Spin-Polarized Inverse Photoelectron Spectroscopy of Solid Surfaces: Ni(110)

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Inverse photoemission spectra have been measured on Ni(110) at 9.7-eV photon energy with a spin-polarized electron source. Consistent with band theory, a d-band–derived peak is observed just above the Fermi level that corresponds to transitions to minority-spin states only, and which increases in intensity and displays a slight (0.1-eV) energy dispersion as the angle of electron incidence is increased. The inelastic background displays an unexpected nonzero ($\sim$ -5%) polarization.

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Measurements of the spin polarization of photoemitted electrons represent a fertile subfield of photoemission spectroscopy (PES), and have provided valuable information on the electronic structure of magnetic materials.[1] Inverse photoemission spectroscopy (IPES), or ultraviolet bremsstrahlung isochromat spectroscopy, is an emerging technique which promises to provide information complementary to that obtained in PES.[2-4] The technique consists of bombarding a sample surface with electrons of variable energy and monitoring the emitted photon flux due to radiative transitions. The important feature of the technique is that it permits investigation of the empty states between the Fermi level and the vacuum level, a range inaccessible in ordinary PES. It is therefore natural to propose that IPES be performed with a source of spin-polarized electrons. Indeed it has been suggested[3] that spin-polarized inverse photoemission spectroscopy (SPIPES) could be an especially effective probe in the case of Ni, where it can be argued that the *holes* in the d band constitute the "active ingredients" in the ferromagnetism.

In this Letter we report the first experimental demonstration of SPIPES. The experiments were performed on Ni which provides an ideal test case. In this ferromagnetic metal, it is thought that the d holes extend only a few tenths of an electronvolt above the Fermi level and that they are 100% minority-spin polarized. The SPIPES data should therefore be particularly clear cut, and we shall show that this is indeed the case. We shall also discuss the relative experimental ease of SPIPES and spin-polarized PES.

The layout of this SPIPES experiment is shown in Fig. 1. The significant additional feature for obtaining spin information in an inverse photoemission experiment is a beam of spin-polarized electrons. We used a GaAs spin-polarized electron source[5] which we modified to increase the beam current by removing a collimating aperture, resulting in an angular spread of the beam from the gun of ± 2.6°. The sample was a Ni(110) crystal magnetized along the $(1\bar{1}1)$ direction by a C-shaped electromagnet as in previous polarized-electron-scattering studies.[6] The crystal assembly was mounted on a manipulator such that it could be rotated about an axis in the crystal surface and normal to the direction of magnetization. Our work is therefore not only the first experimental demonstration of SPIPES but also the first demonstration of *angle-resolved* SPIPES.

The sample was cleaned by prolonged 1-keV Ar-ion bombardment at a temperature of 500 C with subsequent flashing to 600 C. The magnetic state of the sample could be tested independently by measuring a hysteresis curve of the electron-

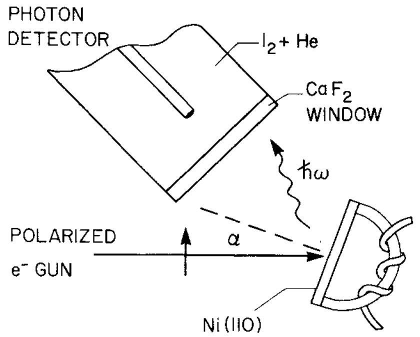

FIG. 1. Schematic of the apparatus for angle-resolved, spin-polarized inverse photoelectron spectroscopy.

beam current absorbed by the sample.[7] The photon detector was a Geiger-Müller counter whose characteristics (a peak sensitivity at $\hbar\omega = 9.7$ eV and a bandpass full width at half maximum of 0.7 eV) have been described elsewhere.[8] The photon detector counts $n_\uparrow$ and $n_\downarrow$ were collected in two separate channels, for the incident spin direction parallel to the majority- and minority-spin directions of the Ni crystal, respectively. Typically a current of 0.5 μA incident on the room-temperature sample produced counting rates of 25–40 counts/sec.

The spin-dependent asymmetry in the photon production is

$$A \equiv \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} = \frac{1}{|P_0 \cos\alpha|}\frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}.$$

The factor $P_0 \cos\alpha$ accounts for the fact that at nonnormal incidence only a component of the incident polarization P_0 is along the magnetization axis. The photon fluxes $N_\uparrow$ and $N_\downarrow$ are the number of photons that would be detected for a 100% polarized incident beam respectively parallel and antiparallel to the majority spin direction. We shall present our results in terms of these corrected quantities $N_\uparrow$, $N_\downarrow$, and A. The statistical uncertainty (one standard deviation) is given by[9] $\Delta A \approx (nP_0^2\cos^2\alpha)^{-1/2}$ where $n = n_\uparrow + n_\downarrow$. By counting for approximately 10 min at one energy a ΔA of 0.03 and a $\Delta n/n$ of 0.007 are obtained. Reversing the magnetic field permits the determination of an apparatus asymmetry or other asymmetry of nonmagnetic character. Any such systematic asymmetry was less than 2%.

