k-dependent exchange splitting of empty bands in nickel

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Spin-polarized inverse photoemission spectroscopy has been used to study the spin-dependent unoccupied electronic structure of nickel. Measurements involved the study of Ni(110) in the $\overline{\Gamma Y}$ azimuth. A k-dependent spin splitting with measured spectral values ranging from 113±20 meV to 337±51 meV has been resolved for a bulk sp-like band. These results are consistent with differential sp/d hybridization. Furthermore, an exchange splitting of 190±30 meV is detected for a Shockley surface state. The experimental observations are in good agreement with calculations employing one-step theory. [S0163-1829(98)02106-7]

I. INTRODUCTION

The electronic basis of bulk, surface, and thin-film magnetism continues to attract considerable interest, with studies of nickel surfaces playing a key role in refining models of the bulk and surface ferromagnetism.[1] It is now well established that the room-temperature bulk $3d$ bands are exchange split into majority- and minority-spin components,[1] the latter being partially unoccupied, in line with the noninteger, $0.6\mu_B$ magnetic moment. It has also been established that low Miller index Ni surfaces are ''magnetically active,'' as evidenced by the exchange splitting of surface states.[1] There are, however, important fundamental factors which have yet to be determined. These include the momentum and energy dependence of bulk and surface states. Here we focus on the exchange splitting of unoccupied bulk bands in nickel.

The reported room-temperature $3d$-band exchange splittings obtained from angle-resolved photoemission measurements range from 0.17 eV (X_2-S_4) to 0.33 eV (X_5-S_3),[1] with little local variation with momentum k within each band. However, a visual inspection of spin-polarized photoemission spectra of Ni(111) suggested a k-dependent exchange splitting of an occupied d band.[2] Studies of the unoccupied states by inverse photoemission spectroscopy (IPE) have monitored the bulk bands as well as surface states.[1,3,4] The exchange splitting of bulk Ni s-p bands has been reported to be 90 meV on the ΓX line[5] and 280 meV in the ΓLWK mirror plane.[6] The extrapolated ground-state exchange splitting of the magnetic Z_2 $3d$ band is 0.28 ±0.05 eV from deconvolution of spin-polarized IPE (SPIPE) data using the maximum entropy method.[7] On the theoretical front, it is found that self-energy corrections are necessary to produce exchange splittings and bandwidths in agreement with experimental results.[8,9] Here we describe an angle-resolved SPIPE study of Ni(110) in the $\overline{\Gamma Y}$ azimuth and corresponding one-step SPIPE calculations. We present results which provide evidence of a k dependence of an sp-like bulk-band exchange splitting.

II. EXPERIMENTAL

The angle-resolved SPIPE measurements employed an instrument which is described elsewhere.[10] Briefly, spin-polarized electrons are generated by photoemission from a negative-electron-affinity GaAs(100) photocathode at room temperature, the spin direction being selected by the helicity of circularly polarized irradiation.[11] Using an analysis similar to that employed by Donath *et al.*,[4] the degree of polarization of the electron beam was estimated to be 25±5%. All of the SPIPE data shown below have been normalized for a hypothetical 100% polarized beam on the assumption of a 25% polarized source.[10] Measurements were made at room temperature in the isochromat mode, with emitted photons counted using a solid-state band-pass detector. This has a detection energy centered at 9.8 eV and a resolution of 0.7 eV [full width at half maximum (FWHM)],[12] which dominates the overall energy resolution of the instrument. Selected measurements employed a modified photon detector with a peak energy of 9.5 eV and an improved resolution of 0.42 eV (FWHM).[12] The photon detector is mounted at 71° to the incoming electron beam direction.

Experiments employed a remanently magnetized 0.7 mm thick Ni(110) picture-frame single crystal with legs in the ⟨111⟩ directions of easy magnetization to minimize stray fields. The sample was magnetized by passing a number of 100 A, 1 ms pulses through a coil which is wrapped around one of the ⟨111⟩ legs. The experimental geometry has the electron spin vector aligned either parallel (or antiparallel) to the [$1\bar{1}0$] azimuth. The sample was cleaned *in situ* by repeated cycles of Ar^+ sputtering (10 min, 500 V, 3 μA) and annealing (870 K, 20 min). Subsequent Auger electron spectra evidenced a clean sample and a sharp 1×1 low-energy electron-diffraction pattern was observed.

SPIPE spectra were calculated using the code PHOTON,[13] which is a modification of a previously published one-step photoemission code.[14] Our calculations assumed a bulk terminated surface and an abrupt surface potential barrier. The latter will introduce an error in the behavior of surface states. The ground-state potentials were obtained[15] using the spin-polarized, self-consistent-field, linear muffin-tin orbital method[16] and the local-spin-density approximation.

