PHYSICAL REVIEW B VOLUME 41, NUMBER 1 1 JANUARY 1990

Cu K-edge x-ray-absorption near-edge structure and electronic structure of $Nd_{2-x}Ce_xCuO_{4-y}$ and $La_{2-x}Sr_xCuO_4$

Nobuhiro Kosugi
Division of Molecular Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Yoshinori Tokura
Department of Physics, The University of Tokyo, Hongo, Tokyo 113, Japan

Hidenori Takagi and Shinichi Uchida
Engineering Research Institute, The University of Tokyo, Hongo, Tokyo 113, Japan

(Received 19 June 1989)

Detailed analyses of Cu K-edge x-ray-absorption near-edge structure (XANES) of electron-doped and hole-doped Cu-based oxides with several Ce/Sr substitution rates, $Nd_{2-x}Ce_xCuO_{4-y}$ and $La_{2-x}Sr_xCuO_4$ have revealed that each Ce/Sr substitution has an effect on ~4–5 Cu sites and that an additional electron or hole supplied with the substitution is distributed mainly to ~4–5 [CuO_2] units, yielding "impurity (localized) states." When $x=0.15$ the "impurity states" amount to ~60–75 % of the whole [CuO_2] units; the interaction and superposition among the localized states are caused to produce bands like Fermi-liquid states. The substitution causes substantial and a little change in the XANES spectra of Nd-Ce-Cu-O and La-Sr-Cu-O, respectively. This means that the electron doping takes place mainly at the Cu site of [CuO_2] in Nd-Ce-Cu-O and that the hole doping in La-Sr-Cu-O takes place mainly at the oxygen site. In the "unreduced" Nd-Ce-Cu-O samples no monovalent species but rather divalent species with relatively large $3d^{10}$ contributions are found. In the "reduced" and superconducting Nd-Ce-Cu-O sample ($x=0.15$), Cu_2O-like monovalent species are found but probably correspond to segregated impurity phases. The essential effect of the reduction to induce the superconductivity in Nd-Ce-Cu-O ($x \sim 0.15$) has not yet been revealed.

I. INTRODUCTION

Recent studies on high-T_c superconducting Cu-based oxides show that the two-dimensional (2D) sheet structure of [CuO_4] squares is indispensable to superconductivity, irrespective of the types of doped carriers, electrons or holes. In 25-K-class electron-doped superconducting Cu-based oxides, i.e., so-called T'-phase compounds such as $Nd_{2-x}Ce_xCuO_{4-y}$ (Nd-Ce-Cu-O, $x \sim 0.15$), electron doping to the 2D [CuO_4] sheet is achieved with Ce^{4+} substitution for Nd^{3+} in Nd_2CuO_4 and subsequent reduction, and in 40-K-class hole-doped superconducting Cu-based oxides, i.e., so-called T-phase compounds such as $La_{2-x}Sr_xCuO_4$ (La-Sr-Cu-O, $x=0.12$–0.22), hole doping to the 2D [CuO_4] sheet is achieved with Sr^{2+} substitution for La^{3+} in La_2CuO_4. On the other hand, in 90-K-class superconducting Cu-based oxides, i.e., so-called 1-2-3 compounds such as $YBa_2Cu_3O_y$ (Y-Ba-Cu-O, $y \sim 7$), the oxygen content y is the key element of hole doping; that is, the hole doping into the 2D [CuO_4] sheet [Cu(2) site] is achieved with hole donation of the electron-deficient 1D CuO chain [Cu(1) site] in Y-Ba-Cu-O ($y \sim 7$). The electron doping which destroys the superconductivity in the 2D [CuO_4] sheet is achieved with electron donation of the electron-rich linear $[CuO_2]^{3-}$ ion [Cu(1) site] in Y-Ba-Cu-O ($y \sim 6$).

The electron or hole-pairing mechanisms in Cu-based oxide superconductors have not yet been settled. Within the rigid-band and single-band models the Sr or Ce substitution, oxygen doping, or reduction introduces holes or electrons into the 2D [CuO_4] sheets in the parent compounds, Nd_2CuO_4, La_2CuO_4, and $YBa_2Cu_3O_y$, and they are distributed in a single band so that each Cu/O atom sees an average change in charge. The correlated models result in mixed-valent Cu/O ions, Cu^+ and Cu^{2+}, O^{2-} and O^-, or $[CuO_2]^{3-}$, $[CuO_2]^{2-}$, and $[CuO_2]^-$. The Ce substitution and the subsequent reduction in Nd-Ce-Cu-O ($x \sim 0.15$) are *both* necessary to induce superconductivity, though either the substitution or the reduction can introduce conductive electrons in Nd_2CuO_4. This indicates breakdown of the rigid-band and single-band models in which both the substitution and the reduction should induce the same change in electronic (band) structure. In the present work, we have studied how the substitution and reduction induce changes in the electronic and geometrical structures in Nd-Ce-Cu-O and La-Sr-Cu-O by means of x-ray absorption near-edge spectroscopy (XANES) at the Cu K edge.

