

X-ray photoelectron spectroscopy of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($x=0$ and 0.15) thin films

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Electronic structure of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($x=0$ and 0.15) thin films was examined by x-ray photoelectron spectroscopy. The films were prepared by rf magnetron sputtering and successive annealing under reducing condition (reduction). The reduced films showed semiconducting and superconducting behaviors depending on the value x . The Cu, O, and Nd core-level spectra revealed that the doped electrons were predominantly in CuO_2 plane of the Nd_2CuO_4 crystal. The Cu core-level spectra from $x=0.15$ films before and after the reduction suggested that the reduction added electrons to $\text{Cu}4s\text{-O}2p$ extended conduction band, and strengthened Cu—O bond covalency to screen the core hole state by mobile itinerant electrons.

I. INTRODUCTION

$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($x=0.15$, $y=0.04$) was discovered as a new n -type (the charge carriers are electrons) high- T_c superconductor.^{1,2} The key issues for n -type superconductivity are (1) the location of the doped electrons and (2) the role of reduction.

n -type superconductivity provides a crucial test for the already proposed theories based on pairing of $\text{O}2p$ holes in p -type superconductors. In n -type superconductors the doped electrons are considered to be positioned at Cu sites because the $\text{O}2p$ level is filled in Nd_2CuO_4 . Experiment of Cu- K edge x-ray absorption spectroscopy on $x=0\text{--}0.20$ bulk samples³ revealed that the electron doping converts some Cu^{2+} into Cu^{1+} but the location of the doped electrons in Cu^{2+} ($3d_{x^2-y^2}$ or $4s$ orbital) is not clear. The change of electron configuration on Cu site before and after the reduction has not yet been reported.

Crystalline thin-film samples provide vital information on physical properties such as the anisotropic two dimensional nature of cuprate superconductor. In this paper we report the core-level x-ray photoemission from highly c -axis oriented $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ thin films and a possible interpretation concerning the effect of the substitution and the role of reduction for obtaining high- T_c superconductivity.

II. EXPERIMENT

$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($x=0$ and 0.15) thin films were prepared by rf magnetron sputtering. Typical conditions of sputtering and successive annealing both in air and in vacuum are listed in Table I. The ratio of Nd:Ce:Cu was determined by electron probe microanalysis (EPMA). The result of the EPMA of the thin films is subjected to some uncertainty (15%). X-ray diffraction patterns of air annealed films indicated the high periodic peaks attributed to (001) diffrac-

tion of the c plane.⁴ c -axis lattice constants of the films with $x=0$ and 0.15 were determined to be 12.15 and 12.06 Å, respectively.⁴ Judging from the ionic radius of Nd^{3+} (1.12 Å), Ce^{3+} (1.14 Å), and Ce^{4+} (0.97 Å), this shrinkage of c -axis lattice constant with x suggests that all Ce ions dissolved in Nd sites were existing in a $4+$ state even before the reduction of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ thin film.

The films were annealed in vacuum (i.e., reducing condition) to obtain high- T_c superconductivity. Gold electrodes were evaporated and the standard four-probe method was used for resistivity measurements. Sharp superconducting transition was observed for reduced $x=0.15$ film.⁵ The onset temperature was 24 K and the zero-resistivity state was obtained at 22 K. Reduced $x=0$ film showed semiconducting behavior.⁵ The reduced $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($x=0$ and 0.15) thin films showed crystallographic and electron transport properties identical to those of the bulk ceramics.^{1,2,4,5}

The diamagnetism of the $x=0.15$ film after the reduction was measured by using an rf SQUID magnetometer with both field cooling at 10 Oe (Meissner effect) and zero field cooling followed by field heating at 100 Oe (shielding effect).⁵ Rapid increase at around 20 K and saturation below 15 K of the diamagnetization was observed in the shielding effect measurement. On the other hand, the observed Meissner signal was very weak. It is well known that this phenomenon is caused by a number of flux trapping sites of thin films.⁶ The critical current density at 4.2 K was estimated to the order of 10^6 A/cm² by using Bean's model.⁷

X-ray photoelectron spectra were collected by a hemispherical electron spectrometer with both unmonochromatized Al and $\text{MgK}\alpha$ radiations in vacuum pressure of less than 3×10^{-8} Pa at 300 K. The sample temperature was controlled by cooling with air through the cooling pipe leading to the suction pump. The measurement of the electron spectra was carried out after *in situ* scraping of the film surface with a diamond file until no further change in photoemission spectra was observed. The components of the substrate (Sr and Ti) were not observed after a number of cycles of scraping because the film thickness varied from 800 to 600

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TABLE I. Preparation conditions.

