Angle-resolved photoemission determination of the band structure and multielectron excitations in Ni

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Angle-resolved photoelectron spectroscopy utilizing polarized synchrotron radiation has been used to determine the electronic energy states of Ni. The dispersion of the sp band and all of the high-symmetry points in the Ni band structure have been determined. The linewidth in the spectra from the various high-symmetry points is used to estimate the magnitude of the exchange splitting throughout the d band. The measured d-band width is 30% smaller than predicted by calculations whereas the sp-band width agrees within 10%. Several peaks in the photoelectron spectra which appear between 6 and 27 eV below the Fermi energy are shown to originate from multielectron excitations.

I. INTRODUCTION

Nickel and copper have become the prototype transition metals for testing the capabilities of angle-resolved photoelectron spectroscopy as an experimental tool capable of determining the electronic states of the surface and bulk. Much experimental and theoretical effort has been expended on the bulk band structures of ferromagnetic nickel¹⁻¹² and of copper¹³⁻¹⁹ as well as on the surface states on Ni (Refs. 20-22) and Cu.^{23, 24} The result of all this work can be easily summarized. Cu works very well. The measured band structure¹⁶ agrees with the calculations of Burdick¹⁷ within ~5% from the bottom of the s band to the Fermi energy. The surface state in the neck of Cu is calculated to be exactly where it is observed. In contrast the same type of theory and experiment applied to Ni fails drastically. The measured exchange splitting is one half of the magnitude of the calculated splitting.⁶ The width of the d band is approximately 30% smaller than the calculated width,^{6,7,10} and the observed surface states have not been satisfactorily explained theoretically. In addition the photoemission spectra of Ni show an energy level ~6 eV below the Fermi energy, which appears to be due to a multielectron excitation.^{25,26} At present it seems that all of these problems are associated specifically with Ni, since for example, the discrepancies between theory and experiment on Fe are much smaller than for Ni.27

All of the apparent discrepancies between theory and experiment on Ni warrant a detailed investigation of the energy bands of Ni. We have used offnormal angle-resolved photoelectron spectroscopy to determine the critical points in the band structures which were not accessible in the previous experiments using normal-emission collection.⁷ Normal-emission measurements at higher photon energies than used previously give the energy dispersion of the sp band down to Γ_1 . We have compiled a list of all of the critical points in the band structure for comparison with theory. The widths of the observed structures in the photoemission spectra are used to extract hole lifetimes and to give a rough estimate of the exchange splitting at points in the band structures below the Fermi energy. The analysis is based on the directtransition model, which allows us to determine the symmetry and energy position and to estimate the lifetime for the final bands in Ni.

We also have investigated the symmetry properties of the peak in the photoelectron spectra of Ni 6 eV below the Fermi energy.²⁵ This structure is incompatible with the one-electron bands of Ni, shows no dispersion, and therefore must result from a multielectron excitation.²⁶ Several other non-one-electron excitations are observed at energies of 13.4, 17.8, 22, and 27 eV below E_F .

II. EXPERIMENTAL PROCEDURE

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin using a grazing-incidence monochromator (Grasshopper²⁸), of a holographically ruled torodial grating monochromator²⁹ coupled to an angleresolved photoelectron detector.³⁰ The angular acceptance was $\pm 2.5^{\circ}$ and the total energy resolution was normally kept at 0.3 to 0.4 eV, but could be improved with subsequent loss of signal. The angle of incidence of the light θ_I is measured relative to the normal of the crystal and can be varied from 0° (s polarization) to ~90°. The crystal can be rotated about its surface normal to adjust the polarization of the incident radiation with respect to the crystal axes. $A_{\mu}[100]$ means the component of the electric field which is parallel to the surface coincides with the [100] crystal direction. The detection angles are denoted by ϕ and θ . Θ is the po-

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lar angle measured relative to the surface normal. ϕ is the azimuth angle measured relative to the plane of incidence of the light with $\phi = 0^{\circ}$ and $\theta = 180^{\circ}$ being perpendicular to the plane of incidence. $\phi = 270^{\circ}$ means the analyzer is oriented towards the incoming light beam.

The sample was a (100) Ni single crystal. It was cleaned *in situ* by Ar-ion sputtering and annealing. Special checks were made to avoid carbon, oxygen, and sulfur contamination. The crystal was oriented by medium-energy (3-keV) electron diffraction. The orientation was verified using angleresolved photoemission. In specific directions strong surface-state emission dominates the spectra near the Fermi energy.²¹ In this energy and momentum range spectra were taken with disordered NO present to destroy the surface state. We are well aware that this procedure might affect the direct interband transitions also, and therefore we crosschecked those data very carefully.

