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by

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SURFACE STATES, SURFACE MAGNETIZATION AND ELECTRON SPIN POLARIZATION IN FERROMAGNETIC 3d METALS

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Abstract

Ab initio spin polarized self-consistent LCAO energy band studies of ferromagnetic 3d transition metal films are reported. These films, 9 layer Ni(001) and 7 layer Fe(001), need to be thick enough to accurately determine the energy dispersion and spatial character of surface states and their effects on the surface magnetism, electron spin polarization, and average exchange splittings. We find the layer spin density moments to show Friedel type oscillations and the surface layer moments for Ni($0.44\mu_\beta$) and Fe ($3.0\mu_\beta$) to be modified from the bulk values of $0.58\mu_\beta$ and $2.2\mu_\beta$ by their respective surface states close to the Fermi energy. Comparisons are made with bulk results, experimental data, and other theoretical results.

The study of surfaces has added a new and exciting dimension to the field of magnetism. This is clear from the wealth of experimental information which has recently been forthcoming to challenge the theoretical understanding of the role of surfaces in magnetism in general, and their importance relative to bulk contributions, in particular. This has provided the stimulus to develop theoretical methods capable of interpreting this wealth of new information. Of particular interest have been the relative roles of bulk and surface contributions since in several important cases agreement between experiment and bulk self-consistent (SC) calculations within the local spin density functional formalism is lacking. The theoretical surface studies share the common problem with bulk studies of treating localized d electrons along with the itinerant s-p electrons, but require, in addition, the treatment of larger numbers of atoms per unit cell.

In our work, spin-polarized self-consistent calculations are made for a single film slab of m layers with the origin of the system midway between the two surface layers; the z axis is normal to the surfaces. With the unit cell a parallepiped (whose 2 dimensions extends to $\pm\infty$), we have periodicity only in the 2 dimensions of the film. The LCAO Bloch basis set consists of 3d, 4s, 4p valence orbitals orthogonalized to the frozen core wavefunctions. The self-consistent potential (with von Barth-Hedin local density exchange-correlation) is obtained iteratively within the superposition of overlapping spherical atomic charge density model with the atomic configurations treated as adjustable parameters and a sampling of 15 equally spaced points in the irreducible Brillouin zone. The spin density is obtained self consistently by minimizing the integrated rms difference between the crystal and superposition spin density. The method has been shown to yield very good results in earlier applications, including oxygen chemisorbed on [1] Ni(001) and thin films[2] of paramagnetic Ni.

For the case of ferromagnetic Ni, we determined the spin-polarized SC band structure of a 9 layer Ni(001) film that is thick enough to accurately determine the energy dispersion and spatial character of SS and their effects on the surface spin polarization, charge distribution and layer projected DOS. Among our major results, we find a pair of majority spin $\bar{M}_3$ surface states (SS) which split away from the bulk bands and cross the Fermi energy, E_F. This creates a majority spin d hole and decreases the surface layer spin mangetization ($0.44\mu_B$) and the exchange splitting (0.41 eV at $\bar{M}_3$SS) from their values

($0.58\mu_\beta$ and 0.63 eV) for bulk ferromagnetic Ni[3]. This slight reduction in surface layer magnetic moment is consistent with field emission[5] experiments. No evidence was found for magnetically 'dead' layers on Ni(001) surfaces. These results may be important (together with escape depth information) for interpreting recent angle resolved photo-emission (ARPE) experiments[4]. Further, the majority spin $\bar{\Gamma}_5$ SS is found to be only weakly localized on the surfaces and to contribute little to the surface projected DOS near threshold. Our result agrees with recent ARPE experiments[6] for Ni(001), where a majority spin SS right below E_F near the zone boundary was found to vanish as it approaches the zone center.

Nearest volume integration yields a practically neutral charge density around each atom (10.02, 9.97, 9.97, 10.02 and 10.05 electrons on surface and subsequent layers) and the spin magnetic moment values shown in Table 1. (Compared to the input superposition charge and spin densities they are converged to within 0.03 electrons and $0.02\mu_\beta$ respectively.) Note that the spin magnetic moments close to the center plane are in very good agreement with the experimental (bulk) value of $0.56\mu_\beta$. The spin density shows the Friedel type oscillations expected from a surface layer. Since the maximum magnetic moment occurs two layers below the surface, the SS responsible for the surface magnetism may be modified in a film less than or equal to 5 layers thick.

The spin density map on the face of the cube [vertical axis along (001)] is shown in Fig. 4. In very good agreement with the bulk results[3], the spin density is larger along the (110) than along the (001) direction. In the interstitial region (where the sp electrons dominate), the spin density, shown as dashed lines, is negative. This opposite polarization of the sp to the d electrons in the surface as well as in the bulk may be important in interpretating spin polarized tunneling[7], field emission[5], and electron capture[8] experiments because the matrix elements for the extended sp electrons may be considerably larger than those for the localized d electrons.

We next carried out a similar spin-polarized self-consistent study of a ferromagnetic 7-layer Fe(001) film. Here we find a large number of SS in the middle of the d bands with the larger magnetic moment ($2.15\mu_\beta$) producing some difference between the two spin states. Comparing our layer projected density of states (DOS) with bulk results, we find SS in the valley of the bulk DOS which seem to penetrate 2 layers below the surface for majority spin. In agreement with bulk results, the spin density for the film is largest along (001) directions and has similar magnitude along the (110) and (111) directions. Negative spin density was found along the (110) direction on the surface and center planes but not in the other planes.