SPIPES data for $N_\uparrow$, $N_\downarrow$, and A are shown in Fig. 2 for two representative angles of incidence. The most prominent result is that the peak seen just above the Fermi level E_F in the $N_\downarrow$ spectra is entirely absent in the $N_\uparrow$ spectra. The width of the peak is dominated by the 0.7-eV bandpass of the detector. This minority peak is found to increase in relative strength with increasing angle of incidence. A is of course strongly nega-

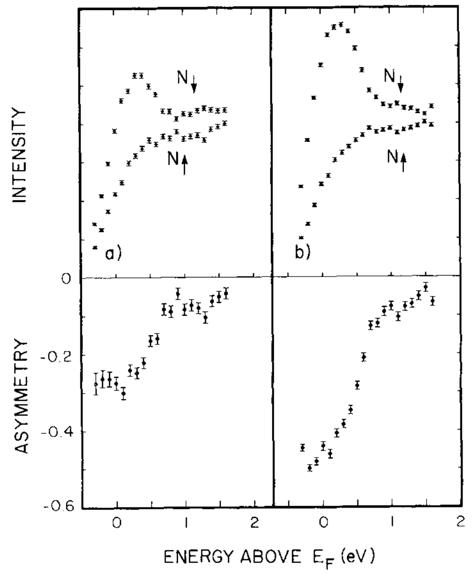

FIG. 2. Experimental results for the photon intensity spectra $N_\uparrow$ and $N_\downarrow$ and for the asymmetry spectrum $A = (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$ taken on Ni(110): (a) angle of electron incidence $\alpha = 0°$; (b) $\alpha = 20°$. The error bars correspond to one standard deviation in the statistical error. Note that A remains negative above the energy range of the d peak.

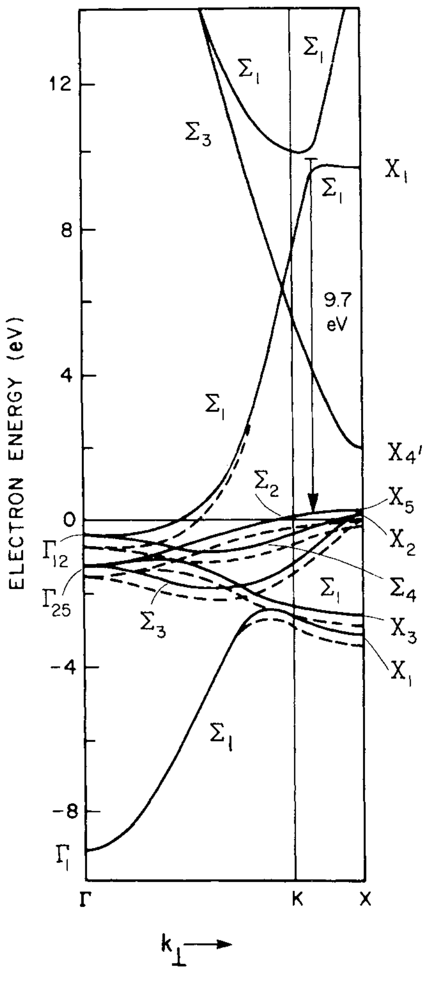

FIG. 3. Band structure of Ni along the ΓKX direction, showing an energetically possible radiative transition at $\hbar\omega = 9.7$ eV for electrons incident normally upon Ni(110). Dashed curves distinguish the majority-spin d bands.

tive in the energy region of the d peak and remains slightly negative at higher energies. This residual asymmetry (~ − 5%) in the inelastic background persists up to 4 eV above E_F which is as high as the A measurements were taken.

The band structure of Ni along the ΓKX line, corresponding to normal electron incidence (parallel wave vector $k_\parallel = 0$) on Ni(110), is shown in Fig. 3. The vertical arrow indicates a direct transition at $\hbar\omega = 9.7$ eV which drops an electron into the minority d bands and which would bring about an asymmetry of the kind observed. Strictly at $k_\parallel = 0$, the transition shown ($\Sigma_1 - \Sigma_2$) is symmetry forbidden.[10] With increasing $k_\parallel$, this selection rule is progressively relaxed and there is an increasing momentum matrix element for the transition, a result confirmed by empirical band calculations using numerical methods described earlier.[11] The observation of some intensity in the d peak even at $k_\parallel = 0$ is presumably a consequence of finite angular resolution. The same empirical band calculations predict that there should be a slight downward dispersion in the d-peak position from 0.21 eV above E_F at $\theta = 0°$ to ~0.1 eV above E_F at $\theta = 20°$. A shift of this sense and magnitude can be discerned on close inspection of the data of Fig. 2.

