Surface Properties and the Photoelectron Spin Polarization of Nickel

D. G. Dempsey and Leonard Kleinman
Department of Physics, University of Texas, Austin, Texas 78712
(Received 20 June 1977)

We calculate the two-dimensional energy bands of a 35-layer (100) Ni film. Surface states exist above the majority-spin d bands throughout the two-dimensional Brillouin zone. Transitions from these surface states into an evanescent LEED (low-energy electron-diffraction) state account for the reversal of photoelectron spin polarization observed 0.1 eV above threshold.

Recently Eib and Alvarado[1] found the polarization of photoelectrons emitted from a (100) single-crystal nickel surface was negative at threshold but changed sign 0.1 eV above threshold. Wohlfarth[2] pointed out he had actually anticipated the experimentally observed polarization reversal.[3] However, Wohlfarth's calculation is based on an overly simplified model density of states (DOS) and requires that Δ, the majority-spin d-band distance from E_F, be 75 meV to have the polarization reversal occur 150 meV above threshold. Band theory indicates that $\Delta > 140$ meV. Furthermore, Smith and Traum[4] point out that if wave vector $\vec{k}$ is conserved in the optical excitation event, it is the joint DOS, not the DOS, which must be used in the polarization calculation. They found the polarization jumped from -100% to $+100\%$ at 0.1 above threshold. They neglected conservation of $\vec{k}$, the transverse component of $\vec{k}$, upon escape. The three-step (excitation, transport, and escape) process which they consider actually contributes nothing to the photocurrent near threshold if $\vec{k}$ is conserved; i.e., electrons which can be excited to positive energies for $\hbar\omega$ close to threshold all have $E < \vec{k}^2$ and cannot escape. We believe that, for an ideal surface, the only allowed photoemission mechanism near threshold is a single-step excitation into an evanescent LEED (low-energy electron-diffraction) state. Note that the three-step process, when allowed, may be considered to be a one-step process going to a propagating (time-reversed) LEED state.[5]

Our earlier parametrized thin-film calculations for Cu[6] and Fe[7,8] suffered from huge sp surface-charge deficits. We have recently shown[9] that if one includes s and p overlap parameters along with the Hamiltonian parameters in the LCAO (linear combination of atomic orbitals) calculation, there exists a continuum of sets of parameters which fit the bulk energy bands equally well. (This corresponds to a continuum in the choice of basis functions ranging from atomiclike wave functions to Wannier functions.) A particular set of bulk Cu parameters yielded surface charge neutrality not only for the (100), (110), and (111) surfaces[9] but for a stepped surface[10] as well. Since without a completely self-consistent calculation one cannot know how much charge is transferred between the sp and d bands at the surface, we base our Ni parameters on Cu as much as possible. We first set[11]

$$H_{pll'm}{}^{\sigma} = H_{pll'm}{}^{\mathrm{Cu}} + \tfrac{1}{2}(\Delta E_l{}^{\sigma} + E_{l'}{}^{\sigma}) S_{pll'm}{}^{\mathrm{Cu}},$$

where $\Delta E_s{}^{\sigma}$, $\Delta E_p{}^{\sigma}$, and $\Delta E_d{}^{\sigma}$ are three parameters chosen to fit the Ni bands[12,13] of spin polarization σ as well as possible. With the thirty-three[14] $H_{pll'm}{}^{\sigma}$ and thirty $S_{pll'm}{}^{\mathrm{Cu}}$ as starting values, we ran our rms-error minimization routine to fit the bulk Ni bands at 43 points in the $\frac{1}{48}$ irreducible Brillouin zone (BZ) with rms errors of 2.56×10^{-3} and 2.45×10^{-3} Ry in the majority- and minority-spin bands.[15] Because Wang and Callaway's energy bands have too large an exchange splitting, we raised the majority-spin intra-atomic d parameter by 0.010 Ry. This yields a splitting of 0.50 eV for the X_5 bulk state in agreement with experiment[12] and a magneton number (0.54) in good agreement with the experimental value[12] of 0.56.