II. EXPERIMENT

The samples used in the present study are the same as in the previous work.[1,2] The substitution rates are as follows: $x=0.0$, 0.05, 0.08, 0.12, 0.15, and 0.20 for $Nd_{2-x}Ce_xCuO_4$ and $x=0.0$, 0.055, 0.10, and 0.15 for

$La_{2-x}Sr_xCuO_4$. To cause electron superconductivity in $Nd_{2-x}Ce_xCuO_4$ ($x=0.15$) the sample prepared in air ("unreduced") was annealed in the reducing atmosphere.[1,2] Let us denote it as $Nd_{2-x}Ce_xCuO_{4-y}$ ($x=0.15$, $y\neq 0$). For comparison, the unreduced sample $Nd_{2-x}Ce_xCuO_4$ ($x=0.12$) was also annealed in the same condition.

Cu K-edge XANES spectra were measured at the beam line 10B of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF).[3] Synchrotron radiation from the electron-positron storage ring (2.5 GeV, average current 200–250 mA) was monochromated with a channel-cut Si(311) crystal monochromator and its nominal resolution was smaller than 1 eV at the Cu K edge. Powder samples were pressed into a pellet with dry BN.

III. RESULTS AND DISCUSSION

A. La_2CuO_4 and Nd_2CuO_4

Figure 1 shows Cu K-edge XANES spectra of the parent (unsubstituted) compounds, together with those of the substituted $x=0.15$ compounds *(vide infra)*. The present "parent" spectra are better in energy resolution than the previous ones.[4] The preedge structure *A* is assigned to the 1*s*-3*d* transition. Because of the planar symmetry of $[CuO_4]$ squares in La_2CuO_4 and Nd_2CuO_4, the intensities originate mainly in electric quadrupole transitions and are correlated with the 3*d* hole densities in the ground states; the 1*s*-3*d* peak intensity for La_2CuO_4 is a little stronger than that for Nd_2CuO_4 and it means that the 3*d* hole density in La_2CuO_4 is larger than that in Nd_2CuO_4. As previously discussed by the present author N. Kosugi and co-workers,[5] the structures *D* and *E* are assigned to 1*s*-4*pσ* transitions to well-screened [through ligand-to-metal charge-transfer (LMCT)] and poorly screened core-hole states and the structures *B* and *C* half-way up the absorption maximum *D* are assigned to 1*s*-4*pπ* transitions to well-screened and poorly screened core-hole states.

The splitting of the shoulder (1*s*-4*pπ*) structure and of the main (1*s*-4*pσ*) structure are characteristic of divalent Cu compounds with the planar coordination around Cu.[5-8] These assignments can be supported by examination of the polarization dependence of XANES and by comparing divalent and monovalent compounds.[9] In Fig. 2, XANES spectra of (c) divalent and (d) monovalent Cu oxides, Sr_2CuO_3 with planar $[CuO_4]$ (no apical coordination) structure and Cu_2O with linear $[CuO_2]$ structure, are compared together with (a) out-of-plane and (b) in-

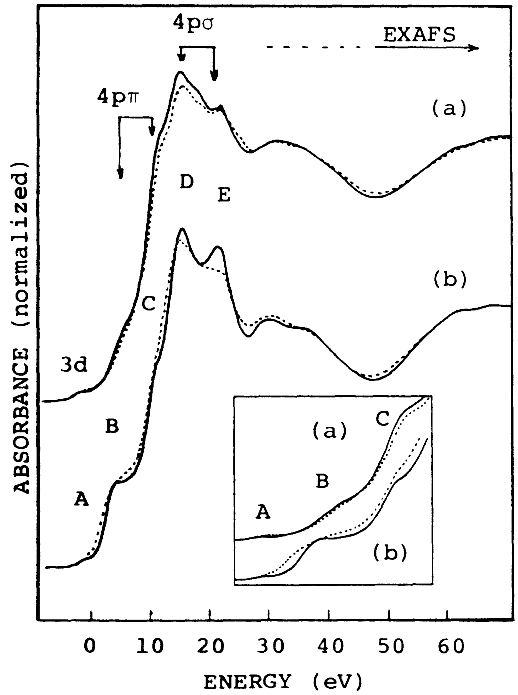

FIG. 1. Cu K-edge XANES spectra of (a) La_2CuO_4 (solid line) and $La_{1.85}Sr_{0.15}CuO_4$ (dashed line), (b) Nd_2CuO_4 (solid line) and $Nd_{1.85}Ce_{0.15}CuO_4$ (dashed line). The 1*s*-3*d* and 4*pπ* regions are insetted on a magnified scale. The excitation energy is relative to the first inflection point at the K edge of Cu foil.

