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Electronic structure and magnetism of the Cu/Ni{100} interface: Self-consistent local-orbital calculations

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The spin-polarized electronic structure of $p(1\times1)$Cu on both sides of a three-layer Ni{100} slab has been calculated using the self-consistent local-orbital method. The Ni layer adjacent to the Cu overlayer has its magnetic moment reduced to $0.37\mu_B$ compared with the bulklike center-plane moment $0.55\mu_B$. The Cu adlayer is essentially unpolarized. We attribute the interface-moment reduction to *sp-d* charge transfer and hybridization of Cu *sp* and Ni *d* levels. The *d*-electron number is 8.91 at the interface, while the central-plane value is 8.74, just as we found earlier for five-layer Ni{100}. All layers are nearly charge neutral. Our results for the magnetic moments agree well with those of Tersoff and Falicov, who did not allow for *sp-d* charge-transfer effects. Adsorbate bands are presented which should be observable in angle-resolved photoemission spectroscopy. These bands may be described as Cu-monolayer bands, shifted and broadened by interaction with the Ni substrate.

I. INTRODUCTION

Recent advances in experimental techniques for measuring spin polarization at solid surfaces have stimulated theoretical efforts to formulate a consistent picture of surface magnetism. For the prototype Ni{100} surface, several self-consistent calculations of the electronic structure and magnetism have been reported,[1-4] all based on local-spin-density-functional (LSDF) theory.[5,6] Ultrathin films were used to simulate the surface behavior; due to the efficient screening in Ni, only the surface density of states (DOS) deviates widely from the bulk DOS. Thus even a three- or five-layer Ni film is thick enough to model the surface magnetic behavior, though thicker films are required to identify surface states which decay slowly into the bulk. Because of the extensive redistribution of charge at the surface, only self-consistent calculations have predictive capabilities.

Two rival computational schemes have been developed for self-consistent determination of surface magnetic behavior. The first approach[2,3] uses a surface-adapted linear augmented plane-wave (LAPW) method including, in some cases, non-muffin-tin terms in the charge density and potential. The self-consistent local-orbital (SCLO) (Refs. 4 and 7) method expands the wave function in atomic orbitals, including core, valence, and virtual orbitals. These orbitals are fitted to a series of even-tempered Gaussians for computational convenience. By expanding potential changes in a Fourier series, matrix elements can be evaluated analytically at all stages of the iterative process by which the LSDF equations are solved. An earlier local-orbital method[1] evaluated these matrix elements by direct numerical integration. However, because of the way in which the charge density was fitted, the calculations were not fully self-consistent.

Two groups[2,3] reported calculations for Ni{100} films using the LAPW method. Both groups found similar electronic structure and obtained a definite surface enhancement of the magnetization. More recently, we performed SCLO calculations for this surface,[4] and found excellent agreement with the LAPW results: the magnetic moments were $0.66\mu_B$, $0.55\mu_B$, and $0.61\mu_B$ per atom on the surface, subsurface, and central layers, respectively. The LAPW results were $0.65\mu_B$, $0.58\mu_B$, and $0.61\mu_B$ (Ref. 2) and $0.64\mu_B$, $0.55\mu_B$, and $0.54\mu_B$ (Ref. 3). By repeating the calculations after omitting hybridization matrix elements, we assessed the relative importance of *sp*-band narrowing and hybridization. Both factors were found to contribute appreciably to the surface-moment enhancement.

Here we report SCLO calculations of the electronic structure and magnetism of the Cu/Ni{100} interface. We have chosen to simulate this system with a $p(1\times1)$ layer of Cu adsorbed on both faces of a three-layer Ni{100} film, denoted as Cu/Ni$_3$. Earlier results derived using a parametrized Hartree-Fock approach by Tersoff and Falicov[8,9] suggest that even a single layer of Cu adsorbed on Ni establishes essentially ideal interface behavior. Of course the Ni$_3$ substrate is too thin to yield a complete description of slowly decaying interface states; nonetheless, the Cu/Ni$_3$ sandwich has the correct bulklike electronic structure and magnetism at the central layer. Also, we note that all layers are essentially charge neutral. Adsorbate bands and magnetic behavior are, we believe, treated accurately in this model.

