Surface magnetism of a Ni overlayer on a Cu(001) substrate

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Self-consistent spin-polarized energy-band studies of a Ni monolayer on each side of a five-layer Cu(001) substrate show that the Ni overlayer is not magnetically "dead"; its moment of $0.37\mu_B$/atom is 40% lower than the Ni bulk value and is similar to the behavior found earlier by Wang and Freeman for the surface layer of a nine-layer Ni(001) film.

The observation of magnetically "dead" layers by Liebermann *et al.*,[1] for less than about 2.5 layers of Ni deposited on a Cu substrate, has attracted a great deal of experimental and theoretical interest. However, conclusions drawn from different experiments and theoretical models appear to contradict each other. For example, whereas the measurement of the anomalous Hall effect by Bergmann[2] confirmed the existence of the dead layers, spin-polarized photoemission measurements cast doubts on it,[3] and electron-capture spectroscopy measurements found that even a monolayer of Ni on Cu is not magnetically "dead," but has a reduced moment.[4] Most recently, Eberhardt *et al.*[5] have obtained direct evidence from photoemission for the nonexistence of dead layers on Ni(110).

On the theoretical side, although the earlier simple models[6] showed that a dead layer may exist on the surface of a magnetic crystal, recent *ab initio* self-consistent spin-polarized calculations[7,8] showed that the surface layer of the Ni crystal is not magnetically dead. Thus, according to Wang and Freeman,[7] the moment of the surface Ni atoms is $0.44\mu_B$ (about 20% less than the moment value of the center atoms of the nine-layer film, $0.54\mu_B$) arising from a majority hole surface state at $\bar{M}$. For a thinner film of Ni(001), Jepsen *et al.*[8] find that the surface moment is $0.61\mu_B$, almost the same as that for the center layer of their thinner (five-layer) film, $0.58\mu_B$.

We have recently completed the first self-consistent spin-polarized calculation on the system of a Ni monolayer on a Cu(001) substrate, consisting of a five-layer Cu(001) slab plus a $p(1\times1)$ monolayer of Ni on each side. We find that the Ni overlayer is not magnetically dead; its magnetic moment of $0.37\mu_B$/atom is reduced by 40% from the theoretical Ni bulk value and is similar to the behavior found earlier for the surface layer of a nine-layer Ni(001) by Wang and Freeman.[7] By contrast, a self-consistent spin-polarized calculation for a monolayer of Ni(001) results in an increased moment of $0.85\mu_B$/atom.

Our self-consistent film linearized-augmented-plane-wave (LAPW)[9,10] method was generalized to deal with the spin-polarization problem. The von Barth–Hedin[11] expression for the spin-dependent exchange and correlation term is used with a core charge density which is computed self-consistently for every iteration in a fully relativistic Dirac-Slater-type atomic-structure program. The valence states are computed semirelativistically; i.e., the Dirac equation is solved including mass-velocity and Darwin terms but without the spin-orbit coupling term. All the warping components of the potential in the interstitial and vacuum region are included in the computation and determined self-consistently by adding to the spin-dependent exchange-correlation term.[11] The Coulomb potential is obtained by a very accurate solution of Poisson's equation.[10] This procedure includes all the contributions of the interstitial and vacuum charge distribution and the spherically averaged monopole pseudocharge inside the muffin-tin regions, and permits a very precise determination of the potential near the surface region and thus gives a good description of the surface states and surface electronic properties. The geometry is assumed to be that of a slab cut from a bulk Cu crystal without any relaxation or reconstruction. This assumption is justified by the good match between the Ni and Cu crystal (the lattice parameter of fcc Ni is only 2.5% less than that of Cu).

For the Ni/Cu system under consideration, the basis size of over 190 LAPW's per z-reflection symmetry type (55 LAPW's per atom) results in eigen-

values converged to better than 3 mRy. 15 $\vec{k}$ points in the $\frac{1}{8}$ irreducible wedge of the two-dimensional Brillouin zone are used to generate the charge density in the self-consistency process. We consider self-consistency achieved when the rms difference between input and output potential is less than 15 mRy. The magnetic moments converge much sooner in the iteration procedure. For the isolated Cu five-layer and Ni monolayer films which are used as comparisons for the composite Ni/Cu system studied, the convergence and self-consistency are much better; e.g., the difference between the input and output potential is less than 4 mRy for the Cu five-layer film, and 1 mRy for the Ni monolayer film.

