Resonant-photoemission study of $Nd_{2-x}Ce_xCuO_4$

H. Namatame, A. Fujimori, and Y. Tokura

Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

M. Nakamura, K. Yamaguchi, and A. Misu

Department of Physics, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

H. Matsubara and S. Suga*

Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo, Tanashi, Tokyo 188, Japan

H. Eisaki, T. Ito, H. Takagi, and S. Uchida

Engineering Research Institute, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

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We have studied the photoemission spectra of $Nd_{2-x}Ce_xCuO_4$ ($0.05 \leq x \leq 0.2$) using synchrotron radiation in the Cu $3p \rightarrow 3d$, Nd $4d \rightarrow 4f$, and Ce $4d \rightarrow 4f$ core absorption regions. The valence-band satellite corresponding to Cu^{2+} shows a resonance behavior. The Nd $4f$-derived photoemission spectrum shows a double-peak structure, which is characteristic of the localized $4f^3$ ground state and strong $4f$-$O 2p$ hybridization. The Ce $4f$-derived photoemission is distributed predominantly near the top of the O $2p$ band. Comparing the results with those of $La_{2-x}Sr_xCuO_4$, we find that the Fermi level is located only ~ 0.7 eV above the top of the valence band in spite of the large (1.5-eV) band gap of Nd_2CuO_4, indicating that the Fermi level of $Nd_{2-x}Ce_xCuO_4$ lies within the band gap of Nd_2CuO_4.

INTRODUCTION

The recent discovery of the electron-doped superconductor $Nd_{2-x}Ce_xCuO_4$ has aroused considerable interest in the search for the mechanism of high-T_c superconductivity in doped Cu oxide systems.[1] The central issue of this new material has been which orbitals are occupied by doped electrons, but no definite answer has been obtained so far. The first CuK-edge x-ray-absorption study by Tranquada et al.[2] revealed an increased amount of Cu^+ (d^{10}) configuration with Ce concentration, whereas a recent work by Kosugi et al.[3] found no significant amount of Cu^+ based on more careful analyses of the spectra. In the Cu $2p$ core-level photoemission study by Fujimori et al.,[4] no Cu^+ signal was found up to $x = 0.15$ (though a weak d^{10} emission was identified for $x = 0.2$), while Uji, Shimoda, and Aoki[5] found in their Cu $2p$ core-level spectra Cu^+ signals whose intensities increased with x although the absolute amount of the signals was small compared to the number of doped electrons. Cu^+ signals have also been reported in the Cu $2p$ core-level study of Grassmann et al.[6] Although a definite answer to the above issue may still be difficult, we have performed a photoemission study of $Nd_{2-x}Ce_xCuO_4$ using synchrotron radiation in order to get more insight into the electronic structure of this material. We have also compared the results of $Nd_{2-x}Ce_xCuO_4$ with those of $La_{2-x}Sr_xCuO_4$ in order to study the position of the Fermi levels with respect to the band gaps of the parent insulating compounds.

EXPERIMENTAL

The measurements were made at BL-2 of the Synchrotron Radiation Laboratory. Photoelectron energies were measured with a double-pass cylindrical mirror analyzer. The total resolution of the analyzer plus monochromator was 0.3–0.4 eV depending on photon energies. $Nd_{2-x}Ce_xCuO_4$ samples were prepared by sintering mixtures of Nd_2O_3, CeO_2, and CuO powders corresponding to different stoichiometries ($x = 0.05, 0.1, 0.15, 0.2$).[7] They were not reduced and thus were not superconducting. A reduced sample with $x = 0.15$, which showed superconductivity, was also studied, but its spectra are not presented here because they do not seem to represent the bulk electronic structure probably due to impurity phases segregated in the grain boundaries[3] as judged from the anomalously weak Cu satellite signals. The samples were introduced from atmosphere to an ultra-high-vacuum sample preparation chamber through an airlock system. The samples were then transferred into an analyzer chamber and set to a liquid-nitrogen cryostat. The sample surfaces in vacuum were degraded so quickly at room temperature that it was necessary to scrape the samples thoroughly with a diamond file at low temperatures. The position of the Fermi level has been determined by measuring the spectra of Au evaporated in the spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows energy distribution curves (EDC's) in the valence-band region taken at $h\nu = 40$ eV for different compositions x's. At this photon energy, emission from the O $2p$ states dominates the spectra with some contributions from the Nd $4f$ states.[8] For contaminated or degraded sample surfaces, a structure appears at a binding energy (E_B) of about 10 eV and a shoulder at $E_B \sim 5$ eV.[9,10] The fact that these features are not observed in
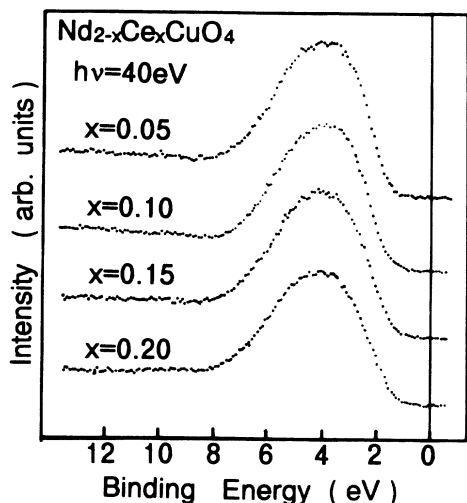
FIG. 1. EDC's of $Nd_{2-x}Ce_xCuO_4$ ($x = 0.05$, 0.10, 0.15, and 0.2) taken at $hv = 40$ eV.