Tersoff and Falicov[8,9] found that Cu suppresses the magnetism of the topmost Ni layer due to *sp-d* hybridization between Cu and Ni on adjoining layers. We undertook our SCLO calculations to check this conclusion in the framework of a fully self-consistent approach. Also, we hoped to identify adsorbate bands which could be mapped out by angle-resolved photoemission experiments, as was recently accomplished[10] for the analogous system Ni$_{0.84}$Cu$_{0.16}$(111).

The SCLO method[7] and its extension to treat spin polarization[4] have been described in detail before. We used 24 basis orbitals per atom, including 4*p*, 4*d*, and 5*s* virtual orbitals in addition to the core and valence orbitals. Fourier integrals of the charge density were computed using a mesh-point separation of 0.248 Å (one-tenth the nearest-neighbor distance). The repeat distance perpendicular to the film was 24.55 Å. The Cu-Ni and Ni-Ni interplanar separations were identical and equal to the spacing of bulk Ni planes. A $\vec{k}$-space sample of 15 special points[11] in the irreducible wedge of the two-dimensional Brillouin zone was used to compute the charge density at each iteration, but a Monte Carlo sampling of 10 000 points in the full zone was used to compute the DOS after the last iteration of the LSDF equations. The iterations were terminated when all matrix elements were converged to within 0.05 eV. Orbital occupation numbers were determined for each layer by numerical integration of the projected DOS up to the Fermi energy E_F. The exchange-correlation potential we used[4] is essentially the one developed by Vosko, Wilk, and Nusair[12] by interpolation of electron-liquid results from the high-density (random-phase approximation) region to low density, where accurate Monte Carlo results are available.[13] The commonly used von Barth—Hedin exchange-correlation potential[5] slightly exaggerates the tendency for correlation to oppose ferromagnetism.

In the next section we present a detailed discussion of our results for the magnetic behavior of Cu/Ni$_3$. In addition, we discuss the origin of the interface-moment reduction by examining orbital occupation numbers and the effects of setting certain hybridization matrix elements equal to zero. The projected DOS and spin-polarized energy bands are presented in Sec. III; adsorbate energy bands are identified. We conclude with a brief summary in Sec. IV.

II. INTERFACE MAGNETISM

The computed spin magnetic moments for Cu/Ni$_3$ are given in Table I for the three inequivalent layers labeled as *S* (surface), $S-1$ (subsurface or interface), and $S-2$ (central layer). The surface (Cu) layer has negligible magnetization. For comparison we also give results for Ni$_3$ and Ni$_5$ films,[4] and for a semi-infinite Cu/Ni{100} interface, found using a parametrized Hartree-Fock method by Tersoff and Falicov.[8,9] Our result for the interface moment $0.37\mu_B$ is 33% smaller than our central-plane moment $0.55\mu_B$. The bulklike behavior of the central layer justifies our use of a five-plane film to simulate the Cu/Ni{100} interface. As shown in Ref. 9 ideal interface behavior is established with only a single atomic layer of Cu.

The strong suppression of interface magnetism contrasts sharply with the definite surface enhancement found for Ni$_3$ and Ni$_5$ films.[2-4] The recent results of Tersoff and Falicov[9] are in reasonable agreement with our results for the interface: their interface moment is $0.39\mu_B$, and bulklike behavior is established at the second or third Ni layer. Earlier results[8] obtained by the same authors (in Ref. 8 but not in Ref. 9, *sp*-*d* charge transfer was allowed) predicted a larger suppression of the interface magnetization—more than 50% compared with their bulk value $0.62\mu_B$.

Two conceptual viewpoints can be used to discuss the physical origin of the interface-magnetism suppression seen in Table I. In the first, the "alchemy" viewpoint, one imagines a conversion of the top layer of Ni{100} into Cu and studies the magnetic behavior of the subsurface (Ni) layer (we ignore possible changes of interlayer spacing since the lattice spacings of Cu and Ni differ by about 2%, and no evidence for substantial relaxation at Cu or Ni{100} surfaces has been found). In the second approach, the "chemisorption" viewpoint, the influence of a Cu adlayer on the properties of a Ni{100} substrate is considered. The first approach is simpler because it entails no change of coordination number for any Ni atom; only the surface chemical species is changed. Now *sp*-electron occupancy plays an important role in magnetic properties because it has a direct bearing on the number of *d* holes and hence the magnetic moment (indeed, we have argued[4] that the surface-induced increase of *sp* occupation partly explains the surface enhancement of the moment for Ni{100}). At the Cu/Ni interface, however, a large change of *sp* occupation compared with the subsurface layer of Ni{100} is not expected since the " box" of atoms confining the nearly-free-electron gas looks essentially the same if some Ni atoms are replaced with Cu atoms. One factor affecting the interface moment[9] from the alchemy viewpoint is the weakening of interlayer *d*-*d* interactions because of the energetic separation of the *d*-band complexes of Cu and Ni. Since the *d*-band DOS of Cu is lower than that of Ni, a definite narrowing of the subsurface DOS, particularly near E_F, is found for Cu/Ni$_3$ when compared with Ni$_5$. As discussed below, this effect reduces the interface magnetic moment by inducing a

