

Interface magnetism in metals: Ag/Fe(001)

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A study of the effect of an ordered overlayer of Ag on the magnetism of an Fe(001) surface is presented. In order to understand the changes induced at the Ag/Fe interface, a series of self-consistent spin-polarized local-spin-density calculations were carried out with the use of our all-electron, full-potential, linearized augmented-plane-wave method. While the charge density is found to approach the bulk value within approximately one layer of the interface, the spin density at the interface is found to be strongly perturbed. An enhancement of the Fe magnetic moment at the interface (to $2.52\mu_B$ /atom) is predicted which, however, is significantly less than that found for the clean Fe(001) surface ($2.95\mu_B$). The role of the Ag overlayer in delocalizing the Fe surface states responsible for the increased surface magnetization and the effect on the single-particle spectra is described and discussed. The effect of the surface and interface on the contact hyperfine fields is evaluated: The (negative) core-polarization contribution is found to scale with the moment, but the valence contribution changes sign from negative in the interior to positive at the surface. The physical basis and the relationship of these results to the interpretation of Mössbauer-effect measurements of the hyperfine field are described.

I. INTRODUCTION

The subject of surface magnetism has generated a great deal of interest both experimentally and theoretically. Developments in both branches have been quite significant in the last few years. On the experimental side,¹ the techniques for preparation and characterization of surfaces have led to reproducible results. On the theoretical side, new techniques for solving the all-electron local-spin-density² equations without shape approximations to the density or potential³⁻⁵ have made possible accurate first-principle determinations of the electronic and magnetic structures of real systems, particularly of the 3d transition metals and their surfaces. The study of the magnetism of the Fe surface has a relatively long history, beginning with the observation of magnetic "dead" layers.⁶ This early result is now believed to be due to impurities; the present experimental⁷ and theoretical⁸ consensus is that there is a $\sim 30\%$ increase in the magnetic moment at the clean surface.

One method not often used for surface studies is the Mössbauer effect. For bulk solids, there is a long tradition of obtaining the magnetic moment from the measured hyperfine fields.^{9,10} The physical basis behind the success of this interpretation is that the dominant term is the (negative) core-polarization contribution which approximately scales with the magnetic moment.¹⁰ (The bulk valence electrons generally give an additional small negative contribution.) Tyson *et al.*¹¹ have performed

Mössbauer measurements of the hyperfine fields, H_{hf} , of ultrathin epitaxial Fe films and found that H_{hf} increased at the surface. However, since Fe is such a good getter and Mössbauer-effect measurements need very long counting times, Tyson *et al.* covered the Fe with Ag overlayers to prevent oxidation. As they point out,¹¹ the conclusion that there is an increased magnetization at the surface must be viewed in light of the possibilities that (1) the film growth is not locally smooth, and more importantly, (2) there may be interactions between the covering layer and the Fe which could affect the surface magnetization.

A further point that may be important, but was not considered experimentally, is that the contributions to H_{hf} may be significantly different at a surface than for a bulk system.¹² In our previous work on the clean Fe surface,⁸ we found that while the magnetic moment increased at the surface, the total contact H_{hf} decreased in magnitude due to a large positive valence contribution. This change in sign of the valence contribution is localized to the surface; even one layer down, the valence contribution is again negative. Hence, while our clean Fe(001) surface results for the moments were in agreement with the conclusions of Tyson *et al.*,¹¹ our results for H_{hf} apparently had the opposite behavior from experiment.

In order to better understand the apparent discrepancies between the experimental and theoretical interpretation of the hyperfine fields, we present a set of self-consistent calculations for a system closely resembling the experimental situation: We treat the case of a thin Fe(001) film with an

Ag overlayer. In this way, we probe the effect of interactions between the overlayer and the Fe substrate. We find that the Ag overlayer strongly affects the Fe surface magnetism and hence clean and Ag-covered Fe(001) films represent different, but individually interesting, systems. In particular, we can reconcile the apparent differences between experiment on Ag/Fe(001) and theory on clean Fe(001) in a simple way—covering the Fe surface with Ag acts to “seal” the surface such that now the Fe at the Ag interface has a negative valence contribution. Then in this case, the experimentally used analysis of assuming a proportionality between the magnetic moment and the hyperfine field is roughly valid.

