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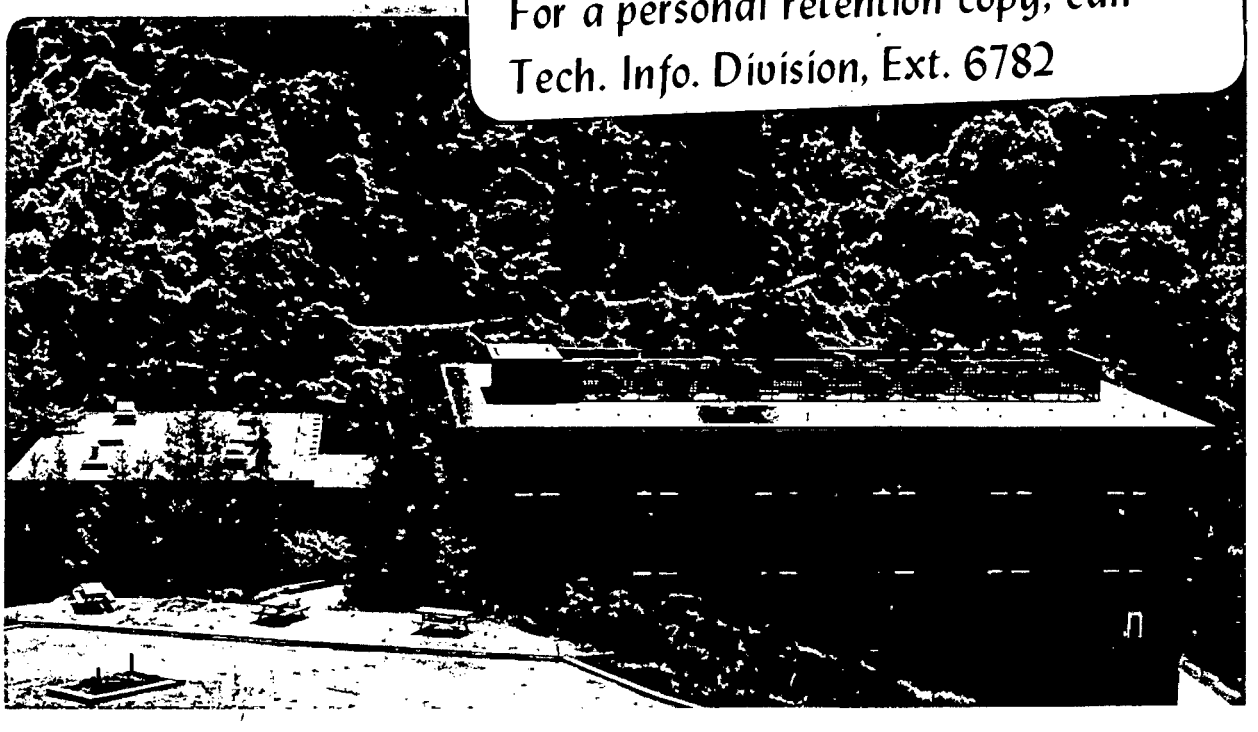

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Calculation of electronic and magnetic properties of Ni films on Cu (100)

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A self-consistent calculation of electronic and magnetic properties of Ni films of various thicknesses on Cu (100) is presented. It is found that: (1) A one-atomic-layer film is not magnetic; (2) Three- or more atomic-layer films are magnetic with essentially full magnetization in the middle layers; (3) The surface layer and the Ni-Cu interface layer both have their magnetization reduced, but by very different mechanisms, which are discussed. Results are consistent with experiments.

Considerable progress has been made, both experimentally[1] and theoretically[2-4], in understanding the properties of transition-metal films and magnetic surfaces. In particular, sensitive experiments reveal a rich behavior with varying thicknesses, substrates and magnetic fields. We report here the results of calculations of the electronic properties of nickel films--with thicknesses from one to four atomic layers--on a Cu (100) substrate. By means of a simple, transparent Hamiltonian and with various film thicknesses we have gained insight into some basic physical effects. In particular we can disentangle the very different effects of the free surface and the Ni-Cu interface.

The magnetic behavior of the surface is dominated by charge transfer from the s-p band to the d band, with a reduction in surface magnetization.