For the pure Cu(001) five-layer film, the spin-polarized calculations yield no magnetic moment, as expected, within the computational uncertainty ($\sim 0.01\mu_B$/atom) for any layer of this slab. The calculated work function, 4.94 eV, is in good agreement with the experimental value, 4.8 eV.[12] Our results, including the work function, density of states, and charge density, are nearly the same as that obtained in a recent self-consistent linear-combination-of-atomic-orbitals (LCAO) calculation.[13] Our results also confirm the existence[13,14] of a surface state above the d-band edge at $\bar{M}$, namely, the $\bar{M}_3$ surface state, which is raised by 0.49 eV above the $\bar{M}_1$ state (both states belong to the degenerate e_g state in a cubic field but their degeneracy is lifted by the reduced symmetry at the surface).

The calculated magnetic moment for the isolated Ni(001) monolayer film is $0.85\mu_B$/atom, which is greater than the bulk Ni moment, $0.62\mu_B$, as obtained from the value of the center layer in a Ni(110) film by the same method,[15] but closer—as expected—to the atomic limit. Within the muffin-tin sphere the total number of electrons is 8.84. A slightly negative polarization is observed in the interstitial and vacuum regions. The exchange splitting is about 0.88 eV for the $3d$ states near the Fermi energy (E_F).

The spin-polarized layer projected density of states of the Cu/Ni system is shown in Fig. 1. The exchange splitting is 0.38 eV near the E_F which is considerably closer to the experimental value for Ni, 0.31 eV.[16] The half-peak width of the Ni $3d$ band is 1.6 eV. The exchange splitting leads to an almost rigid shift between Ni spin-up and spin-down bands; no large difference in the shape between the up- and down-spin density of states (DOS) curves is observed. For the Cu states, there is no exchange splitting even for the interface Cu layer which is adjacent to the magnetic Ni atoms. The DOS curve for the center Cu layer remains the same as that of the pure Cu film.

The band structure of the Ni/Cu film is shown in Fig. 2. The exchange splitting for some surface states close to E_F is 0.39 and 0.35 eV for the $\bar{\Gamma}_4$ and $\bar{\Gamma}_5$