The next section briefly describes the model systems considered and the method used to determine the electronic and magnetic structure of the thin films. In Sec. III, we discuss and compare the charge and spin densities, including the magnetic moments, for the clean and Ag-covered Fe systems. The effect of the Ag overlayer on the single-particle spectra is discussed in Sec. IV, with particular emphasis on surface states and the $3s$ core levels. In Sec. V, we finally discuss the contact hyperfine fields and the relationship to experiment.

II. CALCULATIONAL MODELS

In order to study rather delicate questions concerning the spin density such as the contact hyperfine field, it is necessary to have accurate solutions to the (local-) spin-density-functional equations.² At surfaces, the problem is even more severe than for bulk systems because of the reduced symmetry. For example, in cubic systems such as Fe, the potential and density at a bulk site can only have components corresponding to angular momenta $l=0, 4, 6, 8$, etc. Since the potential outside a charge distribution goes as $r^{-(l+1)}$, the neglect of all terms but the spherically symmetric $l=0$ term will not introduce too large of an error. This is why the commonly used muffin-tin or warped muffin-tin approximations to the potential work well for the close-packed cubic metals. At a surface, however, the first nonzero l is not $l=4$, but rather $l=1$. Hence the standard shape approximations to the potential and density that may be reasonable for bulk systems are suspect at a surface.

In our full-potential linearized augmented-plane-wave (FLAPW) method,⁴ we use an extremely flexible and accurate plane-wave-based basis set to solve the local-spin-density equations, including the nonspherical terms. In this approach, no shape approximations are made to the charge density or potential, Poisson’s equation is solved for a general potential,³ and all matrix elements due to this full potential are rigorously taken into account. All electrons are treated self-consistently, the core fully relativistically and the valence electrons scalar relativistically. We have found that the FLAPW method yields accurate valence spin densities and an accurate treatment of the core polarization, thereby making possible accurate calculations of sensitive quantities like the hyperfine fields at the nuclei.

For this paper, we have performed a series of self-consistent spin-polarized calculations on both clean and Ag-covered Fe(001) films. The series of calculations are

schematically represented in Fig. 1. For the clean Fe(001) surfaces, we have performed calculations on one, five, and seven layers. For the cases of the Ag-covered surfaces we have done two calculations—a five-layer Fe film with an Ag overlayer on each side and a double set of Ag/Fe bilayers. These last two calculations were done in the same structural configuration as the seven-layer clean Fe film. In particular, we have replaced the outermost Fe atoms by Ag, and in the case of the bilayer calculation, we have in addition removed the central layers of Fe. In this way, the computational parameters for the different calculations are the same.

In our earlier study⁸ of the clean Fe(001) surface, we found that the self-consistent contact hyperfine field and charge and spin densities were not very sensitive to the number of basis functions and \vec{k} -point sampling once one reached values for these parameters of about 15 \vec{k} points in the irreducible wedge of the 2D Brillouin zone and ~ 400 basis functions per \vec{k} point, split up into two blocks of ~ 200 basis each using the z -reflection symmetry of the film. The results given in our earlier work⁸ on Fe(001) used 36 \vec{k} points and about 2×250 basis functions per \vec{k} point; for the present calculations, however, we have used the smaller set of parameters. While the contact hyperfine fields are not very sensitive to these computational parameters, they are rather sensitive to convergence, in particular that of the spin density. The root-mean-square difference in the charge density was converged to better than 5×10^{-4} electrons/a.u.³, while the spin density is better converged by an order of magnitude.