Target	Nd _{2-x} Ce _x Cu _{1.5} O _y
Substrate temperature	500 °C
Sputtering gas	Ar
Gas pressure	0.4 Pa
rf input power	160 W
Film thickness	800 nm
Annealing in air	1 atm, 1100 °C, 2 h
Reduction	10 ⁻⁴ Pa, 800-900 °C, 5 min

nm with the scraping but it was thick enough to discuss the chemical state of the film.

III. RESULTS AND DISCUSSION

A. Effect of the substitution

The Cu2p_{3/2} electron spectra for the reduced films are shown in Fig. 1. In the Nd_{2-x}Ce_xCuO_{4-y} system, peak A is the charge transfer satellite which originates from the electron configuration |Cu2p_{3/2}³ 3d¹⁰ O2p⁻¹) (well-screened state) in the final state of photoemission.⁸⁻¹¹ p⁻¹ indicates that one hole exists in the O2p orbital. Peak B observed on higher binding energy side at about 9 eV originates from the |Cu2p_{3/2}³ 3d⁹) electron configuration (poorly screened state) in the photoemission final state.⁸⁻¹¹ Peak B cannot be found in the reduced x = 0.15 film.

Here we consider a prediction of photoemission spectra based on molecular orbital theory. Nd₂CuO₄ has square planer CuO₂ planes with no apical oxygen.^{1,2} The local symmetry around Cu is thus D_{4h}. The Cu3d⁻¹ hole is in the Cu3d_{x²-y²} or shallowest b_{1g} orbital. Upon creation of a Cu2p⁻¹ core hole by photoemission, unfilled 3d level is pulled down (see Fig. 2). The pulled down energy equals Cu2p⁻¹ hole - 3d electron Coulomb energy, and roughly equals the energy difference between peaks A and B in Fig. 1. Since the peak A in Fig. 1 has been assigned to charge transfer satellite,^{10,11} larger relative intensity of peak A compared with that of peak B implies the crossing of the levels, Cu3d

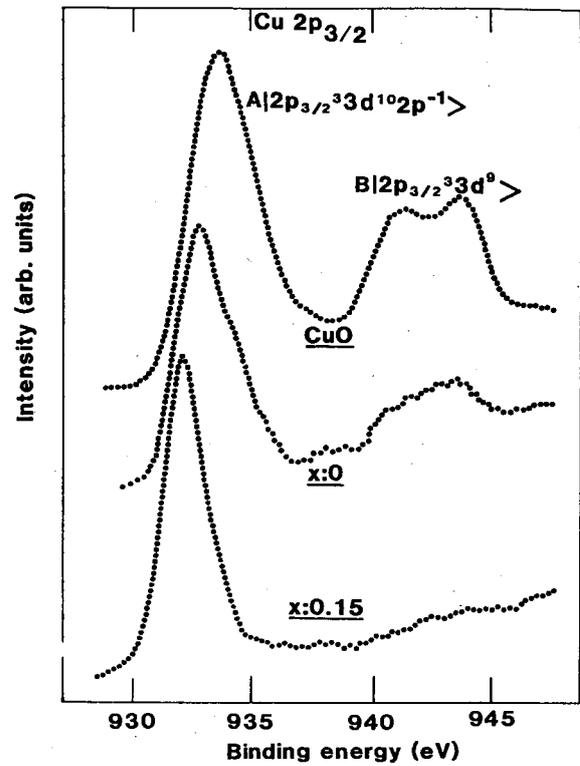


FIG. 1. Cu2p_{3/2} electron spectra for the x = 0 and 0.15 films excited by MgKα radiation. The order of the intensity was 5000-6000 counts. The Cu2p_{3/2} electron spectrum of CuO was also illustrated for convenience of assignment of the electron configuration.