TABLE I. Layer-projected spin magnetic moments (in μ_B/atom) of Cu/Ni$_3$ (three-layer Ni{100} slab with Cu monolayers on each side; all interlayer spacings are equal to the bulk spacing of Ni), obtained from the Löwdin projection method (Ref. 14). Earlier results for a semi-infinite Cu/Ni{100} interface, obtained by Tersoff and Falicov (Refs. 8 and 9) are also given; the results in parentheses are taken from Ref. 8. These results are compared with our earlier calculations (Ref. 4) for three- and five-layer Ni{100} slabs (Ni$_3$ and Ni$_5$). *S* is the surface layer, $S-1$ the subsurface, etc.

Layer	Ni$_3$	Ni$_5$	Cu/Ni$_3$	Cu/Ni (Refs. 8 and 9)
S	0.71	0.66		
$S-1$	0.61	0.55	0.37	0.39(0.30)
$S-2$		0.61	0.55	0.51(0.50)
$S-3$				0.57(0.60)

TABLE II. Layer- and orbital-projected moments of the subsurface planes ($S-1$) of Ni_5 and Cu/Ni_3, obtained by the Löwdin projection method (Ref. 14). Results for the center plane of Cu/Ni_3 are also given; note the similarity between the first and third columns.

	Ni_5	Cu/Ni_3	
Orbital	$S-1$	$S-1$	$S-2$
$3z^2$-r^2	0.052	0.036	0.041
xy	0.142	0.128	0.144
xz,yz	0.143	0.077	0.133
x^2-y^2	0.093	0.055	0.105
sp	−0.020	−0.008	−0.007
$m\,(\mu_B)$	0.0553	0.366	0.550

charge transfer from *sp* to *d* states. The interface moment is also reduced by increased *sp*-*d* hybridization.

From the perspective of the chemisorption approach, one factor suppressing the top Ni-layer magnetism is the confinement of the *sp*-electron gas by the Cu adlayer. This broadens and raises the nominal *sp* band, leading to a decrease in *sp* occupancy and hence a filling of *d* holes. The adlayer also broadens the *d* bands through hybridization and delocalizes the wave functions that extend toward it. Both of these effects also reduce the magnetic moment. Interface magnetism may also be affected by charge transfer between Cu and Ni atoms. Our results show, however, that fewer than 0.04 electrons per atom are transferred from the Ni interface to the Cu overlayer, due to the efficient screening. From either the alchemy or chemisorption perspective, charge-transfer effects are small.

To study the factors affecting interface magnetism we present, in Tables II–IV, atomic-orbital decompositions of the magnetic moments and valence charges of Cu/Ni_3. Again, the Löwdin occupation numbers[14] were used. We begin in Table II with a tabulation of magnetic moment contributions associated with each orbital type. Adopting the alchemy viewpoint, we compare the second-layer moments of Ni_5 with those of Cu/Ni_3. Most of the interface-moment reduction, $0.154\mu_B$, can be attributed to the *xz,yz* orbitals (we use bulk axes, with the *z* axis normal to the film). These orbitals, directed toward surface atoms, are the most affected by the alchemy. On the other hand, the interface *d* orbitals with the weakest coupling to the surface ($3z^2$-r^2 and *xy*) are least affected. The center layer ($S-2$) of Cu/Ni_3, similar to the subsurface layer of Ni_5, is bulklike: the total moment is near the bulk value[15] $0.56\mu_B$, and the equivalent t_{2g} orbitals (xy,xz,yz) have nearly identical contributions to the moment. The *sp*-orbital contributions are small and negative.