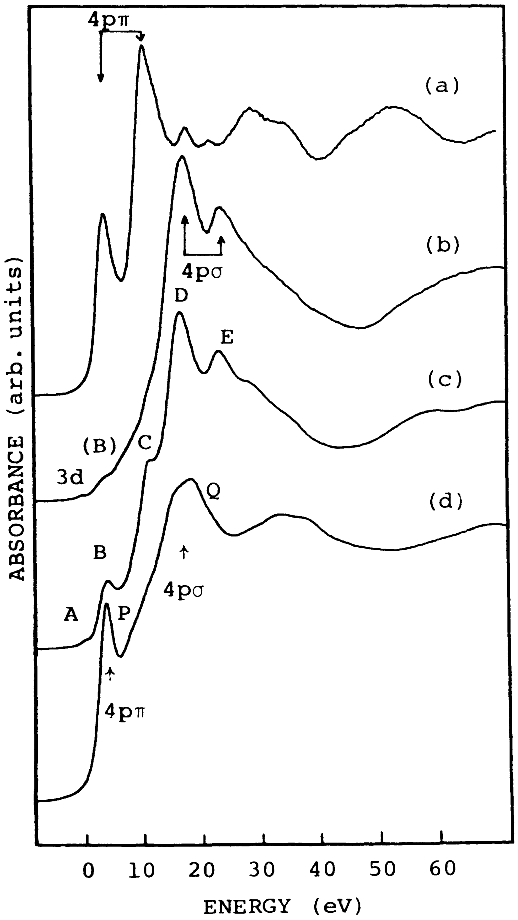

FIG. 2. Polarized Cu K-edge XANES spectra (Ref. 9) of a single crystal of the divalent Cu-based oxide, Sr_2CuO_3: (a) out-of-plane (**E**‖**b**), (b) in-plane (**E**‖**a**), and powder XANES spectra of (c) Sr_2CuO_3, and (d) Cu_2O.

plane polarized XANES spectra of Sr_2CuO_3. We can easily understand that B and C, and D and E are $1s$-π and $1s$-σ transitions, respectively, and that such a splitting (6–7 eV) is not observed in monovalent Cu_2O. It should be noted that the twin-peak structure in divalent Cu compounds is similarly observed in out-of-plane polarized XANES spectra of (creatinium)$_2CuCl_4$ with planar [$CuCl_4$] structure,[6] where the lower $1s$-$4p\sigma$ peak (D, well screened) is shifted down to the higher $1s$-$4p\pi$ peak position (C, poorly screened) due to the weak crystal field of Cl^- ions, and therefore in the powder spectrum of (creat)$_2CuCl_4$, we accidentally find only a single-shoulder structure B, widely assigned to $1s$-$4p\pi$+LMCT core-hole screening ("shakedown" in ionic compounds[6,8,10]).

In Fig. 1, the $1s$-$4p\pi$ transitions are clearly observed in La_2CuO_4 as well as Sr_2CuO_3 and Nd_2CuO_4, though Cu in La_2CuO_4 is coordinated with two apical oxygen atoms below and above the [CuO_4] plane and Cu in Sr_2CuO_3 and Nd_2CuO_4 has no apical oxygen. The reason why the $1s$-$4p\pi$ transitions are not suppressed in La_2CuO_4 is that [CuO_6] octahedron in La_2CuO_4 is elongated in the apical direction: R (in-plane Cu-O) = 1.90–1.91 Å and R (apical Cu-O) = 2.43–2.46 Å. Furthermore, as inset in Fig. 1 on a magnified scale, in (a) La_2CuO_4 and (b) Nd_2CuO_4 the well-screened peaks B are weaker and stronger than the poorly screened peaks C, respectively. It is well known that in Cu $2p$ x-ray photoemission spectroscopy (XPS) of divalent Cu compounds the main peak corresponds to the $\sim 3d^{10}$ (L^{-1}, well screened through LMCT) final state and the satellite band corresponds to the $\sim 3d^9$ (poorly screened) final states,[11,12] and it is seemingly applicable to the Cu K-edge XANES. The screening effect upon core-hole creation is as dominant in divalent Cu compounds in photoabsorption as in photoemission,[5,8,9] though the screening mechanism in core-excited states where an excited electron takes part more or less in core-hole screening is not identical with that in core-ionized states. Therefore, the peak intensity ratio between B and C can be approximately related to the electronic state of the ground state; that is, "divalent" Cu atoms of [CuO_4] in La_2CuO_4 and in Nd_2CuO_4 have large d^9 and $d^{10}(L^{-1})$ components, respectively, in the ground states. This is supported by the observation that the $1s$-$3d$ peak intensity for La_2CuO_4 is stronger than that for Nd_2CuO_4 as above mentioned. These conclusions are consistent with those deduced from the satellite-to-main peak intensity ratios (I_s/I_m) in Cu $2p$ XPS [$I_s/I_m = \sim 0.25$ in Nd-Ce-Cu-O (Ref. 13) and ~ 0.33 in La-Sr-Cu-O (Ref. 14)] and with those deduced from a simple crystal-field consideration: in Nd_2CuO_4 the Cu site with no apical oxygen anions is sharing an electron with the in-plane oxygen ions in [CuO_4] through covalency in the ground state, and the two apical oxygen anions at the Cu site in La_2CuO_4 is repelling electrons on Cu electrostatically and increases ionicity of the Cu—O bond in [CuO_4].

B. $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ (unreduced)

Figure 1 shows Cu K-edge XANES spectra of the substituted compounds ($x = 0.15$) with dashed lines, which are normalized relative to those of the parent compounds ($x = 0$) shown with solid lines. The change of the spectra from $x = 0$ to 0.15 in Nd-Ce-Cu-O is much larger than that in La-Sr-Cu-O. This means that the substitution affects local electronic and geometrical structures around Cu drastically in Nd_2CuO_4 but not so much in La_2CuO_4. This is consistent with the widely accepted thoughts that the electron and hole doping occur mainly at Cu of [CuO_2] in Nd-Ce-Cu-O and at O in La-Sr-Cu-O, respectively.