The Ni-Cu interface is governed by entirely different effects, similar to those in the Ni-Cu alloy[5]. Charge transfer is unimportant. The dominant effect is a considerable change in the local density of states (LDOS) at the nickel site in the interface: a reduction in LDOS at the Fermi level results in a decreased local magnetization.

For the Hamiltonian we chose the parametrized scheme of Slater and Koster[6] (also known as LCAO). The electron-electron interaction was treated in the generalized single-

site model, which has been extensively discussed[7]. In this way

$$H = H_0 + H_{ee} \quad , \tag{1}$$

$$H_{ee} = \sum_{i\sigma\sigma'} \sum_{\mu\nu\lambda\kappa} U_{\mu\nu\lambda\kappa}\, c^{\dagger}_{i\mu\sigma}\, c^{\dagger}_{i\nu\sigma'} c_{i\lambda\sigma'} c_{i\kappa\sigma} \quad , \tag{2}$$

where $c^{\dagger}_{i\mu\sigma}$ creates, at site $\underline{i}$, an electron in an orbital of symmetry μ and spin σ. The one-electron term H_0 is parametrized in terms of one and two-center integrals, chosen so as to give the correct paramagnetic band structure. The interaction term H_{ee} is treated in the Hartree-Fock approximation. The ratios of the screened interaction parameters $U_{\mu\nu\lambda\kappa}$ were chosen from experiment (atomic data[8], solid state Auger measurements[9], etc.) and the overall magnitude was adjusted to give the correct[10] bulk magnetization $\nu \equiv n_{\uparrow} - n_{\downarrow} = 0.56$. Details of the calculation will be presented elsewhere.

Nickel and copper have very similar band structures and lattice constants. The crucial difference is simply that the $\underline{d}$ bands of Cu are deep below the Fermi level, whereas in Ni the $\underline{d}$ bands are not quite full, and there is a large density of states at the Fermi level. Interatomic matrix elements are taken to be the same for Ni and Cu, an excellent approximation especially since the fine details of the

Cu band structure are virtually irrelevant here.

We first calculated bulk and surface properties of pure Ni. The calculation was selfconsistent with respect to magnetization and interband and interatomic charge transfer, within the single-site approximation of (2). For the surface, both for Ni and for the Cu-Ni film system, we treated a semi-infinite crystal using a real-space Green's-function formalism which is described elsewhere[11].

For the electronic structure we found excellent agreement with the fully selfconsistent calculation of the ferromagnetic bulk band structure by Wang and Callaway[12], and of the surface states by Wang and Freeman[2]. We then proceeded to treat the Cu (100) surface with various thicknesses of Ni.

Our main results are summarized in Table I. For one layer of Ni on Cu (100) we find no magnetization. Two layers are at the borderline. We calculate a minute magnetization; but so near the transition quantitative results are unreliable. At three layers, the middle Ni layer has a magnetization approaching that in the bulk. For films of four or more layers, one may view the film as a thick slab, rather bulklike except at the surface and at the Ni-Cu interface. The magnetic moment and d-band occupancy change at the Cu sites are negligible, even at the interface.

Wang et al[3] have calculated the magnetization of a monolayer of Ni on Cu (100), and they find that it retains 60% of the bulk magnetization. As discussed below, our calculation tends to exaggerate the loss of magnetization at the surface because of charge-transfer effects. However, the calculation of Wang et al treats exchange in a local-density-functional approximation[13]. The application of this method to inhomogeneous ferromagnetic systems with localized states is a very new area, and the accuracy in this context is not yet known with any certainty.

Liebermann et al[14] found that thick Ni films on a Cu or Au substrate have their total moment reduced by the equivalent of two "dead layers" at T = 0. We find that, while there are no actual "dead layers" for thick films, the effect of the surface and interface is to reduce the total moment of the film by an amount equivalent to one "dead layer", in qualitative agreement with experiment.

Bergmann[1] has performed sensitive direct measurements of the magnetization of thin Ni films on an amorphous $Pb_{0.75}$ $Bi_{0.25}$ substrate. He finds that ferromagnetism first appears at 2.5 layers of Ni. However, a comparable measurement with a noble-metal substrate has not been performed.

