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Resonant photoemission at the Ni 2*p* core level as a probe of electron correlation effects in nickel

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The observed enhancement in the 3*d*, 3*p*, and 3*s* photoemission structures at resonance with the 2*p* absorption edge of nickel is analyzed using a cluster calculation including multiplet structure. The result strongly supports the view of a localized electronic structure for nickel metal. It is found that the peak splitting in the 3*s* photoemission is due to *d* mixing, whereas the 3*p* photoemission shows the influence of both *d* mixing and electrostatic interaction.

I. INTRODUCTION

The satellite structure in the core-level and valence-band photoemission spectra of nickel has been the subject of intensive studies.¹⁻¹⁶ These structures, which originate from the narrow-band properties of the 3*d* metal, emphasize the importance of electron correlation effects. The satellite at 6 eV below the Fermi level in the valence-band photoemission of nickel is due to a localized two-hole state, which is split from the one-hole band by the large on-site Coulomb interaction in the final state.⁷ The satellite intensity is low, but increases in resonant photoemission by the super-Coster-Kronig decay after the photoabsorption of a core electron at an absorption edge.^{2-4,9,16} At the 3*p* absorption resonance the two-hole final state is enhanced due to a decay $3d^9 \rightarrow 3p^5 3d^{10} \rightarrow 3d^8 k$ (*k* denotes a photoelectron), whereas the one-hole final state shows no enhancement. Unfortunately, the analysis of the resonant spectrum is hampered by the large interference term between the 3*p* deexcitation and the 3*d* photoemission, which are of comparable magnitude.¹⁷ Recently, Tjeng *et al.*¹⁸ observed a giant enhancement of the valence-band photoemission in CuO at resonance with the Cu 2*p* absorption edge. At such a deep edge, the ratio of the cross section for the resonant to direct photoemission is considerably larger than at the 3*p* absorption edge. The interference term is

then negligible, and a straightforward interpretation of the resonant spectrum is possible.

In this paper we use the 2*p* core-level resonance decay to study the 3*s* and 3*p* photoemission. Although the nature of the satellite structure of the valence-band photoemission is well established, the peak splitting in the 3*s* photoemission of 3*d* transition-metal compounds and alloys has not been assigned unambiguously. The splitting has been ascribed to both *d* mixing and exchange interaction. Van Acker *et al.* have studied a large number of iron compounds, but found no simple relation between the magnetic moment of the iron and the 3*s* peak splitting and intensity ratio.¹⁹ In this paper, we analyze the 3*d*, 3*s*, and 3*p* direct and resonant photoemission spectra of nickel metal by comparing experimental results with a cluster calculation including multiplet structure. The resonance enhancement allows us to give clear assignments of the peak structures in the photoemission spectra.

II. EXPERIMENTAL RESULTS

The experiments were performed on a Ni(110) single crystal which was cleaned by repeated cycles of Ar sputtering and annealing. A variable photon energy with a resolution of 1.5 eV was obtained using the spherical grating monochromator of beamline 1.1 at the Synchro-

ron Radiation Source (SRS) in Daresbury.²⁰ The photoelectrons were collected by a hemispherical analyzer with multichannel detection. The intensity was corrected for variations in the incident flux.

Figure 1(b) shows the direct photoemission of the 3d, 3p, and 3s levels at a photon energy of 6 eV below the Ni 2p_{3/2} absorption edge. These x-ray photoemission spectra (XPS) agree with earlier measurements.¹ The high photon energy results in a low intensity, but we only need the position of the direct photoemission contribution in the resonance spectrum. Figure 1(a) shows the resonant photoemission at 852 eV, which is the maximum of the Ni 2p_{3/2} absorption edge. The strong increase of the 3d, 3p, and 3s photoemission is due to the 2p3d3d ($L_3M_{45}M_{45}$), 2p3p3d ($L_3M_{23}M_{45}$), and 2p3s3d ($L_3M_1M_{45}$) decay, respectively, where, e.g., 2p3d3d means that the 2p hole created by the original absorption is filled by a 3d electron while another 3d electron escapes. The structure around 140 eV is due to the 2p3p3p ($L_3M_{23}M_{23}$) decay.