The analysis of the data is based on simple symmetry selection rules using the polarization of the incoming light.^{31,32} These rules can easily be understood from the photoemission matrix element in the dipole approximation,

$$P_{if} = \langle \psi_i | \vec{\mathbf{A}} \cdot \vec{\mathbf{P}} | \psi_i \rangle.$$

 ψ_f and ψ_i are the final- and the initial-state wave functions, \vec{A} is the vector potential of the light, and \vec{P} the momentum operator. If we always collect electrons in a mirror plane, then only even final states can contribute to the detected current, since an odd final wave function is zero in the mirror plane. The whole matrix element must be even under reflection about the mirror plane. The dipole operator $\vec{A} \cdot \vec{P}$ is even (odd) if \vec{A} is parallel (perpendicular) to the collection mirror plane. Therefore only even (odd) initial states can be observed.

We analyze our data using the direct-transition model. The momentum component parallel to the surface k_{\parallel} is conserved during the exit of the electron through the surface. The normal momentum k_{\perp} is changed during the exit since the electron has to escape from the solid. The electron energies are related by the following equations:

$$E_f = E_i + \hbar \omega , \qquad (1)$$

$$E = E_f - V_0. \tag{2}$$

 E_f and E_i are the final- and initial-state electron energies in the crystal, $\hbar \omega$ is the photon energy, and E is the kinetic energy in the vacuum. V_0 is the inner potential which we assume to be independent of the kinetic energy. The objective of the experiment is to determine the energy and momentum \vec{k} of the initial state from the energy and momentum of the emitted electron. The component of momentum parallel to the surface (k_{\parallel}) is conserved, so for a collection angle θ we have

$$k_{\mu}$$
 (inside) = \vec{k}_{μ} (outside) (3)

or

$$\left|k_{ii}\right| = \frac{1}{\hbar} (2mE)^{1/2} \sin\theta .$$
(4)

Equation (4) gives the parallel momentum of the final state outside of the crystal. Since k_{\parallel} is assumed to be conserved in the excitation process this is the k_{\parallel} value of the initial state. The perpendicular component of momentum k_{\perp} is not conserved when the electron crosses the surface barrier into the vacuum. Equation (4a) gives the perpendicular energy inside the crystal:

$$E \text{ (inside)} = E \cos^2\theta + V_0. \tag{4a}$$

The perpendicular component of the momentum can only be determined if the dispersion of the final-state band is known. Two approaches can be used. The first is to use existing band-structure calculations¹¹ and the second is to assume freeelectron final bands. The latter approach has worked very well for Cu (Refs. 15, 16) and Ni.⁷ If you assume a free-electron band structure then

$$\left|k_{\perp}\right| = \frac{1}{\hbar} \left[2m(E+V_{0}) - \hbar^{2}k_{\parallel}^{2}\right]^{1/2}.$$
 (5)

For the specific case of Ni an inner potential of 10.7 eV gives a good fit of the free-electron parabola with the calculated final bands.¹²

Certainly there are deviations from the freeelectron-like behavior, which show up especially close to the zone boundaries. Furthermore, only primary Mahan cones are considered. Higher-order emission involves scattering into different directions, given by a vector of the reciprocal lattice. In the case of Cu this has been observed,³³ but with about one order of magnitude smaller intensity.

Normal emission spectra can probe the band structure along one symmetry direction. For a (100) crystal this is the Δ symmetric band from Γ to X. In normal emission only bands with Δ_1 and Δ_5 symmetry can be excited.³¹ Other bands in this direction and symmetry points in different crystallographic directions can be determined by using other crystal surfaces or collecting data away from the crystal normal. Using different crystal faces in normal emission may produce data that is easier to interpret but many transitions are dipole forbidden.³¹ The number of accessible bands is very restricted. Off-normal data are slightly more complicated to interpret^{34,35}, therefore we will explain our procedure. All of the data are





FIG. 1. Cuts through the extended Brillouin zone of Ni. The vertical axis is k_{\perp} relative to the (100) surface. In (a) the parallel component of the wave vector k_{\parallel} is located in the (100) mirror plane and in (b) in the (110) mirror plane. The circles are contours of constant energy inside the crystal, assuming a free-electron final state. The dashed lines show the \vec{k} vs E location for the observed transition for a fixed collection angle.

taken in an azimuth which corresponds to one of the two mirror planes of this surface [(100) or (110)]. Cross-sectional cuts through the Brillouin zones in these planes normal to the surface are shown in Fig. 1. The parallel momentum which we can determine from the photon energy and collection angle is shown on the horizontal axis [Eq. (4)]. As a first approximation we assume the final-state bands are free electron-like. The various energies are drawn in as circles in Fig. 1. The energies indicated are with respect to the Fermi energy. We have already made one adjustment in Fig. 1; the inner potential is adjusted to make one point at 43-eV kinetic energy agree with the data and calculations.