In the discussion, we will often talk about muffin-tin or atomic spheres. This division is for mathematical convenience and for making a physically appealing decomposition of space. However, the results of the calculation are independent of the choice of the sphere radius, etc., since we treat the full nonspherical charge and potentials everywhere in space. In particular, inside the spheres, we expand the charge and potential in lattice harmonics with $l \leq 8$; higher- l components inside the spheres are treated by the plane-wave representation. For the exchange-correlation functional, we use the spin-dependent part of von Barth and Hedin² and the spin-independent form of Hedin and Lundqvist.¹³

III. CHARGE AND SPIN DENSITIES

The charge and spin densities are the central quantities of density-functional theory² and can be, at least in princi-

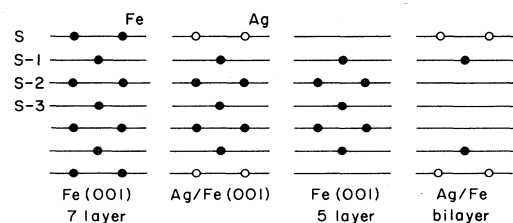


FIG. 1. Schematic representation of the calculations. Solid (open) circles represent Fe (Ag) atoms and the lines correspond to the layers in the film.

ple, directly compared to experimental density maps. In Fig. 2, we show the self-consistent charge densities in a (110) plane for the clean Fe(001) surface⁸ and for the Fe(001) surface with the topmost Fe replaced by an Ag atom. The first point to notice is that at only one layer below the surface, the clean and Ag-covered densities are virtually indistinguishable—the difference in the charge density is localized to this interface layer. The main effect of the Ag on the charge density is to “squeeze” the interstitial density directly below the Ag and to increase the corrugation in the vacuum. These effects are simply related to the larger size of the Ag atom compared to the Fe. These small changes in the charge density, however, are in the region of the dipole barrier and cause the calculated work function to change from 4.29 eV for the clean surface⁸ (experiment:¹⁴ 4.31 eV) to 4.92 eV for the Ag-covered surface.

Figure 3 presents the corresponding spin densities ρ_s for the two surfaces. The spin density⁸ of the clean surface is highly anisotropic and has regions of both positive and negative spin density. Away from the surface layer, the anisotropy¹⁵ (t_{2g} to e_g ratio) in the d band ρ_s and the negative ρ_s between the atom is consistent with that obtained by neutron scattering¹⁶ for bulk Fe. The spin density in the vacuum region is almost entirely positive and indicates a large increase in the magnetic moment at the surface. For the Ag-covered surface, we find that the spin density for the layers below the Ag/Fe interface are the same as for the clean surface. However, at the interface, the spin density is strongly modified. First, there is only a relatively small induced positive spin density on the Ag and the spin density of the Fe at the interface is increased, i.e., the contours are pushed further out towards the vacuum. In contrast to the clean surface, the spin density in the vacuum region is now mainly negative due to the exchange polarization of the Ag sp -electrons towards the unpaired spins of the Fe. As will be seen later, this polarizability of the Ag sp -electrons is important in determining the contact hyperfine fields.

To this point, we have given a qualitative description of the charge and spin densities. In Table I we list the calcu-

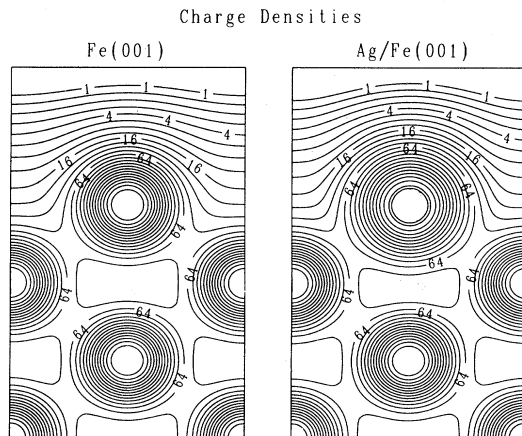


FIG. 2. Total charge densities for Fe(001) and Ag/Fe(001) in a (110) plane. Each contour differs by a factor of $\sqrt{2}$ (in units of 10^{-3} electrons/a.u.³).