We now discuss the physical origin[9] of the interface-moment reduction in the alchemy perspective. As noted above, one effect of the replacement Ni→Cu on the surface is to weaken the interlayer *d*-*d* interaction, particularly near E_F. Thus the subsurface DOS is narrowed compared with its bulklike behavior in Ni_5; it may also be shifted to somewhat higher energy due to its repulsion by the copper *d* bands. Now the center of gravity of the Ni *d*-band is below E_F, so band narrowing fills some *d* holes (the effect may be reduced by the center shift). Since the majority-spin band is already full (except for a small number of hybridization holes), the principal effect is to increase the number of minority-spin electrons, where its DOS has a large peak at E_F. Increasing the *d* charge increases the total charge, and electrostatic shifts that restore charge neutrality push all the subsurface bands to somewhat higher energy. We may expect that, at self-consistency, a net increase of *d* character and corresponding decrease of *sp* character will occur. The magnetic moment and exchange splitting at E_F will be reduced. These trends are evident in Table III, which displays the *d*-band occupation numbers for both spin directions. Again, the subsurface layers of Ni_5 and Cu/Ni_3 are compared. The majority-spin *d*-orbital occupancies are reduced by only 1% in the sandwich, while the minority-spin *xz*, *yz*, and x^2-y^2 orbitals increase their occupancies by 0.057, 0.058, and 0.027 electrons per atom, respectively. These orbitals all make a substantial contribution to the DOS peak at E_F. The last column of Table III shows the contribution of each *d* orbital to the interface-moment decrease. The total deficit, $0.98\mu_B$, is due to a decrease (increase) of 0.054 majority-(0.143 minority-) spin electrons. The net excess of *d* electrons is 0.088 per atom.

Tersoff and Falicov identified a second factor that reduces the interface magnetic moment: increased hybridization between Cu *sp* and Ni *d* orbitals compared with bulk Ni. Hybridization leads to a broadening and rounding of the *d*-band DOS and reduces the effective exchange interaction. To better understand the importance of

TABLE III. Orbital occupation numbers (in electrons/atom) for both spin directions on subsurface ($S-1$) planes of Ni_5 and Cu/Ni_3. The interface-moment reduction is given in the last column. The total *d* charge, n_d, and the *d*-electron moment, m_d, are also given.

	Ni_5		Cu/Ni_3		
Orbital	↑	↓	↑	↓	$\Delta m\ (\mu_B)$
$3z^2$-r^2	0.944	0.895	0.928	0.894	−0.015
xy	0.926	0.783	0.915	0.785	−0.013
xz,yz	0.936	0.792	0.927	0.849	−0.066
x^2-y^2	0.957	0.865	0.947	0.892	−0.037
Total	4.698	4.127	4.644	4.270	−0.198
n_d	8.826		8.914		
$m_d\ (\mu_B)$	0.571		0.374		

TABLE IV. Orbital-projected magnetic moments of the Ni interface layer in Cu/Ni_3, computed when certain Cu-Ni hybridization matrix elements are ignored. H_0 is the Hamiltonian neglecting *sp*-*d* as well as *d*-*d* interactions, H_{dd} and H_{spd} are the hybridization terms. The last column shows results obtained using the full Hamiltonian (see the second column of Table II).

	Magnetic moment (μ_B)			
Orbital	H_0	H_0+H_{dd}	H_0+H_{spd}	H
$3z^2$-r^2	0.034	0.038	0.035	0.036
xy	0.134	0.136	0.128	0.128
xz,*yz*	0.081	0.089	0.062	0.077
x^2-y^2	0.062	0.054	0.060	0.055
sp	−0.003	−0.003	−0.009	−0.008
m (μ_b)	0.389	0.403	0.337	0.366

Cu-Ni hybridization, we successively omitted the following matrix elements of the *self-consistent* Hamiltonian: (a) all Cu-Ni interactions, (b) interactions between Cu *sp* and Ni *d* orbitals (retaining *d*-*d* terms), and (c) *d*-*d* interactions only. The results, given in Table IV, show that these hybridization terms reduce the interface moment. Specifically, *d*-*d* interactions [case (b)] increase the moment of case (a) by $0.014\mu_B$, while *sp*-*d* interactions decrease it by $0.052\mu_B$. When both sets of interactions are included, the moment reduction is only $0.022\mu_B$. Presumably, the increase in case (b) is due to *d*-band broadening, while the decrease in case (a) is caused by hybridization holes in the *d* band.