Figure 1 can be used to give a first-order estimate of \vec{k} knowing E and k_{\parallel} [Eq. (4)]. The dashed

lines on Fig. 1 show the \bar{k} value for the fixed collection angle as a function of E. The determination of \tilde{k} using Fig. 1 is only the first step. Data are taken at a given symmetry point $(K, U, W, \Gamma,$ X, or L) using the photon energy and angle given by Fig. 1. Then a series of energy distributions are recorded for photon energies and collection angles surrounding this point. We vary photon energy and exit angle within reasonable boundaries and search for extremal behavior of the observed structures in the angle-resolved spectra.³⁵ In the extended zone scheme the bands around a zone boundary are continuous, but have extremal energy values. The same is true for the transition matrix element. Furthermore, at the zone boundary gaps in the bands open up. Looking for variations in binding energy and intensities, we can locate the symmetry points rather well. Thus we are free from the assumption of a free-electron final state and can use this data to determine the energy of the final-state band.

III. EXPERIMENTAL DATA

A. Normal emission-sp band

In Fig. 2 we show a set of angle-resolved energy distributions taken in normal emission for photon



FIG. 2. Photoemission energy distributions for normal emission from Ni(100) as a function of photon energy. The light is p polarized.

energies between 20 and 60 eV. Figure 1 shows that in the free-electron final-state model we should map out the band structure along the Δ axis (Γ to X) and that we should pass through Γ at a kinetic energy of ~45 eV (relative to the Fermi energy). Since we are in normal emission only bands with Δ_1 or Δ_5 symmetry can contribute to the signal.³¹ The structure in the energy distributions, shown in Fig. 2, between 0 and -2 eV initial-state energy is due to the upper Δ_1 and Δ_5 bands of Ni. The dispersion of these bands has been mapped out in detail by Himpsel et al.⁷ Therefore we concentrate on the deeper Δ_1 band. The arrows and dashed line show the dispersion of this Δ_1 band as the photon energy is changed. The structure near -6 eV which does not disperse is a multielectron excitation that we will discuss later. The excitation from the sp band reaches a maximum binding energy below the Fermi energy of -8.8 eV at a photon energy of 52 eV. At this point we are exciting states from Γ_1 (bottom of the sp band) to a final band at Γ (Γ_{15} point). Therefore we have determined the bottom of the sp band $(-8.8\pm0.2 \text{ eV})$ and the position of the final-state band at Γ_{15} (43 ± 2 eV). Figure 3 shows portions of the occupied and unoccupied band structure of Ni along the Δ axis. The dashed curve is the free-



FIG. 3. Portions of the band structure of Ni along Γ to X direction. The data points show the measured data for the dispersion of the Δ_1 band and a few critical points. The dashed curve is the free-electron band. The solid curve below E_F is from Wang and Callaway¹⁰ and above E_F from Smulowicz and Pease.¹¹

electron band we have used in Fig. 1. The solid curve at the bottom is the calculated sp band by Wang and Callaway.¹⁰ The solid curves for the unoccupied bands are from Smulowicz and Pease.¹¹

The data points in Fig. 3 show the measured dispersion of the sp band using the free-electron final-state bands. The symmetry point X_1 can not be determined in normal emission because the X_1 to X_1 transition is always dipole forbidden.

The X_1 point shown in Fig. 3 was determined from non-normal emission data. Therefore, our data covers only ~75% of the Δ axis starting at Γ . The agreement between data and theory is reasonably good as long as the band has essentially sp character. The agreement gets worse around the zone edge at X_1 , where the band has considerable *d* character. The experimental dispersion curve has a step behavior near -6 eV. This is an artifact due to the degeneracy with the multielectron excitation shown in Fig. 2. Himpsel *et al.*⁷ have measured the Δ_1 band dispersion in the range $0.7 < \vec{k} < 1.3$ Å⁻¹ and Petroff³⁶ has reported a value of -8.8 eV for Γ_1 .

B. Off-normal emission-d bands

Figure 4 shows an example of off-normal spectra, searching for the X_1 and X_3 points. We start with Fig. 1(a) to give an estimate of the angles and photon energies necessary to reach the X point in the second zone. Figure 4 shows a coarse grid in photon energy keeping the collection angle fixed at 30°. The X_1 point is even with respect to the (100) mirror plane while the X_3 point is odd. The data is taken in the even geometry (\vec{A} parallel to the detection direction) and odd geometry (\vec{A} perpendicular to plane of detection). The final state has to be even with respect to the (100) mirror plane, but in this off-normal geometry a final band with X'_5 symmetry can contribute to the signal from X_1 or X_3 .³⁷



FIG. 4. Photoemission energy distributions showing the search for the X_1 and X_3 symmetry points. The left panel looks at even states and the right at odd states.