Other direct transitions can take place at $\hbar\omega = 9.7$ eV into the other unoccupied d bands (Σ_3 and Σ_4) near the X point, but should contribute only weakly because of poor wave-function-matching possibilities.[11] It is likely that there are contributing transitions involving evanescent rather than Bloch-like band wave functions.[11] This would lead to a removal of $k_\perp$ conservation, where $k_\perp$ is the component of electron wave vector perpendicular to the surface. Our main conclusion, however, should not be affected. The optical selection-rule considerations are rather general, being a consequence of the C_{2v} symmetry of the Σ line. Likewise, the downward energy dispersion with increasing $k_\parallel$ is a general trend and should therefore survive some smearing of the $k_\perp$ quantum number. Even allowing for these complications, we may safely conclude that the main features of the d peak (namely its total minority-spin character, its slight energy dispersion, and its increase in intensity with increasing $k_\parallel$) can all be understood in terms of the Ni band structure.

The polarization asymmetry of the inelastic background is not well understood. The asymmetry in the current absorbed by the Ni crystal in this energy range ($< \frac{1}{2}\%$) and the spin dependence of the electron inelastic-scattering rate[12] are both too small to cause the background asymmetry. The inelastic background is due to a compound process involving a nonradiative decay followed by a radiative transition emitting a photon at $\hbar\omega = 9.7$ eV. The availability of a large density of minority d holes for the final stage of such processes may account for the observed negative polarization.

It is instructive to compare our signal levels (~40 cps for a 0.7-eV bandpass) with those attainable in spin-polarized PES. Note that our IPES experiments are: (1) spin polarized; (2) angle resolved; (3) energy resolved. The counterpart experiments in spin-polarized PES having all three of these features[13,14] are also in their infancy, and have very similar signal levels (~50 cps at ~1-eV bandpass[14]). Our signal levels could be increased by two orders of magnitude or more by increasing the incident polarized electron current; GaAs sources have produced dc beams of up to 400 μA.[15] To fulfill their promise, both of these complementary techniques need to be pushed to higher energy resolution (0.1–0.2 eV). Our encouraging experiences so far indicate that further development of SPIPES will be fruitful and should be no more technically demanding than spin-polarized PES. In particular extending this work to include studies of various adsorbates on Ni should yield valuable information about the importance of the d-band holes in chemisorption.

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Structure-Induced Minimum in the Average Spectrum of a Liquid or Amorphous Metal

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Nonperturbative multiple-scattering theory is used to study the influence of the first peak in the density correlation function, $s(k)$, on the electronic properties of a structurally disordered metal. The present calculations yield a well-defined minimum in the average density of states and a corresponding peak in the electrical resistivity. The position of these structures is directly related to that of the principal peak in $s(k)$.

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In a previous paper[1] we discussed the application of the effective-medium approximation[2] (EMA) to the muffin-tin model of a structurally disordered metal. Our results indicated that the EMA provides a satisfactory description of the average electronic spectrum in the energy range associated with the $l=2$ scattering resonance characteristic of noble- and transition-metal systems. In the present paper we consider strong-scattering effects that are *structural* rather than *atomic* in orgin. In particular, we are concerned with the influence of the first peak in the structure function on the average spectrum. If this peak is centered at K_p, then estimates based on second-order perturbation theory indicate that nearly-free-electron states with wave vectors $k \approx K_p/2$ should be strongly coupled.[3,4] In a rough sense, this coupling is analogous to the band gap that appears in a perfect crystal as $\vec{k}$ approaches the boundary of the Brillouin zone. (Here, of course, $\vec{k}=\vec{K}_n/2$, where $\vec{K}_n$ is a reciprocal-lattice vector.) Since liquid and amorphous systems do not exhibit any long-range order, we cannot reasonably expect a true band gap. However, because the structure function is isotropic, the scattering associated with the first peak in $s(k)$ will not depend on the direction of the electron wave vector and the effects of this scattering will add coherently when the contributions from different wave vectors are summed to produce the total spectrum. The issue then is whether or not this scattering leads to any characteristic structure in the average density of states $\rho(E)$. We emphasize that the calculations described in this paper are nonperturbative and address this issue within a framework that is already known to work well in the strong-scattering regime.

In the following section we describe the effects of the principal peak in $s(k)$ on the density of states, the spectral density function, and the electrical resistivity. In the final section we discuss briefly some physical consequences of these effects. It is to be understood, however, that the purpose of this paper is to clarify a *qualitative* feature of the electronic spectrum in structurally disordered systems, rather than to present results relating to a particular system or experiment.

As described in Ref. 1, muffin-tin EMA calculations are based on a system of coupled nonlinear integral equations. The complexity of these equations implies that there is no explicit relationship between the electronic density of states and the pair distribution function. The character of this relationship can only be studied by examining the results of detailed numerical calculations, and in Fig. 1 we compare the results of three such calculations. Curve 2 is based on the same atom-