

Multiplet Structure in Ni $K\beta$ X-Ray Fluorescence Spectra of Nickel Compounds

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We show that the profiles of the Ni $K\beta_{1,3,\beta'}$ x-ray fluorescence spectra of NiF_2 and NiO , which were long believed to originate from the multiplet splittings due to an exchange interaction between the x-ray hole and valence unpaired electrons, are clearly interpreted by a charge-transfer effect during the photoionization of one of the $1s$ electrons. The profiles of the $K\beta$ x-ray fluorescence spectra of NiCl_2 , NiBr_2 , and NiI_2 are also predicted from the charge-transfer effect. The range of validity of the present theory and its relation to the shakeoff satellites are also discussed.

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Multiplet structures in $K\beta$ x-ray fluorescence spectra (the $3p \rightarrow 1s$ electron transition) of transition-metal compounds are usually interpreted in terms of the splittings due to the exchange interaction $-J(1+4\langle\mathbf{S}\cdot\mathbf{s}\rangle)/2$ between the unpaired $3d$ electrons ($S=1$ for Ni^{2+}) and the x-ray hole ($s = \pm \frac{1}{2}$) in the initial or final state of x-ray emission, where $J = \frac{2}{15} G^1(3p, 3d) + \frac{3}{35} G^3(3p, 3d)$. Then the magnitude of the energy difference between $K\beta$ and $K\beta'$ is given by $\Delta E = J(2S+1)$, and the relative intensity by the ratio of multiplicity $S/(S+1)$.¹ This multiplet theory has been used to calculate the $K\beta, \beta'$ x-ray spectral profiles of many transition-metal compounds.²⁻⁴ Since the above approximation was quite crude, the x-ray spectra were calculated by using the multiplet wave functions in the LS or jj coupling scheme with Coulomb and exchange integrals expressed by Slater-Condon parameters and/or spin-orbit coupling constants in the spherical⁵ or cubic (O_h) symmetry field.⁶⁻⁸ However, these sophisticated calculations gave only an order-of-magnitude agreement between the theory and experiment. A plasmon mechanism was proposed⁹ to interpret the discrepancy. However, the agreement was again unsatisfactory.¹⁰

Recently, a charge-transfer effect was proposed to interpret the satellite structure of the x-ray photoelectron spectra (XPS) of Cu $2p$,¹¹⁻¹³ Ni $2p$,^{13,14} and Ni $3d$.¹⁵ The main line in the Ni XPS of some compounds has been assigned to the transition from the ground state to the well screened state, which is due to a charge transfer from one of the ligands, whereas the satellites in the higher-binding-energy region have been assigned to the transitions from the ground state to the poorly screened states. Though the emission of $K\beta$ x rays is not directly related to the $2p$ XPS, it is natural to assume that one or two electrons are transferred from the ligands during the photoionization of $1s$. Therefore the charge-transfer effect should be incorporated in the interpretation of the $K\beta$ spectral profiles. On this basis, the multiplet structure in the $K\beta, \beta'$ x-ray fluorescence spectra are com-

pletely reanalyzed in this paper, resulting in satisfactory agreement between the theory and experiment.

Figure 1 shows the measured Ni $K\beta$ x-ray fluorescence spectra of NiF_2 and NiO .¹⁶ The spectra were taken with a high-resolution double-crystal $[\text{Si}(220) + \text{Si}(220)]$ x-ray fluorescence spectrometer¹⁷ excited by Rh- or W-