Sweeping the photon energy we see a maximum in the emission intensity when we reach the X point. This gives a value for X_1 of -3.3 ± 0.2 eV and X_3 is at -2.8 ± 0.2 eV. The measured position of the final band X'_5 point is 52 ± 2 eV with respect to the Fermi energy.

The sharp peak at the Fermi level in the odd configuration spectra in Fig. 4 is due to a surface state with odd symmetry.²¹ This surface state was observed only at low photon energies with a maximum cross section around 17-eV photon energy and at a polar angle of about 60°. The cross section dies out rather rapidly towards higher photon energies (30 eV) and suddenly increases again at $\hbar\omega$ around 50 eV, when the normal momentum of

the final-state wave function is approximately equal to the lattice constant *a*. This indicates that the wave function of the surface state extends into the second and third layer of the bulk with a characteristic modulation. The wavelength of this modulation is equal to the lattice constant. Therefore maximum coupling to the final-state wave function is reached, when both initial and final state have the same wavelength normal to the surface. Even though the surface state itself is clearly two dimensional and has no dispersion with normal momentum,²¹ its cross section varies due to the modulation of the surface-state charge density normal to the surface. A similar behavior was found for the Λ_1 symmetry surface state on Ni

TABLE I. Critical-point energies (eV) of occupied Ni bands.

	Exp	eriment						
Symmetry ^b	HKE ^c	This work	FWHM ^d	KSG	WC ^a	vBH	MJW ^e	SP ^f
$\langle \Gamma_1 \rangle$		-8.8 ± 0.2	1.8	-9.16		-8.93	-9.04	-9.04
$\langle \Gamma_{25}' \rangle$	-1.2	-1.1 ± 0.2		-2.15		-2.04	-2.14	-1.97
$\langle \Gamma_{\!\!12} \rangle$	-0.5	-0.4 ± 0.1		-1.01		-0.92	-1.02	-0.93
$\langle X_{i} \rangle$	- 3.8 ^g	-3.3 ± 0.2	1.25	-4.45		-4.30	-4.86	-4.62
$\langle X_3 \rangle$		-2.8 ± 0.2	1.4	-3.94		-3.81	-4.06	-3.81
$\langle X_2 \rangle$		-0.85 ± 0.1		-0.27		-0.18	-0.24	-0.20
X ₅ t	-0.1			-0.51		-0.30	-0.33	
$\langle L_1 \rangle$	-3.4 ^g	-3.6 ± 0.2		-4.78		-4.62	-4.71	-4.53
$\langle L_{3} \rangle$		-1.3 ± 0.1	0.9	-2.17		-2.05	-2.23	-2.07
$\langle L_2' \rangle$	-0.9	-1.0 ± 0.2		-0.64		-0.4	-0.45	-0.58
L ₃ t	-0.15	-0.2 ± 0.1	0.3	-0.68		-0.47	-0.38	
$\langle W_2' \rangle$		-2.6 ± 0.2		-3.73		-3.59	-3.90	-3.70
〈W ₃〉		-1.7 ± 0.2	1.3	-2.91		-2.77	-2.84	-2.68
$\langle W_1 \rangle$		-0.65 ± 0.1	0.8	-1.09		-1.00	-0.92	-1.01
W1 t		-0.15 ± 0.1		-0.51		-0.30	-0.33	
$\langle K_1 \rangle$		-3.1 ± 0.2	1.3	-3.80		-3.66	-4.07	-3.85
$\langle K_1 \rangle$		-2.55 ± 0.1	1.0	-3.58		-3.45	-3.59	-3.39
$\langle K_{3} \rangle$		-0.9 ± 0.2	0.8	-1.94		-1.80	-1.82	-1.72
$\langle K_3 \rangle$		-0.45 ± 0.1		-0.86		-0.77	-0.86	-0.77
$\left< \Lambda_{1} \right>_{\min}$	-1.72			-2.5			-2.5	-2.4
$\left< \Delta_{\mathbf{i}} \right>_{\mathbf{min}}$	-1.2	-1.1 ± 0.2		-1.7			-1.7	-1.6

^a WC: theory by Wang and Callaway using two different potentials, KSG and vBH, Ref. 10.

^b $\langle \rangle$ means average of both spin bands.

^f SP: theory by Smulowicz and Pease, Ref. 11.

^c HKE: experimental work by Himpsel, Knapp, and Eastman, Ref. 7.

^d FWHM is the full width at half maximum (eV) of the observed peaks, which reflects at the critical points to first order the initial-state broadening.

[•] MJW: theory by Moruzzi, Janak, and Williams, Ref. 12.