III. CALCULATIONAL DETAILS

The electronic structure of nickel can be described as a mixture of several 3d configurations. The hybridization in the initial, intermediate, and final state is calculated using a cluster model,^{21,22} where the Hamiltonian H_0 is

$$H_{\text{local}} = \sum_{\nu} E_{d\nu} d_{\nu}^{\dagger} d_{\nu} + \sum_{\nu} E_{c\nu} c_{\nu}^{\dagger} c_{\nu} + \xi_d \sum_{\nu_1 \nu_2} \langle \nu_1 | 1 \cdot s | \nu_2 \rangle d_{\nu_1}^{\dagger} d_{\nu_2} + \xi_c \sum_{\nu_1 \nu_2} \langle \nu_1 | 1 \cdot s | \nu_2 \rangle c_{\nu_1}^{\dagger} c_{\nu_2} \\ + \sum_{\nu_1 \nu_2 \nu_3 \nu_4} \langle \nu_1 \nu_2 | Q_{cd} | \nu_3 \nu_4 \rangle d_{\nu_1}^{\dagger} d_{\nu_2} c_{\nu_3}^{\dagger} c_{\nu_4} + \sum_{\nu_1 \nu_2 \nu_3 \nu_4} \langle \nu_1 \nu_2 | U_{dd} | \nu_3 \nu_4 \rangle d_{\nu_1}^{\dagger} d_{\nu_2} d_{\nu_3}^{\dagger} d_{\nu_4}, \quad (2)$$

$$H_{\text{bulk}} = \sum_{\nu} E_L L_{\nu}^{\dagger} L_{\nu}, \quad (3)$$

$$H_{\text{mix}} = \sum_{\nu} V_{\nu} (d_{\nu}^{\dagger} L_{\nu} + L_{\nu}^{\dagger} d_{\nu}), \quad (4)$$

$$H_{\text{mol. field}} = -g\mu_B H \sum_{\nu} \langle \nu | S_z | \nu \rangle (d_{\nu}^{\dagger} d_{\nu} + L_{\nu}^{\dagger} L_{\nu}), \quad (5)$$

$$H_{\text{pes}} = E_k k^{\dagger} k, \quad (6)$$

where $d^{\dagger}$, $c^{\dagger}$, $L^{\dagger}$, and $k^{\dagger}$ are the creation operators for a valence, core, bulk, and continuum hole with energy E_d , E_c , E_L , and E_k , respectively. The index ν labels all orbital and spin quantum numbers. The Hamiltonian H_{local} describes the localized states, which are split by spin-orbit interactions $1 \cdot s$ with parameters ξ_d and ξ_c , and electrostatic interactions with matrix elements Q_{cd} given by the Slater integrals F^0 , F^2 , G^1 , and G^3 , and U_{dd} given by the Slater integrals F^0 , F^2 , and F^4 . The Hartree-Fock values for the Slater integrals and spin-orbit constants, which were obtained from Cowan's code,²³ are given in Table I. In the cluster calculations the Slater integrals were reduced to 80% to include intra-atomic correlation effects.²⁴ The Hamiltonian H_{bulk} describes the states formed by a combination of appropriate symmetry of orbitals on the adjacent sites, which are hybridized with the

FIG. 1. Measured 3d, 3p, and 3s photoemission of nickel metal (a) at $h\nu = 846$ eV; (b) in resonance with the Ni 2p_{3/2} absorption edge at $h\nu = 852$ eV. The strong increase of the 3d, 3p, and 3s photoemission is due to the 2p3d3d ($L_3M_{45}M_{45}$), 2p3p3d ($L_3M_{23}M_{45}$), and 2p3s3d ($L_3M_1M_{45}$) decay, respectively, where, e.g., 2p3d3d means that the 2p hole created by the original absorption is filled by a 3d electron while another 3d electron escapes. The structure around 140 eV is due to the 2p3p3p ($L_3M_{23}M_{23}$) decay.

