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Auger decay of quasiparticle states: Calculation of the Ni $3p$ photoemission spectrum in $NiCl_2$

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We have calculated the Ni $3p$ x-ray photoemission spectrum (XPS) in $NiCl_2$, taking into account the lifetime of Ni $3p$ hole states due to the $M_{2,3}M_{4,5}M_{4,5}$ super-Coster-Kronig decay process. We show that the LS-term dependence of the lifetimes strongly affects the whole spectral shape because the multiplet splitting of the $3p$ XPS is large. This indicates a breakdown of the assumption that the lifetimes of final states are the same, which has been widely adopted in the analysis of core-level excitation spectra.

In general, quasiparticle states in solids and atoms have their characteristic lifetimes due to Coulomb interaction with other quasiparticles. In atomic systems, the decay process is called Auger decay.[1] For example, the lifetime of atomic Zn $\underline{3p}3d^{10}$ states is due mainly to the Coulomb interaction with $3d^8\varepsilon f$ states, where $\underline{3p}$ denotes a $3p$ hole and εf denotes a continuum state with f symmetry, and, consequently, it was derived that the difference in the lifetime for the $\underline{3p}_{3/2}3d^{10}$ and $\underline{3p}_{1/2}3d^{10}$ final state is very small.[2] In general, when the outer shells are fully occupied in the ground state as in the rare gases, and the kinetic energy of the Auger electron is far above the vacuum level, the lifetimes of the shallow core-hole states separated by the spin-orbit splitting do not differ so much from each other.[3,4] However, the situation can be much different when the relevant outer shells are incompletely filled. In the following, we can show that the lifetime strongly depends on the multiplet terms in the $3p$ x-ray photoemission spectrum (XPS) for transition-metal (TM) systems (both ions and solids) with unfilled $3d$ orbitals. Since the Slater integrals between $3p$ and $3d$ orbitals are so large that the multiplet splitting of Ni $\underline{3p}3d^8$ states extends over 20 eV, for example, the observation of multiplet-term dependence of the lifetime can be expected. Moreover, in solids, the solid-state hybridization can affect the spectral shape of the $3p$ XPS. In this paper, we start with the Ni $3p$ XPS in a free Ni^{2+} ion in order to show the role of the term-dependent lifetime. Afterward, we calculate the Ni $3p$ XPS in $NiCl_2$, showing the charge-transfer (CT) effects due to the hybridization between Ni $3d$ and Cl $3p$ orbitals as well.

We calculate the Ni $3p$ XPS in $NiCl_2$ in terms of a $NiCl_6$ cluster model. The applicability of such cluster models has recently been established very well for the analysis of the $2p$ XPS of late TM compounds.[5-15] Since CT is allowed between Ni $3d$ states and ligand $3p$ orbitals, the ground state can be described by a linear combination of $3d^8$, $3d^9\underline{L}$, and $3d^{10}\underline{L}^2$ electron configurations, where $\underline{L}$ denotes a ligand hole and $3d^8$ denotes the state in which the Ni ion has the $3d^8$ configuration and the ligand orbitals are full. The basis wave functions for the final states are obtained by annihilating a $3p$ electron in these configurations. We denote the CT energy from the ligand state to the $3d$ levels as Δ. In the limit of the hybridization strength between the Ni $3d$ and Cl $3p$ orbitals $V \rightarrow 0$, the energy differences between those electron configurations are given as $E[d^9\underline{L}]-E[d^8]=\Delta$ and $E[d^{10}\underline{L}^2]-E[d^9\underline{L}]=\Delta+U_{dd}$, where $E[d^{10}\underline{L}^2]$, $E[d^9\underline{L}]$, and $E[d^8]$ represent the configuration-averaged energies of $3d^{10}\underline{L}^2$, $3d^9\underline{L}$, and $3d^8$, respectively, and U_{dd} is the correlation energy between $3d$ electrons. When a core hole is created, the energy differences are obtained by replacing Δ with $\Delta_f \equiv \Delta - U_{dc}(3p)$ in these expressions, where $U_{dc}(3p)$ is the core-hole potential acting on $3d$ electrons. In the present analysis, $U_{dc}(3p)$ is the parameter to be determined, since we estimated that $\Delta=1.3$ eV, $U_{dd}=7.3$ eV, and $V=1.7$ eV from the analysis of the Ni $2p$ XPS and $3s$ XPS.[13] Although the estimated values for Δ, U_{dd}, and V can depend somewhat on the analyses,[6,13] those minor differences do not affect the following results. For simplicity, we also neglect the difference in hybridization strength for $3d(e_g)$ and $3d(t_{2g})$ orbitals.