^g These values are extrapolated.



FIG. 5. Plot of the variation between the experimentally determined critical points (E_m) in the band structure of Ni and the theoretical calculation of Wang and Callaway¹⁰ using the vBH potential (E_c) . (a) is the % deviation and (b) is the energy discrepancy, both as a function of the calculated energy below the Fermi energy.

(111),²⁰ the cross section of which modulates according to the distance between two L points in the final-state wave function.³⁷

The values for the critical points at X and W[Fig. 1(a)] were checked by using a different scan. The value of k_{\parallel} was fixed at 1.78 Å⁻¹ [X point in Fig. 1(a)]. Then the photon energy was changed always adjusting the collection angle according to Eq. 4 to keep k_{\parallel} fixed. This mode sweeps k_{\perp} , i.e., a vertical line on Fig. 1. All of the measured critical points for the occupied bands of Ni are tabulated in Table I. Our experimental values are compared to those of Himpsel, Knapp, and East man^7 and to four different calculations. $^{10,\,11,\,12}~\mbox{In}$ Fig. 5 we compare our measurements to the calculations of Wang and Callaway using the von Barth-Hedin (vBH) potential.¹⁰ This figure shows the difference between the measured and calculated energies as a function of the calculated energy in Fig. 5(b) and the % error in Fig. 5(a). Figure 5(b) indicates that the discrepancy with theory increases with increasing energy below the Fermi energy to an energy of ~ -4 eV then the discrepancy decreases. At the bottom of the sp band there is very good agreement between theory and experiment. This figure shows what is already known, the measured d band is narrower than the calculated d band. Figure 5(a) presents the % deviation of the calculations and measurements. This figure shows that the % error is larger near the Fermi energy and then decreases monotonically with decreasing energy below the Fermi energy. The data presented in this fashion shows that these calculational schemes do not handle the d electrons in Ni properly. We will discuss the origin of this problem later.

C. Final states

We have already described the determination of Γ_{15} and X'_5 in the unoccupied band structure of Ni (see Fig. 3). More detailed information about the final band structure can be obtained if we plot the intensity of a given initial state as a function of photon energy. Such a plot for normal emission is shown in Fig. 6. The initial energy is the Fermi energy. In normal emission we follow the band structure along the Δ axis (Fig. 1).

The data shown in Fig. 6 refers to the third zone in the extended zone scheme (Fig. 1). From de Haas-van Alphen data we expect two bands, the Δ_1 and Δ_5 bands, to cross the Fermi level.^{10, 38} These bands are split due to the exchange splitting, but since three of the four bands are very close to each other, we expect only two Fermi level crossings at $\vec{k} = 2.71 \ (2\pi/a) \ (1,0,0)$ and $\bar{k} = 2.77 \ (2\pi/a)(1, 0, 0)$. For a free-electron-like state this would result in a transition energy of $h\nu = 79 \text{ eV} (83 \text{ eV})$. These transitions are marked by arrows in Fig. 6. This seems to fit rather well with the main peak. The shoulder could be explained by a secondary Mahan cone, which involves an additional lattice vector $\vec{G} = (\vec{2}, 2, 2)$ (marked by parallel lines). These are the closest energy bands one can find in the free-electron approximation. All other lattice vectors would result in a



PHOTON ENERGY $h\omega$ (eV)

FIG. 6. Intensity of Fermi-energy electrons as a function of photon energy for normal emission.

TABLE II.	Final states in Ni.
State	Energy (eV)
Γ ₁₅	43±2
Γ_{15}	23 ± 2
X _i	9.8 ± 0.5
X_5'	52 ± 2
L'_2	22.3 ± 1
L_2'	77
W ₃	30 ± 2
K	61 ± 2

larger energy separation. These transitions are expected to be weaker, and therefore could account for a shoulder on the main peak. On the other hand, a calculation for a real LEED final state could give several possible final bands in this energy range. This has been observed for Cu.³³ If the main peak is due to transitions into a single final band, the lifetime of an electron in this state can be estimated by taking the FWHM of the peak.³⁹ A rough estimate gives a lifetime $\tau = \hbar/\Gamma = 6 \times 10^{-16}$ sec. Taking the group velocity of the free-electron band, this results in a scattering length of $l = v_e \tau = 4$ Å, a reasonable value. If more than one final band contributes to the observed transition, the calculated escape depth would increase since the width of each single transition would be smaller and therefore its lifetime larger.

Table II lists all of the points in the final band structure that we have determined. X_1 is measured by looking at the shape of the low-energy secondaries. There is an appreciable decrease in the intensity of the secondaries below approximately 4.5 eV. We have taken the halfway point of this decrease to be X_1 .