and O2p, at the time of photoionization. However the levels with the same symmetry do not cross each other (avoided crossing), thus the hole in the Cu3d_{x²-y²} (b_{1g}) orbital is transferred to the O2p orbital which has b_{1g} symmetry and is a linear combination of four O2p orbitals in the CuO₄ cluster. The bonding molecular orbital, b, and antibonding molecular orbital, a, of the CuO₂ plane in the ground state are expressed as a linear combination of the Cu3d and O2p orbitals,^{10,11}

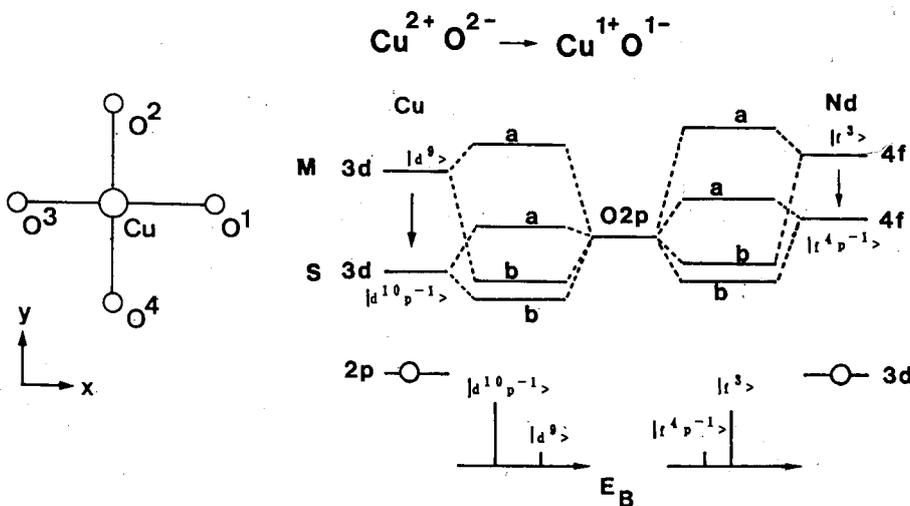


FIG. 2. Schematic picture of Cu2p and Nd3d ionization in the Nd_{2-x}Ce_xCuO_{4-y} system. |Cu3d) = d_{x²-y²} and |O2p) = (-p_x² + p_y² + p_x² - p_y²)/2. The Cu2p peaks S and M are antibonding and bonding orbitals in b_{1g} symmetry, respectively. They originate from the electron configurations of |Cu2p_{3/2}³ 3d¹⁰ O2p⁻¹) and |Cu2p_{3/2}³ 3d⁹) in the final state of photoemission, respectively. The Nd3d peaks S and M originate from the electron configurations of |Nd3d_{5/2}⁵ 4f⁴ O2p⁻¹) and |Nd3d_{5/2}⁵ 4f³) in the final state of photoemission, respectively.

$$b = p \cos \Theta + d \sin \Theta,$$

$$a = -p \sin \Theta + d \cos \Theta,$$

where d and p represents the $\text{Cu}3d$ and $\text{O}2p$ orbitals, respectively. Here we neglect the small overlap $\langle p|d \rangle$. In the $\text{Cu}2p^{-1}$ hole state, the bonding and antibonding orbitals become

$$b' = p \cos \Theta' + d \sin \Theta',$$

$$a' = -p \sin \Theta' + d \cos \Theta'.$$

If we express $\Theta'' = \Theta' - \Theta$, then we get

$$\Phi_M = A\Phi_1 \cos \Theta'' + A\Phi_2 \sin \Theta'',$$

$$\Phi_S = -A\Phi_1 \sin \Theta'' + A\Phi_2 \cos \Theta'',$$

where Φ_1, Φ_2, Φ_M , and Φ_S are Slater determinants shown in Fig. 3. A is an annihilation operator to remove a $\text{Cu}2p_{3/2}$ electron. From this the relative intensity in the $\text{Cu}2p_{3/2}$ spectrum is $I_S/I_M = \tan^2 \Theta''$.⁹ The intensity ratio of peak A to B (I_S/I_M) is proportional to the square of the increment of covalency which is represented by the increment of the molecular orbital coefficient ($\tan^2 \Theta''$) from the initial state to the final state of photoemission.⁹ The stronger the covalency due to a core hole, the stronger the peak A becomes. Consequently the Cu valence fluctuation takes place easily in the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ covalent system.