Figures 3 and 4 show Cu K-edge XANES spectra of unreduced $Nd_{2-x}Ce_xCuO_4$ ($x = 0, 0.05, 0.08, 0.12, 0.15, 0.20$) and $La_{2-x}Sr_xCuO_4$ ($x = 0, 0.055, 0.10, 0.15$), respectively. Furthermore, we have obtained difference spectra to investigate the substitution dependence of the XANES: [$Nd_{2-x}Ce_xCuO_4$ ($x \neq 0$)] − [Nd_2CuO_4] and [$La_{2-x}Sr_xCuO_4$ ($x \neq 0$)] − [La_2CuO_4]. The difference spectra for Nd-Ce-Cu-O shown in Fig. 3 agree with the previously reported ones by Tranquada *et al.*[4] The change in the spectra for La-Sr-Cu-O is small and noisy, but for Nd-Ce-Cu-O the change is appreciable and indi-

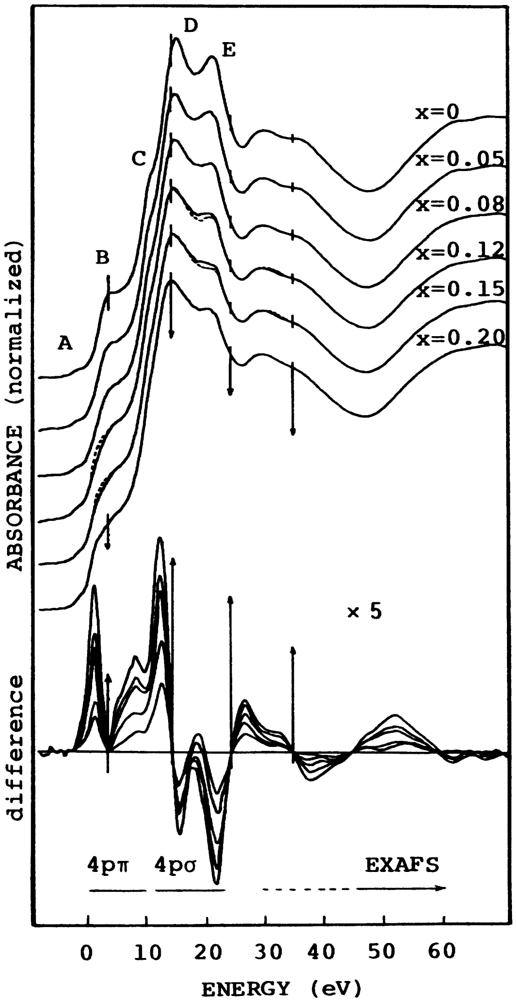

FIG. 3. Cu K-edge XANES spectra of $Nd_{2-x}Ce_xCuO_4$ and difference spectra: [$x \neq 0$(unreduced)] − [$x = 0$(parent)]. Some isosbetic points are indicated by arrows. Dashed lines correspond to the spectra of reduced samples ($x = 0.12, 0.15$).

increase of the 1*s*-4*p*π region and the decrease and/or shift of the 1*s*-4*p*σ region with the substitution. It should be noticed that peaks in the difference spectra do not always correspond to real peaks in the absorption spectra.

We have found isosbetic points in the difference spectra. Some of them are shown by arrows in Figs. 3 and 4. The existence of the isosbetic points indicates that the spectra for the substituted systems consist of two components, parent and additional ones, and the former decreases and the latter increases with the substitution. Furthermore, the uniformity of the substituted samples indicates that the additional components introduced with the substitution are not segregated impurity phases but uniformly or randomly distributed "impurity states." Instead of discussing the difference spectra, we have tried to extract XANES spectra for the impurity state from the spectra of the parent (unsubstituted) and substituted compounds. The extracted XANES spectra for the additional components (impurity state) can be obtained as follows:

$$([Nd_{2-x}Ce_xCuO_4]-b[Nd_2CuO_4])/a \ ,$$

$$([La_{2-x}Sr_xCuO_4]-b[La_2CuO_4])/a, \quad (a=1-b) \ .$$

However, we cannot know the value of a in advance. Let us suppose a is proportional to $x, a=kx$, where the coefficient k is an unknown parameter but becomes a very significant one; for example, if $k=0.5$, an extra electron (hole) yielded with the Ce(Sr) substitution for Nd(La) would fill only a single Cu atom, irrespective of the substitution rate x.