III. RESULTS AND DISCUSSION

SPIPE data recorded in the $\overline{\Gamma Y}$ azimuth of Ni(110) are shown in Fig. 1. The labeling of the bands in Fig. 1 (B_1, B_2,

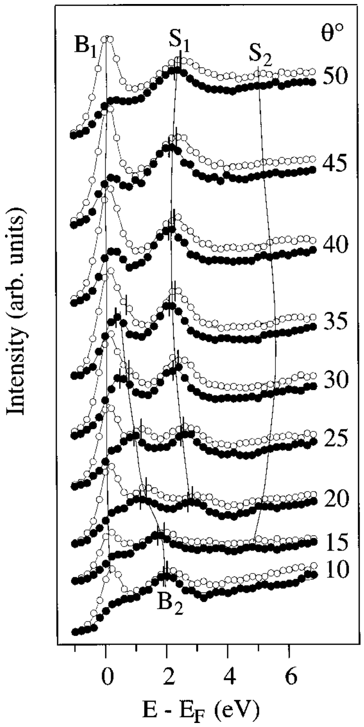

FIG. 1. Spin-polarized IPE spectra ($h\nu = 9.8$ eV) of Ni(110) in the $\overline{\Gamma Y}$ azimuth as a function of the electron incidence angle with respect to the surface normal, θ. Fitted functions are shown as lines through the experimental points and the peak positions from the fitting procedure are shown as vertical lines. Experimental majority (minority) spectra are shown as full (empty) circles.

S_1, and S_2) follows the assignment of earlier IPE data.[17] B_1 and B_2 represent transitions into bulk states in the ΓKLU mirror plane, with B_1 arising from transitions into empty minority-spin d bands. B_2 was concluded to arise from states having mainly s-p character.[17]

S_1 and S_2 have been associated with transitions into surface states, being observed in an inverted Shockley gap of the projected bulk band structure.[17–19] While S_1 is clearly distinguishable in our spin-polarized data, S_2 is barely distinguishable above the noise level. S_1 is totally quenched by an exposure of 0.2 L of O_2, while S_2 is hardly affected.[17] The latter behavior, along with the $k_\parallel$ dispersion of S_2 led to its assignment as an image potential state.[17]

In order to determine the magnitude of the exchange splitting of B_2 and S_1, a function was fitted to each spectrum. The function consists of three gaussians representing B_1, B_2, and S_1, a linear background, and a step function convoluted by the photon detector response function[12] to represent the Fermi edge. All parameters for the gaussians and the linear background were free to vary within the fit, while the width of the convoluted step function was held constant. Although a linear function does not perfectly reproduce the background, this approximation is thought adequate to determine the peak positions, whose main dependence on the background lies in its slope. The result of this procedure is shown in Fig. 1, where the fitted function is compared to the experimental data.

The dispersion of the final-state bands derived from the peak positions in Fig. 1 is displayed in an $E(k_\parallel)$ diagram in Fig. 2. Here they are compared with the projected bulk band

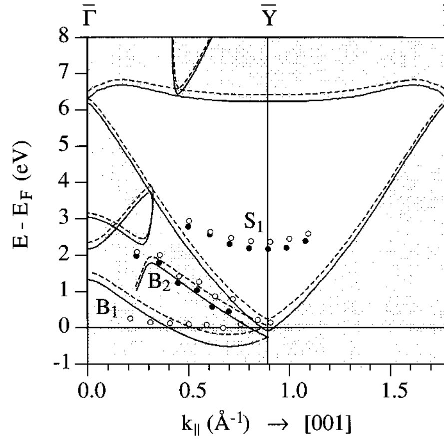

FIG. 2. $E(k)$ diagram showing the projection of the (majority-spin) bulk bands (shaded area) of Ni(110) onto the $\overline{\Gamma Y}$ line and final-state bands where they are accessible via transitions with $h\nu = 9.8$ eV. The latter were obtained using a combined interpolation scheme (Ref. 19) and are shown as full and dashed lines for the majority and minority components, respectively. Experimental peak positions obtained from the data shown in Fig. 1 are shown as circles.

structure and some possible direct radiative transitions with photon energy 9.8 eV. The latter were calculated[20] employing a combined interpolation scheme based on the $E(k)$ relations in Ref. 8.

In general, corresponding minority- and majority-spin states measured at the same angle of incidence lie at a slightly different k because of their difference in energy. The measured separation of the two spin states only corresponds to the exchange splitting if the corresponding final-state bands are flat in the region of k sampled. At an electron incidence angle of 40°, the Shockley surface state S_1 appears close to the $\bar{Y}$ point in the surface Brillouin zone. At this point the dispersion is reasonably flat and the measured separation of 190 ± 30 meV corresponds to the exchange splitting.