In the sudden approximation, the photoemission intensity is given by

$$I_{\mathrm{XPS}}(E_B)=\sum_f |\langle f|a_{\mathrm{core}}|g\rangle|^2 \frac{\Gamma_f/\pi}{(E_B-E_f+E_g)^2+\Gamma_f^2}, \quad (1)$$

where E_B is the binding energy, and the ground and final states are described by $|g\rangle$ and $|f\rangle$ (with energies E_g and E_f, respectively). a_{core} is the annihilation operator of a core electron. The symmetry of the ground state is $^3F_4$. The expression for Γ_f is given by

$$\Gamma_f = \pi \sum_A \left| \left\langle A \left| \frac{1}{r} \right| f \right\rangle \right|^2 \delta(E_A - E_f) \ , \tag{2}$$

where $|A\rangle$'s denote the states accessible by the Auger transition. In the present calculation, we take into account the process $3\underline{p}3d^n\underline{L}^{n-8} \rightarrow 3d^{n-2}\underline{L}^{n-8}\varepsilon\nu$ with $n=8,9,10$. We note that the Auger electron state ($\varepsilon\nu$) is free-electron-like since its kinetic energy is about 80 eV, corresponding to the binding energies of the $3p$ core levels. Although ν can be p, f, and h in the present case, the decay process to εf is so dominant that the others can be safely negelected. The Hamiltonian matrix elements, as well as the wave functions for the continuum states, are calculated by Cowan's[16] computer programs. The Slater integrals are scaled down to 80% of the Hartree-Fock values.

First we show the experimental Ni $3p$ XPS for $NiCl_2$ in Fig. 1,[17] where we find that the spectrum extends over 20 eV. The spectrum consists of four parts: The first peak at E_B (relative binding energy) $= -8$ eV, the second peak at $E_B = -3$ eV, the third structure at $E_b = 0 \sim 5$ eV, and the fourth peak at $E_B = 13$ eV. This large extension in energy is due primarily to the large Slater integrals between $3p$ and $3d$ electrons.

We show the results for the free Ni^{2+} ion in Figs. 2(a), 3(a), and 3(b). The continuous spectrum in Fig. 2(a) is obtained by convoluting the line spectrum in Fig. 2(a) with a Lorentzian function of a constant width $\Gamma = 1.0$ eV [half width at half maximum (HWHM)], while that in Fig. 3(a) is obtained taking into account the *LS*-term dependence of the lifetime (Γ^{-1}) which is shown in Fig. 3(b). In Fig. 2(a), the second and third structures are fairly conspicuous. In Fig. 3(a), on the other hand, we can see that the spectra except for the first peak are much broadened due to the term dependence of the lifetime shown in Fig. 3(b), where the lifetime of the first structure is several times longer than those of the other structures. Therefore the *LS*-term dependence of the lifetime is large enough to affect the spectral shape of $3p$ XPS.

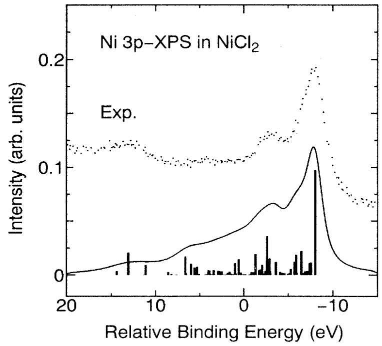

FIG. 1. Experimental and theoretical Ni $3p$ XPS in $NiCl_2$. The experimental data (dots) are taken from Ref. 17. The theoretical spectrum (solid curve) is obtained by convoluting the line spectrum with Lorentzian and Gaussian functions, where the multiplet-term dependence of the lifetime shown in Fig. 5(b) is taken into account. The instrumental resolution is taken to 0.5 eV (HWHM).