The upper part of Fig. 5 shows the dependence of the extracted XANES spectra for the additional components on k for Nd-Ce-Cu-O ($x=0.12$). When $k=2$-2.5 the extracted spectra give reasonable features compared with known spectra for several Cu-based oxides,[5] though there remains some arbitrariness. The lower part of Fig. 5 shows the extracted XANES spectra for the additional components in the other Nd-Ce-Cu-O ($x=0.05, 0.08, 0.15$) when $k=2$. They seem to be almost independent of x considering that large errors are included for small x. This means that each Ce^{4+} ion substituting Nd^{3+} changes 4–5 [CuO_2] units and that an additional electron supplied with the substitution is distributed mainly to 4–5 [CuO_2] units (there might be a little contribution from the oxygen atoms covalently bonded with Cu in the 2D [CuO_4] plane with no apical coordination). The local change in electronic structure could be related to a local geometrical change at least within a [CuO_4] cluster. Such

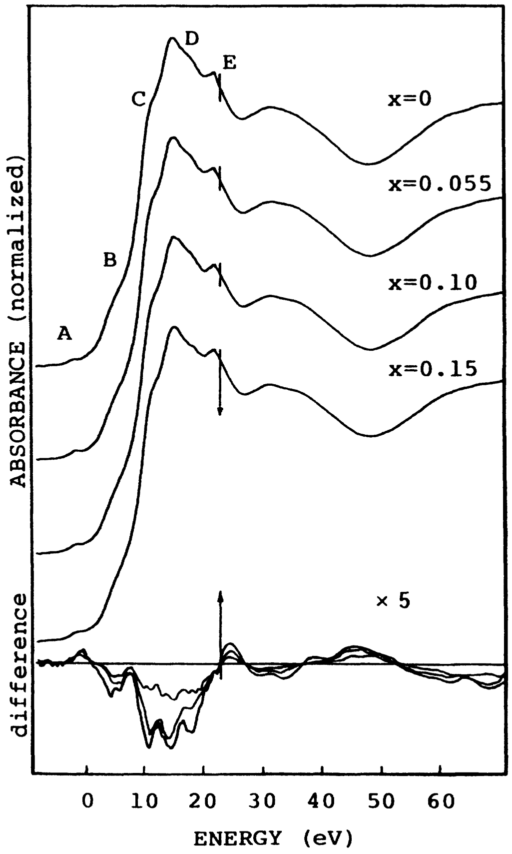

FIG. 4. Cu K-edge XANES spectra of $La_{2-x}Sr_xCuO_4$ and difference spectra: [$x\neq0$(substituted)]$-$[$x=0$(parent)].

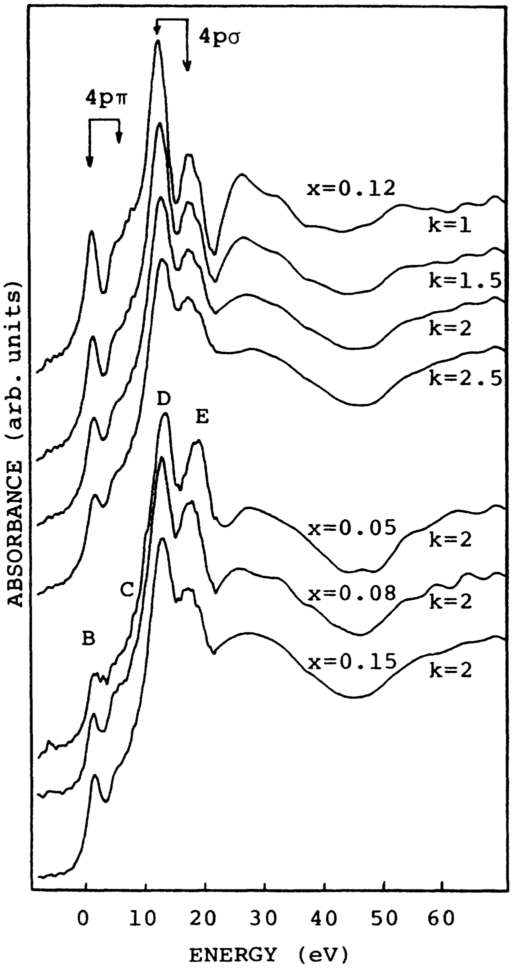

FIG. 5. Extracted XANES spectra for additional components (impurity state) introduced with the substitution from the spectra of the parent (unsubstituted) and Ce-substituted Nd_2CuO_4: ($[Nd_{2-x}Ce_xCuO_4]-b[Nd_2CuO_4]$)/$a$ ($a=1-b=kx$).

a local structural change is consistent with considerable difference between the parent and extracted XANES spectra, but is not inconsistent with the result of x-ray crystallography which shows that the *c* axis shrinks with the increase in substitution (12.15 Å for $x=0$, 12.05 Å for $x=0.20$), because x-ray crystallography sees an average structure and inner-shell absorption spectroscopy, EXAFS (extended x-ray absorption fine structure) and XANES sees local electronic and geometrical structures within a time scale of $\sim 10^{-16}$ sec; for example, in solid solution, the former supports the virtual-crystal approximation, often called Vegard's rule, but the latter does not.[15]

