. We also pointed out the existence of the insulator-to-metal transition around $x=0.16$.[5] The UPS result, which indicates the growth in $N(E_F)$ with increasing x, is consistent with the results of the transport properties. However, no drastic differences of the electronic structure between $x=0$ and 0.2, which might be related to such insulator-to-metal transition, were observed.

Figure 8 shows the UPS results for Nd_2CuO_4, $Nd_2CuO_{3.8}F_{0.2}$, and $Nd_{1.85}Ce_{0.15}CuO_4$. Although the difference in shape around 5 eV between $Nd_{1.85}Ce_{0.15}CuO_4$ and $Nd_2CuO_{3.8}F_{0.2}$ may suggest the characteristic difference between the Cu $3d$–O $2p$ and

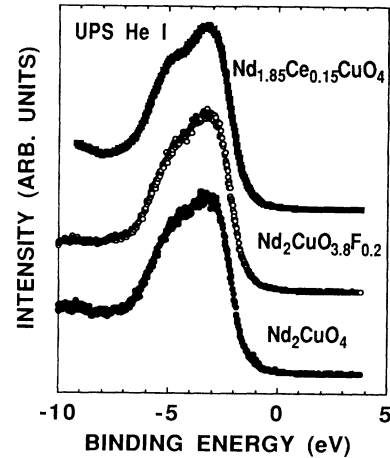Cu $3d$–F $2p$ hybridization, the overall shapes of the three spectra are quite similar, especially in the vicinity of E_F. This indicates that the electronic structures of $Nd_2CuO_{4-x}F_x$ should be approximately the same as those of $Nd_{2-y}Ce_yCuO_4$. In fact, the calculated electronic structure using the tight-binding approximation showed[14] that there were no significant differences between $Nd_{2-y}Ce_yCuO_4$ and $Nd_2CuO_{4-x}F_x$. Furthermore, the calculation indicated that E_F shifted by 0.34 eV towards the high binding-energy side (comparing with Nd_2CuO_4) and the value of $N(E_F)$ was 0.71 states/(eV unit-cell) for $Nd_2CuO_{3.6}F_{0.4}$, if the F^- ions were doped into only the O(1) sites. Of course, at this moment, it is difficult to estimate the value of $N(E_F)$ only from the UPS measurements. Nevertheless, the measured photoelectron spectra for $Nd_{2-y}Ce_yCuO_4$ (Refs. 11 and 12) and $Nd_2CuO_{4-x}F_x$ seem to be in good agreement with the calculated one.

IV. SUMMARY

A photoelectron-spectroscopic study was made in order to investigate both the fluorine sites in and the electronic structure of superconductive $Nd_2CuO_{4-x}F_x$ ($x=0$, 0.1, 0.16, 0.2, and 0.3). The x-ray photoelectron spectroscopic (XPS) results for F $1s$ spectra showed a possibility that the doped fluorine ions were not located on the O(2) sites around the Nd^{3+} ion but rather on the O(1) sites in the CuO_2 planes. Although the XPS spectra for Nd $3d$ and O $1s$ exhibited no significant changes due to F doping, the amount of Cu^+ ions was found to increase with x from the XPS spectra for Cu $2p$. In the ultraviolet photoelectron-spectroscopic measurements, it was observed that the density of states in the vicinity of the Fermi level also increases with x, as reported for other high-T_c superconductors.

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