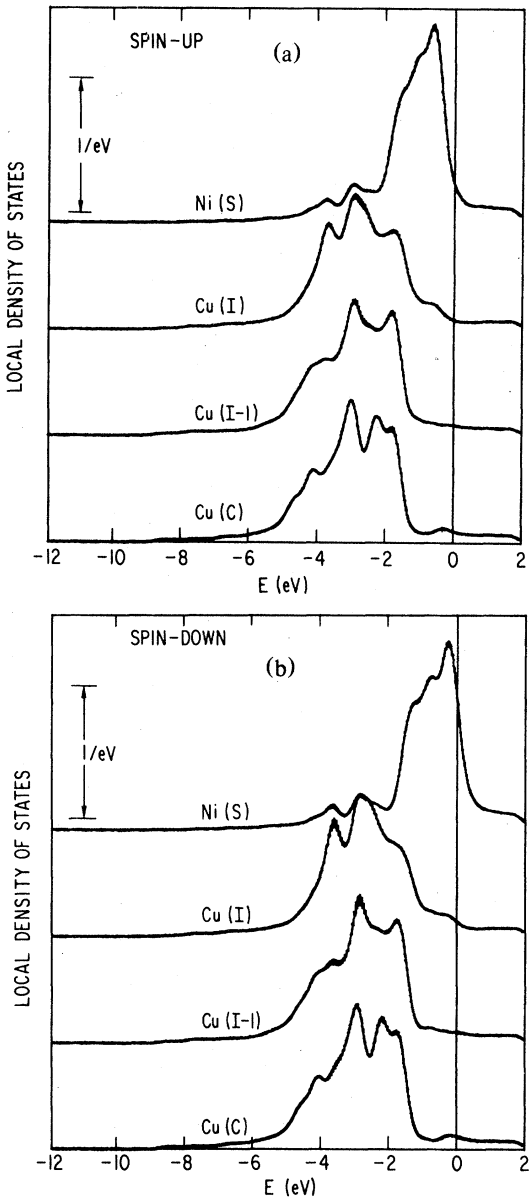

FIG. 1. Spin-polarized layer projected density of states of a five-layer Cu(001) slab covered with a $p(1\times1)$ monolayer of Ni on each side: (a) spin up (majority), (b) spin down (minority). The curves for the surface Ni layer, Ni(S), the interface Cu layer, Cu(I), to the center layer of Cu, Cu(C), are all shown.

states, 0.28 eV for the $\bar{M}_1$ state and 0.39 eV for the $\bar{M}_3$ state, and 0.38 for the $\bar{X}_2$ state. The $\bar{M}_3$ surface state is now 0.87 eV above the corresponding $\bar{M}_1$ state because of the combined surface-interface effects. For the isolated Ni monolayer film, this crystal-field splitting of these states is still stronger; here the $\bar{M}_3$ state is 1.22 eV above the $\bar{M}_1$ state. This surface state is similar in nature to the surface state at $\bar{M}$ above the d-band edge for the clean

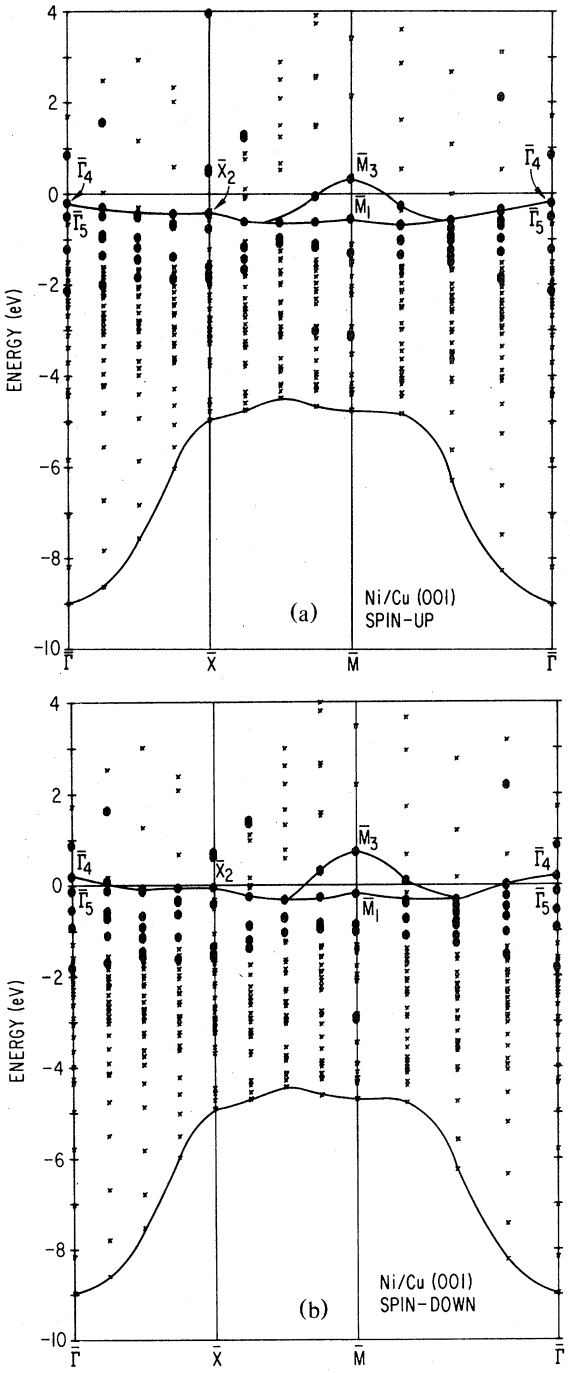

FIG. 2. Band structure of a five-layer Cu(001) slab covered with a $p(1\times1)$ monolayer of Ni on each side: (a) spin up (majority), (b) spin-down (minority). Solid circles denote states with more than 60% of electron in the surface Ni overlayer.