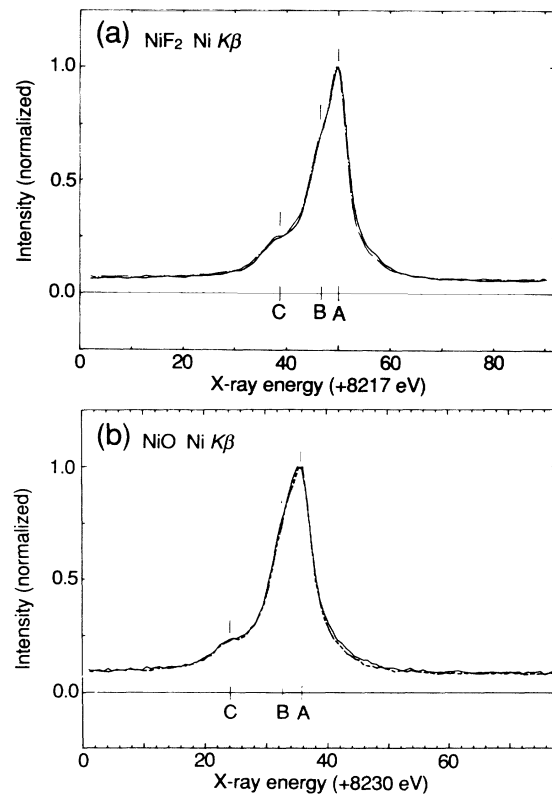


FIG. 1. Measured Ni $K\beta$ spectra of (a) NiF_2 and (b) NiO taken from Ref. 16. The solid-line spectra are excited by Rh-anode tube ($\text{Rh } K\alpha$, 20.2 keV), while the dashed- and dotted-line spectra are excited by W-anode tube to avoid the shakeoff process.

anode tubes. Since the energy of $W L\alpha$ (8.396 keV) is slightly above the Ni K absorption edge (8.330 keV), the W -tube excitation partially avoids the excitation of multiple ionizations (shakeoff process). The shakeoff satellites in these $K\beta$ spectra are weak due to the charge-transfer effect as discussed later. The $K\beta$ spectra of NiF_2 and NiO have roughly three peaks in the $K\beta_{1,3,\beta'}$ region: a strong main peak (denoted by A in Fig. 1, usually called $K\beta_{1,3}$)¹⁸ and two peaks on the shoulders at about 4 (B in Fig. 1) and 12 eV (C in Fig. 1, usually called β') below the main peak. These three peaks are also recognized in the spectra of the same compounds in other works.¹⁹⁻²¹

Figure 2 shows the calculated multiplet structures for the transitions $\underline{1s}3d^2 \rightarrow \underline{3p}3d^2$ (${}^2SPDFG, {}^4PF \rightarrow {}^2SPDFGH, {}^4SPDFG$), $\underline{1s}3d \rightarrow \underline{3p}3d$ (${}^{1,3}D \rightarrow {}^{1,3}PDF$), and $\underline{1s} \rightarrow \underline{3p}$ (${}^2S \rightarrow {}^2P$), where the underline denotes the hole(s). The radiations resulting from all electric-dipole transitions between the two configurations are shown. The multiplet energies and wave functions were calculated by diagonalization of the matrix, the elements of which are tabulated by Condon and Odabasi.²² The Slater-Condon parameters in the $\underline{1s}$ and $\underline{3p}$ hole states were calculated from the one-electron wave functions of free ions by the $X\alpha$ method.²³ The dipole transition intensity for LS coupling was taken from Goldberg.²⁴ The calculated spectra have been checked by a sum rule. The transition energy of the center of gravity of each multiplet was calculated by the $X\alpha$ program based on Slater's transition-state theorem.²⁵

In the old theory, the $K\beta$ x-ray spectra of weak-ligand-field nickel compounds such as NiF_2 or NiO were believed to originate from the transition $\underline{1s}3d^2 \rightarrow \underline{3p}3d^2$.⁶⁻⁸ Comparing Fig. 1 with Fig. 2(a), one can assign the $K\beta$ main peak (peak A in Fig. 1) as the transition $|\underline{1s}3d^2, {}^4PF\rangle \rightarrow |\underline{3p}3d^2, {}^4DFG\rangle$, peak B as $|\underline{1s}3d^2, {}^4F\rangle \rightarrow |\underline{3p}3d^2, {}^4D\rangle$, and peak C mostly as $|\underline{1s}3d^2, {}^2F\rangle \rightarrow |\underline{3p}3d^2, {}^2G\rangle$ within the framework of the old theory.²⁶ However, the agreement between the experiment and the calculation with the old theory is unsatisfactory since the experimental main peak (peak A in Fig. 1) is significantly narrower than the calculated one.