written as

$$H_0 = H_{\text{local}} + H_{\text{bulk}} + H_{\text{mix}} + H_{\text{mol. field}} + H_{\text{pes}}, \quad (1)$$

where

d states on the central site. This hybridization is described by H_{mix} . In the cubic symmetry of the face-centered-cubic metal the transfer or mixing integral is given by the parameters $V(e)$ and $V(t_2)$.²⁵ The Hamiltonian $H_{\text{mol. field}}$ describes the molecular field, which can be treated as a magnetic field acting on the spin only. The Hamiltonian H_{pes} describes the photoemission state.

The initial state i_{ν} is given as

$$|i_{\nu}\rangle = \alpha_{\nu} |3d^8(\nu)\rangle + \beta_{\nu} |3d^9\bar{L}(\nu)\rangle + \gamma_{\nu} |3d^{10}\bar{L}^2(\nu)\rangle. \quad (7)$$

The configurations $3d^8$, $3d^9\bar{L}$, and $d^{10}\bar{L}^2$ have average energies 0, $\Delta - U$, and $2\Delta - U$, respectively, where $\Delta = E_d - E_L$ is the transfer energy, and U is the effective $F^0(d, d)$ Coulomb interaction. The ground state has an

TABLE I. Hartree-Fock values (eV) of the Slater and spin-orbit parameters for the initial, excited, and final state in the Ni 2*p* resonant photoemission process, obtained by Cowan's code (Ref. 23).

Configuration	F^2	F^4	$\zeta(p)$	$\zeta(3d)$	F^2	G^1	G^2	G^3
Ni 3 <i>d</i> ⁷	13.278	8.294		0.091				
Ni 3 <i>d</i> ⁸	12.234	7.597		0.083				
Ni 3 <i>d</i> ⁹				0.074				
Ni 2 <i>p</i> ⁵ 3 <i>d</i> ⁹			11.507	0.102	7.721	5.787		3.291
Ni 2 <i>p</i> ⁵ 3 <i>d</i> ¹⁰			11.509					
Ni 3 <i>p</i> ⁵ 3 <i>d</i> ⁸	13.317	8.319	1.397	0.092	14.333	17.717		10.798
Ni 3 <i>p</i> ⁵ 3 <i>d</i> ⁹			1.366	0.084	13.633	16.900		10.277
Ni 3 <i>p</i> ⁵ 3 <i>d</i> ¹⁰			1.345					
Ni 3 <i>p</i> ⁴ 3 <i>d</i> ⁹	16.136		1.408	0.093	14.372	17.750		10.824
Ni 3 <i>p</i> ⁴ 3 <i>d</i> ¹⁰	15.910		1.378					
Ni 3 <i>s</i> ¹ 3 <i>d</i> ⁸	13.387	8.364		0.093			13.562	
Ni 3 <i>s</i> ¹ 3 <i>d</i> ⁹				0.085			12.880	

energy E_g . The final-state configurations d^7k , $d^8\bar{L}k$, and $d^9\bar{L}^2k$ of the valence-band photoemission have energies 0, $\Delta - 2U$, and $2\Delta - 3U$, respectively. The final-state configurations cd^8k , $cd^9\bar{L}k$, and $cd^{10}\bar{L}^2k$ of the core-level photoemission have energies 0, $\Delta - U - Q$, and $2\Delta - U - 2Q$, respectively, where Q is the effective $F^0(p, d)$ Coulomb interaction.²⁶

