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Characteristics of Resonant Photoemission of Metallic, Molecular, and Correlated Solid Systems

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Inner-shell photoabsorption spectroscopy and photoemission spectroscopy are powerful tools to investigate the origin of electronic and magnetic properties in transition metal compounds. In the present study, we have investigated Ni 3p and 3s photoemission at the Ni 2p edge of some Ni-containing solid systems with different electronic properties to get a unified view for the resonant behavior. The systems chosen are NiO as a correlated system, Ni as a metallic system, and $K_2Ni(CN)_4$ as a molecular system.

Experiments were performed at BL1A soft x-ray beamline. A pair of beryl $(10\bar{1}0)$ crystals were used in the double crystal monochromator. The Ni 2p photoabsorption spectra were measured by monitoring the total electron yield. A SCIENTA SES200 electron energy analyzer was used to measure the photoelectron spectra. The total energy resolution in the photoelectron spectra was about 0.7 eV.

The Ni 2p photoabsorption spectra for the three systems are different as shown in Fig.1. In NiO the shoulder and weak features arise from correlation and multiplet effects [1]. In Ni metal the absorption is dominated by the broad conduction band. In $K_2Ni(CN)_4$ the strong extra features arise from the single electron transition MLCT (Metal-to-Ligand Charge Transfer) [2]. Fig. 2 shows off- and on-resonant Ni 3p, 3s photoemission spectra at the photon energy marked in Fig. 1. The on-resonant photoemission spectra of Ni metal and $K_2Ni(CN)_4$ are nearly the same and resemble the normal Auger spectra. That is, the correlation and multiplet interaction seem to be reduced in the metallic and molecular systems. On the other hand, the on-resonant spectra of NiO show more complicated features than those of Ni metal and $K_2Ni(CN)_4$, due to strong correlation and multiplet interaction [3].

The resonant behavior (photon energy vs. kinetic energy of the enhanced satellite bands) is quite different in the three systems as shown in Fig. 3. The resonant photoemission features in Ni metal and $K_2Ni(CN)_4$ nearly coincide with the normal Auger lines in energy. In $K_2Ni(CN)_4$ the resonantly enhanced satellite states have a character of combination of the normal Auger final state with the one-electron (excitonic electron) state, which is localized within a unit of $Ni(CN)_4^{2-}$ ion and is bound by the core holes, forming a series of core excitons converging to the Ni 2p ionized state in the photoexcitation and to the normal Auger final state in the resonant photoemission [4]. The binding energy of the one-electron state by the double holes in the Auger final state is larger than that by the single hole in the photoexcitation. Therefore, the resonantly emitted satellite electron decreases its kinetic energy for the higher excitation energy.

In Ni as a metallic system, the intermediately photoexcited, resonantly enhanced satellite, and normal Auger states are embedded in the continuum band and are well screened by the conduction electron. Therefore, the resonantly emitted satellite electrons show nearly the same kinetic energy as the normal Auger electrons. This is true in the broad band metallic system even if there should be several photoexcited and satellite states near the threshold due to multiplet and/or excitonic effects.

On the other hand, since in NiO the correlation and multiplet interaction are very important, there is neither clear one-to-one correspondence between the photoexcited states and the resonantly enhanced satellite states nor relation between the satellite electrons and the normal Auger electrons as shown in Fig. 3(a).

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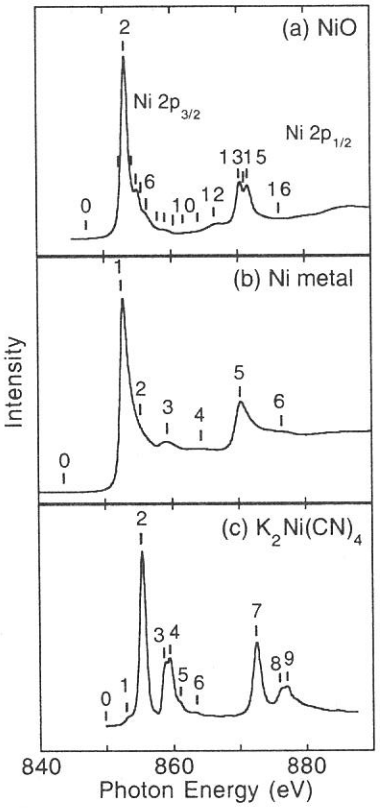

