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Ni overlayer on a Cu{100} substrate: Magnetism and surface states

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Self-consistent local-orbital (SCLO) calculations were performed for a $p(1\times1)$ monolayer of Ni on a three-layer Cu{100} substrate. The magnetic moment of the supported monolayer was found to be $0.24\mu_B$, compared with the value $0.98\mu_B$ obtained for the free monolayer. Factors which suppress the magnetism include hybridization of Ni and Cu orbitals, and surface *sp*-*d* charge transfer. Energy bands computed for the Ni/Cu sandwich include surface-state bands which closely resemble those obtained earlier for the free Ni monolayer, except for their much smaller exchange splittings.

I. INTRODUCTION

When thin Ni films are supported by a substrate, the magnetic behavior is influenced by the deposition technique as well as the nature of the substrate. Liebermann, Clinton, Edwards, and Mathon,[1] who electroplated Ni onto Cu and Au, found that the surface layers were magnetically "dead." Pierce and Siegmann,[2] by measuring photoelectron spin polarization, concluded that magnetic order exists for Ni films of greater than two layers thickness on Cu; Rau and Eichner[3] found that even the bilayer film is magnetic. The spin polarization of electrons tunneling through an aluminum substrate was studied by Meservey, Tedrow, and Kalvey.[4] In this case the loss of magnetic order occurs when the Ni-film thickness is reduced below three layers. On still another substrate, a Pb-Bi alloy, Bergmann[5] found that Ni overlayers of greater than 2.5 layers thickness had magnetic moments. This conclusion was based on anomalous-Hall-effect measurements. More recently,[6] the same method was used to show that Ni on the surface of Mg, In, and Sn is not magnetic when its thickness is less than about 2.5 atomic layers, while on noble-metal substrates even a monolayer is magnetic.

Theoretical studies have also shown that substrate composition strongly influences Ni-film magnetism. Tersoff and Falicov[7,8] found in their parametrized Hartree-Fock calculations that *sp*-*d* hybridization across the Ni/substrate junction tends to suppress the film magnetism. Since hybridization strength is substrate dependent, the disparate results summarized above are to be expected. In particular, substrates with higher *sp*-electron density are more effective in suppressing the magnetism of the supported film.

Here we report self-consistent local-orbital (SCLO) calculations for Ni on Cu{100} that complement earlier calculations by Tersoff and Falicov,[7,8] and by Wang, Freeman, and Krakauer.[9] The latter authors' self-consistent linearized augmented-plane-wave (LAPW) results predicted a magnetic moment of $0.39\mu_B$ per atom for a Ni monolayer, compared with the value $0.48\mu_B$ obtained in Ref. 7. The moment found by us for this system is $0.24\mu_B$, about one-fourth the result for the isolated monolayer.[10] We also computed surfacelike energy bands for Ni/Cu{100}. Except for their much smaller exchange splittings, these bands closely resemble those for an isolated Ni monolayer. They should be detectable by angle-resolved photoemission spectroscopy (ARPES).[11]

The SCLO method, including its generalization to treat spin polarization, has been discussed previously.[10,12] For the present application, we used 15 special points[13] in the two-dimensional Brillouin zone (2D BZ) for the determination of the (iterated) charge and spin densities. We considered only a three-layer Cu{100} "substrate" with $p(1\times1)$ Ni monolayers on both sides. All interlayer spacings were set equal to the bulk spacing in Cu. This system is thick enough to simulate bulklike behavior at the center of the film but not thick enough to yield a complete understanding of interface states.[7] Both surface states and magnetic behavior should be given accurately in our five-layer model, however.

II. MAGNETISM

The magnetic moment of a Ni monolayer supported on Cu{100} (denoted as Ni/Cu) was found to be $0.24\mu_B$, roughly one-fourth the value $0.98\mu_B$ for the free monolayer,[10] and 36% the value we obtained earlier[14] for the surface layer of a five-layer Ni film, $0.66\mu_B$. Our results are compared with other calculations[7,9,15] in Table I. Note that we predict a much smaller magnetic moment for the supported monolayer than do the other groups.[7,9] For Ni (Refs. 7, 14, and 15) and Cu/Ni,[7,16] on the other hand, there is much better agreement among theoretical results (LAPW calculations have not been reported for Cu/Ni). A possible reason for the discrepancy in the case of Ni/Cu is discussed below.