The $\text{Nd}3d_{5/2}$ electron spectra of the reduced films are shown in Fig. 4. It is well known that the spectra of $3d$ levels in the rare earths are split into several lines due to charge transfer (shakedown) satellites. Charge transfer takes place from the $\text{O}2p$ level to the core-ionized Nd atom. The $\text{Nd}3d_{5/2}$ spectra of the films showed similar shape comprising a small shoulder peak at around 977.5 eV and an intense peak at around 981.7 eV. If we assume that the well-screened state has lower binding energy, the higher and lower binding energy peaks correspond to $|\text{Nd}3d_{5/2}^5 4f^3\rangle$ and $|\text{Nd}3d_{5/2}^5 4f^4 \text{O}2p^{-1}\rangle$ electron configurations, respectively.¹² The peak shape of the $\text{Nd}3d_{5/2}$ spectra was invariant with x .

The fairly intense charge transfer satellites for both $\text{Cu}2p_{3/2}$ and $\text{Nd}3d_{5/2}$ are observed for the $x = 0$ and 0.15 films. Figure 2 is a schematic picture of $\text{Cu}2p$ and $\text{Nd}3d$ ionization in the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ system. The $\text{Cu}3d$ and $\text{Nd}4f$ orbitals are pulled down by the core holes to below and above the $\text{O}2p$ valence orbital, respectively. The charge transfer satellite intensity in the $\text{Cu}2p_{3/2}$ spectra became greater for the $x = 0.15$ film but that in the $\text{Nd}3d_{5/2}$ spectra was invariant with x . This fact suggests that the electrons

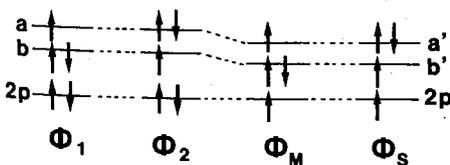


FIG. 3. Electron configurations for the Slater determinants, $\phi_{1,2}$ and $\phi_{M,S}$. a and b are antibonding and bonding orbitals in the ground state, respectively. a' and b' are the relaxed antibonding and bonding orbitals due to the $\text{Cu}2p$ hole, respectively. S and M are $|\text{Cu}2p_{3/2}^{-1} 3d^{10} \text{O}2p^{-1}\rangle$ and $|\text{Cu}2p_{3/2}^{-1} 3d^9\rangle$ in the final state of photoemission, respectively.

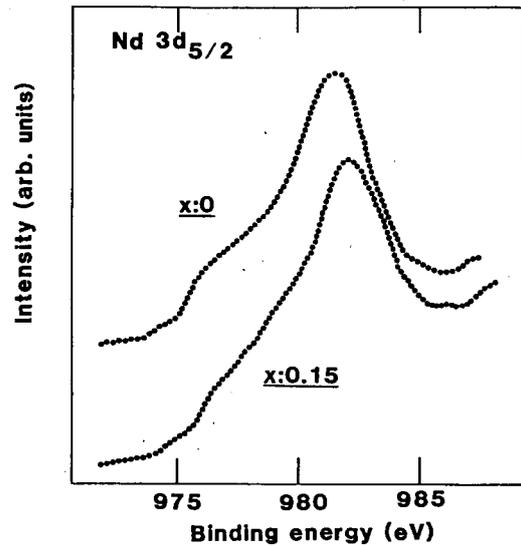


FIG. 4. $\text{Nd}3d_{5/2}$ electron spectra for the $x = 0$ and 0.15 films excited by $\text{MgK}\alpha$ radiation. The order of the intensity was 5000–20 000 counts.

doped by replacing Nd^{3+} for Ce^{4+} enter the $\text{Cu} - \text{O}$ bond and are delocalized on the CuO_2 plane.