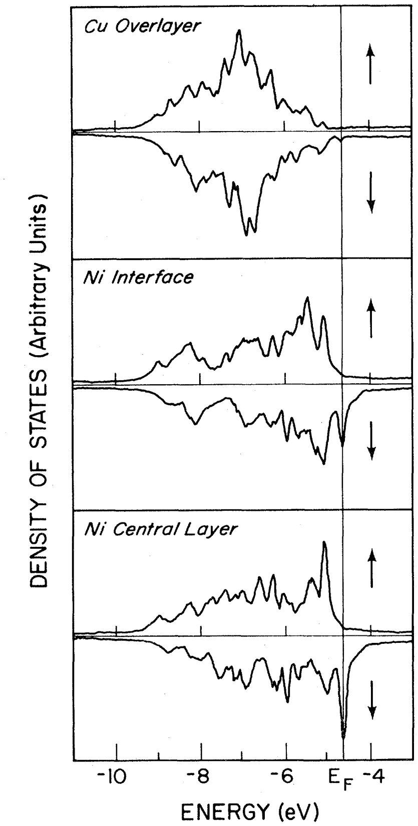

FIG. 1. Layer-projected DOS of Cu/Ni_3 in the *d*-band region for majority (↑) and minority (↓) spins, obtained using the Löwdin projection technique (Ref. 14). The energy zero is the vacuum level.

A precise assessment of the relative importance of charge transfer and hybridization effects does not seem possible since both interact with one another in a highly nonlinear fashion. In our judgment both factors should be included in a fully self-consistent calculation. Because the parametrized model of Ref. 9 is not well-suited to treat charge transfer accurately at the surface, *sp* and *d* occupancies were frozen at their bulk values (by adjusting on-site potentials). With this constraint, the computed interface-moment reduction was about 30%, in agreement with our result in which the charge transfer was computed self-consistently. Yet when this constraint was not used, Tersoff and Falicov[8] predicted a reduction of about 50%. In most other respects, e.g., energy bands and DOS, there is no significant disagreement between our results and those of Ref. 9.

III. DOS'S AND SURFACE BANDS

The layer-projected DOS of Cu/Ni_3 is shown in Fig. 1 for both spin directions. Note that the work function, 4.7 eV, is close to that of the isolated Cu monolayer, 4.6 eV (the value for Ni_5 is 5.0 eV). The surface DOS shows the expected narrowing compared with the inner planes; its center of gravity is about 1 eV lower than that for the Ni planes, and the exchange splitting is negligible. Compared with the bulklike DOS of the central layer (see Fig. 1), the interface DOS is somewhat narrower. The latter resembles the surface DOS of Ni_5, with higher amplitude near E_F than at the *d*-band minimum; see Fig. 2 for a comparison.

The spin-polarized energy bands of Cu/Ni_3 are given in Figs. 3 and 4. Not surprisingly, they appear to be an

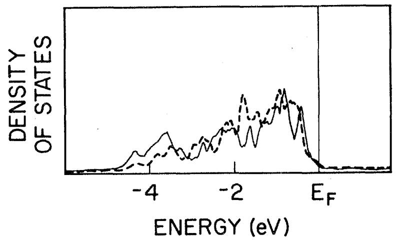

FIG. 2. Interface DOS in the *d*-band region for majority-spin states in Cu/Ni_3 (solid line). The surface DOS of $Ni_5\{100\}$ (dashed line) is shown for comparison.