We now consider the important physical mechanisms underlying the magnetic behavior of the film. From Table I

we see that for films of three or four layers the Ni atom at the Ni-Cu interface has its moment reduced by about $\Delta\nu = 0.25$. This is not due to local d-band filling, which amounts to no more than 0.07 electrons.

The cause of this reduced magnetization can be seen in Figure 1. There we show the LDOS at various sites for a three-layer Ni film on Cu (100). The Ni bulk density of states is also shown. For the Ni atom at the interface (layer 3) the LDOS loses some structure, specifically some of the peaking at high energy characteristic of the ideal fcc lattice. This smoothing-out reduces the LDOS at the Fermi level, and is the primary cause of the reduced magnetization at the interface.

We must stress that this is essentially the familiar problem of magnetism in Ni-Cu alloys. There, ferromagnetism disappears at a Cu concentration of 0.6, though there is apparently not significant filling of the local Ni-d-bands[5] as was once thought[15]. The loss of the characteristic fcc structure in the Ni and Cu LDOS at the interface is reminiscent of that in alloys[16], as seen for example in the calculation of Stocks *et al*[17].

The physical effects at the *surface* of an Ni film or crystal are of a very different nature. While the magnetization at the surface, as at the interface, is reduced, the physical cause here is a transfer of electrons from the s-p to the d bands at the surface. This is simply

the transition-metal version of the dipole layer found in s-p metals [11]. Comparison with the results of Wang and Freeman suggests that we overestimate this effect somewhat. This is natural, because of our choice of a minimal basis of Wannier-like orbitals [18].

The crucial point to note is that the demagnetization at the surface is much less than the d-band filling (Table I). This is because of a second competing effect at the surface -- the d band narrows because of lower coordination, and the hybridization between the local s-p and d bands is thereby reduced. This narrowing and dehybridization increases the LDOS at the Fermi level, both in the minority and majority spin bands, and leads to enhanced magnetization.

This effect is beautifully illustrated in the calculation of Noffke and Fritsche [4] for the unsupported monolayer Ni film. There the density of states at the Fermi level is very large because of the drastic band narrowing, so that despite a d-band filling of 0.3 electrons relative to the bulk, the magnetization is enhanced by almost 50%. For the surface, on the other hand, it is the d-band filling which dominates.

Wang and Freeman [2] point out the role of a majority-spin surface state in reducing the surface magnetization. However this surface state does not contain enough hole states to account for most of the effect at the surface.

In conclusion, we have illustrated the development of ferromagnetism with film thickness for up to 4 atomic layers of Ni on Cu (100), and we have brought out three important physical points: First, the similarity of the interface to the Ni-Cu alloy, and the importance of changes in the shape of the LDOS; second, the dominance of charge transfer from the s-p band to the d band in reducing surface magnetization; and third, the importance of band narrowing and dehybridization at the surface as a competing effect, which tends to enhance the magnetization.

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TABLE I

Spin imbalance and d-band occupancy for Ni films on a Cu substrate

Layer from the surface	Number of Ni layers in film	$\nu \equiv n\uparrow - n\downarrow$	$\Delta\nu$ (a)	Δn_d (b)
1	1	0.00	0.56	0.41
1	2	0.07	0.49	0.36
2	2	0.08	0.48	0.10
1	3	0.39	0.17	0.34
2	3	0.47	0.09	0.03
3	3	0.34	0.22	0.07
1	4	0.38	0.18	0.34
2	4	0.55	0.01	0.01
3	4	0.49	0.07	0.01
4	4	0.30	0.26	0.07

(a) $\Delta\nu$ is the reduction is spin imbalance from the Ni bulk value

(b) Δn_d is the increase in d-band occupation from the Ni bulk value

FIGURE CAPTION

Figure 1 LDOS for Ni bulk and for a three-layer Ni film on Cu (100). (a) Ni bulk. (b) Layer 1 -- Ni film surface. (c) Layer 2 -- Ni film middle layer. (d) Layer 3 -- Ni film interface layer. (e) Layer 4 -- Cu substrate interface layer. Solid (dotted) lines indicate minority (majority) spins. LDOS shown is broadened by an imaginary part of 0.01 Ry in the energy.