TABLE I. Surface-layer magnetic moments (μ_B) for a $p(1\times1)$ monolayer of Ni on a Cu{100} substrate, and for the Ni{100} surface (Ref. 14). The magnetic moment of the interface (Ni) layer of Cu/Ni{100} is also given (Ref. 16). Results obtained by two other theoretical groups (Refs. 7, 9, and 15) are shown in the second and third columns.

Layer	SCLO	LAPW (Refs. 9 and 15)	Tersoff and Falicov (Ref. 7)
Ni/Cu(*S*)	0.24	0.39	0.48
Ni(*S*)	0.66	0.64	0.74
Cu/Ni(*I*)	0.37	· · ·	0.39

TABLE II. Orbital-projected surface magnetic moments (μ_B) for Ni on Cu{100}, and for the Ni{100} surface (Ref. 14). Results are also shown for the interface (Ni) layer of Cu/Ni{100} (Ref. 16). Only d-orbital contributions are listed, as determined from the Löwdin projections (Ref. 19). Bulk coordinate axes are used with the z axis normal to the surface plane.

Film	$3z^2$-r^2	xy	xz or yz	x^2-y^2	Total
Ni/Cu(S)	0.026	0.059	0.025	0.108	0.242
Ni(S)	0.085	0.163	0.139	0.141	0.667
Cu/Ni(I)	0.037	0.128	0.077	0.055	0.374

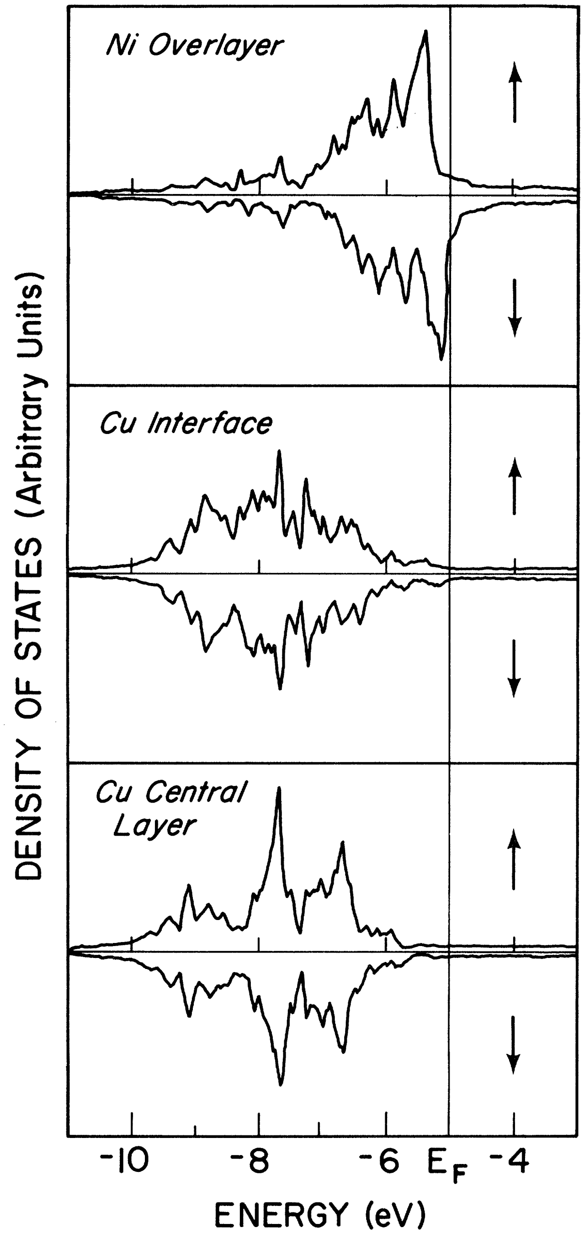

FIG. 1. Layer-projected densities of states (DOS) of the Ni/Cu{100} sandwich, for majority (↑)- and minority (↓)-spin electrons, obtained using the Löwdin projection analysis (Ref. 19). The energy zero is the vacuum level.

Table II lists the individual d-orbital contributions to the moments given in the first column of Table I. For the supported Ni monolayer, all d orbitals exhibit a reduced magnetism compared with their behavior on the Ni{100} surface; the xy, xz, and yz contributions are all reduced by more than $0.1\mu_B$. These large reductions are consistent with several characteristics of the surface density of states (DOS) shown in Fig. 1: the small exchange splitting, the large number of majority-spin (↑) d holes, and the absence of prominent peaks above E_F. The $d\uparrow$ holes arise primarily from an xy-like band near $\bar{M}_3$ and xz,yz bands near $\bar{\Gamma}_5$ in the 2D BZ; see Fig. 2. As expected, the surface (Ni) DOS is narrower than the DOS of interior (Cu) planes, due to reduced coordination. The center-plane DOS resembles that computed earlier[12] for Cu{100} films, though a thicker substrate is probably required to achieve truly bulklike behavior at the film center.