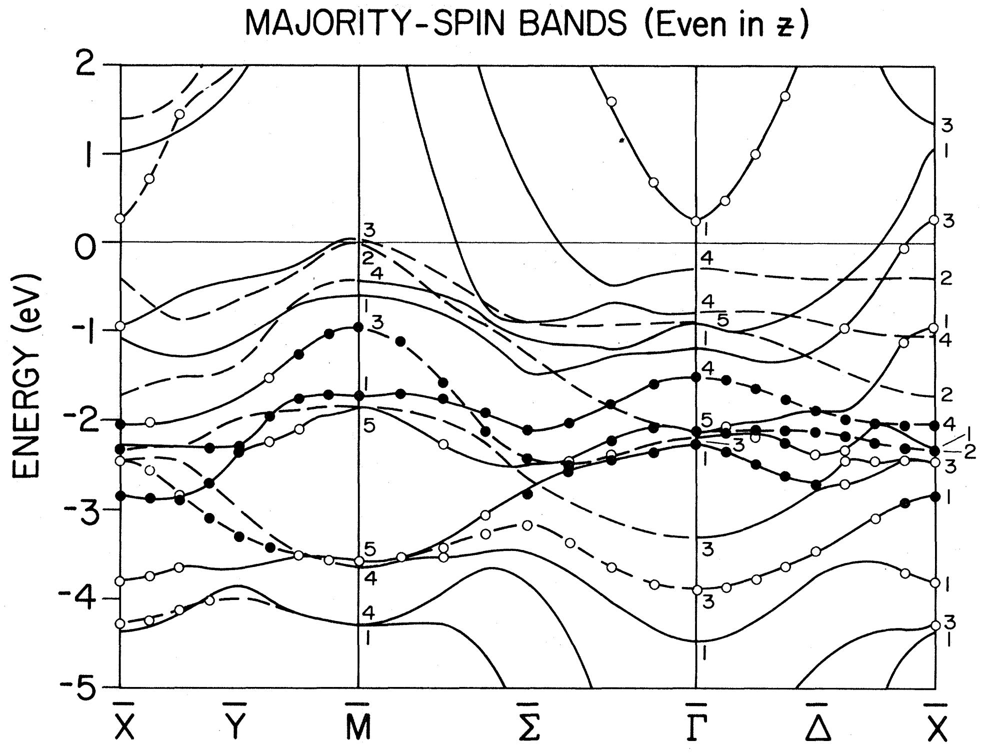

FIG. 3. Majority-spin energy bands of the Cu/Ni_3 film in the two-dimensional Brillouin zone adopted in Ref. 4. Symmetry labels agree with standard usage (Ref. 16), and even (odd) bands, with respect to vertical reflection planes, are denoted by solid (dashed) lines. Only bands of even z-reflection character are given. The Fermi energy is the energy zero. Closed circles denote states with 70% or higher surface character; open circles indicate 50—70 % surface character.

amalgamation of the bands for (a) the isolated Cu monolayer, and (b) the Ni_3 film. Energy levels with 70% or more probability on Cu atoms are denoted with closed circles; those with 50—70 % Cu character are denoted with open circles. Some portions of the Cu-like bands have a clear correspondence with monolayer results,[7] for example, the portions near $\bar{\Gamma}_4$ and $\bar{M}_3$. Other portions mix more strongly with Ni levels, and their dispersion is quite