Fig. 1. Photoabsorption spectra at the Ni $2p_{3/2}$ and $2p_{1/2}$ edges for (a) NiO, (b) Ni metal, and (c) $K_2Ni(CN)_4$.

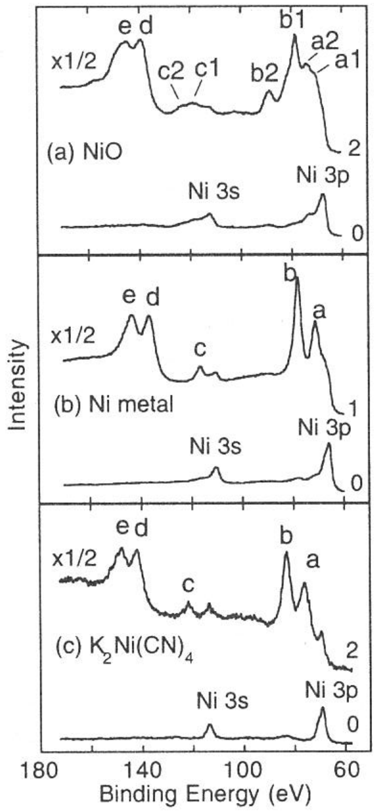

Fig. 2. Off-resonant and on-resonant photoemission spectra in the Ni 3p and 3s region at the Ni $2p_{3/2}$ absorption edge marked in Fig. 1 for (a) NiO, (b) Ni metal, and (c) $K_2Ni(CN)_4$.

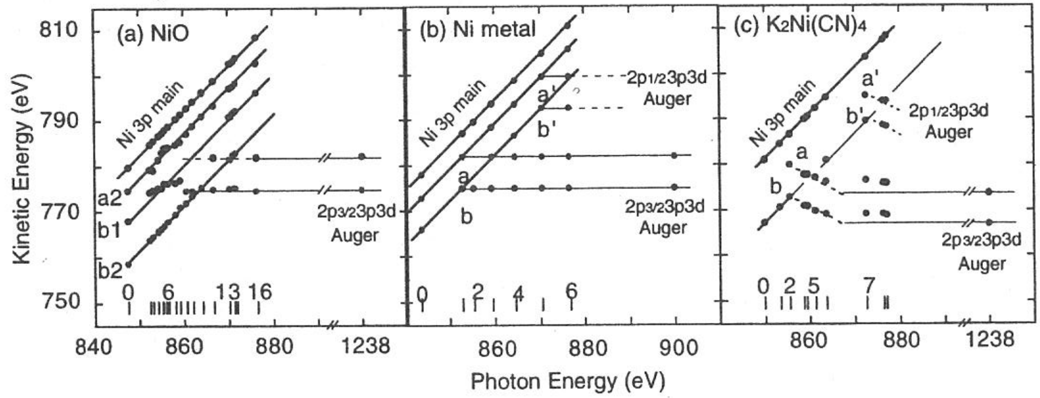

Fig. 3. Resonant behavior of satellite photoelectrons in the Ni 3p region at the Ni 2p excitation for (a) NiO, (b) Ni metal, and (c) $K_2Ni(CN)_4$. Photon energy dependence of the electron kinetic energy, ΔK.E./Δhν. The energy uncertainty is about 0.2 eV.