The peak positions for the sp-like bulk band feature B_2 are readily determined only for the lower angles of incidence. For higher angles it is masked in the minority-spin channel by the $3d$ peak (B_1). Nevertheless, as evidenced by the results displayed in Fig. 3, where additional peak positions from spectra taken with better resolution have been included, the B_2 exchange splitting increases with increasing $k_\parallel$. This is consistent with the results of the combined interpolation scheme which are reproduced in Fig. 3. A selection of the spectra taken with higher resolution are shown in Fig. 4.

The error bars shown in Fig. 3(b) were determined by the following procedure. To each data point in the IPE spectra we superimposed a random noise value from a statistical distribution equal to that of the statistical error in the experimental data. The pseudoexperimental spectrum obtained in this fashion was then fitted with a least-squares procedure, using the fitting function described above. This procedure was repeated 2000 times for each spectrum, whereby a distribution of best-fit peak positions was obtained for each feature. The standard deviation of this distribution was then used as our error bars for the peak positions of B_2.

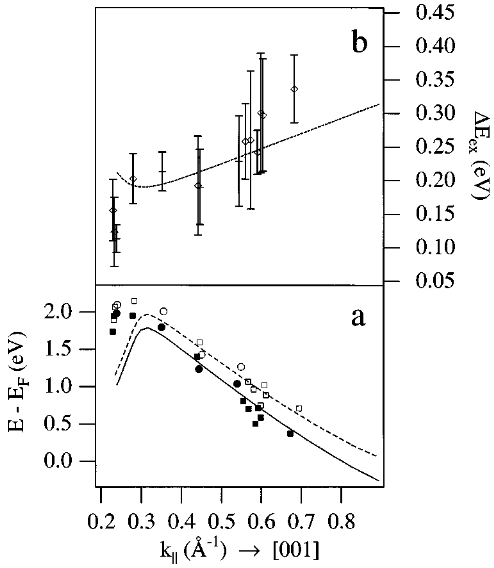

FIG. 3. (a) $E(k_\parallel)$ diagram of experimental (circles) and theoretical (lines) positions of transitions into B_2. Square symbols represent data taken with the 9.5 eV detector. (b) Exchange splitting of B_2 as a function of $k_\parallel$. The diamond symbols are derived from the data taken with the 9.5 eV detector. The error bars for the spin splittings are derived from the standard deviation of the peak positions from a set of 2000 least-squares fits performed for each pseudoexperimental spectrum, where random noise of an identical distribution to the statistical error in the experimental data has been added to each data point. The dashed line refers to the spin splitting of transitions into the theoretical bands (Ref. 20).

Due to the opposite sign of the slope of the initial and final band dispersions, the correct exchange splitting for the B_2 final band should be larger (smaller) than our measured values if the initial band splitting is smaller (larger) than the final band splitting. The large observed variation with k, however, can only be explained if either the initial or final band exchange splitting is varying with k. This is an experimental observation of a k-dependent exchange splitting of an sp-like bulk band.

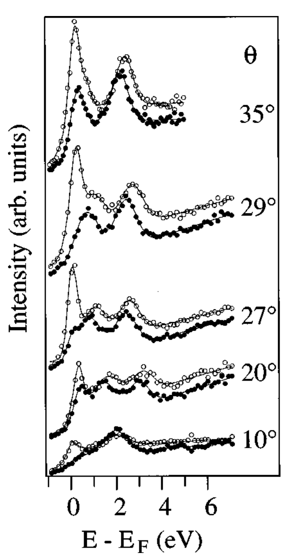

FIG. 4. Higher-resolution spin-polarized IPE spectra ($h\nu = 9.5$ eV) of Ni(110) in the $\overline{\Gamma Y}$ azimuth as a function of the electron incidence angle with respect to the surface normal θ. Fitted functions are shown as lines through the experimental points. Experimental majority (minority) spectra are shown as full (empty) circles.

In qualitative terms, a k variation of the exchange splitting of the final band can be understood by observing that the nearly-free-electron wave vector of the incident electron inside the crystal for small $k_\parallel$ would locate the transition close to the ΓX line, where a mainly p-like band splitting of about 90 meV has been observed.[5] For increasing $k_\parallel$, the transition will move towards the ΓL line leading the final state to gradually acquire more d character and hence a larger exchange splitting. The initial band splitting in the region between the ΓX and ΓL lines is expected to be about 160 meV, the value estimated for the ΓX line.[5]

