Spin Separation in a Metal Overlayer

Roy Richter, J. G. Gay, and John R. Smith
Physics Department, General Motors Research Laboratories, Warren, Michigan 48090
(Received 27 March 1985)

The electronic properties of a ferromagnetic Fe monolayer epitaxially adsorbed on a Ag{100} substrate have been computed fully self-consistently. The minority *d*-band spin states of the Fe overlayer were found to be separated energetically from the majority-spin band. The magnetic moment per overlayer atom is $3.0\mu_B$, 36% larger than that of bulk iron.

PACS numbers: 75.50.Bb

We have carried out a calculation of the electronic structure of an Fe monolayer on Ag{100} and have found unusual and perhaps unique magnetic properties. Despite the tendency of nonmagnetic substrates to quench ferromagnetism, we found a 36% enhancement of the Fe magnetic moment in the monolayer over that in bulk Fe. Further, we find spin splittings of the Fe *d* bands of 2 to 3 eV. These splittings are sufficient to completely separate the majority- and minority-spin *d* bands of the Fe.

In the considerable literature on ferromagnetic overlayers on nonmagnetic substrates (see Refs. 1–6, and references therein), no overlayer moment has been found to be higher than that of the corresponding bulk. Also spin separation of overlayer bands has not been seen. Recent activity in magnetic overlayers was initiated by Liebermann *et al.*[7,8] They deposited Fe on Ag, Cu, and Au substrates and reported magnetic "dead" layers in the two Fe atomic layers closest to the substrate. Dead layers were also found for Ni and Co overlayers. These results were contradicted by a number of other experimental findings. Walker, Guarnieri, and Semper[9] found no nonmagnetic layer of Fe deposited on Ag{111}, and similarly Bergmann[10] found that the first monolayer of Fe on Pb-Bi showed a magnetic moment. More recently, Meservey, Tedrow, and Kalvey[11] found ferromagnetism in Fe only one atomic layer thick on Al as did Bergmann[12] for Fe on In, Sn, Pb, and Pd substrates. There is now experimental evidence that one to two monolayers of Ni on noble metals can remain ferromagnetic,[2,4,13] while Ni dead layers may be found[10,11,12] on Pb-Bi, Al, Mg, In, Sn, and Pb substrates. For the case of the solid-vacuum interface, we know that the magnetic moment of the surface layer of Ni{100} (see Ref. 14, and references therein) and Fe{100} is actually enhanced relative to the bulk.[15]

There are at least two competing factors affecting the overlayer magnetic moment.[5,6] Magnetic moments generally increase with decreasing coordination number as illustrated in Table I. An overlayer has a lower coordination number than the bulk, and it is lower the higher the index of the plane. A nonmagnetic substrate will generally tend to lower the moment of the overlayer, and experimental evidence suggests the substrate tends to be more effective the higher the substrate *sp*-conduction-electron density. We suspect that *d*-*d* coupling between the magnetic overlayer and a nonmagnetic substrate could also act to lower the overlayer moment significantly.

With the above in mind, we chose Fe on Ag{100} as a likely candidate to have a relatively large moment on the Fe overlayer. We suspected that the overlayer *d* band would be sufficiently narrow so that it would not overlap the Ag{100} *d* band, thus minimizing the *d*-*d* coupling effect. The Fe-Fe spacing in the overlayer is larger than that of the Fe bulk, which also reduces the *d*-*d* coupling. The experimental results also suggest that Fe is less sensitive than Ni to demagnetization effects coming from substrate-overlayer *spd* hybridization. In addition, Ag has a relatively low *sp*-conduction-electron density. Finally, it is known[18] that a monolayer of Fe can be grown epitaxially on Ag{100}, so the system can be realized experimentally.

The calculation was done using our self-consistent local orbital method.[19] The method has been used to

TABLE I. Magnetic moment per iron atom and total energy change due to spin polarization for various configurations. The geometry for all configurations is {100}.

	Magnetic moment (μ_B)	E(ferro) − E(para) (eV/Fe atom)
Fe atom[a]	4	
Fe monolayer[b]	3.4	−1.3
Fe on Ag	3.0	−1.2
Fe surface[c]	2.9	
Ag on Fe[d]	2.5	
Fe bulk[e]	2.2	

[a]The orbital angular momentum is assumed to be quenched as it is in the solid.