Using these parameters, we calculated the energy bands of a 35-layer (100)Ni film at $N = 576$ points in the 2D BZ. We calculated the local DOS for symmetry α, spin σ, and plane i, using the formula

$$\mathfrak{N}_{i\alpha\sigma}(E) = N^{-1} \sum_{j\beta n\vec{k}} C_{\alpha i}{}^{n\vec{k}\sigma} S_{ij}{}^{\alpha\beta}(\sigma, \vec{k}) \times C_{\beta j}{}^{n\vec{k}\sigma} \delta(E - E_{n\vec{k}}), \quad (1)$$

where $C_{\alpha i}{}^{n\vec{k}\sigma}$ is the coefficient of the ith planar (α, σ) Bloch function appearing in the nth eigenfunction at $\vec{k}$, and $S_{ij}{}^{\alpha\beta}(\sigma, \vec{k})$ is the overlap of two planar Bloch functions. A preliminary calculation found a surface surplus of 0.1135 majority[16]

TABLE I. Surface intera-atomic d parameter shifts (in Ry) and charge associated with each d orbital in the surface and central planes. (xy and x^2-y^2 are referred to the square 2D lattice which is rotated 45° with respect to the cubic lattice.)

	shift	ρ(surf)	ρ(cent)
$(xy)\uparrow$	0.030	0.9417	0.9461
$(xy)\downarrow$	0.020	0.8731	0.8784
$(xz, yz)\uparrow$	0.052	0.9545	0.9265
$(xz, yz)\downarrow$	0.038	0.7879	0.7803
$(x^2-y^2)\uparrow$	0.022	0.9108	0.9261
$(x^2-y^2)\downarrow$	0.013	0.8049	0.7811
$(3z^2-r^2)\uparrow$	0.035	0.9496	0.9454
$(3z^2-r^2)\downarrow$	0.024	0.9085	0.8791
Total		8.873	8.770

d, 0.4507 minority d, 0.0398 s, and a deficit of 0.1388 p electrons per surface atom. By shifting surface intra-atomic d parameters as shown in Table I, we achieved surface charge neutrality. In Fig. 1 we show the majority-spin bands along symmetry lines in the 2D BZ. In Fig. 2 we show the surface and center plane DOS. The Fermi energy obtained by integrating the total DOS up to 10 electrons per atom is -0.3804 Ry (cf. work function[4] of 5.15–5.20 eV). In Table I, we show the contribution of each d orbital to the center and surface planar charge. The surface d excess of 0.103 electron per atom compensates an sp deficit of 0.101 electron per atom.

For the Wohlfarth mechanism which conserves neither $\vec{k}$ nor $\bar{k}$, the photocurrent of spin σ due to transitions occurring in the ith plane is proportional to

$$J_{i\sigma}(\omega) = \int_{\hbar\omega}^{E_F} \mathfrak{N}_{i\sigma}(E)\, dE, \tag{2}$$

where $\mathfrak{N}_{i\sigma} = \sum_\alpha \mathfrak{N}_{i\alpha\sigma}$. The photocurrent from all planes is proportional to

$$J_\sigma = \sum_i J_{i\sigma} \exp(-i/l), \tag{3}$$

where the planes are numbered inward from the (zeroth) surface plane, l is the escape in interplanar spacings (l is between[1] 3 and 6), and

$$P = (J_\uparrow - J_\downarrow)/(J_\uparrow + J_\downarrow). \tag{4}$$

For our $\bar{k}$-conserving process replace $\mathfrak{N}_{i\sigma}$ in (2) by

$$\mathfrak{D}_{i\sigma}(E) = N^{-1} \sum_{j\alpha\beta n\bar{k}} C_{\alpha i}^{n\bar{k}\sigma} S_{ij}^{\alpha\beta}(\sigma, \bar{k}) \times C_{\beta j}^{n\bar{k}} \delta(E - E_{n\bar{k}} + \bar{k}^2)\theta(E_F - E_{n\bar{k}}), \tag{5}$$