D. Exchange splitting

Ni is ferromagnetic and therefore all bands are split by the exchange splitting. Experimentally this has been observed in the vicinity of the L point in the (110) plane^{5,6} and the values claimed are between $\Delta_x = 0.3$ and $\Delta_x = 0.5$ eV. Owing to the fact that the lifetime broadening of the measured bands increases with distance below the Fermi energy, the exchange splitting can only be resolved near the Fermi energy. For higher binding energies in Ni the lifetime broadening is larger than the exchange splitting and therefore we only see one wide peak for each spin split band. In Fig. 7 we show the measured width (FWHM) for those initial-state bands where we can extract the width without too many assumptions about the background. We did not include structures. which show up only as a shoulder on a peak. The width is increasing from $\Delta E = 0.3$ eV close to the Fermi level (L_3^{\dagger}) to $\Delta E =$ 1.8 eV at the bottom of the sp band (Γ_1). The lifetime of the initial state is determined mainly by Auger transition. In the case of Ni these transitions most likely end with one electron in the unfilled portion of the d bands. The density of these unfilled d bands is very large but concentrated almost like a δ function in energy at the Fermi level. Therefore in a first order approximation one expects from a phase space argument the lifetime broadening to increase linearly with the distance from E_F . The L_3^{\ddagger} level is a band with electrons of only one spin direction and at the bottom of the sp band (Γ_1) the exchange splitting is vanishing. A calculation¹⁰ gives a value of 40 meV at Γ_1 compared to 340 to 530 meV in the *d* bands. If we connect the measured points at L_3 and Γ_1 with a straight line to approximate the lifetime broadening, we get an estimate of the exchange splitting of the other bands by the deviation of the measured FWHM from this line. The dot-dashed lines in Fig. 7 show the expected width for two different exchange splittings, assuming the inherent width to depend linearly upon the binding energy. We calculate the total width of a peak. which is a superposition of two Gaussians showing the inherent lifetime width separated by an exchange splitting of 0.4 and 0.6 eV, respectively. These curves indicate that the exchange splitting near the bottom of the d bands may indeed be a little larger than at the Fermi energy as predicted by theory.¹⁰

It obviously is more desirable to observe the exchange splitting directly. Two spectra, which show the exchange splitting measured at different points in the Brillouin zone, are shown in Fig. 8.



FIG. 7. Full width at half maximum (FWHM) of critical point structures (Table I) in a photoemission energy distribution as a function of its energy below the Fermi energy.



FIG. 8. Angle-resolved photoemission spectra showing exchange splitting near the Fermi energy. The split bands are marked by arrows. The electrons are detected in the (110) plane (a) and in the (100) plane (b) normal to the crystal surface.

As previously mentioned, the exchange splitting only can be resolved for bands close to E_F , where the exchange splitting is comparable to the lifetime broadening. Looking at the band-structure calculations and de Haas-van Alphen data one finds only a few points in the whole Brillouin zone, where such an attempt might be successful. One of those regions is close to the L point. At L itself the minority L_3 band is above E_F , but it crosses E_F not far away from the L point. Previous results show this splitting going from L in the (110) plane in $[\overline{112}]$ directions.^{5,6} In Fig. 8(a) we show the exchange splitting of the same bands but going in the [110] direction from L. Fitting the curve shown in Fig. 8(a) with Lorentzians we obtain a value of $\Delta_{z} = 0.25 \pm 0.05$ eV for the exchange splitting. Since the transitions out of the two bands are not at the same point in k space, we obtain a vertical exchange splitting of $\Delta_r = 0.26 \pm$ 0.05 eV after correction. Assuming a free-electron-like final state, we calculate the observed transition to be at

$$\mathbf{k} = (2\pi/a)[(\frac{1}{2}, \frac{1}{2}, \frac{3}{2}) + 0.09(1, 1, 0)]$$

Since there are no calculated final bands available, this is the best estimate we can give for the point in \vec{k} space for the transition. The Fermi-level crossing of the $L_3 \neq$ band is located¹³ at

 $\vec{\mathbf{k}} = (2\pi/a)[\frac{1}{2}, \frac{1}{2}, \frac{3}{2} + 0.075(1, 1, 0)]$

as measured by de Haas-van Alphen data. The exchange splitting at L is in good agreement with previous results^{5,6} and differs drastically from theoretically predicted values. The closest calculated value is 0.6 eV (L_3), Ref. 10. This might be an indication that the treatment of the exchange and correlation effects by whatever potential is used is too crude at the present stage. The strong deviations of the measured *d*-band critical points from the calculated points might have the same explanation.