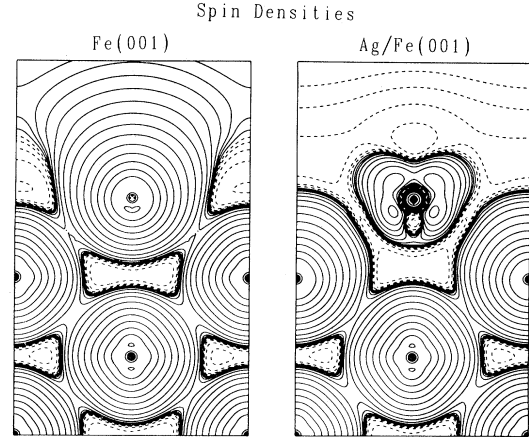


FIG. 3. Total spin densities. Solid (dotted) lines mark the zero and positive (negative) 2^n ($n=0,1,2,\dots$) contours in units of 10^{-4} electrons/a.u.³

lated results for the total charge and spin inside the muffin-tin spheres for the different calculations. As seen in our earlier work,⁸ at the clean Fe surface there is a decrease in the total charge inside the sphere mainly due to a loss of p -like charge. Moreover, the charge density approaches the bulk value very rapidly, i.e., the screening length is on the order of the interlayer spacing: The Fe charge density is approximately bulklike as long as it has a complete shell of nearest neighbors (at least one layer down from the surface).

If we consider the effect of creating a surface, the fact that this result is independent of whether the nearest neighbors are Ag or Fe is not too surprising: In creating a surface, the periodicity in the normal direction is disrupted resulting in a leakage of charge out into the newly created vacuum region. It is this leakage of charge that is responsible for the formation of the dipole barrier, and hence the work function. Since metallic screening lengths are of the order of interatomic spacings, it is mainly the charge density associated with the surface atoms that is perturbed by the creation of a surface. If the surface is coated with Ag (or another metal), it is now mainly the Ag, not the Fe, electrons that will leak into the vacuum; the charge density of the interfacial Fe is perturbed due to the presence of a nearest-neighbor Ag instead of another Fe. It is obvious that this perturbation is much smaller than that involved in creating a surface; hence we expect the Fe layer at the Ag interface to be more bulklike than the Fe layer at a clean surface. These results then lead to a picture in which the noble metal seals the Fe surface by partially restoring the bulk periodicity without strongly perturbing the Fe. Further evidence for this picture is given by the results of the bilayer calculation: Both the charges on the Ag and Fe spheres are nearly the same as if they were at the terminating end of a thick slab. [The work function of the bilayer is close to the Ag/Fe(001) calculation because the reference vacuum level is on the Ag site of the bilayer.] Since Ag seals the surface, it is clear that an Ag-coated Fe surface should have different electronic and magnetic properties than a clean Fe surface.

TABLE I. Layer decomposition of the charges and the magnetic moments (in μ_B) in the muffin-tin spheres for the clean Fe(001) system (one-, five-, and seven-layer films) and for the Ag/Fe system [bilayer of Ag and Fe, and overlayer of Ag on a five-layer Fe(001) slab Ag/5 Fe]. For the Ag/Fe systems, the surface layers (S) are Ag, and the subsurface layers ($S-1$, etc.) are Fe. The work functions ϕ in eV are also given for each calculation.

	Ag/Fe(001)			Fe(001)	
	Ag/5 Fe	Bilayer	Seven layer	Five layer	Monolayer
Charges in spheres					
S	9.55	9.56	6.78	6.80	6.50
$S-1$	7.08	6.81	7.05	7.05	
$S-2$	7.07		7.05	7.05	
$S-3$	7.05		7.05		
Moments					
S	0.08	0.05	2.98	2.94	3.18
$S-1$	2.52	2.80	2.35	2.32	
$S-2$	2.37		2.39	2.52	
$S-3$	2.27		2.25		
ϕ					
	4.92	5.05	4.29	4.57	4.47