The direct photoemission intensity is determined by the fractional parentage of the ground state to the final states. The photoabsorption decay is governed by the Auger matrix elements. By exciting an electron from a 2*p* core level into the 3*d* valence band, the resonance process creates the excited states $2p^53d^{10}\bar{L}$ and $2p^53d^9$ with an energy separation of $\Delta - Q$. The $2p^53d^{10}\bar{L}$ excited state decays by Auger transitions to the *two-hole* final states $d^8\bar{L}k$, $3p^5d^9\bar{L}k$, $3s^1d^9\bar{L}k$, and $3p^4d^{10}\bar{L}k$. The $2p^53d^9$ excited state decays to the *three-hole* final states d^7k , $3p^5d^8k$, $3s^1d^8k$, and $3p^4d^9k$. These two- and three-hole configurations are the final states of the 3*d*, 3*p*, and 3*s* photoemission and the configuration interaction satellite of the 3*s* photoemission, respectively. The *one-hole* final states $d^9\bar{L}^2k$, $3p^5d^{10}\bar{L}^2k$, and $3s^1d^{10}\bar{L}^2k$ are only ac-

cessible by direct photoemission. Thus, the core-hole decay spectrum displays a resonance enhancement of the two- and three-hole states, but not of the one-hole final states.

The spectra were calculated by taking into account radiative transitions to first order and Auger transitions to infinite order, as has been described in detail in Ref. 27. The direct photoemission has dipole matrix elements $\langle l||r||k \rangle$ with $k = l \pm 1$. The $l_1l_2l_3$ decay has Auger matrix elements $R(l_1, l_2; l_3, k)$ with $k = 0, 2, \dots, k_n$ for k_n even, and $k = 1, 3, \dots, k_n$ for k_n odd, where $k_n = l_1 + l_2 + l_3$. The Hartree-Fock values for the dipole transitions and Auger matrix elements, which were obtained from Cowan's code,²³ are given in Table II. The decay rate is proportional to the square of the Auger matrix elements.

The valence-band photoemission was calculated using the parameters $\Delta = -0.75$, $U(3d, 3d) = 1.50$, $Q(2p, 3d) = 2.5$, $V(e) = 1.6$, $V(t_2) = 0.8$, $g\mu_B H = -0.5$ eV, which produced a ground state with 16% d^8 , 49% d^9 , and 35% d^{10} character. The Fermi level was taken at the binding energy of the lowest photoemission state.

TABLE II. Hartree-Fock values of the dipole and Auger matrix elements for the Ni 2*p* resonant photoemission, obtained by Cowan's code (Ref. 23).

Transition	Reduced-matrix element
2 <i>p</i> → 3 <i>d</i>	$\langle 2p r 3d \rangle = -0.177\,23$ a.u.
2 <i>p</i> 3 <i>d</i> 3 <i>d</i> decay	$\langle 3d r \epsilon_p \rangle = 0.000\,621$ a.u./eV ^{1/2} $\langle 3d r \epsilon_f \rangle = -0.003\,525$ a.u./eV ^{1/2} $R^{1,3}(2p, 3d; 3d, \epsilon_p) = -0.053\,04, -0.043\,41$ eV ^{1/2} $R^{1,3}(2p, 3d; 3d, \epsilon_f) = 0.191\,25, 0.117\,49$ eV ^{1/2} $R^3(2p, 3d; 3d, \epsilon_h) = 0.060\,71$ eV ^{1/2}
2 <i>p</i> 3 <i>p</i> 3 <i>d</i> decay	$\langle 3p r \epsilon_s \rangle = 0.001\,494$ a.u./eV ^{1/2} $\langle 3p r \epsilon_d \rangle = -0.005\,667$ a.u./eV ^{1/2} $R_{d,e}^1(2p, 3p; 3d, \epsilon_s) = -0.030\,59, -0.075\,87$ eV ^{1/2} $R_{d,e}^1(2p, 3p; 3d, \epsilon_d) = 0.047\,75, 0.037\,31, 0.087\,83, 0.033\,03$ eV ^{1/2} $R_{d,e}^1(2p, 3p; 3d, \epsilon_g) = -0.86\,80, -0.102\,64$ eV ^{1/2}
2 <i>p</i> 3 <i>s</i> 3 <i>d</i> decay	$\langle 3s r \epsilon_p \rangle = -0.003\,251$ a.u./eV ^{1/2} $R_{d,e}^1(2p, 3s; 3d, \epsilon_p) = -0.001\,437, -0.048\,67$ eV ^{1/2} $R_{d,e}^1(2p, 3s; 3d, \epsilon_f) = 0.030\,88, 0.103\,37$ eV ^{1/2}
2 <i>p</i> 3 <i>p</i> 3 <i>p</i> decay	$R^{0,2}(2p, 3p; 3p, \epsilon_p) = 0.072\,26, 0.039\,07$ eV ^{1/2} $R^2(2p, 3p; 3p, \epsilon_f) = 0.096\,29$ eV ^{1/2} $R^1(3p, 3p; 3s, 3d) = 19.3468$ eV

