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Energy bands of (111) ferromagnetic Ni films

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Using the same bulk Ni linear-combination-of-atomic-orbitals (LCAO) parameters and two-center surface shift parameters that we used for (100) and (110) Ni films, we have calculated the energy bands and planar densities of states for a 32-layer (111) Ni film. Our calculated thin-film bands fail to account for the photoelectron-spin-polarization reversal observed by Eib and Alvarado; this failure is attributed to errors in the bulk energy bands from which the LCAO parameters were obtained and is not believed to be an intrinsic error in the thin-film calculation.

I. INTRODUCTION

We[1] have recently calculated the energy bands of ferromagnetic 35-layer (100) and 47-layer (110) Ni films using the parametrized extended Huckel method.[2] The bulk linear-combination-of-atomic-orbitals (LCAO) Hamiltonian and overlap parameters were obtained by fitting the energy bands of Wang and Callaway[3] to within an rms error of 2.5×10^{-3} Ry. Because the bulk s and p parameters can correspond to any of a continuum of sets of basis functions between Wannier at one extreme and atomic at the other, one has sufficient freedom in choosing those parameters that they can be chosen to be valid not only in the bulk but for all surfaces as well,[1,2] including stepped surfaces.[4] For reasons described in Ref. 1 this cannot be done for $3d$ parameters and so we found a set of first-neighbor potential parameters associated with the missing atoms outside the surface from which intra-atomic d-parameter shifts could be calculated at the surface. These potential parameters were chosen to yield (100)-surface charge neutrality and to cause the occurrence of a surface state above the top of the majority-spin d bands. With this surface state we were able to reproduce the observed[5] photoelectron-spin-polarization reversal which occurs 0.1 eV above threshold for (100) Ni.

We here calculate the energy bands and planar densities of states (PDOS) of a 32-layer (111) Ni film using the same set of bulk parameters together with the missing-atom potential parameters multiplied by a single parameter (whose value is 0.98) chosen to achieve surface charge neutrality. Thus this calculation involves only one new parameter. The photoelectron-spin-polarization reversal observed for (100) Ni is also observed[5] for (111) Ni. We find the needed surface state again occurs along the top of the majority-spin d bands; however, because the highest point in the d bands does not occur at the center of the (111) two-dimensional Brillouin zone (2D BZ), we cannot reproduce the observed (111) photoelectron spin polarization. Very recently Himpsel and Eastman[6] have determined that the bulk majority-spin L_3 level, contrary to the Wang-Callaway (WC) bands,[3] lies only 0.15 eV below E_F, essentially degenerate with the X_5 level. Thus the highest point in the d bands should occur at the center of the 2D BZ for both the (100) and (111) faces and the surface state found in this calculation can play a major role in the photoelectron-spin-polarization reversal.

II. RESULTS

Multiplying the two-center potential parameters associated with missing atoms outside the surface (from Table III of Ref. 1) by 0.98 we obtained the three independent diagonal and one off-diagonal intra-atomic (111)-surface matrix-element shifts shown in Table I. Using the bulk parameters listed in Table I of Ref. 1 and the surface parameter shifts we calculated the energy bands for a 32-layer (111) Ni film at 61 points in the irreducible $\frac{1}{12}$ hexagonal 2D BZ. Our technique for making the Hamiltonian (and overlap) matrices real and a listing of the symmetrized basis functions are given in our[7] (111) iron paper; although the (111) is the most open of the high-symmetry bcc faces, and the tightest packed of the fcc, the symmetry is identical in the two cases.

TABLE I. Intra-atomic d-matrix-element shifts in Ry for the (111) surface plane. The orbitals are referred to the 2D lattice with $\vec{z}=(1,1,1)/\sqrt{3}$, $\vec{x}=(1,\bar{1},0)/\sqrt{2}$, and $\vec{y}=(1,1,\bar{2})/\sqrt{6}$.