Although the density for the Fe at the Ag interface is already rather bulklike, the spin density is not. This result is not unexpected since while small relative shifts of the majority and minority densities may cause only small changes in the total charge density, these shifts can yield large spin densities. From the results for the clean Fe(001) surface given in Table I, we see that there is a large increase in the moment at the surface. As discussed previously,⁸ there is a small Friedel oscillation of the magnetic moments and the moment at the center of the seven-layer film is slightly too large compared to bulk results. This latter effect suggests a small size effect in the seven-layer film. This is more obvious in the five-layer case where the increase in the central-layer moment is more pronounced—as is the Friedel oscillation. However, the magnetic moments in the surface (S) and subsurface ($S-1$) Fe spheres are in very good agreement with each other, demonstrating that the surface spin density and magnetic moments are given correctly. At the clean surface, we find that there is a large increase in the magnetic moment to $\sim 2.95\mu_B$ /atom; for an unsupported Fe monolayer, with effectively two free surfaces, the moment increases even further to $\sim 3.2\mu_B$. (If we reduce the dimensionality even further, we find that the moment of a linear chain¹⁷ of Fe increases further still to $\sim 3.3\mu_B$ while the free atom has a moment of $4\mu_B$.)

Now let us consider the effect of Ag on a single layer of Fe. The Fe moment is reduced from both the monolayer and free-surface results to $2.80\mu_B$ and a small moment is induced on the Ag. Hence, we would expect that the effect of putting Ag on an Fe substrate is to decrease the magnetic moment of the Fe at the interface from the free-surface value. This expectation is borne out by the calculations for the Ag overlayer on the five-layer Fe; the Fe at the interface now has a moment of $\sim 2.5\mu_B$, which is still a substantial ($\sim 10\%$) increase in the moment compared to bulk. Very recent results^{1,18} obtained by doing direct-magnetization measurements have obtained an in-

crease in the magnetic moment at the Fe(110)-Ag(111) interface of about 10%. Although direct comparison is difficult due to the different orientation of the films, the rough agreement between theory and experiment is encouraging. Note that for the five-layer Fe slab covered with Ag, there is no Friedel oscillation in the moment and the agreement in the $S-2$, $S-3$ moments between these results and the seven-layer Fe(001) slab is excellent. If we attribute the large oscillations of the clean surface to the Fe conduction electrons spreading out into the vacuum region, we have further evidence that the Ag has sealed the surface; in this context, the Ag has stabilized the response of the Fe charge and spin densities to the perturbation caused by the creation of the surface.

From these discussions and results, it is obvious that the Fe at the interface between Ag and Fe is quite different than an Fe at the clean surface. Hence, measurements that probe the Ag/Fe or similar interface cannot be compared directly to the free Fe surface. It may well be that a number of different overlayers will yield comparable results for the interface Fe properties, especially if these adsorbates are chosen so that they do not interact strongly with the Fe. Before discussing the contact hyperfine field (and the relationship to the Mössbauer experiments), we digress briefly and discuss the single-particle spectra, focusing on the surface states and the Fe 3s core-level splittings.

IV. SINGLE-PARTICLE SPECTRA

In our previous work⁸ on the clean Fe(001) surface, we saw a variety of surface states both above and below the Fermi level, E_F . Recently, Turner *et al.*¹⁹ reported energy dispersions along $\bar{\Gamma}$ to \bar{X} determined by angle-resolved photoemission. They found a surface state (resonance) just below E_F existing in the entire region from $\bar{\Gamma}$ to \bar{X} and a lower broad-band surface state with a dispersion

from -2 to -3 eV below E_F . (All energies will be given with respect to E_F .) These states were also found in our self-consistent calculation of the clean Fe(001) surface.⁸

In Fig. 4, we give the majority (partial) local density of states (LDOS) in the surface and subsurface atomic spheres for both the clean and Ag-covered surfaces. Note that the labels S (surface) and $S-1$ (subsurface) correspond to the position from the surface. The LDOS is dominated by the d density of states, with the $s-p$ giving a small background. The LDOS for the $S-2$ layers for the two systems are very similar and bulklike, including their position relative to E_F , and hence are not shown. First note that for the clean Fe(001) surface, there are surface states within the valley between the bonding and antibonding bulk peaks. For the second layer, the LDOS is already reasonably bulklike. In the case of Ag/Fe(001), the surface LDOS is mainly Ag-like, as expected, but with some Fe d weights 2 to 4 eV below E_F . The LDOS of the Fe at the interface does not look like either the LDOS of the S or $S-1$ Fe of the clean surface. If, however, one compares the average of the S and $S-1$ Fe LDOS with that of the $S-1$ Ag/Fe, then one finds good agreement in the position and height of the main features in the LDOS above about -3 eV if the Ag/Fe LDOS is shifted by -0.3 eV to greater binding energy. (This shift is due to the dipole layer.) For energies between about -3 to -4.5 eV, there is a loss of states in Ag/Fe compared to clean Fe, but a gain of states below -5 eV. These differences are due to the hybridization of the Ag and Fe d bands.