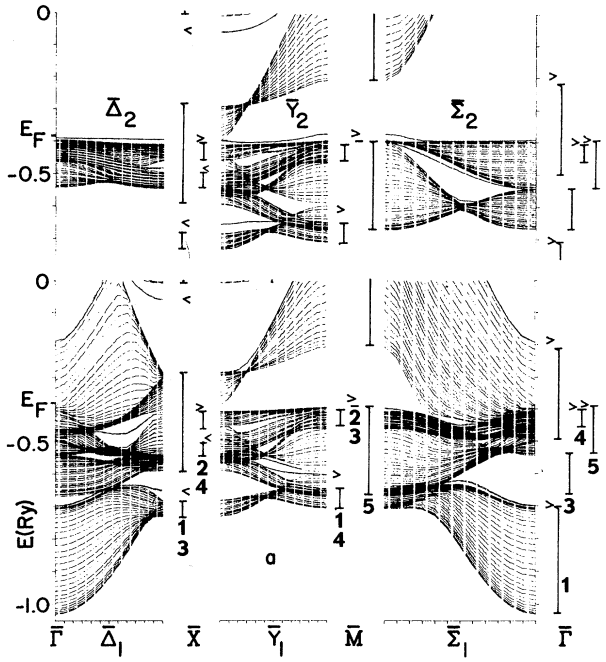

FIG. 1. Majority-spin sub-bands of $\bar{\Delta}_1$-$\bar{Y}_1$-$\bar{\Sigma}_1$ and $\bar{\Delta}_2$-$\bar{Y}_2$-$\bar{\Sigma}_2$ symmetry. Solid lines represent surface-state bands. At symmetry points surface states are represented by arrowheads. When two symmetries span the same energy range, a left-pointing arrowhead represents a surface state of the higher index symmetry, e.g., < represents $\bar{\Gamma}_3$ whereas > represents $\bar{\Gamma}_1$. The minority-spin bands differ mainly in that the $\bar{\Delta}_2$ and $\bar{\Sigma}_2$ surface bands do not extend to $\bar{\Gamma}$ so the $\bar{\Gamma}_5$ ss is missing. The top of the minority-spin d band continuum is 0.022 Ry above E_F.

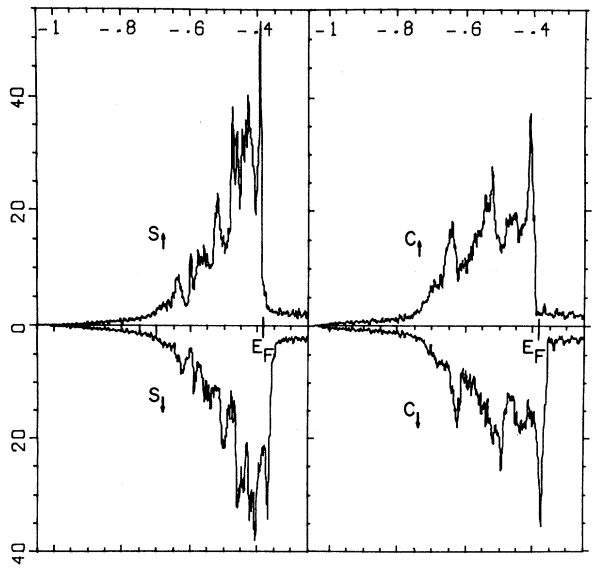

FIG. 2. Surface (S) and center (C) plane majority (↑) and minority (↓) spin density of states in units of electrons per atom per rydberg.

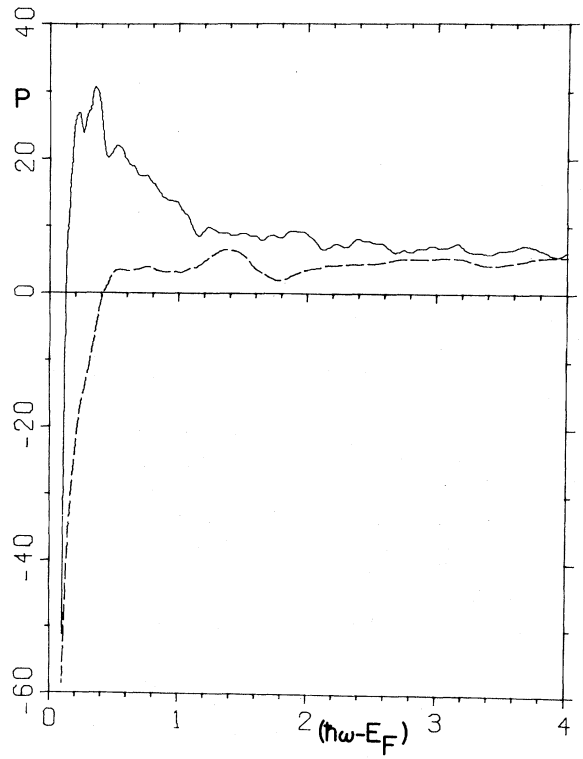

FIG. 3. The Ni photoelectron spin polarization calculated according to the wave-vector–nonconserving Wohlfarth mechanism with $l = 4.5$ (dashed curve) and calculated for $\bar{k}$-conserving transitions into evanescent LEED states (solid curve).