It is noticed, in the extracted XANES spectra for the impurity state introduced with the substitution in Nd-Ce-Cu-O as shown in Fig. 5, that the well-screened peaks *B* and *D* are considerably strong but the poorly screened peaks *C* and *E* are remaining. The twin-peak structure both in the $1s$-$4p\pi$ region (*B* and *C*) and in the $4p\sigma$ region (*D* and *E*) is found, irrespective of the value of *k*. Therefore, Cu atoms in the impurity state have more $3d^{10}$ contribution than in the parent compound but are still divalent. The present conclusion disagrees with that by Tranquada *et al.*[4] who discussed the difference spectra and concluded that the extra electrons introduced with substitution fill $3d$ holes on the Cu atoms and convert some divalent Cu^{2+} ions to Cu^{+}. They found that the peak position of *B* in Fig. 5, which corresponds to the lowest peak in the difference spectra shown in Fig. 3, is nearly the same as that of a $1s$-$4p\pi$ peak typically observed in monovalent Cu_2O with linear $[CuO_2]$ coordination, but ignored the $1s$-$4p\pi$ transitions to the poorly screened ($\sim 3d^9$) core-hole states (*C*), and they assigned the $1s$-$4p\sigma$ transitions to the well-screened ($\sim 3d^{10}$) core-hole states (*D*) as the transitions to the poorly screened ($\sim 3d^9$) ones. The present result does not exclude the contribution of Cu $4s$,[13] but the observation is inconsistent with that of Cu $2p$ XPS by Fujimori *et al.*[13] who reported that the satellite-to-main peak intensity ratio remains unchanged with the Ce substitution. This discordance probably arises from the spectroscopic difference in sensitivity to electronic and structural changes; for example, as insetted in Fig. 1 on a magnified scale, the intensity ratios between peaks *B* (well screened $4p\pi$) with *C* (poorly screened $4p\pi$) in Cu K-edge XANES of Nd_2CuO_4 and La_2CuO_4 are more sensitive to the electronic and structural changes than the intensity ratios between satellite and main peaks in Cu $2p$ XPS.[13,14]

Figure 6 shows extracted XANES spectra for the additional components (impurity state) with the substitution in La-Sr-Cu-O, similarly to the extracted spectra in Nd-Ce-Cu-O shown in Fig. 5. The extracted spectra in La-Sr-Cu-O are also reasonable when $k=2$–2.5. The shoulder structures which correspond to the $1s$-$4p\pi$ transitions are obscure behind the noise level but it is clearly observed that the $1s$-$4p\sigma$ transition to the well-screened state *D* is a little weakened compared with that for the parent compound. This means that Cu atoms in the impurity state have more $3d^9$ contribution than in the parent compound and that the substitution of Sr for La causes the hole doping mainly in oxygen atoms but also a little in Cu atoms. It is, however, impossible to elucidate the Cu $3d$ hole state quantitatively from the well-screened–to–poorly-screened peak intensity ratio of the $1s$-$4p\sigma$ transitions which are not only overlapping the continuum transitions but also interacting with the continuum through the interchannel coupling. This effect explains why the relative intensities of the well-screened and poorly screened peaks are different between $1s$-$4p\pi$ and $1s$-$4p\sigma$.

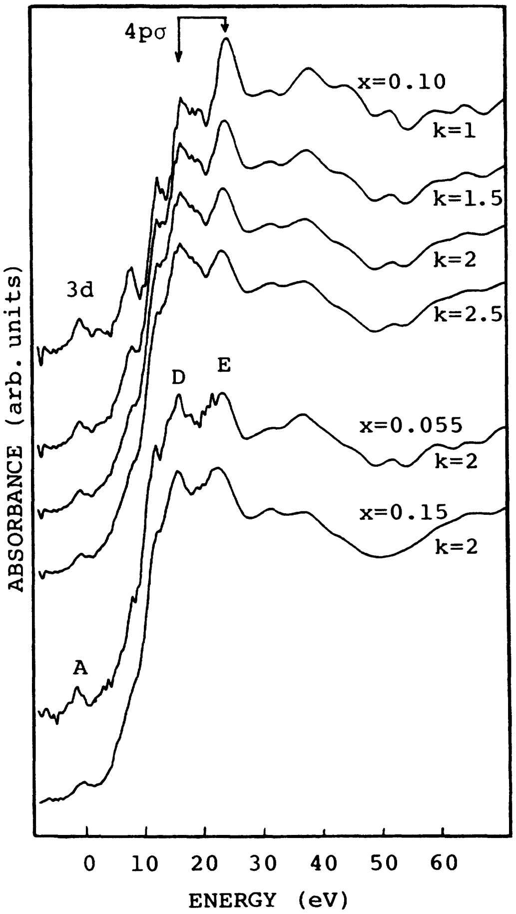

FIG. 6. Extracted XANES spectra for additional components (impurity state) introduced with the substitution from the spectra of the parent (unsubstituted) and Sr-substituted La_2CuO_4: $([La_{2-x}Sr_xCuO_4]-b[La_2CuO_4])/a$ ($a=1-b=kx$).

The $1s$-$3d$ peak *A* seems to be weakened and strengthened in the extracted XANES spectra for the additional components in Fig. 5 (Nd-Ce-Cu-O) and in Fig. 6 (La-Sr-Cu-O), respectively, relative to the parent spectra shown in Fig. 1. The observation is consistent with the above conclusion. However, we could not observe the systematic dependence in $1s$-$3d$ peak intensity on the substitution rate (x). The noise level in $1s$-$3d$ bands may be strengthened in the extracted spectra for the additional components.