the spectra indicates that the sample surfaces were clean enough during the measurement. (These features were clearly observed in the previous measurements carried out at room temperature.[6,7]) The line shapes are similar for the different compositions, having the peak position at $E_B \sim 4$ eV. Namely, we find no rigid band behavior in the Fermi-level shift as unoccupied states are filled by doped electrons.

In Fig. 2, spectra taken at photon energies in the Cu $3p \rightarrow 3d$ core absorption region are shown for the unreduced $x = 0.15$ sample. The constant initial state (CIS) spectrum for the satellite peak at $E_B = 13.3$ eV shows a clear resonance at $hv \sim 74$ eV. As the same resonance is known to occur at $hv \sim 74$ eV for the satellite of CuO at $E_B = 12.9$ eV,[11] the present satellite is assigned to a $3d^8$ final state of Cu^{2+}. Its resonance enhancement is attributed to an interference between the direct d-electron photoemission from Cu^{2+} and the $3p \rightarrow 3d$ absorption followed by a super Coster-Kronig decay,

$$3p^6 3d^9 + hv \rightarrow 3p^5 3d^{10} \rightarrow 3p^6 3d^8 + \epsilon l .$$
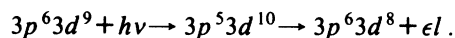
(The weak shoulder at $hv \sim 76$ eV is a Cu $3p$ spin-orbit partner of the 74-eV peak.) As for Cu_2O, a satellite is located at $E_B = 15.3$ eV and is enhanced at a higher photon energy, $hv \sim 76.5$ eV.[11] A CIS spectrum was measured for $E_B = 15.7$ eV, but we found no clear structure around $hv = 76.5$ eV for every sample, as in Fig. 2. Unfortunately, it is difficult to conclude about the existence of Cu^+ from these results due to the weakness of the Cu^+ resonance (twice as weak as that of Cu^{2+})[11] and the small maximum Cu^+ concentration ($< 20\%$).

The main valence-band peak at $E_B \sim 4$ eV is the O $2p$ band or the $d^9\underline{L}$ final states, where $\underline{L}$ denotes a ligand hole. The difference spectrum ($hv = 74-71$ eV) shown in Fig. 2 is negative around $E_B = 4$ eV because the photoionization cross section of the O $2p$ states dominating in this region increases with decreasing photon energy. The CIS spectrum near the top of the valence band, $E_B = 1.6$ eV, shows only a very weak, broad antiresonance dip around
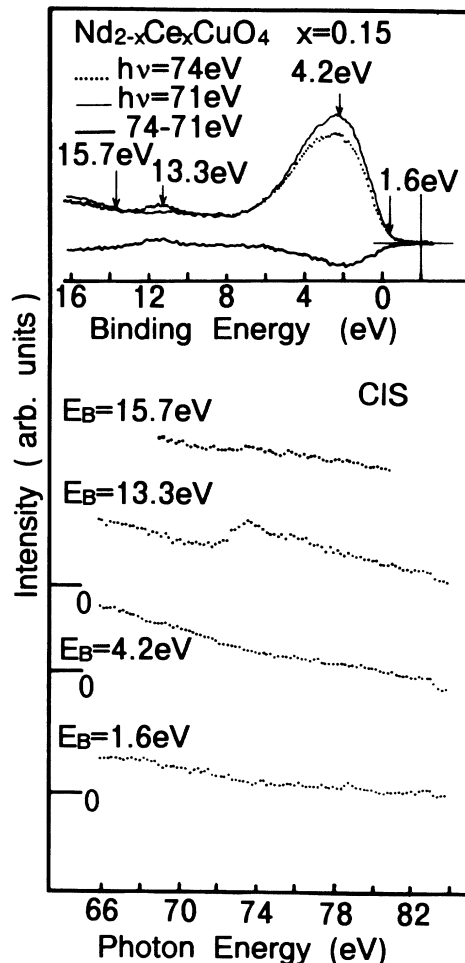

FIG. 2. Top: EDC's of $Nd_{2-x}Ce_xCuO_4$ ($x = 0.15$) taken in the Cu $3p \rightarrow 3d$ absorption region. Bottom: CIS spectra for the binding energies indicated by the arrows in the top panel. The CIS spectra have been so scaled as to give approximately the same magnitudes. Zero for each CIS spectrum is shown.