From these results, we see that the Fe at the Ag interface is neither bulklike nor surfacelike, but has features of both. In particular, the surface states that give rise to the increased surface magnetism⁸ are still present, but are not as localized as they are for the clean surface. Hence, the increase in the magnetization at the interface is less pronounced than at the clean surface. The same observation holds for other surface states. This delocalization of the

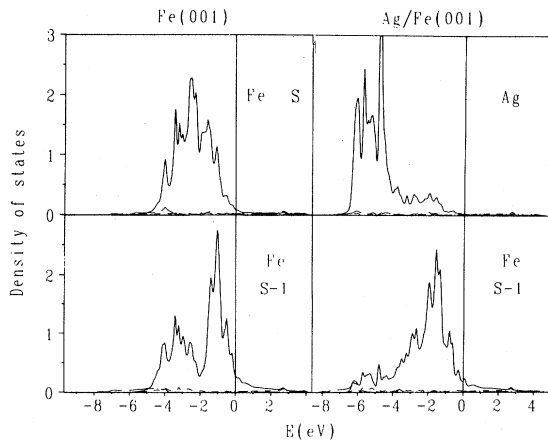


FIG. 4. Majorities local partial density of states (in states/eV spin) in the surface (S) and subsurface ($S-1$) atomic spheres. Energies are measured with respect to the Fermi level. The d ($s-p$) partial densities of states are given by the solid (dotted) lines.

surface states is due to the partial reimposition of bulk boundary conditions by the Ag, i.e., the Fe electrons are now more itinerant than they are at the clean surface. That the Ag does not have the same effect of reimposing the bulk conditions as an Fe is hardly surprising. Having discussed the valence spectra, let us now shift our attention to the localized $3s$ core levels.

The splitting of the $3s$ core levels in Fe is often used as a measure of the magnetic properties of Fe.²⁰⁻²² A complicating feature of this procedure, however, is that final-state correlations²¹⁻²³ are very important in determining the splittings; these effects can cause the experimental spectra to differ by a factor of 2 from the initial-state splittings.²¹ Our calculations give the initial-state splittings only, and hence cannot be directly compared to experiment. However, one hopes that these final-state effects remain approximately constant so that changes in initial-state splittings and shifts are also reflected in the experimental spectra.

With this complication in mind, we now consider the initial-state splittings and shifts of the $3s$ core levels for the clean and Ag-covered Fe(001) surfaces. The calculated exchange splitting of the $3s$ level is ~ 2.6 eV for the Fe up to one layer from the vacuum or Ag interfaces. That the exchange splitting is approximately constant is simply the result of the magnetic moments having approximately the bulk value up to the interface layers. At the clean and Ag-covered surfaces, the exchange splittings of the $3s$ level have increased to 3.2 and 2.8 eV, respectively. Again these increases just reflect the increase in the magnetic moments at the interfaces, and scale approximately with the magnitude of the moments. (At the clean surface, this scaling is not as accurately obeyed as for the Ag-covered surface.)

Although the $3s$ level as measured by photoemission is quite wide (full width at half maximum²¹ of ~ 3.3 eV), it is possible to see core-level shifts much smaller than this value. Since each spin has a different potential it is not necessary that the two spins have the same core-level shifts. This is, in fact, borne out by the calculations. The minority spin Fe $3s$ level shows only a very small surface to bulk shift of < 0.1 eV to greater binding energy for both the clean and Ag-covered surfaces. The majority spin levels have corresponding shifts of 0.7 and 0.3 eV to greater binding energy, respectively. Note that this difference in the majority spin $3s$ core-level shift is just equal to the corresponding differences in the exchange splittings. We know of no compelling reason why the minority $3s$ core-level shifts should be approximately 0, with the majority shifts then determined by the exchange splitting. This is different than the situation for the Ni(001) surface,²⁴ where both majority and minority levels shift; the different behavior seen in Fe and Ni is perhaps related to the fact that bulk Fe is a weak ferromagnet, whereas Ni is a strong ferromagnet.