C. $Nd_{2-x}Ce_xCuO_{4-y}$ (reduced)

As shown by dashed and solid lines in Fig. 3, the spectra for the reduced Nd-Ce-Cu-O samples ($x=0.12, 0.15$)

are not identical with those for the unreduced ones, whereas Tranquada *et al.*[4] reported that the spectra of the oxidized and reduced samples for $x=0.15$ were identical. This discordance probably arises from the difference in energy resolution. Similarly to the above procedure, we have tried to extract XANES spectra for reduced components. The extracted XANES spectra for the reduced components can be obtained as follows:

$$\{[\mathrm{Nd}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_{4-y}(\text{reduced})]-$$
$$b[\mathrm{Nd}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_4(\text{unreduced})]\}/a\ ,$$

where $a=1-b$. As shown in Fig. 7, the extracted XANES spectra for the reduced components show a single $1s$-$4p\pi$ (P) and a single $1s$-$4p\sigma$ (Q) transitions, irrespective of the values of a. This indicates that the reduction yields monovalent species unlike the Ce substitution. Examination on various values of a has revealed that the reduced components correspond mainly to $\mathrm{Cu_2O}$-like species as shown in Fig. 7.

In Fig. 7 the extracted spectra are best fitted to the spectrum of pure $\mathrm{Cu_2O}$. The resultant values of a are 0.07–0.08. This means that $y=0.24$–0.28 (for example, $[\mathrm{CuO}_{3.72}]=0.92[\mathrm{CuO_4}]+0.04[\mathrm{Cu_2O}]$). The values of y obtained with the XANES analysis is much larger than that obtained with the iodometric titration technique,[2] which has revealed that the oxygen content decreases from $y=0\sim0.01$ to $y\sim0.04$ after the reduction when $x\sim0.15$. Most of the oxygen deficiencies correspond to a tiny $\mathrm{Cu_2O}$ impurity phase (1–2 %) found with powder x-ray diffraction;[2] that is, $0.99[\mathrm{CuO_4}]+0.005[\mathrm{Cu_2O}]=[\mathrm{CuO}_{3.965}]$. This is consistent; there is no remarkable difference found in the lattice parameters between the samples before and after the reduction.[2] The discordance of the values of y obtained with the XANES analysis and with the iodometric titration and powder x-ray diffraction techniques probably arises from the difference in sensitivity to impurity phases and from the experimental and analytical errors.

On the other hand, Cu $2p$ XPS spectra for unreduced and reduced samples ($x=0.15$) show that the satellite-to-main peak intensity ratios I_s/I_m are 0.25 and 0.21, respectively,[13] indicating that monovalent species are included up to 16% after the reduction and $y=0.56$ if they are all $\mathrm{Cu_2O}$ ($[\mathrm{CuO}_{3.44}]=0.84[\mathrm{CuO_4}]+0.08[\mathrm{Cu_2O}]$). Fujimori *et al.*[13] concluded that the small value of I_s/I_m in the reduced sample is likely due to extrinsic Cu^+ contamination since a prolonged reduction of the same sample in $\mathrm{CO_2}$ resulted in detectable monovalent impurity phases. The values of y obtained with XPS are much larger than those obtained with XANES, iodometric titration, and powder x-ray diffraction. This probably means that the monovalent species are impurity phases such as surface contamination and grain-boundary segregation since photoabsorption (transmission-mode) and photoelectron spectroscopies are bulk sensitive and surface sensitive, respectively, and there is extrinsic Cu^+ contamination mainly at the surface and grain boundary.

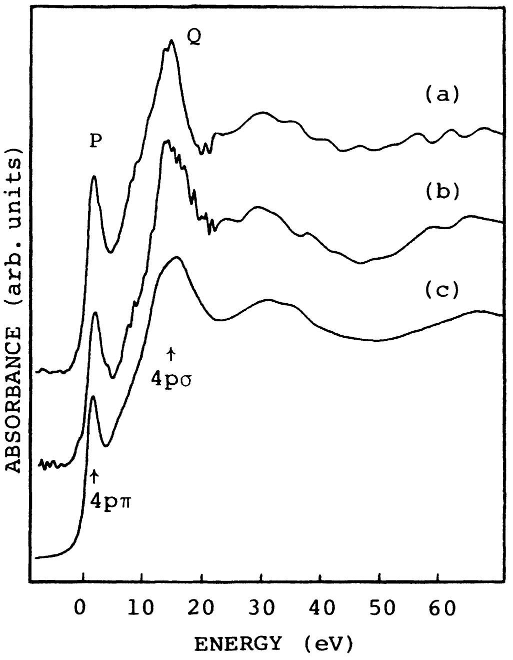

FIG. 7. Extracted XANES spectra for additional components (impurity state) introduced with the reduction from the spectra of the unreduced and reduced $\mathrm{Nd}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_4$: $([\mathrm{Nd}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_{4-y}(\text{reduced})]-b[\mathrm{Nd}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_4(\text{unreduced})])/a$ where $a=1-b$. (a) $x=0.12$, $a=0.08$; (b) $x=0.15$, $a=0.07$; (c) $\mathrm{Cu_2O}$.