$h = 74$ eV. A similar behavior has been reported for states near the Fermi level of $Bi_2Sr_2CaCu_2O_8$,[12] which are assigned to A_1-symmetry singlet $d^9\underline{L}$ states ($^1A_1$) in the CuO_2 planes.[13,14] So we may tentatively assign the top of the valence band of $Nd_{2-x}Ce_xCuO_4$ to $^1A_1$ states.

Photoemission spectra originating from the rare-earth $4f$ states can be obtained from the difference between spectra taken with photon energies at and off the rare-earth $4d \rightarrow 4f$ core absorption peaks utilizing the interference between the direct $4f$-electron photoemission and the $4d \rightarrow 4f$ transition followed by a super Coster-Kronig decay,

$$4d^{10} 4f^n + hv \rightarrow 4d^9 4f^{n+1} \rightarrow 4d^{10} 4f^{n-1} + \epsilon l .$$
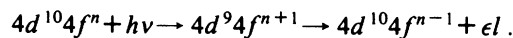
When taking the difference spectra, the hv dependence of the O $2p$ band intensity has been taken into account according to Ref. 15 by using a CIS spectrum of $La_{2-x}Sr_xCuO_4$. (Detailed results on single-crystalline $La_{2-x}Sr_xCuO_4$ measured at liquid-nitrogen temperature will be reported elsewhere.[16]) Figure 3(b) shows Nd $4f$ on- and off-resonance spectra and their difference spec-
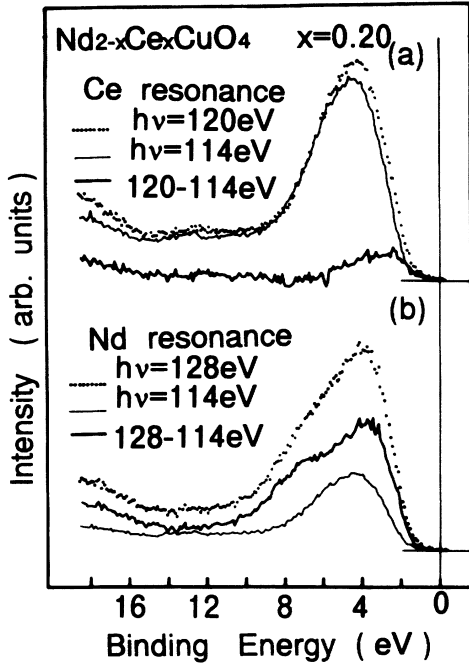
FIG. 3. EDC's of $Nd_{2-x}Ce_xCuO_4$ ($x = 0.20$) taken in (a) the Ce $4d \rightarrow 4f$ absorption region and (b) in the Nd $4d \rightarrow 4f$ absorption region.

FIG. 4. Top: Comparison of EDC's for $Nd_{2-x}Ce_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ which have been shifted so as to align the tops of the valence bands. Bottom: Schematic representation of the electronic structure near the Fermi levels in the two compounds.

trum ($hv = 128-114$ eV). The difference spectrum, which represents the Nd $4f$-derived photoemission, has a double-peak structure in agreement with the previous result.[6] The double-peak structure is characteristic of a localized $4f^3$ ground state.[15] The higher-binding energy peak is due predominantly to final states in which the $4f$ hole is screened by charge transfer from the ligand O $2p$ orbitals ($4f^3\underline{L}$ final states) and the lower-binding energy component to the bare $4f$ hole ($4f^2$ final states).[15] Figure 3(a) shows Ce $4f$ on- and off-resonance spectra and their difference ($hv = 121-114$ eV) which represents the Ce$4f$-derived photoemission and is found to increase with x. Although the formal valence of Ce is 4+ ($4f^0$), analyses of Ce core levels have revealed that approximately 0.5 of $4f$ electrons exist in the ground state as a result of hybridization with O $2p$ states.[4-6,17] These hybridized $4f$ states are distributed predominantly near the top of the O $2p$ band, as would be expected from the band-structure calculation of CeO_2 (Ref. 18), according to which nonbonding O $2p$ states (as opposed to the rare-earth $5d$-O$2p$ bonding states) are distributed near the top of the O $2p$ band and have a tendency to hybridize with the $4f$ states because of symmetry.