Having described above the interpretation of the $K\beta$ spectra within the old multiplet theory, we will next interpret the $K\beta$ profiles by the charge-transfer effect. The total electronic wave function of a core hole (\underline{c}) state is expanded in terms of the ground-state wave function $|\underline{3d}^8\rangle$ and one-electron ($|\underline{3d}^9\underline{L}\rangle$) and two-electron excitation configurations ($|\underline{3d}^{10}\underline{L}^2\rangle$);

$\Phi_f = C_{i1}|\underline{c}3d^8\rangle + C_{i2}|\underline{c}3d^9\underline{L}\rangle + C_{i3}|\underline{c}3d^{10}\underline{L}^2\rangle$ ($i = 1, 2, 3$), where L denotes a linear combination of ligand valence orbitals. The Ni $2p_{3/2}$ XPS of many compounds exhibits

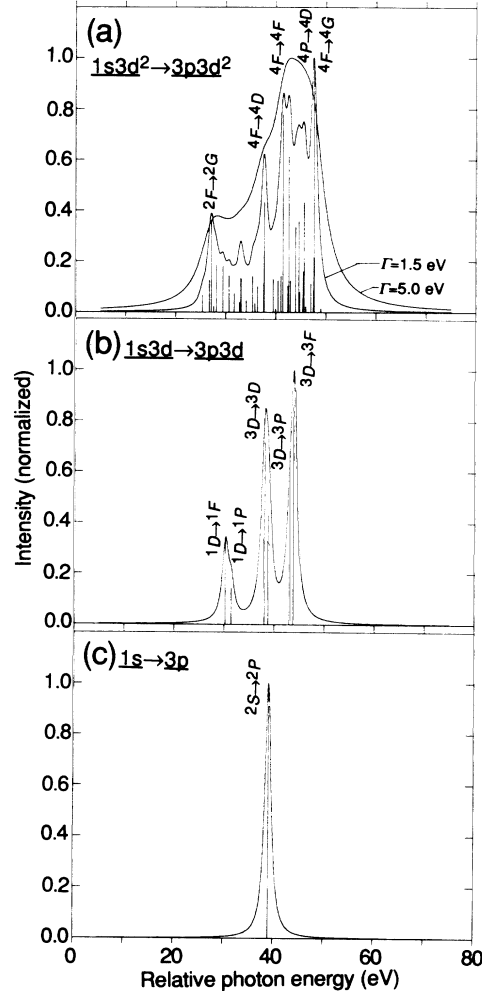


FIG. 2. Calculated spectra of (a) $\underline{1s}3d^2 \rightarrow \underline{3p}3d^2$, (b) $\underline{1s}3d \rightarrow \underline{3p}3d$, and (c) $\underline{1s} \rightarrow \underline{3p}$. The calculated multiplets are broadened by 1.5-eV FWHM Lorentzian functions for (a), (b), and (c), and also a 5-eV Lorentzian function for (a).

three peaks which have been assigned to the transitions from the ground state to the $|\underline{2p}3d^8\rangle$, $|\underline{2p}3d^9\underline{L}\rangle$, and $|\underline{2p}3d^{10}\underline{L}^2\rangle$ states.¹⁴ If $c = 2p_{3/2}$, then the relative intensities of the three observed Ni $2p_{3/2}$ lines are $|C_{11}|^2 : |C_{21}|^2 : |C_{31}|^2$ in the sudden approximation.¹¹ If we assume that the valence electrons feel approximately the same core-hole potential from a $\underline{1s}$, $\underline{2p}$, or $\underline{3p}$ hole,²⁷ then the $|C_{ij}|^2$ of $\underline{1s}$ and $\underline{3p}$ hole states can be estimated from the $2p$ XPS. The $K\beta$ spectrum is expressed as

$$\sum_{ij} |\langle \underline{3d}^8 | r | \Phi_i^{1s} \rangle|^2 \times |\langle \Phi_i^{1s} | r | \Phi_j^{3p} \rangle|^2 \delta(h\nu + E_j - E_i),$$

where E_i and E_j are the total energy of the i th $\underline{1s}$ and the j th $\underline{3p}$ hole states, respectively, and the phase memory is lost at the multiplication mark (\times). Then one obtains the relative intensity of each $K\beta$ component,

$$I(\underline{1s}3d^8 \rightarrow \underline{3p}3d^8) : I(\underline{1s}3d^9\underline{L} \rightarrow \underline{3p}3d^9\underline{L}) : I(\underline{1s}3d^{10}\underline{L}^2 \rightarrow \underline{3p}3d^{10}\underline{L}^2) = |C_{11}|^2 : |C_{21}|^2 : |C_{31}|^2.$$

Consequently, the $K\beta$ spectra of Ni^{2+} in nickel compounds are a mixture of the spectra of Figs. 2(a)–2(c).