We have identified two factors which suppress the magnetism of the supported monolayer: hybridization of Cu and Ni states, and sp-d surface charge transfer. The effects of hybridization have been discussed in Ref. 7: broadening

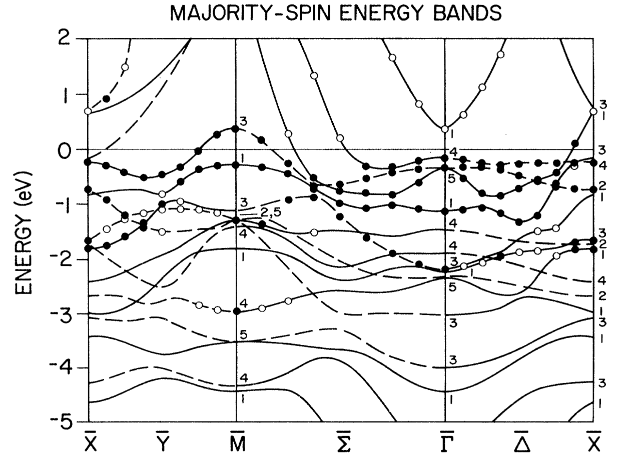

FIG. 2. Spin-polarized energy bands of the Ni/Cu sandwich, in the two-dimensional Brillouin zone adopted in Ref. 14. Symmetry labels agree with standard usage, and even (odd) bands, with respect to vertical reflection planes, are denoted by solid (dashed) lines. Only majority-spin bands with even z-reflection symmetry are given. The energy zero is the Fermi energy. Full circles denote states with 70% or more surface character; empty circles indicate 50–70% surface character.

and rounding of the DOS near E_F, which weakens the effective exchange interaction and prevents the magnetization from going to saturation (full majority-spin d band). Regarding surface sp-d charge transfer (interlayer charge transfer is not significant, i.e, the layers are charge neutral to within 0.02 electrons), we find that the supported Ni monolayer has 8.95 d electrons per atom, compared with the value 8.77 for the free monolayer.[10] This increase of d occupancy occurs entirely in the minority-spin band (the $d\uparrow$ band is essentially full in the isolated monolayer); thus the magnetic moment of the supported monolayer decreases. The basic mechanism leading to sp-d surface charge transfer is substrate-induced broadening of the sp band: The broader sp band loses electrons, hence the d band fills to maintain charge neutrality; the effect is slightly reduced by hybridization. The more-localized d levels experience much less broadening than the extended sp states. An alternative explanation of the surface sp-d charge transfer is based on the "alchemy" viewpoint. Imagine that the interior planes of a Ni slab are converted into Cu, leaving the surface Ni intact. In this picture, the sp bands are relatively unaffected, while the Ni d band is narrowed due to its weakened interaction with subsurface d levels, which are offset energetically by about 2 eV. Since the d band is almost full, narrowing tends to increase its occupation at the expense of the sp band. Table III shows that the supported monolayer has 8.95 d electrons compared with the value[14] 8.84 at the surface of Ni{100}. This transfer of 0.11 d electrons is slightly larger than we found[16] for interface Ni atoms in Cu/Ni (0.09 electrons).

As noted above, we predict a smaller magnetic moment for the supported monolayer than do Refs. 7 and 9. A possible cause of these discrepancies is the differing amounts of sp-d charge transfer present in these calculations. Charge transfer was not allowed for (by constraint) in Ref. 7. The d-electron projection inside the muffin-tin sphere obtained in Ref. 9 for a Ni bilayer on Cu was only 0.04 electrons per atom larger than the "bulk" value found at the center plane of Ni{100}; no result for the supported monolayer was reported. Also, while we found a surface d-electron excess of 0.1 electrons per atom for Ni{100},[14] the LAPW calculation predicted[15] no change of occupancy at the surface inside the muffin-tin spheres. Our treatment of surface sp-d charge transfer is supported by the work function we obtained for Ni/Cu, 4.9 eV, which lies between the experimental values for Ni{100}, 5.0 and 5.2 eV,[17] and for Cu{100}, 4.6 and 4.8 eV (Ref. 18) (no experimental value of the work function for Ni/Cu{100} has been reported). The work function was not computed in Ref. 7, while the LAPW results[9] for the supported monolayer and bilayer are 5.45 and 6.10 eV, respectively.