[b]At the Ag lattice constant 5.449 bohr. The bulk Fe lattice constant would give a square surface lattice constant of 5.405 bohr.

[c]Reference 15. These authors report $2.98\mu_B$ for the Fe{100} surface layer computed within the muffin-tin spheres only. As the spin density outside the spheres is largely negative, we infer the value 2.9.

[d]Reference 16. Value is for top (interface) Fe layer.

[e]Reference 17.

calculate the electronic structure of a number of d-band metal surfaces and interfaces and is established as an accurate and reliable technique. In several instances our calculations have predicted the existence of surface-state bands which were subsequently observed experimentally.[20] A spin-polarized version applied to the Ni{100} surface[14] has yielded a structure in close agreement with those found using linear augmented-plane-wave schemes. The Ceperley-Alder[21] local-density expression for the exchange-correlation potential was used. The calculation

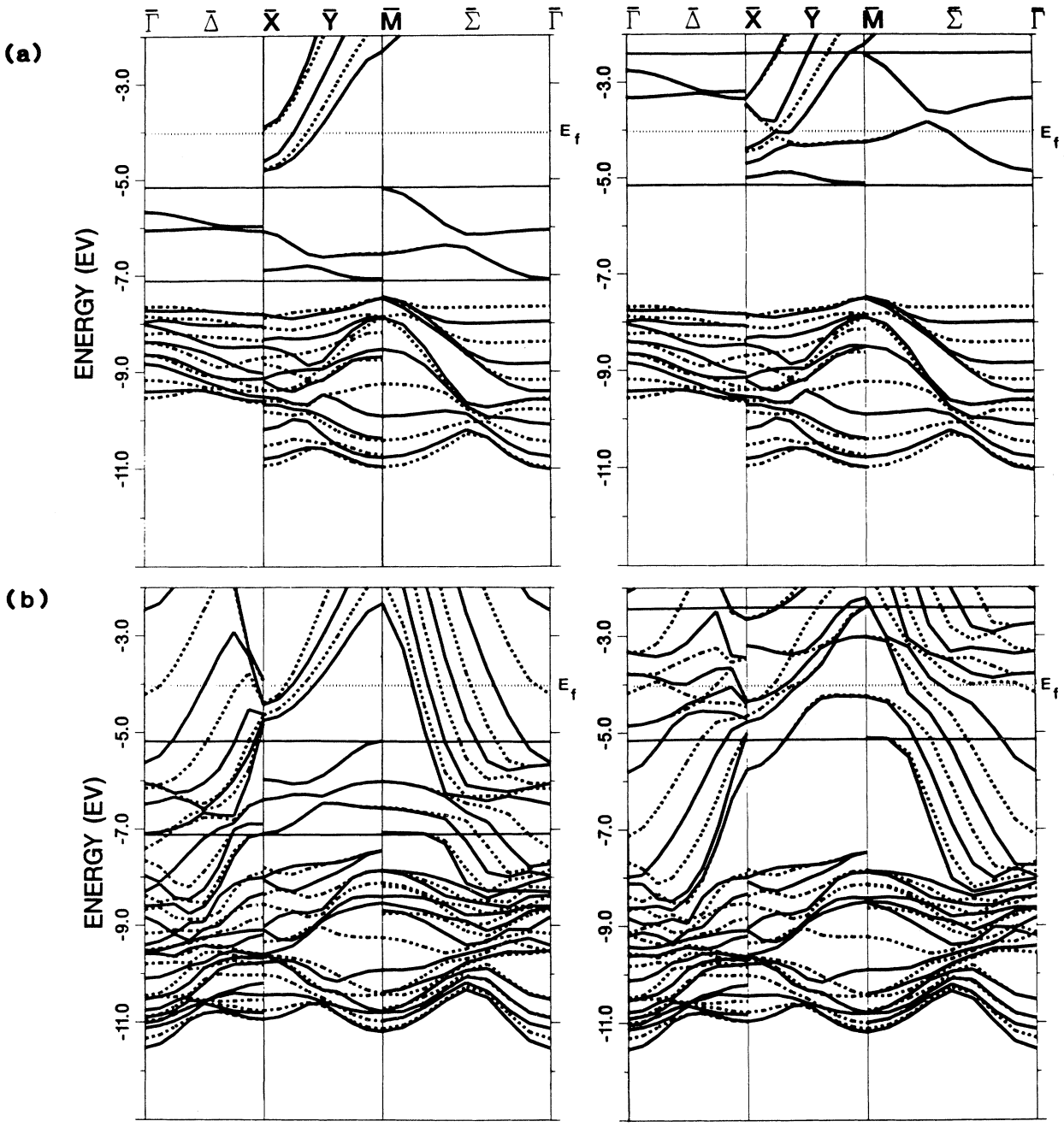

FIG. 1. Electron energy bands along high-symmetry directions for a monolayer of Fe on Ag{100}. Majority-spin bands are on the left and minority-spin bands are on the right. In (a) are those bands that are odd with respect to reflection in the mirror plane perpendicular to the surface and (b) exhibits the even bands. The Fe d bands lie essentially within the horizontal solid lines. The solid (dashed) energy bands correspond to wave functions symmetric (antisymmetric) with respect to reflection in the $z = 0$ plane.

was carried out for a thin film consisting of seven layers of fcc Ag{100} with monolayers of fcc Fe{100} epitaxially adsorbed on either side of the film. The Ag-Fe plane spacing was reduced from the fcc Ag-Ag spacing by 0.508 bohr to account for the smaller atomic diameter of Fe.

The resulting energy bands are shown in Fig. 1. The majority-spin bands are given in the left panels and the minority-spin bands are on the right. Figure 1(a) exhibits those bands which are even with respect to reflection in the mirror plane and 1(b) the odd bands. The Fe *d* bands are essentially contained between the horizontal solid lines. We see that the Fe *d* bands lie above the Ag *d* bands and are quite narrow. Also note that the Ag minority-spin *d* bands differ relatively little from the majority-spin bands, while the *sp* bands show larger differences. The most striking feature of Fig. 1 is the large splitting between minority- and majority-spin *d* bands of Fe. This splitting is slightly larger than the Fe *d*-band width, leading to a separation of majority- and minority-spin bands.

This separation is depicted in Fig. 2 in terms of minority- and majority-spin densities of states as projected on the Fe overlayer. From this plot it is clear that the two spin bands are resolved in the overlayer, and this is the only example of such a separation in a ferromagnetic overlayer on a nonmagnetic substrate to our knowledge.

Because the Fe *d* bands do not overlap the Ag *d* bands even after spin polarization, one would not expect spin polarization to have a large effect on the binding of the Fe to the Ag. The total energy differences (ferromagnetic minus paramagnetic) listed in Table I bear this out. We see that while the total energy of the Fe/Ag{100} system is lowered by 1.2 eV per Fe atom as a result of spin polarization, that of the isolated Fe{100} monolayer is lowered by 1.3 eV. Thus the change in binding energy of the Fe layer to the Ag is -0.1 eV; i.e., the bond is weakened slightly.

Let us now consider the magnetic moments per atom in the film. The Ag atoms all have magnetic moments less than $0.03\mu_B$. The Ag seems very hard to spin polarize, as expected. The Fe atoms have magnetic moments of $3.0\mu_B$. We calculate $3.4\mu_B$ for an isolated Fe{100} monolayer using the Ag{100} lattice spacing. The lowering of the magnetic moment from $3.4\mu_B$ when the isolated Fe{100} monolayer is placed on the Ag{100} surface is due to the effect of the nonmagnetic substrate. There is a charge transfer to the Fe of 0.15 electrons, which helps to lower the Fe moment. It is interesting that the magnitude of this suppression is very close to the increase due to lowered coordination number for the isolated monolayer relative to the surface layer[15] of Fe{100} ($0.4\mu_B$ vs $0.5\mu_B$, respectively; see Table I).

It is informative to compare the Fe on Ag{100} case

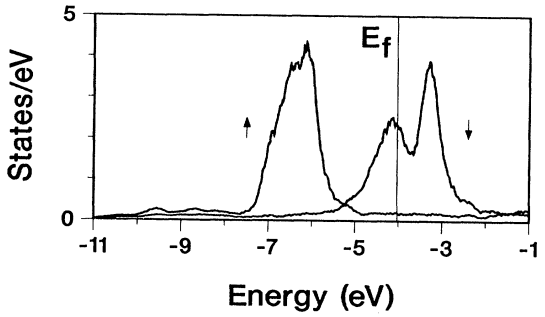

FIG. 2. Densities of states for majority and minority bands as projected on the Fe monolayer.