Cu(001) films[9,13,14] and the $\bar{M}_3$ surface state on a pure Ni(001) film.[7,9] Also, similar to the pure Ni film result,[7] in the Ni/Cu system the spin-up $\bar{M}_3$ surface state lies above E_F and creates a majority spin hole that leads to a decrease of the magnetic moment.

Table I lists the total number of the valence electrons inside the muffin-tin spheres. Surface atoms usually lose some electrons, as can be seen by comparing the surface and center layers of the pure Cu film, and by comparing the isolated Ni monolayer with the bulk Ni.[15] But the Ni atom on a Cu substrate has almost the same total number of electrons as that of the bulk atom. This means that the loss of its electrons to the vacuum region is compensated by gaining some electrons from the Cu substrate. This outward electron transfer is consistent with the increase of the computed work function, which is 5.45, or 0.51 eV larger than for our clean Cu(001) and close to the Ni(001) work function, 5.2 eV.

Although the total number of electrons remains the same for the Ni atom on the Cu substrate, its magnetic moment decreases appreciably. This is because the surface state near $\bar{M}$ creates some majority spin holes.[7] The spin-up electron occupation decreases by 0.12 in comparison with the bulk Ni atom (Table II). This effect is further enhanced by the decrease of the exchange splitting which leads to an increase of the minority spin electrons. The muffin-tin magnetic moment decreases to $0.39\mu_B$, or 37% less than the computed bulk value.[15] The Cu atoms show no magnetic moment within the computational error $0.01\mu_B$. On the other hand, for the isolated Ni monolayer, the loss of electrons plays an important role in determining its magnetic properties. Because Ni has a nearly filled majority-spin d band, and the DOS at E_F is larger for minority than for majority spin band, any decrease of the total number of electrons should cause an increase of the magnetic moment since the minority band loses more electrons. It is also to be noted that, although the magnetic moment is quite different for the different systems, the Stoner-Hubbard parameter $I=\Delta E/\mu$ is almost identical for either the isolated monolayer or the Ni overlayer on a Cu substrate, and it also equals the value for bulk Ni.[17]

TABLE I. Total number of the valence electrons inside touching muffin-tin spheres; note that the Ni(001) monolayer result is 8.84 and the LAPW "bulk" Ni value [for the center layer of a Ni(110) film of Ref. 15] is 9.22, by layers from the interface (I) or Surface (S).

		Ni on Cu(001)	Pure Cu(001)
Ni		9.21	
Cu	Interface or surface	10.35	10.21
	$I-1$ or $S-1$	10.37	10.37
	Center	10.39	10.38

TABLE II. The number of the valence electrons, e_{MT}, and the magnetic moment, μ_{MT}, inside the Ni muffin-tin spheres, total magnetic moment, μ, exchange splitting, ΔE, and the Stoner-Hubbard parameter I defined as $\Delta E/\mu$ for the Ni atom on the Cu substrate and in an isolated monolayer film.

		Ni on Cu(001)	Ni on Ni(001)[a]	One-layer Ni	Bulk Ni[b]
e_{MT}	Total	9.21		8.84	9.22
	Spin up	4.80		4.85	4.92
	Spin down	4.41		3.99	4.30
μ_{MT} (μ_B)		0.39		0.86	0.62
μ (μ_B/atom)		0.37	0.44	0.85	
Δ_E (eV)		0.38	0.41	0.87	
I (eV/μ_B)		1.03	0.93	1.02	

[a]Surface layer of a nine-layer Ni(001) film from a self-consistent LCAO calculation (Ref. 7).
[b]Center layer of a five-layer Ni(110) film from a self-consistent LAPW calculation (Ref. 15).

In conclusion, our results show that a Ni monolayer on the Cu(001) substrate is not magnetically dead, and its reduced magnetic moment is in agreement with electron-capture measurements.[4]

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