TABLE III. d-orbital occupation numbers (electrons per atom) computed in the Löwdin representation (Ref. 19), for Ni/Cu{100}, Ni{100}, and Cu/Ni{100}. S denotes the surface layer, S-1 the subsurface and S-2 the center layer.

Layer	Ni/Cu	Ni (Ref. 14)	Cu/Ni (Ref. 16)
S	8.949	8.838	9.679
S-1	10.927	8.826	8.915
S-2	10.904	8.736	8.742

III. SURFACE BANDS

Spin-resolved energy bands for the Ni/Cu sandwich are given in Fig. 2. Only majority-spin states with even reflection symmetry in the z-axis normal to the surface are shown. As a rough means of identifying the surface bands, filled (open) circles are used to denote states with 70% or more (50–70%) Ni character, as determined from the Löwdin projection analysis.[19] The Ni-like bands bear a striking similarity to the two-dimensional energy bands of the free Ni{100} monolayer calculated earlier,[10] except that the exchange splittings are much smaller, about 0.25 eV near E_F. The persistence of Ni-like and Cu-like bands is consistent with the DOS in Fig. 1, which indicates that the substrate DOS is weak in the energy region near E_F where the overlayer DOS is substantial. Note that the overlap of Cu and Ni DOS is minimized at the Ni/Cu interface because the surface-induced narrowing of Ni bands tends to draw these bands away from the Cu bands which lie about 2 eV lower.

To illustrate the close correspondence of the surface bands in Fig. 2 with the monolayer bands of Ref. 10, we superimposed them in Fig. 3; the latter bands[10] were given a rigid shift to align the $\bar{M}_3$ level with Fig. 2. This shift produces a nearly perfect coincidence of several bands near E_F, including the $\bar{Y}_1\bar{M}_3\bar{\Sigma}_2$, $\bar{Y}_1\bar{M}_1\bar{\Sigma}_1\bar{\Gamma}_1\bar{\Delta}_1$, $\bar{\Sigma}_1\bar{\Gamma}_4\bar{\Delta}_2$, and $\bar{\Gamma}_5\bar{\Delta}_2$ bands. The bands at lower energy, such as $\bar{Y}_2\bar{M}_4\bar{\Sigma}_1$ and $\bar{\Sigma}_2\bar{\Gamma}_3\bar{\Delta}_1$, which overlap the Cu bands, are distorted somewhat. Many of these bands should be detectable using ARPES, since they occur well above the Cu substrate levels.

An important feature of the energy bands in Figs. 2 and 3 is that a substantial portion of the majority-spin d levels lie above E_F, i.e., are unoccupied. The other systems we studied,[10,14,16] Ni{100} and Cu/Ni{100}, had almost no $d\uparrow$ holes (except for a small number of hybridization holes): The $\bar{M}_3$

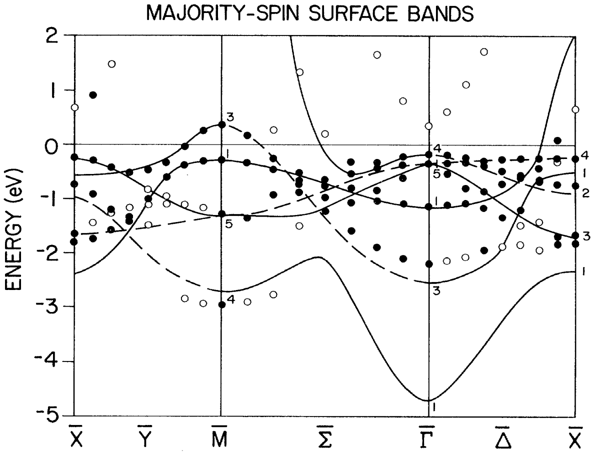

FIG. 3. Energy bands of the free Ni{100} monolayer (Ref. 10), superimposed on surface states of Ni/Cu taken from Fig. 2 (denoted by circles). A rigid shift was applied to the monolayer bands, in order to align the two sets of bands at the M_3 level.

level was at or below E_F. In this situation, the magnetic moment is saturated (Hund's rule). For the Ni/Cu system, the factors discussed above, hybridization and *sp*-*d* charge transfer, weaken the effective exchange interaction enough to cause a breakdown of Hund's rule.

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