	Majority	Minority
xy/xy $(x^2-y^2)/(x^2-y^2)$	0.0127	0.0068
xz/xz yz/yz	0.0381	0.0279
$(3z^2-r^2)/(3z^2-r^2)$	0.0387	0.0283
xy/xz $yz/(x^2-y^2)$	-0.0052	-0.0043

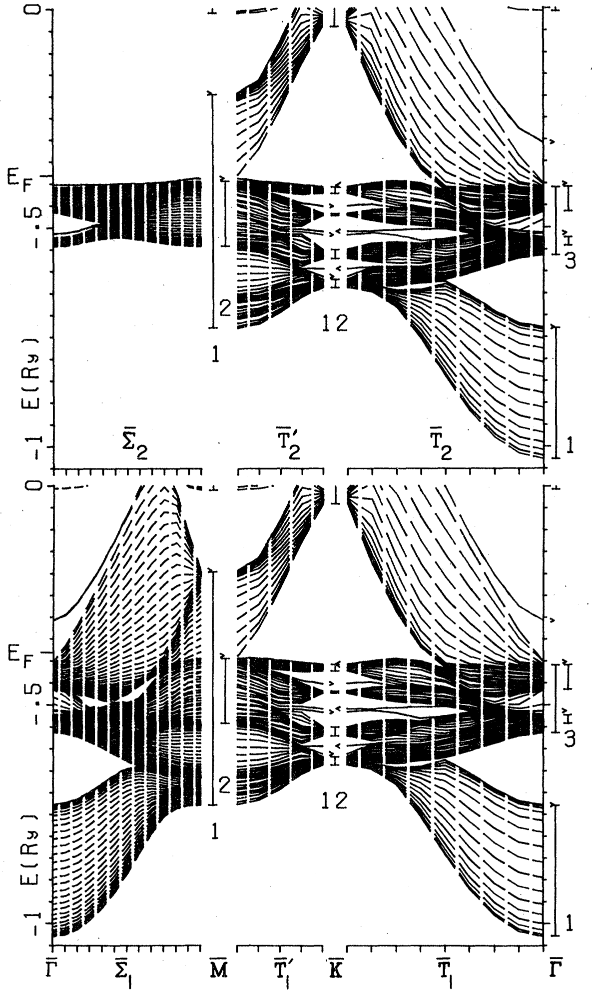

FIG. 1. Majority-spin subbands of $\bar{\Sigma}_1$-$\bar{T}_1'$-$\bar{T}_1$ and $\bar{\Sigma}_2$-$\bar{T}_2'$-$\bar{T}_2$ symmetry for a 32-layer (111) Ni film. Vertical lines at the $\bar{\Gamma}$, $\bar{M}$, and $\bar{K}$ symmetry points represent the energy range of the bulk bands which project into the various 2D symmetries. At symmetry points surface states are represented by arrowheads. When two symmetries span the same energy range, a left-pointing arrowhead represents the higher index symmetry, e.g., <, represents $\bar{K}_2$ whereas > represents $\bar{K}_1$.