The resistivity measurement and the core-level electron spectra revealed that electron doping to the CuO_2 plane in Nd_2CuO_4 crystal by substituting Nd^{3+} for Ce^{4+} gave rise to high- T_c superconductivity and large $\text{Cu} - \text{O}$ bond covalency. Superconductivity originates from the ground state $\text{Cu}^{1+} - \text{Cu}^{2+}$ charge fluctuation due to strong $d-p$ hybridization in the CuO_2 plane for n -type (electron-doped) superconductors. This is just like the $\text{Cu}^{2+} - \text{Cu}^{3+}$ charge fluctuation for p -type (hole-doped) cuprate superconductors.^{13,14} But there is still controversy over where the doped holes are dominantly located in p -type cuprate superconductors.^{15,16}

B. Effect of the reduction

The $\text{Cu}2p_{3/2}$ spectra for the $x = 0.15$ film before and after the reduction are shown in Fig. 5. The peak A, $|\text{Cu}2p_{3/2}^3 3d^{10} \text{O}2p^{-1}\rangle$ (well-screened state), was obviously enhanced and the peak B, $|\text{Cu}2p_{3/2}^3 3d^9\rangle$ (poorly screened state), was depressed by the reduction for the $x = 0.15$ film. The $x = 0$ film showed similar spectral change with the reduction but the degree of the change was much smaller than that of $x = 0.15$ film.

We have to consider ground states for the understanding of the observed effects of reduction appeared in the spectra of excited states mentioned above because of the superconducting transition takes place in the ground state. In charge transfer compounds such as cuprate superconductor, the charge transfer from the $\text{O}2p$ level to the $\text{Cu}3d$ level occurs even in the ground state. It is obvious that the reduction process introduces electrons into the CuO_2 plane in the crystal as seen in the x-ray photoemission spectra mentioned above the electronic transport properties as described later. We consider the possibility of entering the doped electrons into σ bound orbital rather than into π bound orbital. The $\text{Cu}3d_{x^2-y^2} - \text{O}2p$ antibonding orbital cannot accept doped

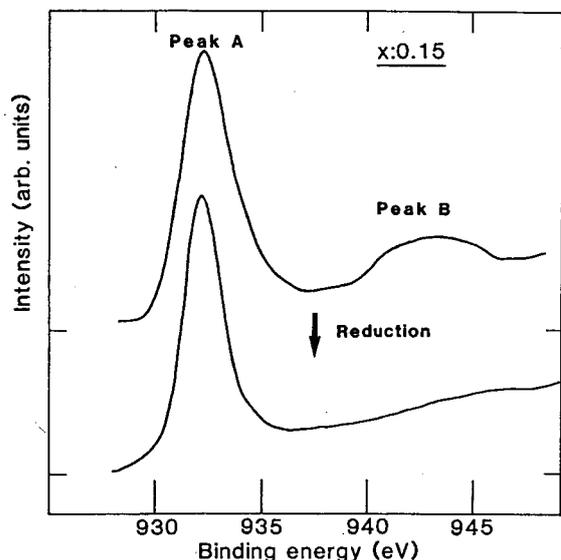


FIG. 5. $\text{Cu}2p_{3/2}$ electron spectra for the $x = 0.15$ film before and after the reduction excited by $\text{MgK}\alpha$ radiation. The order of the intensity was 5000–6000 counts.

electrons except by expanding Cu-O distance in the square CuO_2 plane. Doping of electrons into antibonding orbital weakens the strength of Cu—O bond. But $\text{Cu}4s\text{-O}2p$ bonding orbital can accept electrons. When the electrons are doped to the $\text{Cu}4s\text{-O}2p$ bonding orbital in the ground state, the Cu—O σ bond is strengthened and then the covalency of Cu—O bond is enhanced. The increase in Cu—O bond covalency in the ground state results in the enlargement of peak A in the final state of photoemission.

Before the reduction the temperature dependence of the resistivity of the film showed semiconductorlike behavior, but the shrinkage of the c -axis lattice constant indicated that the doped Ce^{4+} ions replaced the Nd^{3+} ions in the crystal. The excess electrons introduced by the substitution do not act as charge carrier and are localized at around Ce^{4+} ions in the crystal before the reduction. By the reduction the temperature dependence of the resistivity became metallic and the resistivity decreased in normal state, and the superconducting transition was realized. This suggests that the doped electrons become charge carrier and are delocalized in the crystal by the reduction. The $\text{Cu}4s\text{-O}2p$ hybridization forms a broad s - p conduction band (crystal orbital) due to the overlapping of each molecular orbital in the solid state. The reduction process transfer the electrons in the localized impurity level into the s - p conduction band and caused the delocalization of electrons on the CuO_2 plane in the crystal. The enhancement of electron delocalization on the CuO_2 plane in the ground state induces the increase of well-screened core hole state by mobile itinerant electrons in the photoemission final state.