For the 3p and 3s photoemission calculations we had to reduce the calculation by using spherical symmetry with $V=1.8$ eV and $g\mu_B H=0$, resulting in somewhat different weights of 14% d^8 , 48% d^9 , and 38% d^{10} .²⁸ The value of $Q(3p,3d)$ and $Q(3s,3d)$ used in XPS was 4.5 eV, which is 2 eV larger than in x-ray-absorption spectroscopy (XAS), to account for the increased effective nuclear charge after electron emission.²⁹

The core-hole lifetime and apparatus broadening were included by a convolution of the calculated line spectra with a Lorentzian of $\Gamma=1.5$ eV and a Gaussian of $\sigma=1$ eV.

IV. RESULTS AND DISCUSSION

The calculation of the 2p absorption spectrum has been reported earlier.^{29,30} The spectrum is split by core-hole spin-orbit interaction into a $2p_{3/2}$ and $2p_{1/2}$ peak with an energy separation of 17.3 eV. Both peaks have a small satellite structure at 4–6-eV higher energy.³¹ The main peaks have predominantly $2p^5 3d^{10} \bar{L}$ character, whereas the satellite structures have mainly $2p^5 3d^9$ character. We will present only the decay from the main $2p_{3/2}$ peak, because the $2p_{1/2}$ core hole decays dominantly by a Coster-Kronig transition $2p_{1/2} 2p_{3/2} 3d$, and for the satellites the intensity is low. The direct and resonant photoemission spectrum are shown in Figs. 2 and 3, respectively, where the calculations have been compared with the experimental results from Fig. 1. The $2p_{3/2} d^{10} \bar{L}$ decay gives 38% 3d photoemission, 30% 3p photoemission, 2% 3s photoemission, and 28% goes into the $2p 3p 3p$ decay. The remaining 2% goes into the $2p 3s 3s$ and $2p 3s 3p$ decay. We will discuss the various levels separately.

A. Valence band

The direct photoemission (Fig. 2) of the valence band shows a main peak with predominantly $3d^9$ character (from here on, we omit $\bar{L}$ and k in the notation). At 6 eV below the Fermi level is the two-hole satellite, which is visible as a small shoulder. In the resonance spectrum (Fig. 3) the final states with two or more d holes are enhanced. The largest increase is in the 6-eV satellite, which is broadened by the d - d Coulomb interactions. To a lesser extent the main peak is also enhanced by the presence of a small amount of d^8 character. The intensity of the $3d^7$ final state at ~ 15 eV is small due to the low amount of $2p^5 3d^9$ character in the excited state and the interference with the two-hole final state.