Figure 3 shows the calculated $K\beta$ spectra for various mixing ratios of the three configurations d^8 [Fig. 2(a)], d^9 [Fig. 2(b)], and d^{10} [Fig. 2(c)]. The mixing ratio of the spectrum in Fig. 3(a) is taken from the $2p_{3/2}$ x-ray photoelectron spectrum of NiF_2 , which has two peaks:¹⁴ The main line (857 eV) is assigned to the transition from the ground state to the $|2p3d^9\bar{L}\rangle$ final state, while the higher-binding-energy peak (862.5 eV) to the $|2p3d^8\rangle$. The calculated spectrum in Fig. 3(a) (including the charge-transfer effect) reproduces the experimental spectra (Fig. 1) much better than Fig. 2(a) (without the charge-transfer effect).

The spectra in Figs. 3(b) and 3(c) are calculated with mixing ratios close to those of NiCl_2 or NiBr_2 and NiI_2 , respectively. The mixing ratios are taken from the $2p$

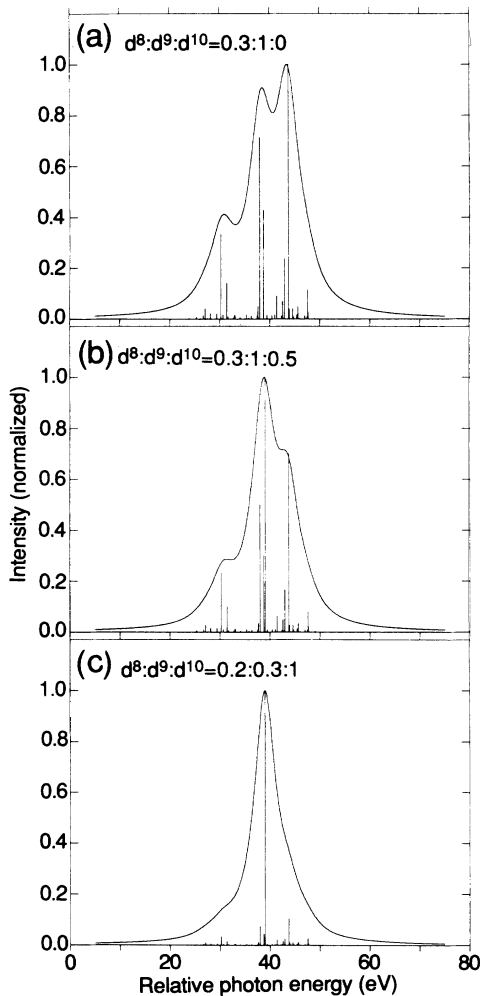


FIG. 3. Calculated Ni $K\beta$ spectra for various mixing ratios of the three configurations ($|3d^8\rangle$, $|3d^9\rangle$, and $|3d^{10}\rangle$). The calculated multiplets are broadened by 5-eV Lorentzian functions. The mixing ratios are those of (a) NiF_2 and NiO , (b) NiCl_2 and NiBr_2 , and (c) NiI_2 .

XPS.¹⁴ Therefore, these spectra will reproduce the $K\beta$ spectra for NiCl_2 or NiBr_2 [Fig. 3(b)] and NiI_2 [Fig. 3(c)],²⁸ though high-resolution spectra of these crystals have not yet been measured due to decomposition during measurements.