IV. CONCLUSION

Cu K-edge XANES spectra have been measured for electron-doped and hole-doped Cu-based oxides with several Ce/Sr substitution rates, $\mathrm{Nd}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_{4-y}$ (Nd-Ce-Cu-O) and $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_4$ (La-Sr-Cu-O). We have tried to extract XANES spectra for the uniformly or randomly distributed impurity state introduced with the substitution from the spectra of the parent (unsubstituted) and substituted compounds:

$$\{[x\neq0\ (\text{substituted})]-b[x=0\ (\text{parent})]\}/a\ ,$$
$$(a=1-b=kx)\ .$$

This approach is rationalized by the existence of isosbetic points in the difference spectra between $[x\neq0]$ and $[x=0]$. When $k=2$–2.5, the extracted spectra are almost independent of x and give reasonable features compared with known spectra for several Cu-based oxides. This means that each $\mathrm{Ce}^{4+}/\mathrm{Sr}^{2+}$ ion substituting $\mathrm{Nd}^{3+}/\mathrm{La}^{3+}$ changes 4–5 Cu sites and that an additional electron or hole supplied with the substitution is distributed mainly to 4–5 $[\mathrm{CuO_2}]$ units, yielding impurity (localized) states. When $x=0.15$, the impurity states amount to 60–75 % of the whole $[\mathrm{CuO_2}]$ units; the interaction and superposition among the localized states are caused to produce bands such as Fermi-liquid states.[16]

In the extracted XANES spectra in Nd-Ce-Cu-O the well-screened peaks B and D are considerably strong but the poorly screened peaks C and E are remaining. This means that Cu atoms in the impurity state have more $3d^{10}$ contribution than in the parent compound but are still divalent. The present conclusion disagrees with that by Tranquada *et al.*[4] On the other hand, in La-Sr-Cu-O the change in XANES is much smaller than in Nd-Ce-Cu-O, but it is observed that the $1s$-$4p\sigma$ transition to the well-screened state D in the extracted spectra is a little weakened compared with that for the parent compound. This means that Cu atoms in the impurity state in La-Sr-Cu-O have a little more $3d^9$ contribution than in the parent compound and that the substitution of Sr for La causes the hole doping mainly in oxygen atoms but also a little in Cu atoms.

From the XANES spectra of the reduced and superconducting Nd-Ce-Cu-O sample ($x = 0.15$) and the unreduced and nonsuperconducting sample, we have successfully extracted an XANES spectrum of Cu_2O-like monovalent species. However, they probably correspond to segregated impurity phases. The essential effect of the reduction to induce the superconductivity in Nd-Ce-Cu-O has not yet been revealed.

ACKNOWLEDGMENTS

One of the authors (N.K.) acknowledges the Morino Foundation for Molecular Science for supporting part of the present work. The present work was performed under the approval of the Photon Factory Advisory Committee (Proposal Nos. 87-U002, 87-132, and 88-U004).

---

[1] Y. Tokura, H. Takagi, and S. Uchida, Nature **337**, 345 (1989).

[2] H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).

[3] H. Oyanagi, T. Matsushita, M. Ito, and H. Kuroda, KEK Repot, No. 30, Vol. 80, 1984.

[4] J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang, and M. Croft, Nature **337**, 720 (1989).

[5] N. Kosugi, H. Kondoh, H. Tajima, and H. Kuroda, Chem. Phys. **135**, 149 (1989).

[6] N. Kosugi, T. Yokoyama, K. Asakura, and H. Kuroda, Chem. Phys. **91**, 249 (1984); T. Yokoyama, N. Kosugi, and H. Kuroda, *ibid.* **103**, 101 (1986).

[7] T. A. Smith, J. E. Penner-Hahn, M. A. Berding, S. Doniach, and K. O. Hodgson, J. Am. Chem. Soc. **107**, 5945 (1985).

[8] N. Kosugi, in *Core-level Spectroscopy in Condensed Systems, Springer Series in Solid-State Sciences*, edited by J. Kanamori and A. Kotani (Springer, Berlin, 1988), Vol. 81.

[9] N. Kosugi, H. Kondoh, and H. Kuroda, J. Chem. Phys. (to be published).

[10] R. A. Bair and W. A. Goddard III, Phys. Rev. B **22**, 2767 (1980).

[11] S. Larsson, Chem. Phys. Lett. **40**, 362 (1976).

[12] G. van der Laan, C. Westra, C. Haas, and G. A. Sawatzky, Phys. Rev. B **23**, 4369 (1981).

[13] A. Fujimori, Y. Tokura, H. Eisaki, H. Takagi, S. Uchida, and E. Takayama-Muromachi (unpublished).

[14] A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, Phys. Rev. B **35**, 8814 (1987).

[15] J. C. Mikkelsen, Jr. and J. B. Boyce, Phys. Rev. B **28**, 7130 (1983).

[16] H. Matsuyama, T. Takahashi, H. Katayama-Yoshida, T. Kashiwakura, Y. Okabe, S. Sato, N. Kosugi, A. Yagishita, K. Tanaka, H. Fujimoto, and H. Inokuchi, Physica C (to be published).