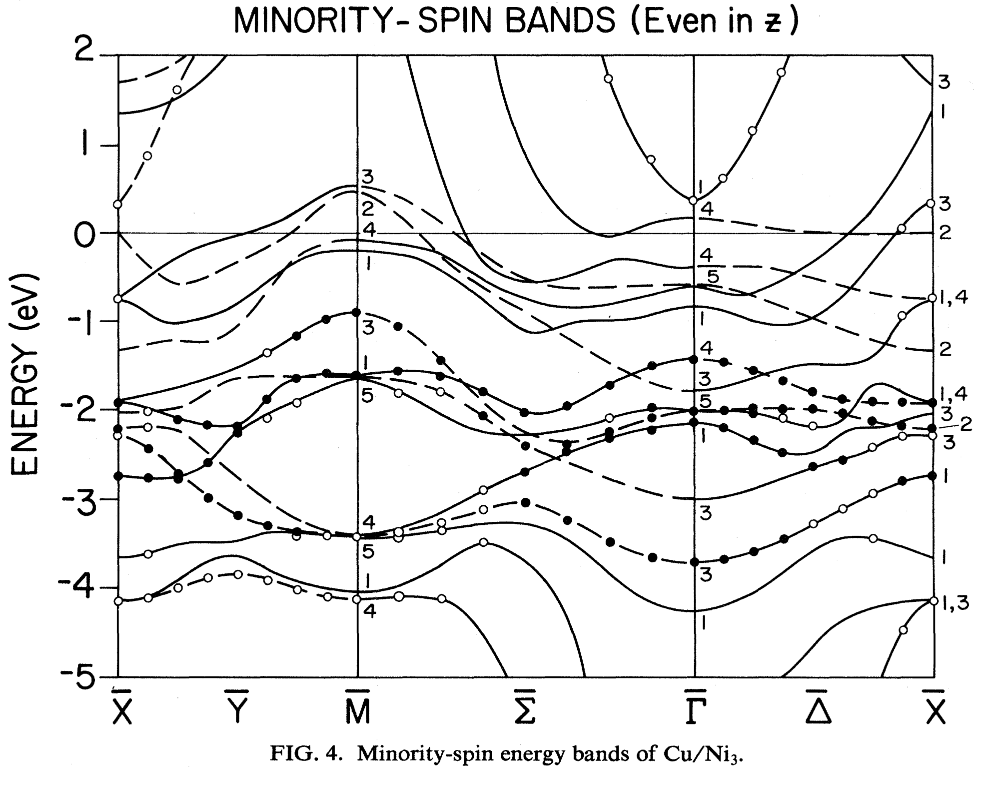

FIG. 4. Minority-spin energy bands of Cu/Ni_3.

different from the monolayer case. The *sp* bands and some *d* bands hybridize to such an extent with Ni bands that they cannot be considered surface bands. Finally, most of the bands within 1 eV of E_F have mainly Ni character, as expected. Those levels in Figs. 3 and 4 with mainly Cu character should be detectable in angle-resolved photoemission spectroscopy as surface bands. They should be sensitive to adsorption or sputtering, and their dispersion should be independent of the photon energy. The use of polarized light should aid in their identification. Analogous bands were mapped out[10] for $Ni_{0.84}Cu_{0.16}(111)$, where surface segregation produces a Cu-rich outer layer. In this system, the measured dispersion bore a striking resemblance to the calculated energy bands of a free Cu(111) monolayer. The best agreement between calculated and measured bands was obtained when the former were shifted rigidly downward in energy by 1.24 eV; the shift was attributed to the substrate.[10] For the {100} film studied here, the monolayer dispersion is both broadened and shifted by contact with the underlying Ni.

Our model film is not thick enough to permit straightforward identification of interface states; i.e., states concentrated on the subsurface Ni layer. These were discussed in Ref. 9. An exceptional case is the $\bar{M}_2$ level near E_F in Fig. 3, which by symmetry constraints has all its amplitude on the second plane. As noted in Ref. 9, the $\bar{M}_2$ interface state should be detectable in photoemission experiments.

IV. SUMMARY

We have presented SCLO results for Cu/Ni_3, a system which simulates the ideal Cu/Ni{100} interface. In agreement with Tersoff and Falicov,[8,9] we find that the Cu adlayer suppresses the magnetic moment of the top Ni layer by more than 40%, while bulklike behavior is observed at the central layer. The Cu layer is almost unpolarized, with a moment of less than $0.01\mu_B$. We discussed the interface-moment reduction from the alchemy perspective: Replacing a surface Ni layer with Cu weakens the interlayer *d*-*d* interaction, which narrows the subsurface DOS and reduces the corresponding magnetic moment. Band narrowing causes charge to flow from *sp* to *d* orbitals, contradicting a basic assumption used by Tersoff and Falicov.[9] Charge transfer between layers is unimportant because it is small. A discussion from the chemisorption viewpoint was also given. Here the main issue is the effect of the adsorbed Cu on the moment of the ideal Ni surface. Compression of the *sp*-electron gas by the adlayer and hybridization are the crucial factors that reduce the interface moment.

Turning now to the electronic structure, the interface DOS we computed is considerably narrower than the second-layer DOS of Ni_5, due to the weaker *d*-*d* interaction between Cu and Ni. The effect is most noticeable near E_F where there are no Cu-like bands. The exchange splitting is reduced at the interface Ni, in proportion to the magnetic moment. The center-layer DOS is similar to that of Ni_5, though the Fermi peak is somewhat sharper. The energy bands of Cu/Ni_3 are an amalgam of Cu-monolayer bands and Ni_3 bands. Three kinds of *d* bands were noted: bands that could be associated with definite monolayer bands, those that could not but had Cu character (major fraction of the probability density on Cu atoms), and those that had Ni character. The existence of the second class of bands proves that Cu-*d*-Ni-*d* interactions cannot be neglected, though their effect on the interface magnetism is small. The adsorbate bands should be detectable in angle-resolved photoemission spectroscopy.

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