IV. SUMMARY

In this paper we reported the results of x-ray photoemission from $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ crystalline thin films and a possible interpretation of the change of the photoemission spectra due to the substitution and reduction. The resistivity measurement and the core-level electron spectra revealed that the electron doping to CuO_2 plane in Nd_2CuO_4 crystal by substituting Nd^{3+} for Ce^{4+} gave rise to high- T_c superconductivity and large Cu—O bond covalency. The reduction changed the electron transport properties from semiconductorlike behavior to superconductor for the $x = 0.15$ film and reduced the normal state resistivity of the films. After the reduction the spectral intensity of the well-screened state was enhanced and that of the poorly-screened state was depressed in the $\text{Cu}2p_{3/2}$ electron spectra of the films. The reduction is considered to cause the doping of electrons from impurity level into $\text{Cu}4s\text{-O}2p$ bonding orbital and, as a result, strengthen of Cu—O σ bond, and the core hole state is screened well by mobile itinerant electrons. Our results indicate that we must reconsider the importance of Cu valence fluctuation from $1 + (d^{10})$ electron configuration) to $2 + (d^9)$ and/or from $2 +$ to $3 + (d^8)$ due to strong $\text{Cu}3d\text{-O}2p$ hybridization of cuprate high- T_c superconductors.

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- ¹Y. Tokura, H. Takagi, and S. Uchida, *Nature* **337**, 345 (1989).
- ²H. Takagi, S. Uchida, and Y. Tokura, *Phys. Rev. Lett.* **62**, 1197 (1989). The deficiency of oxygen, $y = 0.04$, was determined by iodometric titration.
- ³J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang, and M. Croft, *Nature* **337**, 720 (1989). The Cu-K edge x-ray absorption revealed that the doped electrons occupies the $\text{Cu}3d$ orbital and the valence of Ce is $3.5 +$, but Takagi *et al.*² have reported that all Ce ions dissolved in Nd sites were present in the $4 +$ state.
- ⁴S. Hayashi, H. Adachi, K. Setsune, T. Hirao, and K. Wasa, *Jpn. J. Appl. Phys.* **28**, L962 (1989).
- ⁵H. Adachi, S. Hayashi, K. Setsune, S. Hatta, T. Mitsuyu, and K. Wasa, *Appl. Phys. Lett.* **54**, 2713 (1989).
- ⁶S. Hatta, K. Hirochi, H. Adachi, T. Kamada, Y. Ichikawa, K. Setsune, and K. Wasa, *Jpn. J. Appl. Phys.* **27**, 1646 (1988).
- ⁷C. P. Bean, *Phys. Rev. Lett.* **8**, 250 (1962).
- ⁸J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G. A. Sawatzky, and M. T. Czyzyk, *Phys. Rev. B* **38**, 11322 (1988).
- ⁹S. Asada and S. Sugano, *J. Phys. Soc. Jpn.* **41**, 1291 (1976); S. Sugano, *Jpn. J. Appl. Phys. Suppl.* **17-2**, 38 (1978).
- ¹⁰S. Larsson, *Chem. Phys. Lett.* **40**, 362 (1976).
- ¹¹G. van der Laan, C. Westra, C. Hass, and G. A. Sawatzky, *Phys. Rev. B* **23**, 4369 (1981); J. Zaanen, C. Westra, and G. A. Sawatzky, *Phys. Rev. B* **33**, 8060 (1986).
- ¹²G. Wendin, Ed., *Breakdown of the One-Electron Pictures in Photoelectron Spectra* (Springer, Berlin, Heidelberg, New York, 1981), p. 96.
- ¹³S. Kohiki, K. Hirochi, H. Adachi, K. Setsune, and K. Wasa, *Phys. Rev. B* **39**, 4695 (1989).
- ¹⁴S. Kohiki, T. Wada, S. Kawashima, H. Takagi, S. Uchida, and S. Tanaka, *Phys. Rev. B* **38**, 8868 (1988).
- ¹⁵J. Kondo, *J. Phys. Soc. Jpn.* **58**, 2284 (1989).
- ¹⁶J. B. Torrance and R. M. Metzger, *Phys. Rev. Lett.* **63**, 1515 (1989).