The surface layer spin density (c.f. Table 1) shows an increase to $\sim 3.0\mu_\beta$ compared to bulk. This result is only semi-quantitatively correct because the Friedel oscillation penetrates deeper in Fe than was expected from the Ni results. Thus, a thicker film is required. The surface moment reduction in Ni(001) and its increase in Fe(001) may be consistent with the experiments of Bergmann[5] showing that Ni films less than 2 layers thick possess no moment whereas the first layer of an Fe film does. Here, Mössbauer or other hyperfine measurements may illucidate the surface magnetism in Fe.

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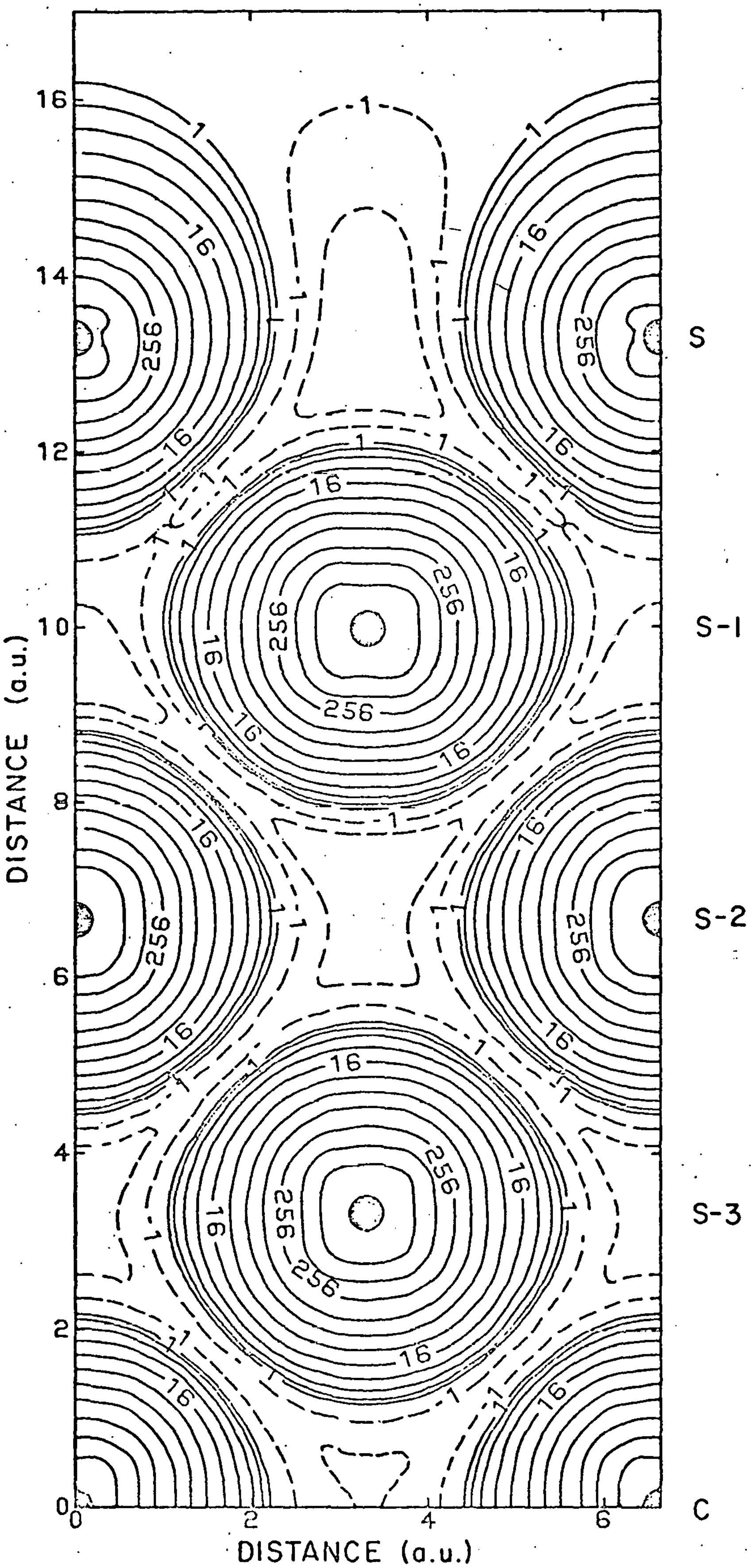
Figure Caption

Fig. 1. Self-consistent spin density map in units of 0.0001 a.u. in the (110) plane. Each contour line differs by a factor of 2. The dashed lines indicate nagative spin density.

Table 1. Layer spin magnetic moment in μ_β in 9-layer Ni(001) and 7-layer Fe(001) (s=surface layer and c=center layer).

	s	s-1	s-2	s-3	c	bulk theory	bulk exp.
Ni	0.44	0.59	0.62	0.56	0.54	0.58	0.56
Fe	3.01	1.69	2.13	—	1.84	2.16	2.12



DISTANCE (a.u.)
DISTANCE (a.u.)
0
2
4
6
8
10
12
14
16
1
16
256
S
S-1
S-2
S-3
C