The $K\beta$ spectra should be calculated with the above charge-transfer effect for the *charge-transfer semiconductors*²⁹ (usually late transition-metal compounds, $Z \geq 25$), while for the *Mott-Hubbard insulators*²⁹ (usually early transition-metal compounds, $Z \leq 25$) the old multiplet theory is valid for the calculation of the $K\beta$ spectra. This is because, for charge-transfer semiconductors, the energy difference between the $3d$ and the ligand p orbitals is small (the $3d$ orbital energy is slightly higher than that of the ligand p orbitals) and the ligand p electrons are strongly attracted by the $3d$ holes. Thus at the creation of a core hole by photoionization, the $3d$ orbital crosses the ligand p orbitals because the $3d$ orbitals are pulled down by the core-hole potential, and at the moment of the level crossing, the ligand p electron(s) is (are) transferred to the unoccupied $3d$ orbital(s) of the nickel ion with the probability $|C_{i1}|^2$. On the other hand, for Mott-Hubbard insulators, the energy difference between the $3d$ and the ligand p orbitals is large while the Coulomb attraction energy between a ligand p electron and a $3d$ hole is small. Hence at the moment of photoionization, the ligand p electrons are hardly transferred to the nickel $3d$ orbital. The charge-transfer peak ($d^9 + d^{10}$ for Ni^{2+}) in XPS is always stronger than the peak which reflects the ground-state valence electron configuration (d^8 for Ni^{2+}). Therefore the calculated x-ray emission spectra of late transition-metal compounds should be completely reanalyzed on the basis of the charge-transfer effect.

The shakeoff process at the moment of $1s$ photoionization of a free ion usually leaves one additional hole in the outermost orbitals with a probability of 20%–40% for a single ionization event. Therefore, for the divalent nickel compounds, the states expected after the $1s$ photoionization are $|1s3d^8\rangle$ (single ionization) and $|1s3d^7\rangle$ (shakeoff of one of the $3d$ electrons). However, the shakeoff hole in the $3d$ orbital is easily transferred to one of the ligand orbitals due to the charge-transfer effect described above. Thus shakeoff satellites become weak for the charge-transfer semiconductors.

In summary, the line shapes of the x-ray fluorescence spectra of Ni $K\beta$ for NiF_2 and NiO have been successfully interpreted by the charge-transfer effect at the moment of $1s$ photoionization. The three peaks in the experimental spectra (A , B , and C in Fig. 1) do not originate from the exchange interaction among one $3p$ hole and two $3d$ holes, but are mostly due to the exchange interaction between one $3p$ hole (the x-ray hole in the final state) and one $3d$ hole (the other $3d$ hole is filled by an electron transferred from one of the ligand ions). The x-ray fluorescence spectra of late transition-metal compounds cannot be interpreted by a simple multiplet

theory, but should be interpreted by the charge-transfer effect at the creation of a core hole. The degree of charge transfer reflects the electronic structure of the compounds through the mixing ratio of the configuration interaction. Consequently, the line shape of the x-ray fluorescence spectra is a source of information of the electronic structure of the compounds. The $K\beta$ spectra of NiCl_2 , NiBr_2 , and NiI_2 are also predicted from the charge-transfer effect.

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²⁶The spectrum of a free ion in Fig. 2(a), which is folded with a Lorentzian function, is similar to that calculated by Asada, Satoko, and Sugano for $10Dq=0$ (Fig. 1a of Ref. 6). NiF_2 and NiO are coordinated by six ligand ions with O_h symmetry with similar weak ligand-field splittings ($10Dq \approx 0.9$ eV). From the DV- $X\alpha$ calculations, $10Dq$ is only slightly (30%) increased after the creation of a core hole, because the charge transferred from the ligand ions screens the core-hole potential. Therefore, the ligand field used by Asada, Satoko, and Sugano (2 eV; Ref. 6) was too strong. Consequently, we believe it is enough to calculate the free-ion spectrum for the interpretation of the $K\beta$ line shapes of ionic nickel compounds such as NiF_2 and NiO .
²⁷The mixing ratio is approximately the same between $1s$ and $2p$ hole states, but may be slightly different between $2p$ and $3p$ hole states.
²⁸For NiCl_2 , NiBr_2 , and NiI_2 , since the covalency increases in this order, the effects associated with ligand fields will be largest for NiI_2 . This may be a source of difference between the prediction and the experiment.
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