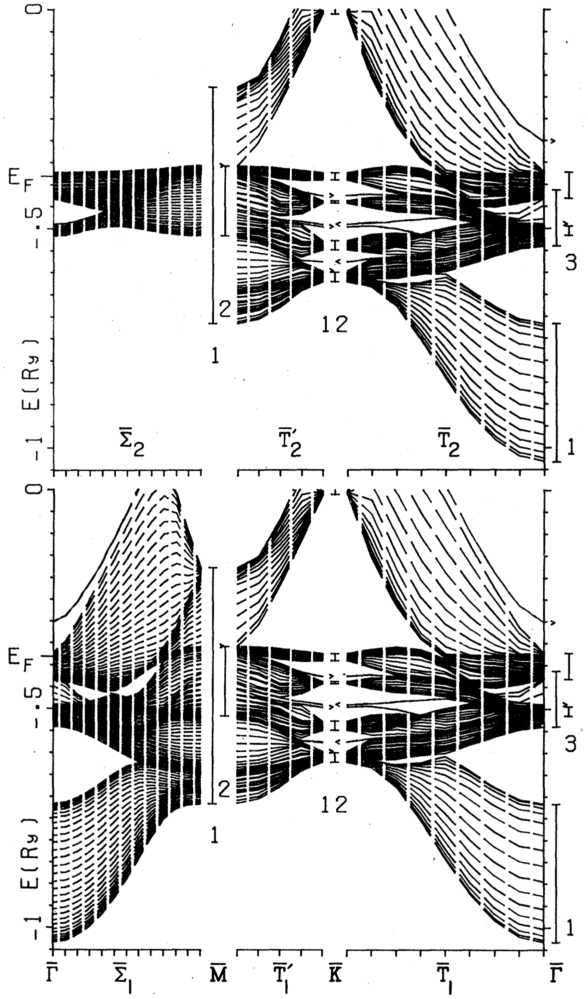

FIG. 2. Minority-spin subbands for a 32-layer (111) Ni film.

In Figs. 1 and 2 we show the majority- and minority-spin energy bands. There are seven $\bar{T}'$-$\bar{K}$-$\bar{T}$ surface state bands lying in three d-band gaps in both the majority and minority bands. (Remember[8] that $\bar{T}_1$, $\bar{T}_2$ and $\bar{T}_1'$, $\bar{T}_2'$ form pairs of surface states on opposite faces of the film.) There is a $\bar{\Sigma}_1$-$\bar{\Gamma}_1$-$\bar{T}$ surface state band running along the bottom of the lowest majority-spin gap. The surface matrix-element shifts for the minority spins are not strong enough to push this surface band out of the continuum. A $\bar{\Gamma}_3$-$\bar{\Sigma}_2$ surface band exists in the only $\bar{\Sigma}_2$ gap for both spins. A $\bar{T}'$ surface band which extends to $\bar{M}_1$ for majority but not minority spins runs for a short distance along the bottom of the highest $\bar{T}'$ gap. A free-electron $\bar{T}$-$\bar{\Gamma}_1$-$\bar{\Sigma}_1$ surface band extends from about -0.4 Ry at $\bar{\Gamma}_1$ nearly up to the vacuum level for both spins. Finally, there is a $\bar{\Gamma}_3$-$\bar{\Sigma}_2$-$\bar{M}_2$-$\bar{T}'$-$\bar{K}_2$-$\bar{T}$ surface state band pushed out of the top of the majority-spin d bands everywhere along the symmetry lines except for the 80% of the $\bar{T}$ line closest to $\bar{\Gamma}$. Because $\bar{\Gamma}_3$ is twofold degenerate it connects not only to the $\bar{\Sigma}_2$ surface band but also to a $\bar{\Sigma}_1$ surface resonance which extends about 25% of the way to $\bar{M}$. In the $\bar{T}$ direction it persists as $\bar{T}_1$ and $\bar{T}_2$ resonances[9] about 65% of the way to $\bar{K}$. It was a surface state (resonance) band like this that enabled us to reproduce the photoelectron-spin-polarization curve[5] for (100) Ni. That curve changes sign with an almost vertical slope just 0.1 eV above threshold. We argued that because of the conservation of the transverse component of wave vector $\bar{k}$, all electrons emitted near threshold must come from the region around $\bar{\Gamma}$ in the 2D BZ. Furthermore for the (100) film there were no propagating bulk states near threshold (i.e., near $E=0$ and $\bar{k}=0$) so that the transition had to occur into an evanescent low-energy electron diffraction state right at the surface. Thus it was necessary to have a majority-spin surface state at $\bar{\Gamma}$, less than 0.1 eV below the Fermi energy. Although there has been no data published on the (111) photoelectron polarization, it is reported[5] to be nearly identical to the (100). Here the $\bar{\Gamma}_3$ surface state lies 0.29 eV below E_F and the top of the majority-spin d bands at $\bar{\Gamma}$ lies 0.10 eV below that. Thus even though a majority-spin bulk band begins just below $E=0$ at $\bar{\Gamma}$, there is no way we can account for the (111)-face photoelectron-spin-polarization reversal at 0.1 eV above threshold with these bands. Because the (111) $\bar{\Gamma}$ states arise from points between Γ and L in the three-dimensional BZ whereas the (100) $\bar{\Gamma}$ states arise from points between Γ and X and because the WC d bands are highest at X, the top of (100) d bands occurs at $\bar{\Gamma}$ but the top of the (111) d bands occurs elsewhere. Very recently Himpsel and Eastman[6] have interpreted their photoemission data to say that the bulk majority spin L_3 level lies only 0.15 eV below E_F, about degenerate with X_5, contrary to WC. If this is the case, then our $\bar{\Gamma}_3$ surface state should lie only 0.05 eV below E_F and would completely account for the photoelectron-spin-polarization reversal. They further find, contrary to WC, that the majority spin L_2' level lies below L_3 and that the free-electron surface state in the L_2'-L_1 gap also lies below L_3. This forces the surface state band to move downward in energy away from $\bar{\Gamma}$ rather than sweeping upward toward the vacuum level as we have found it. In fact, if their ordering of the bulk bands and the $\bar{\Gamma}_1$ surface state is correct, it could not form a surface state band; the $\bar{\Gamma}_1$ surface state however could join to a very strong surface resonance band which would be experimentally indistinguishable from a surface state band. WC had an exchange splitting of about 0.64 eV; we[1] were able to reduce that to 0.50 eV by shifting their majority d bands upward. We could not further reduce it without spoiling agreement with the experimental magneton number. Himpsel and Eastman[6] find the exchange splitting to be less than 0.5 eV but that the d bands are also narrower than WC's which enables the magneton number to be preserved. If the exchange splitting and d-band width were small enough (which is contrary to other recent experimental evidence[10]), the photoelectron spin polarization could be explained without requiring a majority-spin surface state band at the top of the d bands. It seems to us