(BL1A) Ni-Ni chemical bond in $[Ni_2(napy)_4Br_2][B(C_6H_5)_4]$ studied by Ni 2*p* photoabsorption

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Since the recognition of the structural and theoretical significance of the Re-Re bond [1], various complexes containing metal-metal bonding have been synthesized and a large number of experimental and theoretical studies have been done to characterize the metal-metal bonding [2,3]. In contrast to the metal-metal bonds of early transition elements, such as Cr, Mo, W, Re, and Ru, the Ni-Ni bonding is not well characterized [3]. In order to elucidate character of the Ni-Ni chemical bond, linearly polarized Ni 2*p* photoabsorption spectra of $[Ni_2(napy)_4Br_2][B(C_6H_5)_4]$ (napy: 1.8-naphthyridine), which has Ni-Ni bond (2.415 Å) being shorter than Ni-Ni bond in Ni metal (2.50 Å).

The sample was prepared as described in ref. [4]. A single crystal (about 1 x 5 x 5 mm) was obtained by slow recrystallization from acetone solution. The structure consists of binuclear complex cations $[Ni_2(napy)_4Br_2]^{1+}$ and $[B(C_6H_5)_4]^{1-}$ anions (Fig. 1) [4]. The molecular axis z chosen as Fig. 1 was determined by the X-ray diffraction analysis. Ni 2*p* photoabsorption spectra were measured at the BL1A soft x-ray beamline with a pair of beryl $(10\bar{1}0)$ crystals by monitoring total electron yields.

Fig. 2 shows the Ni 2*p* photoabsorption spectrum of powder $[Ni_2(napy)_4Br_2][B(C_6H_5)_4]$. The intensity ratio of the Ni $2p_{3/2}$ region to the Ni $2p_{1/2}$ region is larger than statistical value 2, indicating that the complex cation has unpaired electrons. This is consistent with the effective magnetic moment, 4.19 BM, for a $[Ni_2(napy)_4Br_2]^{1+}$unit [4].

In a simple diatomic system Ni_2, the Ni 3*d*-3*d* chemical bonding gives bonding and antibonding orbitals, σ and σ^* (d_{z2}), π and π^* (d_{xz}, d_{yz}), δ and δ^* (d_{xy}, d_{x2-y2}), where the degeneracies of the π, π^*, δ, and δ^* orbitals are removed in $[Ni_2(napy)_4Br_2]^{1+}$ because of imperfect eclipsed ligand geometry (Fig. 1). For the $[Ni_2(napy)_4Br_2]^{1+}$ cation, there are 3 holes in these '3*d*' orbitals ('3*d*' is not purely atomic), since the Ni atoms have the formal oxidation number +1.5. In order to elucidate the symmetries of the holes, the linearly polarized Ni 2*p* photoabsorption was measured. As shown in Fig. 2, distinct polarization dependence is observed. The lowest band A is strong in the $E\perp z$ direction, where E denotes the electric vector of incident photon, and very weak in the $E//z$ direction. Therefore, the band A is clearly assigned to the transition of d_{xy} or d_{x2-y2} symmetry. This indicates that some holes are located in 'δ' orbitals. On the contrary, the band B is strong in the $E//z$ direction and weak in the $E\perp z$ direction. This implies that the other holes are located in the σ^* orbital with d_{z2} symmetry.

The intensity ratio of band A to B is estimated to be about 2 from the curve fitting of the spectrum of the powder sample. Based on the polarization dependence and intensity of band A and B, it is reasonable to say that one hole is located in the σ^* orbital and two holes in δ-symmetry orbitals, though we cannot distinguish between $\delta^3\delta^{*3}$ and $\delta^4\delta^{*2}$ configurations.

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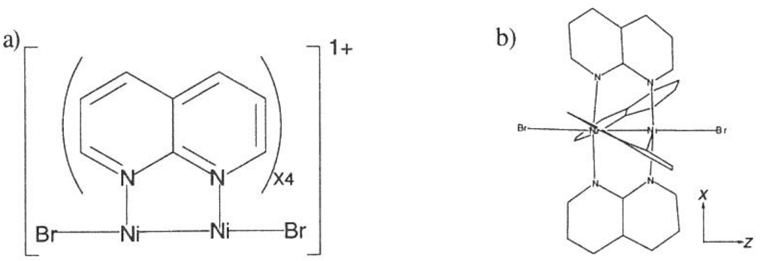

Fig. 1 The molecular structure of $[Ni_2(napy)_4Br_2]^{1+}$ (a) and the structure determined by X-ray diffraction analysis (b) [4].