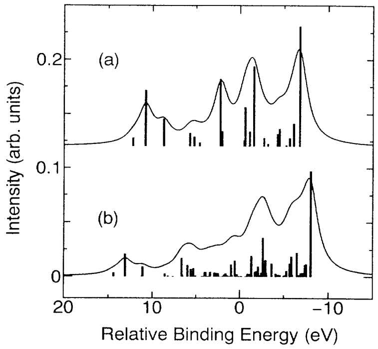

FIG. 2. Theoretical Ni $3p$ XPS with constant lifetime for free Ni^{2+} ion [Fig. 2(a)] and $NiCl_2$ [Fig. 2(b)]. The continuous spectra are convoluted from the line spectra with a Lorentzian function of width 1.0 eV (HWHM). For (b), the CT energy ($\Delta = 1.3$ eV), the correlation energy ($U_{dd} = 7.3$ eV), the hybridization strength ($V = 1.7$ eV), and the core-hole potential energy ($U_{dc} = 5.5$ eV) are used.

We find that the atomic calculation shown in Figs. 2(a) and 3(a) roughly reproduces the energy extension of the experimental spectrum for $NiCl_2$, though the spectral shapes do not reproduce the experiment very well. This point can be improved by taking into account the solid-state hybridization effects and the effect of the core-hole potential (U_{dc}).[11] In Fig. 4, we show the U_{dc} dependence of Ni $3p$ XPS with fixed values of Δ, U_{dd}, and V. We can see that the spectral shape and the intensity of the first peak change considerably. In the case of $U_{dc} = 3.5$ eV, the second peak seen in the experiment splits into two peaks. In the case of $U_{dc} = 7.5$ eV, the second peak is fairly sharp and strong. With increasing U_{dc}, the $3\underline{p}3d^9\underline{L}$ final state becomes lower than the $3\underline{p}3d^8$. In the cases of $U_{dc} = 5.5$ and 7.5 eV, the energy of the $3\underline{p}3d^9\underline{L}$ final state is apparently lower than the $3\underline{p}3d^8$, so that the character of the first peak is mainly the $3\underline{p}3d^9\underline{L}$ and that of the

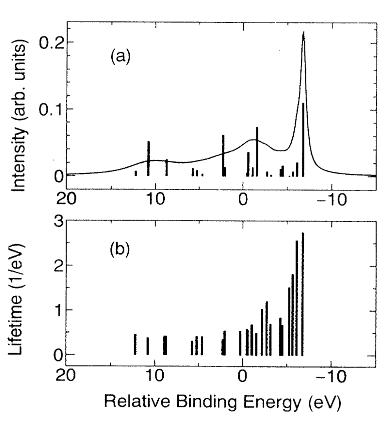

FIG. 3. Theoretical Ni $3p$ XPS for a free Ni^{2+} and the lifetime of each multiplet term. The solid curve in (a) is convoluted from the line spectrum, taking into account the *LS*-term dependence of the lifetime (Γ^{-1}) shown in (b).

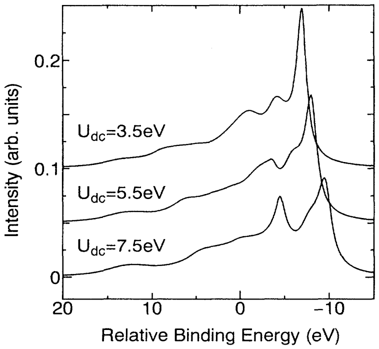

FIG. 4. U_{dc} dependence of Ni $3p$ XPS. The other parameter values are the same as those in Fig. 2(b).

second one is the main peak in the free ion.

We show the spectrum for $U_{dc} = 5.5$ eV in Fig. 5(a) together with the term dependence of the lifetime in Fig. 5(b). Comparing Fig. 3(b) with Fig. 5(b), the lifetime for the main peak in the free ion is longer than that in $NiCl_2$. This is due to the hybridization effect of $\underline{3p}3d^9\underline{L}$ states whose lifetimes are shorter than those for $\underline{3p}3d^8$ in general. With increasing U_{dc}, as can be seen in Fig. 4, the lifetime for the main peak becomes short and that for the first satellite becomes long, reflecting the $\underline{3p}3d^8$ character in each peak. For comparison, we show in Fig. 2(b) the continuous spectrum calculated with a constant Γ and with $U_{dc} = 5.5$ eV. When we compare Fig. 2(b) with Fig. 5(a), we can see the importance of the term dependence of Γ.

Among the three cases shown in Fig. 4, the case of $U_{dc} = 5.5$ eV reproduces the experimental spectrum best. Moreover, taking into account the instrumental resolution of 0.5 eV (HWHM), we get the solid curve in Fig. 1. The value of $U_{dc}(3p) = 5.5$ eV is somewhat smaller than $U_{dc}(2p) = 7.5$ eV and $U_{dc}(3s) = 6.5$ eV,[13] which reflects the larger radial extension of the $3p$ wave functions. It is also reasonable that $U_{dc}(3p)$ (= 5.5 eV) for $NiCl_2$ is smaller than that for $CuCl_2$ (= 6.4 eV),[18] since $U_{dc}(2p)$ also decreases on going from Cu to Ni dihalides[9,13] because the Cu ions are more contracted.