In Fig. 4, an EDC of $Nd_{2-x}Ce_xCuO_4$ is so drawn that its valence-band top coincides with that of $La_{2-x}Sr_x$-CuO_4.[16] The valence-band emission is wider for Nd_{2-x}-Ce_xCuO_4 due to the contributions form the Nd $4f$ emission on the high-binding energy side of the O $2p$ band (see Fig. 3). In addition to this, the O$2p$-band line shapes may be different between the two compounds because of the different environments of the oxygen atoms in the LaO and NdO planes. However, at least it is obvious from Fig. 4 that the Fermi energy position with respect to
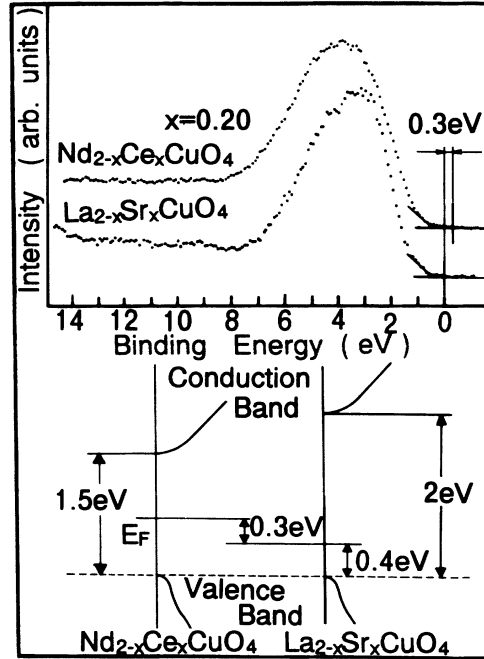
the valence-band top is shifted upward by 0.3 ± 0.1 eV in going from $La_{2-x}Sr_xCuO_4$ to $Nd_{2-x}Ce_xCuO_4$. Although the exact position of the valence-band top is difficult to define from the EDC's themselves (one may be able to put an upper limit of 0.8 eV on the separation between the valence-band top and the Fermi level), the 0.3-eV shift indicates that the Fermi level of $Nd_{2-x}Ce_xCuO_4$ is located at least 0.3 eV above the top of the valence band of host Nd_2CuO_4. On the other hand, Nd_2CuO_4 is known to have a 1.5-eV band gap between the valence band ($d^9\underline{L}$) and the conduction band (probably d^{10}).[19] Thus we can safely conclude that the Fermi level of $Nd_{2-x}Ce_xCuO_4$ is located not at the bottom of the conduction band but within the host band gap. Although the Fermi edge is not clear in the present spectra, it has recently been reported that clear Fermi edges can be observed with high photon energy ($hv \sim 1500$ eV) for doped $Nd_{2-x}Ce_xCuO_4$ but not with ultraviolet photons.[20] As illustrated in Fig. 4, optical absorption studies on doped $La_{2-x}Sr_xCuO_4$ have suggested that new states are formed ~ 0.4 eV above the top of the valence band, in which states the Fermi level is located,[21] whereas La_2CuO_4 has a band gap of 2 eV.[19] If we combine the value of ~ 0.4 eV with the 0.3-eV Fermi-level shift, we can estimate the Fermi-level position in $Nd_{2-x}Ce_xCuO_4$ to be 0.7 eV above the valence-band top.

The origin of the gap states which pin the Fermi level is not clear at this moment. One possibility is that these states are due to electron correlation effects induced by carrier doping in the charge-transfer insulators.[22] Another possibility is that they are impurity levels formed within the band gap due to the electrostatic potentials of the sub-

stitutional Ce or Sr ions as in doped semiconductors.[23] Doped carriers will occupy the impurity levels and pin the Fermi level. Such carriers are necessarily localized around the impurities at least for low doping levels, but at higher doping levels they might be ionized and could supply their electrons or holes to the d^{10} conduction band or to the $d^9\underline{L}$ valence band.[23]

In summary, we have measured photoemission spectra of $Nd_{2-x}Ce_xCuO_4$ using synchrotron radiation. A clear resonance is observed for the Cu^{2+} satellite. From the difference spectrum between the on- and off-resonance spectra in the rare-earth $4d \rightarrow 4f$ core absorption region, the Nd and Ce $4f$-derived photoemission spectra have been obtained. The Nd $4f$ spectrum shows a double-peak structure characteristic of the localized $4f^3$ ground state and strong $4f$-ligand hybridization in the final state. The Ce $4f$ states are states distributed predominantly near the top of the valence band. From comparison between the EDC's of $Nd_{2-x}Ce_xCuO_4$ and $La_{2-x}Sr_xCuO_4$, the Fermi level is found to be shifted by only 0.3 ± 0.1 between the two compounds, even though the band gaps of Nd_2CuO_4 and La_2CuO_4 are as large as 1.5-2 eV. From this observation, we conclude that the Fermi level of $Nd_{2-x}Ce_xCuO_4$ as well as that of $La_{2-x}Sr_xCuO_4$ lies within the band gap between valence and conduction bands.

ACKNOWLEDGMENTS

*Present address: Department of Materials Physics, Osaka University, Toyonaka 560, Japan.

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