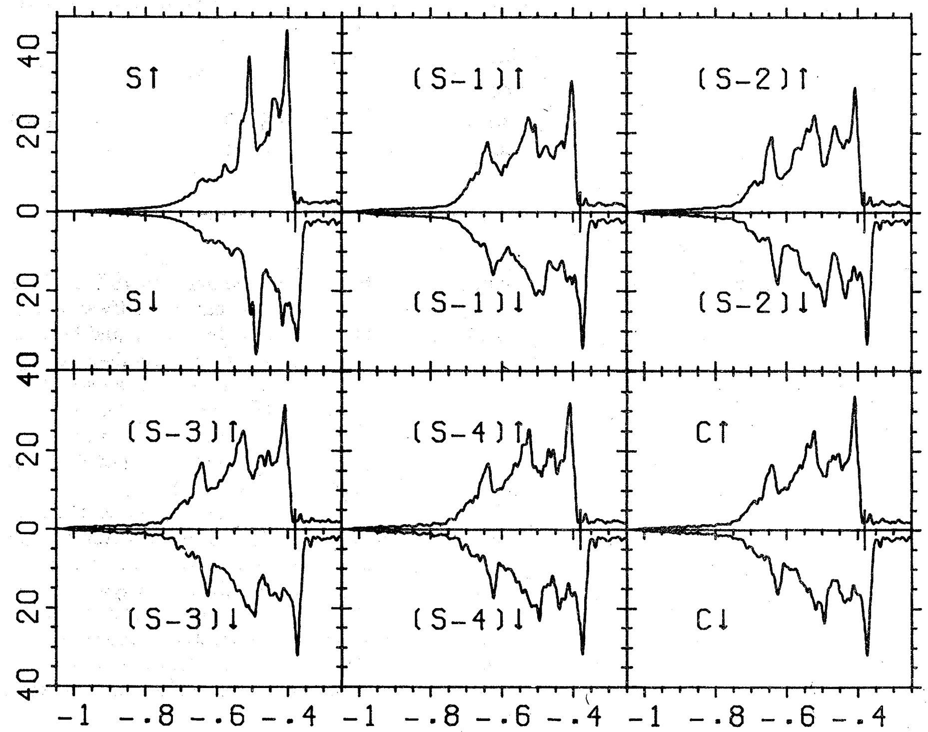

FIG. 3. Majority- (↑) and minority- (↓) spin PDOS for the surface (S) and next four interior (S-n) and central (C) planes of (111) Ni in electrons per atom per rydberg. The large mark on the abscissa is at $E_F = 0.3805$ Ry.