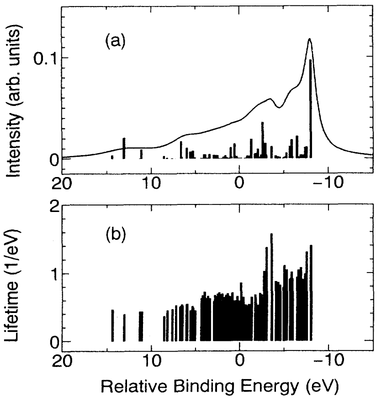

FIG. 5. Theoretical Ni $3p$ XPS and the lifetime of each multiplet term. The parameter values are the same as those in Fig. 2(b). The solid curve in (a) is convoluted from the line spectrum, using the LS-term dependence of the lifetime (Γ^{-1}) shown in (b).

The reason why the term-dependent Γ is so important for TM $3p$ XPS is the following: In the case of shallow core-level excitations, in general, the Slater integrals are larger than the spin-orbit splitting of core-hole states so that the LS scheme approximately describes the eigenstates of the systems. Since the Auger decay is due to the Coulomb interaction, there is no Auger matrix element between different LS eigenstates, giving strict selection rules for the Auger decay process. As a result, we get the significant LS-term dependence of the lifetime; in other words, the final-state dependence of the lifetime in the Ni $3p$ XPS. In the case of TM $2p$ XPS, on the other hand, the term dependence of the lifetime is averaged out because the large spin-orbit interaction of the $2p$ core mixes the LS states. Moreover, decay processes other than the Coster-Kronig decay ($\underline{2p}3d^8 \rightarrow 3d^6\varepsilon f$) can contribute to the core-hole lifetime, so that the energy dependence of Γ is much weakened.

Concerning the final-state-dependent Γ, we would like to suggest a link between the present $3p$ XPS and valence-band photoemission spectra. It is well known that there are so-called correlation satellites about 6–7 eV higher than the main peak in the valence-band photoemission spectra of various Ni compounds[19–25] and Ni metal.[26] In NiO, Fujimori and Minami[27] ascribed it to the $3d^7$ final states and used the energy-dependent lifetime in their spectral calculation. We would like to suggest that the lifetime of these final states can be determined by an interatomic Auger decay process by analogy to the present $3p$ XPS. In this case, one of two ligand electrons occupies a $3d$ hole in the final state and the other is scattered into the conduction band. This process would give an appreciable contribution to the lifetime of the correlation satellites and would introduce an energy-dependent lifetime. This kind of analogy may be extended further to a lower excitation region. In metals, for example, it is well known that Γ is scaled proportionally to the square of the energy in the vicinity of the Fermi energy according to the Fermi-liquid theory.[28] Although the energy dependence of Γ is not quadratic in the case of $3p$ XPS, the Fermi-liquid theory and the present case have some analogies in the sense that the decay of quasiparticles is due to Coulomb interaction, and moreover in the sense that the selection rules for decay processes determine the lifetime of quasiparticle states.

In summary, we have calculated the Ni $3p$ XPS in a free Ni^{2+} ion and that in $NiCl_2$. The LS-term dependence of the lifetimes significantly affects the spectral shape. The assumption that the lifetimes of final states are the same, which has been widely adopted in the analysis of core-level excitation spectra, evidently breaks down in the case of Ni $3p$ XPS. In the case of $NiCl_2$, the final-state effects due to the core-hole potential (U_{dc}) and the solid-state hybridization (V) are important for Ni $3p$ XPS just as in Ni $2p$ XPS and Ni $3s$ XPS. Although the term dependence of Γ in $NiCl_2$ is obscured to some extent by the hybridization effect, it is still important in discussing the spectral shape.

The term dependence of Γ shown in this paper has also been calculated for the 4d XPS in rare-earth metals by the present authors,[29] and will be published elsewhere. Therefore the term dependence of Γ is general, at least for shallow core-level excitation spectra in strongly correlated systems. Although the average value of Γ has been calculated often by many authors, for example for TM 3p shells,[30,31] the present result evidently demonstrates the importance of the term dependence of Γ.

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