B. 3p photoemission

The 3p direct photoemission spectrum (Fig. 2) shows a $3p^5 d^{10}$ main peak with a maximum at 67.3 eV, and a high-energy tail which corresponds to the $3p^5 d^9$ state. The latter state is split by the 3p-3d electrostatic interaction into three more or less distinct structures, viz. $^1D+^3F$, which is hidden under the main peak, $^3P+^3D$, and $^1F+^1P$. In the resonance spectrum (Fig. 3) the $^3P+^3D$ and $^1F+^1P$ structures are strongly enhanced. The intensity increase of the main line is due to a small amount of $3p^5 d^9$ character. The weak structure at 90 eV

FIG. 2. Photoemission of nickel metal at $h\nu=846$ eV (a) experimental results; (b) calculational results from a cluster model, where the ground state has d weights of 14% d^8 , 48% d^9 , and 38% d^{10} .

is due to the $3p^5 d^8$ final state.

Although the calculation correctly predicts the satellite structure of the 3p photoemission, the separation between the main and satellite peak is 3.5 eV larger than in the experiment. The same effect occurs in the valence-band spectrum if the molecular field is reduced to zero. A calculation which includes the magnetic exchange interaction might also give an improvement in the 3p photoemission, but is too large for the moment.

C. 3s photoemission

The 3s photoemission calculation has to include the configuration interaction with the $3p^4$ final states. The direct 3s photoemission spectrum (Fig. 2) shows a main peak at 111.4 eV, which has $3s^1 d^{10}$ character, and a small satellite with $3s^1 d^9$ character, which contains a 3D and a 1D state. In the resonant spectrum (Fig. 3) only the satellite is enhanced, which proves it is $3s^1 d^9$. This demonstrates that the 3s peak splitting is due to d mixing and

FIG. 3. Photoemission of nickel metal in resonance with the Ni $2p_{3/2}$ absorption edge at $h\nu=852$ eV (a) experimental results; (b) calculational result from a cluster model, where the ground state has d weights of 14% d^8 , 48% d^9 , and 38% d^{10} .

not to exchange interaction. The $3p^4d^{10}$ configuration is split by the $3p$ - $3p$ electrostatic interaction into 3P , 1D , and 1S states, where the first peak is at 134.2 eV. The $3p^4d^{10}$ state can be reached by decay from the $2p^53d^{10}$ intermediate state, as well as by intra-atomic configuration interaction with the $3s^1d^9$ final state of the $3s$ photoemission. This configuration interaction has a large matrix element [$R^1(3p, 3p; 3s, 3d)$ in Table II] which pushes the 1D peak of the $3s^1d^9$ structure toward the 3D peak and the 1D peak of the $3p^4d^{10}$ structure toward the 1S peak. This effect destroys the usefulness of the 1D - 3D splitting to determine the $3s$ - $3d$ exchange, because the original splitting of 3.8 eV is reduced by the configuration interaction such that in our case the peaks are no longer separable.^{32,33} The structure at 160 eV is the $3p^4d^9$ state.

V. CONCLUSIONS

The strong photoemission enhancements which are observed in resonance with the $2p_{3/2}$ absorption edge have

been ascribed to Auger decay from an excited state with mainly $2p^53d^{10}$ character, whereas the $2p^53d^9$ contribution gives much weaker structures at ~ 20 -eV higher binding energies. The excellent agreement between experiment and localized model calculations supports the idea of a correlated electronic structure for nickel metal. The resonant photoemission enables us to verify the assignments of the core-level structures. The resonant photoemission shows that the $3s$ splitting in nickel is due to d mixing instead of exchange interaction.

Similar effects as for nickel are expected for other $3d$ metals. Small enhancements in $3p$ resonant photoemission have been observed in all $3d$ transition-metal elements^{16,34-40} and from the magnitude of the reduced-matrix elements it can be derived that the enhancements at the $2p$ resonance will be orders of magnitude larger.²⁸ This makes it possible to study the valence and core-level structure of transition-metal compounds and alloys in extreme detail.

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