V. CONTACT HYPERFINE FIELDS

The largest contribution to the hyperfine fields¹⁰ is generally the Fermi contact term H_{hf} . This term is given in terms of the spin density at the nucleus $m(\vec{r}=\vec{0})$ as

$$H_{\text{hf}} = \frac{8\pi}{3} \mu_B m(\vec{r}=\vec{0}) = 524m(\vec{r}=\vec{0}) \text{ kG}$$

if $m(\vec{r}=\vec{0})$ is given in atomic units. There are two contributions to the contact term for transition metals:¹⁰ (1) the large negative polarization of the core s electrons due to the d moment and (2) a valence contribution from the valence “ s -like” electrons. The valence contribution in bulk ferromagnetic materials such as Fe and Ni is also negative. This negative polarization of the valence s electrons in the bulk is due to the predominance of the indirect (or covalent) polarization²⁵ associated with the opposite spin-conduction electrons over the direct (Hund’s rule) coupling to the unpaired d electrons. In a free atom, however, the direct polarization of the s level will dominate and produce a positive contribution to H_{hf} . As we will see below, these two effects in the valence contribution are important for hyperfine studies at surfaces.

Table II presents the calculated contact hyperfine fields broken down into layer core and valence contributions for the different systems studied. First let us consider the core terms. This term scales approximately with the magnetic moment¹⁰ regardless of the local (metallic) environment for all the systems studied here; the calculated value of the core contribution is ~ -130 kG/unpaired spin and is very close to the free-atom value calculated earlier.¹⁰ This scaling is the basis for the standard interpretation relating Mössbauer data to the magnetic moments:¹ Since generally the bulk valence contribution is small, the larger the magnitude of the measured (negative) hyperfine field is, the larger the moment is. This analysis has been very successful for bulk systems and lead Tyson *et al.*¹¹ to interpret their Mössbauer data of Fe films covered with Ag as suggesting that the free Fe surface has an increased moment.

While our results⁸ for the clean surface do show a large enhancement of the surface magnetic moment, the total calculated H_{hf} is smaller in magnitude (-252 kG) due to a large *positive* ($+140$ kG) valence contribution. From Table II, we see that the surface Fe has a positive valence contribution while the subsurface valence contributions are again negative. (The positive value at the central layer of the five-layer film is due to a size effect—the film is too thin to stabilize the Friedel oscillation of the conduction electron term.) These results can be understood simply in terms of our earlier discussion. For atoms below the surface, the indirect polarization should be dominant, yielding a negative contribution. Then the standard interpretation relating the measured H_{hf} to the magnetization should be valid. At the surface, however, the s density is more nearly atomiclike and hence we have a positive valence contribution to H_{hf} . In the sense that the bands narrow at the surface and that the magnetic moments are more atomiclike, this is a consistent picture. Moreover, we now see that the standard interpretation of the data is *not* valid at the surface.

In order to understand the experimental results, we consider the Ag/Fe system. First, let us look at the bilayer. The Fe core contribution again scales as expected and there is a small induced core polarization on the Ag. The conduction term on the Fe is large and positive again due to the direct (atomlike) polarization. The Ag valence contribution is very large and negative. This result is completely in accord with our model. The noble metal s - p electrons act as an electron gas that the Fe d moment can couple to, giving rise to a Ruderman-Kittel-Kasuya-Yosida²⁶ interaction. Since this interaction is such that at the nearest neighbor it yields a negative electron spin density, we expect a large and negative valence contribution to H_{hf} for Ag.

TABLE II. Calculated contributions to the contact hyperfine field in kG with the same labeling as in Table I. For the Fe core contributions, the hyperfine field per unpaired spin is given below in parentheses.