The exchange splitting varies throughout the d bands. We show in Fig. 8(b) the exchange splitting of the topmost Z_1 band measured approximately halfway between W and X. Taking a free-electron-like final-state band we locate the observed transition at

$$\mathbf{k} = (2\pi/a)[(1, 0, \frac{3}{2} + 0.2(0, 0, 1))]$$

If we take the only available calculated final band¹¹ we obtain a value of

 $\vec{\mathbf{k}} = (2\pi/a)[(1, 0, \frac{3}{2} + 0.175(0, 0, 1))]$

very close to the value as approximated by the assumption of a free-electron-like final state. A-gain the measured exchange splitting of $\Delta_x = 0.28 \pm 0.05$ eV differs roughly by a factor of 2 from theoretically predicted values. Table III lists the

Symmetry	Position in \mathbf{k} space	Measured splitting (meV)	Correction ^a (meV)	Δ_x (meV)	Ref.
<i>Z</i> ₁	$\frac{X \to W}{a} [(1, 0, \frac{3}{2}) + 0.175(0, 0, 1)]$	290 ± 50	-9	281± 50	
L	$\frac{L \to \Delta}{a \left[\frac{1}{2}, \frac{1}{2}, \frac{3}{2}\right] + 0.09(1, 1, 0)]}$	250 ± 50	+8	258± 50	
L	$\frac{2\pi}{a}(0.14,-0.43,-0.43)$	510 ± 50	-20	490 ± 50	5
L	$L \rightarrow 1, 1, 2$ in (110) plane	300 ± 100	+ 50	350 ± 100	5
L	$L \rightarrow 1, 1, 2$ in (110) plane	280 ± 30	+ 30	310 ± 30	6

TABLE III. Exchange splitting.

^a The corrections for the fact that the exchange-split bands observed in the spectra are due to transitions in slightly different \hat{k} points are made assuming free-electron-like final states.

experimentally determined exchange splitting in Ni. We list the region in \vec{k} space where the determination was made, the measured splitting and the corrections due to the different position in \vec{k} space of the transitions out of the two bands.

E. Multielectron excitations

Finally we report the observation of multielectron excitations or shake-up processes in Ni. A drastic resonance of a peak located 6 eV below E_F has been observed at the threshold of the Ni-3p excitations.²⁵ X-ray photoemission (XPS) spectra of Ni core levels as well as the valence-band spectra⁴⁰ show a characteristic satellite connected with all the main lines. This satellite is not due to a plasmon excitation, but rather an excited state of the core or valenceband hole.^{40,41} XPS of Zn impurities in Ni (Ref. 42) support this model strongly, since satellites are not observed for all impurity emission lines. Therefore the 6 eV satellite can be correlated with the hole and is not due to "extrinsic" plasmon scattering. Off-resonance ultraviolet-photoemis-



FIG. 9. Angle-resolved photoemission spectra showing the multielectron excitation at -6.3 eV. In the odd geometry there are no bulk states to be excited. In the even geometry the *sp* band can be excited in this energy range.



FIG. 10. Normal-emission EDC's of Ni(111) and Ni(110) taken in (67 eV) and off resonance (55 eV) with the 3p excitations. The multielectron shake-up structures are marked by arrows. Both curves are normalized to equal height of the *d*-band emission.

sion (UPS) valence-band spectra of Ni single crystals as well as submonolayer Ni films^{4, 36, 43} also show a peak located at 6 eV below E_F , but the interpretation is difficult, since the lowest Ni *sp* band shows up in the very same region of the spectra. We have used the polarization of the synchrotron radiation to discriminate against emission from the Ni *sp* band. In Fig. 9 we show sets of energy distributions taken in the [100] azimuth and picking up emission from odd or even bands, respectively. Clearly a structure at an apparent binding energy of -6.3 eV shows up in both sets of data, which cannot be attributed to any interband transition. The same structure shows up in the spectra shown in Fig. 2.

Penn²⁶ has attributed the 6 eV peak to a shake-up structure or as he calls it, a two-hole state in the d bands. Two d electrons are simultaneously excited, one of them into the continuum and the other one into the empty d states right above the Fermi level. This leads to a shake-up peak about 6 eV below E_{F} .