though that, more likely than not, the surface band is needed. What is becoming increasingly clear is that the photoelectron spin polarization can be explained entirely within one-electron theory without recourse to many body effects.[11]

In Fig. 3 we show the PDOS for the surface and next four interior planes as well as the central[12] plane. In Table II we list the charge on the surface, first interior and central planes broken into *sp* and *d* contributions. The net deficit on the surface plus first interior planes means that our surface parameter shifts were slightly too large; the multiplicative factor should have been about 0.96 rather than 0.98. The Fermi energy is –0.3805 Ry in agreement with the (100) and (110) calculations. [We did not rigidly shift the (111) bands in order to account for the difference between the (100) and (111) work functions.] An additional indication of the numerical consistency of the calculation is that the *sp*↑, *sp*↓, *d*↑, *d*↓ breakdown of the central plane charge is the same for all three films. The surface plane *sp* to *d* charge transfer is seen to be 0.06 electrons per atom compared with 0.10 and 0.16 for the (100) and (110) faces. This is a consequence of surface effects being weaker for more tightly packed faces. Another indication of the strength of the surface perturbation comes from the size of the surface shift needed to restore surface charge neutrality. It is easy to see in our two-center approximation that the sum of the *diagonal* matrix-element shifts is independent of the positions of the missing first neighbors.[13] Thus the sum of the diagonal matrix-element shifts is proportional only to the number of missing first neighbors and the factor by which the two-center potential parameters were multiplied to obtain charge neutrality. Thus the relative strengths of the surface shifts are $3 \times 0.98 = 2.94$, $4 \times 1 = 4$, $5 \times 0.886 = 4.43$ and $1 \times 0.886 = 0.886$ for the (111), (100), and (110) surface planes and the (110) first interior plane.

TABLE II. Charge in the surface, first interior, and central planes of (111) Ni broken into majority- and minority-spin and *sp*- and *d*-basis-function contributions.

	$\rho\,(S)$	$\rho\,(S\text{-}1)$	$\rho\,(C)$
sp↑	0.5764	0.5940	0.5997
sp↓	0.6018	0.6229	0.6307
d↑	4.6852	4.6852	4.6702
d↓	4.1444	4.0713	4.1012
Total	10.0078	9.9734	10.0018

In conclusion, we have calculated the energy bands and PDOS of the three faces of ferromagnetic Ni. These calculations are completely consistent with one another and with the WC bulk energy bands. We have found, besides the usual surface states which occur in band gaps, a surface state band running along the top of the *d* bands which explains the photoelectron-spin-polarization reversal observed in (100) Ni. It does not explain the reversal observed in (111) Ni; this failure is believed to be due to errors in the WC energy bands and not an intrinsic failure of the thin-film calculation.

ACKNOWLEDGMENT

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[8] See Ref. 26 of Ref. 2.

[9] Another very strong resonance band emanates from the lower Γ_3 aurface state running as a $\bar{\Sigma}_1$ resonance 25% of the way to $\bar{M}$ and as a $\bar{\Sigma}_2$resonance from the end of the $\bar{\Sigma}_2$ surface state to 75% of the way to $\bar{M}$. It runs as T_1, T_2 resonances halfway to $\bar{K}$, splitting and running around both the top and bottom of the long gap at about –0.5 Ry. Yet another strong resonance starts at –0.65 Ry as $\bar{M}_1$ and runs as a T_1', T_2' band over 75% of the way to $\bar{K}$. Very similar resonances are also observed in the minority spin bands.

[10] E. Dietz, U. Gerhardt, and C. J. Maetz, Phys. Rev. Lett. 40, 892 (1978).

[11] L. Kleinman, Phys. Rev. B 17, 3666 (1978).

[12] Since we have an even number of planes in this film, by central plane we mean either of the planes of atoms adjacent to a plane through the center of the film.

[13] The sum of the squares of the five *d* functions has spherical symmetry as does the potential of the missing first neighbor. Thus the sum of the matrix elements depends only on the distance of the missing first neighbor.