	Ag/Fe(001)			Fe(001)		
	Ag/5 Fe	Bilayer	Seven layer	Five layer	Monolayer	
Total						
	S	-587	-664	-252	-228	-101
	$S-1$	-335	-221	-395	-419	
	$S-2$	-339		-327	-295	
	$S-3$	-359		-366		
Conduction						
	S	-553	-635	+143	+166	+323
	$S-1$	-7	+142	-89	-117	
	$S-2$	-31		-16	+33	
	$S-3$	-64		-75		
Core						
	S	-34	-29	-395	-394	-424
				(-134)	(-134)	(-133)
	$S-1$	-328	-363	-306	-302	
		(-130)	(-130)	(-130)	(-130)	
	$S-2$	-308		-311	-328	
		(-130)		(-130)	(-130)	
	$S-3$	-296		-291		
		(-130)		(-130)		

The results for our thicker Ag-covered film are qualitatively the same as for the bilayer. As was seen for the bilayer, the valence contribution to the Ag H_{hf} is large and negative. The Fe core contribution again scales with the moment and now all the valence contributions are negative. These contributions then yield total Fe H_{hf} that are of the order of the bulk value. That the total hyperfine field at the interfacial Fe is not larger in magnitude than the bulk, as found in experiment, may be due to either (1) the fact that the experiments were done on Fe (110) films as opposed to the (100) face studied here or (2) a residual finite-size effect. On the close-packed (110) face, the valence s density should be more nearly electron gaslike than that on the more open (100) face; hence the negative valence contribution should be larger in magnitude. On the other hand, a finite-size effect cannot be ruled out since the valence H_{hf} contribution is not yet constant in the middle of the film. Regardless of the origin of the differences, our results do give a consistent explanation of the Mössbauer data. The observed increase in H_{hf} at the Ag/Fe interface does correspond to an increased magnetization of the outermost Fe. Had the same experiment been done for a clean surface, which has an even larger increase in the magnetic moment, one would have found instead a *decrease* in H_{hf} . The use of the standard model^{1,11} would have then lead one to the wrong conclusion.

As one final point of contact between our results and the Mössbauer experiments, we consider the total density at the nucleus which is related to the isomer shift. Tyson *et al.*¹¹ have deduced from their measurements that there is a decrease in the s charge density at the nuclei near the interface. Our results, in agreement with the experiments, also give a decrease in the contact density at the surface and interface: The outermost Fe in the clean and Ag-covered films show decreases of 0.2 and 0.4 electrons/a.u.³, respectively, from the "bulk" value of 14 494.6 electrons/a.u.³ calculated for the contact density at the center of the films.

VI. SUMMARY

We have presented a set of self-consistent spin-polarized local-spin-density calculations for the clean and Ag-covered Fe(001) system in order to obtain a better understanding of magnetism at vacuum-metal and metal-

metal interfaces. The results show that the charge density quickly approaches the bulk value within approximately one layer of the interface, but the spin density has a larger screening length. We find that there is an increase of the Fe magnetic moment at the Ag interface by about 10% compared to an increase of 30% for the clean surface. The single-particle spectra (both valence and core) are modified at the interface; in particular the Fe LDOS at the Ag interface is neither bulklike nor surfacelike, but rather has features of both.

One of the main motivations behind the present work was the Mössbauer measurements¹¹ of the hyperfine field in thin Fe films. These experiments showed an increase in magnitude of the (negative) H_{hf} at the Ag/Fe interface, which was interpreted as indicating an increased magnetic moment at the Fe surface. In our earlier study⁸ of the clean Fe(001) surface, however, we found a decrease in H_{hf} due to a large positive valence contribution although the magnetic moment increased. As we have shown here, coating the Fe surface with Ag causes the Fe valence contribution at the interface to be negative again; this result then resolves the apparent contradiction between theory for the clean Fe surface and experiment for the Ag/Fe system. These results, however, point out that the contributions to the hyperfine field at the surface are different than those in the bulk and that it is dangerous to apply the simple bulk interpretations of the data to surface work. Furthermore, the first-principle results we have presented here not only give a simple and consistent explanation of this and other available experimental data^{1,11,18,19} on the Fe(001) and Ag/Fe(001) systems, but also demonstrate quite clearly that surfaces and interfaces are different, and individually interesting, systems.

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