where θ is a step function. Also replace l^{-1} in (3) by twice the decay constant[17] of the evanescent LEED state, $2\alpha = 0.8$ bohr$^{-1} = 2.66/$(interplanar spacing). Before calculating P we rigidly raised the majority-spin bands by 0.004 Ry (which raised E_F by 0.0004 Ry). The Wohlfarth polarization is dominated by interior-plane contributions due to the large value of l, and its curve in Fig. 3 bears very little resemblance to the experimental data.[1] We also show the polarization P calculated from the $\mathfrak{D}_{i\sigma}$'s, almost all of which arises at the surface because of large value of 2α. P starts rising rapidly 0.08 eV above threshold[18] when the majority-spin $\bar{\Gamma}_5$ surface state (ss) begins to contribute, and reverses sign 0.12 eV above threshold. It reaches a maximum value of 32% compared to the experimental maximum of about 36%. The peak of our P curve is not so broad as the experimental curve. This is a consequence of using the threshold value of α everywhere. As the energy increases, more LEED states with differing α's become available until at about 1 eV above threshold transitions to propagating LEED states occur.

Edwards and Hertz[19] have proposed a many-electron explanation of the spin-polarization reversal based on the single-band Hubbard Hamiltonian. The self-energy of majority-spin holes due to spin-wave scattering into minority-spin hole states causes the majority-spin band's leading edge to move closer to E_F. This may account for the total shift of 0.014 Ry that we had to give Wang and Callaway's majority-spin d bands to obtain agreement with the spin-polarization data. Because there are no propagating final states near threshold (i.e., there is a gap around $E=0$, $\bar{k}=0$ in Fig. 1), even if many-body effects were dominant, the appropriate quantity to calculate is not the total DOS but rather the many-body surface $\mathfrak{D}_{i\sigma}(E)$.

There are many ss throughout the 2D BZ in Fig. 1, most of which would occur without the surface-parameter shifts. The twofold degenerate $\bar{\Gamma}_5$ ss and the $\bar{\Gamma}_4$ ss which lie 0.08 and 0.18 eV below E_F for the majority spin are forced out of the continuum by the surface-parameter shifts. These ss are highly localized.[20] Only a single ss exists above the $\bar{\Delta}_2$ and $\bar{\Sigma}_2$ sub-bands but equally localized resonances exist in the $\bar{\Delta}_1$ and $\bar{\Sigma}_1$ continua in the same energy region. Were the peak in the majority-spin DOS to lie even closer to E_F, it could not account for the rapid rise in P. Many-body effects which might cause such a shift are accompanied by lifetime effects which reduce the peak height (see Fig. 6 of Ref. 19), further reducing the rise of P. Therefore we believe that our extremely localized ss are essential for the rapid increase of P. Our eight[21] surface-parameter shifts were chosen to yield these ss[22] and to give surface charge neutrality. They were also chosen so that the largest shifts are for functions with charge lobes pointing toward missing neighbors, but those functions with the largest shift still have the largest surface excess charge (in Table I) even after the shift. Note that we did not choose our surface shifts to be excessively large in order to obtain the ss. Had we chosen our bulk parameters to yield a smaller sp surface charge deficit, the d surface-parameter shifts would have had to be even larger to restore surface charge neutrality. Thus, although our surface parameters are somewhat arbitrary, they satisfy several criteria, are reasonable in every respect, and are as accurate as one could demand with the current state of the art.[23]

This work was supported by the National Sci-

ence Foundation under Grant No. DMR73-02449-A02.

[1]W. Eib and S. F. Alvarado, Phys. Rev. Lett. 37, 444 (1976).

[2]E. P. Wohlfarth, Phys. Rev. Lett. 38, 524 (1977).