with the case of Ag on Fe{100} (Ref. 16). We see from Table I that the magnetic moment of the Fe overlayer is 20% larger than that of the Fe interface layer. Clearly the Fe coordination is lower for Fe on Ag{100} than for Ag on Fe{100}, helping to increase the magnetic moment. Note the suppression due to the presence of the nonmagnetic Ag{100} substrate is the same as that due to a Ag{100} overlayer ($0.4\mu_B$). This is at first thought surprising, because one might expect the *d*-*d* coupling between the Ag and Fe to be larger for Ag on Fe{100} than for Fe on Ag{100} due to larger *d*-band overlap in the former case. However, the *d*-band overlap turns out to be quite small for Ag on Fe{100} as well.[16,22] Presumably the magnetic suppression is primarily due to Ag(*sp*)-Fe(*d*) hybridization in both cases, which may explain why it has the same magnitude.

The unusual magnetic properties we calculate for Fe on Ag{100} make it a prime candidate for study using spin-polarized photoemission or other spin-sensitive probes. The separation of the Fe spin bands should be easily observed and confirmed in such experiments.

[1]J. S. Moodera and R. Meservey, Phys. Rev. B **29**, 2943 (1984).

[2]I. Kramer and G. Bergmann, Phys. Rev. B **27**, 7271 (1983).

[3]R. Miranda, D. Chandesris, and J. Lecante, Surf. Sci. **130**, 269 (1983).

[4]C. Rau and S. Eichner, J. Magn. Magn. Mater. **35**, 25 (1983).

[5]J. Tersoff and L. M. Falicov, Phys. Rev. B **26**, 6186 (1982).

[6]D. Wang, A. J. Freeman, and H. Krakauer, Phys. Rev. B **24**, 1126 (1981).

[7]L. N. Liebermann, D. R. Fredkin, and H. B. Shore, Phys. Rev. Lett. **22**, 539 (1969).

[8]L. Liebermann, J. Clinton, D. M. Edwards, and J. Ma-

thon, Phys. Rev. Lett. **25**, 232 (1970).

[9]J. C. Walker, C. R. Guarnieri, and R. Semper, in *Magnetism and Magnetic Materials—1972,* edited by C. D. Graham and J. J. Rhyne, AIP Conference Proceedings No. 10 (American Insitute of Physics, New York, 1973), p. 1539.

[10]G. Bergmann, Phys. Rev. Lett. **41**, 264 (1978).

[11]R. Meservey, P. M. Tedrow, and V. R. Kalvey, J. Appl. Phys. **52**, 1617 (1981).

[12]G. Bergmann, J. Magn. Magn. Mater. **35**, 68 (1983).

[13]D. T. Pierce and H. C. Siegmann, Phys. Rev. B **9**, 4035 (1974).

[14]X. Y. Zhu, J. Hermanson, F. J. Arlinghaus, J. G. Gay, Roy Richter, and J. R. Smith, Phys. Rev. B **29**, 4426 (1984).

[15]S. Ohnishi, A. J. Freeman, and M. Weinert, Phys. Rev. B **28**, 6741 (1983).

[16]S. Ohnishi, M. Weinert, and A. J. Freeman, Phys. Rev. B **30**, 36 (1984).

[17]J. Callaway and C. S. Wang, Phys. Rev. B **16**, 2095 (1977). These authors used three exchange-correlation potentials, and the result listed is an average of their three results for bulk Fe.

[18]G. C. Smith, H. A. Padmore, and C. Norris, Surf. Sci. Lett. **119**, L287 (1982).

[19]J. R. Smith, J. G. Gay, and F. J. Arlinghaus, Phys. Rev. B **21**, 2201 (1980).

[20]P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. B **20**, 3059 (1979); S. D. Kevan and D. A. Shirley, Phys. Rev. B **22**, 542 (1980); D. Westphal and A. Goldman, Surf. Sci. **95**, L249 (1980); E. E. Koch, J. Barth, J. H. Fock, A. Goldman, and A. Otto, Solid State Commun. **42**, 897 (1982); A. Goldman and E. Bartels, Surf. Sci. Lett. **122**, 1629 (1982).

[21]S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1700 (1980), from calculations by D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[22]M. Weinert, private communication.