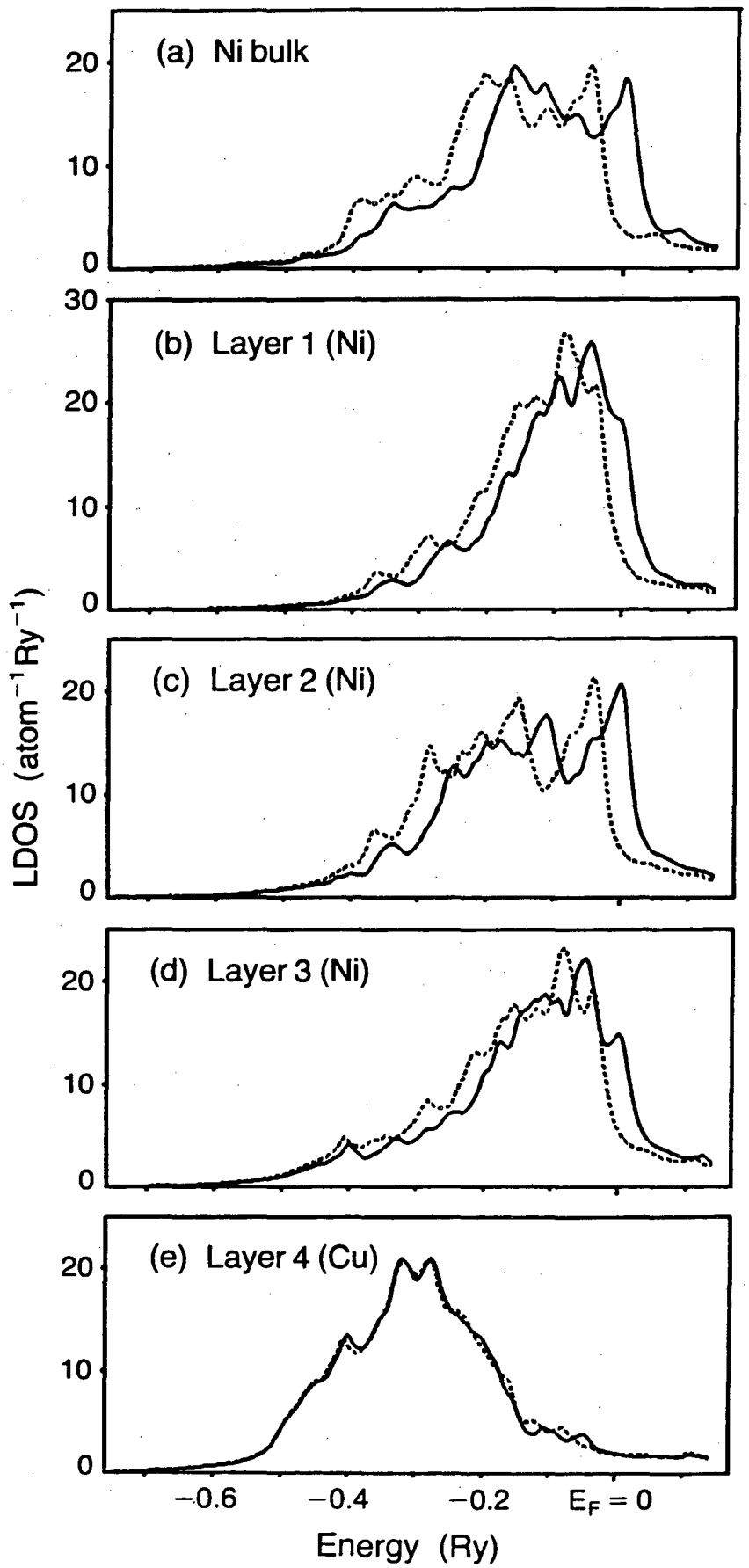
(a) Ni bulk
(b) Layer 1 (Ni)
(c) Layer 2 (Ni)
(d) Layer 3 (Ni)
(e) Layer 4 (Cu)
LDOS (atom^{-1}Ry^{-1})
0
10
20
30
−0.6
−0.4
−0.2
$E_F = 0$
Energy (Ry)

Figure 1

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