Near the $\overline{Y}$ point it is likely that the majority-spin part of B_2 falls below the Fermi level since no peak can be observed near E_F in the majority-spin channel of the appropriate spectrum in Fig. 1 (angle of incidence about 50°). If this is the case, the bulk band corresponding to the B_2 feature will contribute to the magnetic moment. Considering the expected surface state near the Fermi level at $\overline{Y}$,[18,19] and the strong sensitivity of B_2 to adsorption of O_2,[17] it seems reasonable to conclude that there is a significant surface contribution to this feature. Hence, B_2 would also contribute to the surface magnetic moment. A surface state has already been shown to contribute to the magnetic moment at $\overline{\Gamma}$ on Ni(111), where a projection of the same bulk band gap $(L_{2'}-L_1)$ occurs. On the other hand, a surface state near the Fermi level in the $L_{2'}-L_3$ gap is expected to have a smaller exchange splitting than the d bands on the basis of its pd hybridization character.[19] It might therefore be expected that the exchange splitting of B_2 decreases again at $\overline{Y}$. Whether or not this is the case cannot be assessed from our data, because B_2 coincides with B_1 at $\overline{Y}$.

In order to test our ideas regarding the assignment of bulk and surface features in the experimental spectra, we compare the experimental results with calculations performed using the PHOTON code. The calculated spectra, shown in Fig. 5, correspond to the sum of the intensity of emitted s- and p-polarized light. The feature in the calculated spectra at highest energy above E_F exhibits similarities with the surface state S_1 in the experiment. The calculated layer photon current for this feature was found to have a maximum at the surface, consistent with its surface character. Moreover, modifications to the surface barrier in the calculations were found to shift the energy position of this feature, while the other features remained unaffected. The image potential state feature S_2 cannot be accurately reproduced by the calculations since it arises from a Coulombic surface barrier.[1]

The middle peak, appearing at 10° incidence angle in the calculated spectra and dispersing down towards the Fermi level with increasing angle, reproduces the sp-like band feature B_2 in the experimental angle-resolved SPIPE spectra. The spin splitting of this feature is marginally larger in the calculated version but the trend of its $k_\parallel$ dependence is identical. The agreement between peak position and dispersion is thought excellent. Moreover, the surface contribution to this calculated feature does indeed increase near $\overline{Y}$ as predicted in Refs. 18, 19.

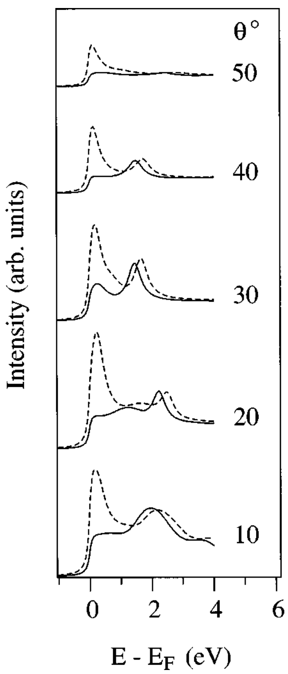

FIG. 5. Calculated spin-polarized IPE spectra of Ni(110) for $h\nu = 9.8$ eV, consisting of the sum of emitted light with s and p polarization. Full (dashed) lines represent majority (minority) spin spectra.

The peak just above the Fermi level in the calculated minority-spin spectra is observed in the s-polarized component. According to symmetry selection rules,[21] this calculated feature would therefore be due to transitions into a band with S_4 symmetry. In the present calculation no self-energy corrections were carried out due to incompatibility with the present code, and hence the calculated S_4 band extends to above the Fermi level. In contrast, experimental photoemission results[22] and band-structure calculations with self-energy corrections[8,23] indicate that the highest point of the minority-spin S_4 band lies *just below* the Fermi level. It was therefore suggested by Woodruff *et al.*[24] and Donath *et al.*[4] that the IPE peak just above the Fermi level for normal incidence on Ni(110) is due to ''density of states'' transitions in which k conservation is largely relaxed and the initial state is of the evanescent type. This would explain the similarity of our calculations and the experimental results in the region of B_1.

IV. SUMMARY AND CONCLUSIONS

We have resolved a k-dependent exchange splitting of an empty bulk sp-like band. The splitting is observed to vary from 113 ± 20 meV to 337 ± 51 meV. This experimental observation is in good agreement with the results from a combined interpolation scheme calculation and the results from calculated one-step SPIPE spectra. It is concluded from the sensitivity of this band to adsorption of O_2 in conjunction with the distribution of calculated layer photocurrents that there is significant surface contribution to this band near $\overline{Y}$. Furthermore, in the latter region it is concluded that this sp-like band is contributing to the surface magnetic moment as observed by the lack of intensity in the experimental SPIPE majority-spin channel. An exchange splitting of 190 ± 30 meV is observed for a Shockley surface state in the projected $(L_{2'} - L_1)$ bulk band gap.

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