[3]E. P. Wohlfarth, Phys. Lett. 36A, 131 (1971).

[4]N. V. Smith and M. M. Traum, Phys. Rev. Lett. 27, 1388 (1971).

[5]D. J. Spanjaard, D. W. Jepsen, and P. M. Marcus, Phys. Rev. B 15, 1728 (1977).

[6]K. S. Sohn, D. G. Dempsey, L. Kleinman, and E. Caruthers, Phys. Rev. B 13, 4640 (1976), and 14, 3185, 3193 (1976).

[7]D. G. Dempsey, L. Kleinman, and E. Caruthers, Phys. Rev. B 12, 2932 (1976), and 13, 1489 (1976), and 14, 279 (1976).

[8]D. G. Dempsey and L. Kleinman, J. Phys. F 7, 113 (1977).

[9]D. G. Dempsey, and L. Kleinman, Phys. Rev. B (to be published).

[10]K. S. Sohn, D. G. Dempsey, L. Kleinman, and G. P. A. Alldridge, Phys. Rev. B (to be published).

[11]To shift the bands rigidly by an amount ΔE, one must change the Hamiltonian parameters by an amount $\Delta H_{pll'm} = \Delta E S_{pll'm}$, where $S_{pll'm}$ is the overlap between l and $l' = s$, p, or d basis functions with azimuthal quantum number m, p neighbors apart.

[12]C. S. Wang and J. Callaway, Phys. Rev. B 15, 298 (1977).

[13]Wang and Callaway performed the calculation with two different exchange potentials. We fit their vBH bands. We thank Dr. Wang and Professor Callaway for giving us their eigenvalues and eigenfunctions throughout the BZ.

[14]There are ten two-center parameters per neighbor and s, p, and d intra-atomic parameters for each spin. There are actually two d intra-atomic parameters but for the $3d$ metals we have always found them to be essentially equal.

[15]The third-neighbor overlap and Hamiltonian parameters are all small, and a reasonable fit could have been obtained without them; also, all dd and ds overlaps vanish so that there are effectively 35 parameters. A table of these parameters will be published elsewhere.

[16]The majority-spin d bands are filled; there are, however, about 0.3 majority-spin d electrons per atom hybridized into bands above E_F. The surface majority-spin d-electron surplus arises from a decrease in hybridization at the surface.

[17]There are no positive-energy states at $\bar{\Gamma}$ below 0.16 Ry. We estimate $\alpha = (\delta E)^{1/2}$, where δE is the distance in energy to a propagating state.

[18]Because only single point in the 2D BZ ($\bar{k} = 0$) contributes within 0.04 eV of threshold and because of the discreteness of the sp bands in a 35-layer film, we happen not to obtain any majority-spin sp contribution near threshold, and the calculated $P_{\text{threshold}} = -100\%$. (The Wohlfarth calculation which samples the entire 2D BZ yielded $P_{\text{threshold}} = -82\%$ due to majority-spin sp contributions.) In order to reduce the noise in $\mathfrak{D}_{i\sigma}(E)$, we doubled the number of points sampled in the 2D BZ for $\bar{k}^2 < 0.08$ Ry.

[19]D. M. Edwards and J. A. Hertz, J. Phys. F 3, 2191 (1973).

[20]The $\bar{\Gamma}_5$ ss has 47, 24, and 13% of its density on the first three planes while $\bar{\Gamma}_4$ has 80, 16, and 3.4%.

[21]After completing this calculation we realized we could calculate these four parameters per spin from three parameters ($\sigma > \pi \gg \delta$) associated with the missing first-neighbor atoms. This also allows us to calculate the diagonal and off-diagonal matrix elements which occur between d functions at lower-symmetry faces. The (100) parameters are multiplied by a single factor for each new face to obtain charge neutrality. This factor is within 11% of unity for the (110) face, which is another indication of the reasonableness of these parameters.

[22]Because of the narrowness of the $\bar{M}_2$ continuum, the $\bar{M}_2$ ss occurs with infinitesimal surface shifts; however, for the ss band to extend all the way to a $\bar{\Gamma}_5$ ss, the (xz, yz) surface shifts must be 0.042 Ry or more.

[23]There are no self-consistent calculations for ferromagnetic surfaces in existence, nor are there any accurate ones likely for some time to come.