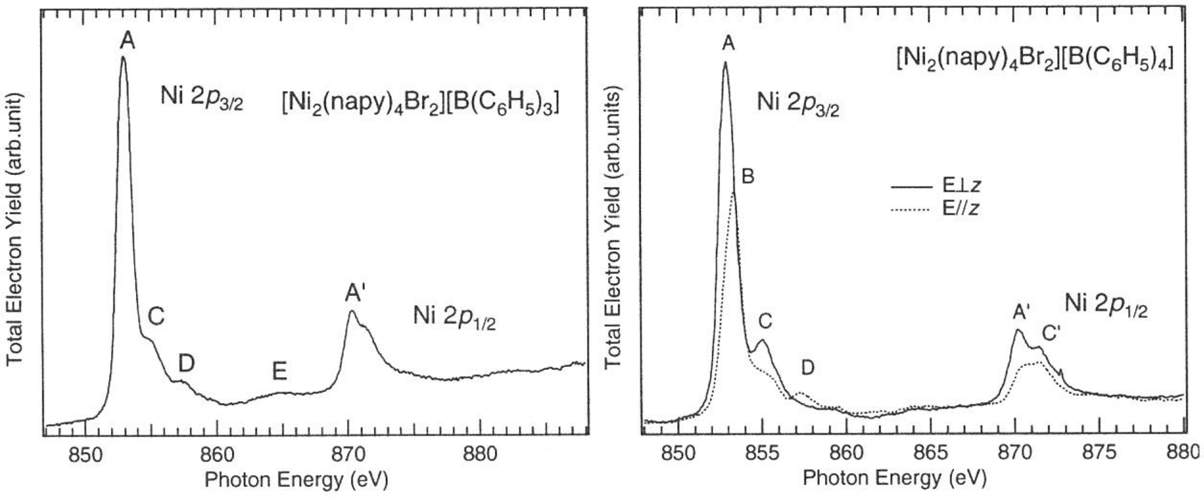

Fig. 2. Ni $2p$ photoabsorption spectrum of powder $[Ni_2(napy)_4Br_2][B(C_6H_5)_4]$ (left) and polarized Ni $2p$ photoabsorption spectra of a single crystal for the E//z and E⊥z directions (right), where E and z denote the electric vector of the incident photon, and the molecular axis chosen as Fig. 1, respectively.

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Al-K XANES Spectra of Al1-xGaxN Solid Solusions

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Introduction

AlN and GaN are becoming to be fundamental compound semiconductors which have a large band gap to give new promising electronic devices. On designing these devices, the knowledge of electronic structure is necessary to make the best of these materials. Electron correlation is not main phenomena in semiconductors. Its electronic structure will be explained by using the idea of density of states (DOS). In this study, Al-K edge spectra give directly p type unoccupied partial density of states (PDOS) at Al site, which will constitute one set of DOS information with that at N site. How is the rate of covalent bond in these materials, in comparison with the typical covalent bonding in Si and Ge.

Anisotropic spectra in regard to c-axis is expected on Al-K edge, because AlN takes wurtzite crystal structure. The measured spectra will be decomposed into polarized components which will reveal the relation of remarkable peaks between the decomposed components and an original spectra.

Spectral change of Al-K edge in Al1-xGaxN by increasing concentration of Ga element gives the local arrangement of wave function at Al site, which shows the rate of bonding in these materials. Putting all accounts together the results from the above mentioned points of view in our study, a better understanding of the electronic structure in AlN will be obtained.