The structure at an apparent binding energy of -6.3 eV is not the only one which is observed. In Fig. 10 we show angle-resolved spectra of Ni(111) in normal emission which exhibit additional shakeup features marked by the arrows. At the photon energy chosen ($\hbar\omega = 67 \text{ eV}$) the 3p excitation is just allowed, and enhancement of the multielectron excitations is observed. We also observe these excitations at photon energies away from the 3pthreshold. The peak at -13 eV has been reported previously,^{4, 36} but only in connection with the 3pthreshold. None of the other structures, which are summarized in Table IV, have been observed previously. The relative intensity of these shake-up peaks varies with photon energy. Therefore only at certain photon energies are all peaks visible

Shake-up structure	Possible atomic energy ^a transition		
6.3 eV	$3d^84s \rightarrow 3d^84p$ (5.3 eV) $3d^84s \rightarrow 3d^74s^2$ $3d^84s \rightarrow 3d^74s4p$ (>6.4 eV) estimated		
13.4 eV	$\begin{array}{l} 3d^{8}4s \rightarrow 3d^{7}4s5s \\ 3d^{8}4s \rightarrow 3d^{8}5p \ (10.3 \leqslant E \leqslant 17.05 \text{ eV}) \\ 3d^{8}4s \rightarrow 3d^{7}4s5p \ (\geqslant 11.4 \text{ eV}) \end{array}$		
17.8 eV	$3d^84s \rightarrow 3d^8 \in l \ (17.05 \text{ eV})$		
22 eV	$3d^84s \rightarrow 3d^74s \in l (23.7 \text{ eV})$		

TABLE IV.

^a According to Ref. 45.

simultaneously.

The 3d wave functions are very localized and can be regarded almost like a core-electron wave function.⁴⁴ This is indicated by the narrowness of the d bands. Under the assumption that the interaction with the neighbor atoms is negligible, one can try to understand the shake-up processes in an atomic-like picture. A configuration interaction calculation such as the one done for Ni,44 but extended to higher energies, should be able to explain the shake-up and resonance phenomena. We here restrict our interpretation to a comparison with Moore's tables.⁴⁵ The difficulty involved is to get the proper ground-state configurations for the solid. The ground-state configuration could vary between $3d^84s^2$, $3d^94s$, and $3d^{10}$. Following Goddard^{44,46} we assume the ground-state configuration to be $3d^94s$. After excitation of one d electron we get the Ni⁺ atom in the configuration $3d^84s$. Excited states $3d^74s^2$ or $3d^74s4p$ can be estimated to have an energy of about 6 eV above the ground state of Ni⁺ after Moore's tables.⁴⁵ This corresponds very well to the energy of the first shake-up structure (6.3 eV). If we however try to follow Penn's model²⁶ we would have to assume an ionic ground state $3d^84s$ with a maximum energy spread between $3d^8({}^3F)4s$ and $3d^8({}^1G)4s$ of 3.0 eV. This consideration makes the interpretation of Penn rather unlikely, which involves as excitation of a d electron from the bottom of the d bands to the empty d states at the Fermi level. From these atomic considerations an excitation 3d - 4s or 3d - 4p seems more likely to be the origin of the shake-up peak. If this is the case, the shake-up structures do not depend on the presence of a dband hole at E_F and should be seen in other materials. The structures might, however, be much weaker because the second condition for its occurrence are very well localized d bands, which are almost like core electrons. In this respect Ni is certainly one of the best examples. Other shakeup structures and possible final-state assignments are given in Table IV. Following Goddard⁴⁴ we assume an initial configuration of $3d^94s$. This leaves after ionization of a *d* electron an atom in the configuration $3d^84s$ behind. In Table IV we only consider shake-up transitions starting from this configuration. The structure at -22 eV coincides with emission from 0 2s. However, we do not attribute it to oxygen impurities since we observe the Λ_1 surface-state emission, which is very sensitive to any kind of contamination.²⁰

Recently the 6-eV resonance feature has been observed for Ni phthalocyanine, an organic compound, which contains isolated Ni atoms.⁴⁷ The photoelectron spectra show the same resonant behavior at -6 eV as bulk Ni when scanning through the 3p threshold. This clearly approves the atomic-like interpretation of the shake-up structures observed here.

IV. DISCUSSION

The issue is why do band-structure calculations work quite well for Cu and Fe, but fail for the dbands of Ni. The explanation seems to be given by calculations by Upton and Goddard on small Ni clusters.⁴⁴ These generalized valence band-configurational interaction calculations illustrate how important many-body effects are in describing the 3d orbitals of Ni. The reason that Ni is more sensitive to these effects than say Cu or Fe is that the $4s^23d^8$ ground state of a Ni atom is only 0.03 eV lower in energy than the $4s^{1}3d^{9}$ configuration. Upton and Goddard's calculations show that when Ni bonds to Ni the lowest configuration on each atom is $4s^{1}3d^{9}$. The consequence of this is that the d orbitals are more localized than typical Hartree-Fock orbitals used in band-structure calculations and the bonding is predominantly $s-s.^{46}$ Therefore the correct d orbitals obtained from an "effective potential" consistent with these calculations would produce a narrower d band and consequently a smaller exchange splitting in Ni than that given by conventional band calculations. The strong localization of the d bands also explains the presence of so many shake-up features in the spectra, which can be interpreted in an atomic-like picture.

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