Experimental

The sample takes a film form where c-axis of single crystal is perpendicular to the surface. The polarized ($c \perp E$ and $c \parallel E$) and non-anisotropic components were obtained by decomposing the spectra measured at various tilt angle of c-axis from the direction of incident light.

The measurement were carried out at BL7A and BL1A beam lines of UVSOR. Absorption measurements were done by the method of total electron yield, using qurtz crystal as a monochromator crystal. Samples with small content of Al were measured during a period of good machine stability, when the noise level of drain current is the order of 10^{-2} pA. The obtained signals were averaged to get reliability. The correct positions of the edge were determined by comparison with Al_2O_3 as a standard at BL1A beam line, where the high brightness of the monochromator system allows a rapid scan.

Results and Discussion

The summary of our results is mentioned as follows, including also the content of the previous report [1]. Al-K edge spectra (c⊥E) of Al1-xGaxN were obtained as shown in Fig. 1. Main peaks in the spectra (a, c and f) are retained, though the percentage of Al changes from100 to 5 %. This result and a small (0.2 eV) difference of edge position (chemical shift) suggest that PDOS at Al site is almost composed of Al wave functions and that the bonding character around Al is ionic. As shown in Fig.2, c⊥E and c∥E polarized components (XY and Z) and non-anisotropic component (NA) were obtained by the numerical decomposition using the method of the least square fitting. The result of the decomposition is supported by the fact that the synthesized spectrum from the three components (XY, Z and NA) at a magic angle (where the anisotropy of spectrum disappears in wurtzite structure) fairly coincides with p type PDOS calculated by a band theory [2]. Therefore, the obtained three components give us a new step for the further precise study of Al-K edge in this material.

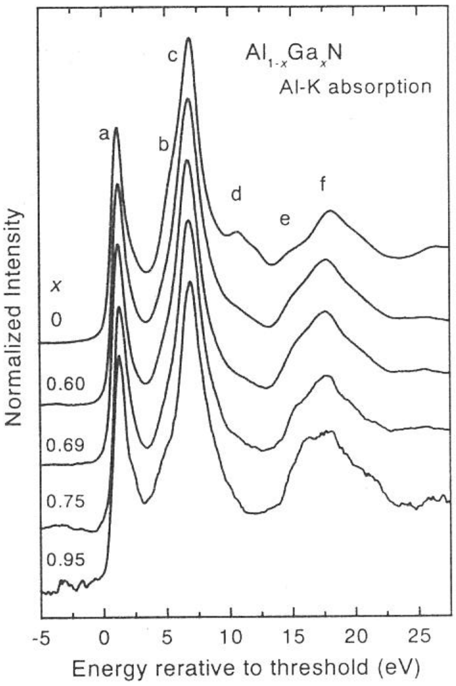

Fig. 1

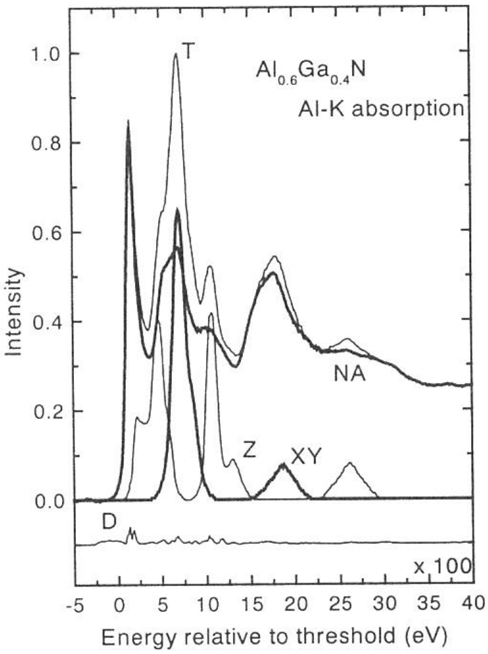

Fig. 2

The authors would like to thank Dr.S.Tanaka, Dr.Aoyagi (RIKEN) for supply of AlN and AlGaN samples.

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