PHYSICAL REVIEW B, VOLUME 64, 144419

# First-principles study of hyperfine fields in a Cd impurity in the Fe/Ag(100) interface

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(Received 21 November 2000; published 20 September 2001)

Monolayer-resolved hyperfine fields (HFF's) at the Fe/Ag(100) interface have recently been determined using $^{111}$In probe atoms, which decay to $^{111}$Cd, in perturbed $\gamma\gamma$ angular-correlation spectroscopy (PAC). Isolated radioactive probe atoms in PAC allow to sense the presence of HFF's at the Fe and induced HFF's at the Ag layers but, poses a complementary physical problem to that of the HFF's at the host Fe/Ag system: that of an impurity within the layers. Using density-functional theory (DFT) within the generalized gradient approximation (GGA) and a supercell approach, we investigate this problem. Similarly as experimentalists insert the probe atom on a layer-by-layer growth, preparing samples with radioactive probe atoms either in the Fe/Ag interface, or in the second (from the interface) Ag layer, or embedded within the bulk Fe, our supercell methodology can simulate each of these systems. The theoretical approach has the advantage of having the capability of distinguishing between two different cases at the interface: Cd in the Fe or Ag side. This allows us to make a clear assignment of the measured HFF's. We discuss: (i) the relation of the HFF in the Cd probe with that of the original host atom, (ii) the precision of state of the art DFT-GGA calculations to obtain quantitative predictions of HFF's in very complex systems such as interfaces and the effect of lattice relaxations (interlayer spacings, lateral displacements). The importance of including spin-orbit coupling and the influence of additionally considering orbital polarization are assessed.

DOI: 10.1103/PhysRevB.64.144419 PACS number(s): 75.70.Cn, 76.80.+y

## I. INTRODUCTION

Effects like giant magnetoresistance and oscillatory interlayer coupling together with possible applications to magnetic-recording technologies have made the experimental and theoretical studies of the magnetic properties of ultrathin films and artificial structures of considerable interest. Most interesting are artificial structures consisting of ferromagnetic layers separated by nonmagnetic spacers. The underlying physics can be understood with the help of, e.g., Mössbauer studies of the local hyperfine fields (HFF's) in the ferromagnetic films and near the interface. In these experiments, what happens in the nonmagnetic layers close to the interface cannot be resolved. The use of radioactive probe atoms in perturbed $\gamma\gamma$ angular-correlation (PAC) spectroscopy represents instead a very sensitive tool to sense the presence of HFF's at the buried probe atom in not necessarily magnetic layers. Individual atomic layers can be characterized, since probe atoms can be deposited at any time during the preparation of the samples.

In recent PAC experiments[1] with $^{111}$In probe atoms, the Fe/Ag(100) interface has been studied complementing previous Mössbauer spectroscopy experiments using $^{57}$Fe as a probe,[2,3] and low-temperature nuclear-orientation (LTNO) experiments.[4]

In Mössbauer experiments about 1 monolayer (ML) of probe atoms is needed to get a sufficiently strong signal whereas in PAC spectroscopy this number is reduced to the order of $10^{-4}$ ML. The insertion of an isolated probe different from the host atoms in PAC experiments poses a complementary problem: that of an impurity embedded in different layers.

Experimental results agreed on the presence of two well-defined measured HFF's at the Fe/Ag interface. Liu and Gradmann[2] concluded that the presence of two different components was a property of a structurally homogeneous Fe/Ag(100) interface without providing any indication for an attribution of either component. In the Mössbauer experiment by Schurer *et al.*[3] several frequencies were observed and associated with the presence of different Fe sites with different nearest-neighbor configurations, i.e., a nonhomogeneous interface.

In the PAC investigation[1] the two well-defined measured HFF's are assigned to Cd probe atoms sitting at different sides of the interface. The component with the highest frequency (which coincides with the value measured in bulk Fe), was assigned to probe atoms in the Fe layer at the Fe/Ag interface, and the other one to those atoms in the Ag layer adjacent to the interface. Moreover, the experiments by Runge *et al.*[1,5] were performed in such a way that the measured hyperfine fields directions, both at the Fe and Ag layer, were in the plane of epitaxial growth and are oriented along the [100] direction of the iron lattice corresponding to the [110] direction of the silver lattice. This represents a different situation to that found in the LTNO experiments[4] on the Fe/Ag(100) interface, which reported HFF's at the Ag side that are directed *out of the plane* of the multilayer.

The measured hyperfine fields give information on the electronic properties of solids that cannot be obtained by other methods, but in general the interpretation of measured values is not straightforward. All-electron *ab initio* theoretical studies based on spin-density-functional theory (DFT) within the generalized gradient approximation (GGA) can be used as complementary tool for the investigation of HFF's. Within spin DFT, spin-orbit (SO) coupling is the only effect considered responsible for orbital magnetization and to be included in the evaluation of the orbital and magnetic dipole contributions to HFF's. However, the predicted orbital magnetic moments are often found to be up to approximately 50% too small when compared to experimental values. To correct for this deficiency, one can include the so-called orbital-polarization (OP) term in an *ad hoc* manner.[6–8] During the last decade, calculations of hyperfine parameters in solids (electric-field gradients, isomer shifts, and hyperfine fields) have become available using different implementations of these *ab initio* methods[9,10] and proved to be accurate and reliable. In particular, HFF's of impurities in bulk, at the surfaces or as adatoms of ferromagnetic hosts have been extensively theoretically studied (see, e.g., Refs. 11 and 12). Most recently, first-principles calculations of lattice relaxations and HFF's of impurities in bulk Fe have been performed.[13,14] The Fe/Ag interface was first studied in the pioneering work of Freeman and co-workers[15] and by Guo and Ebert,[16] and most recently by Rodriguez *et al.*[17] The results of those DFT calculations suggested that, as far as the orbital magnetic moments are concerned, it is necessary to invoke the orbital-polarization correction in order to bring the calculated moments in line with the experimental values. Nevertheless, the OP correction induced changes in the orbital and dipolar contributions to the HFF's tend to enlarge the discrepancy between theoretical and experimental HFF's values. Moreover, the calculated HFF field decreases on the Fe side of the interface and increases on the Ag side, i.e., a different behavior than the PAC assignment for the Cd atom probe.

In this paper a theoretical study based on spin-DFT-GGA electronic structure calculations of the problem of the HFF's in Cd embedded in the Fe/Ag interface is undertaken in an attempt to understand the results of the recent PAC determinations.

Two important issues are discussed: (i) the relation of the HFF in the Cd probe with that of the original host (Fe or Ag) atom, (ii) the precision of state-of-the-art *ab initio* calculations to obtain quantitative predictions of HFF's in very complex systems such as interfaces in order to complement and help clarify experimental findings. In particular, the importance of lattice relaxations (interlayer spacings and lateral relaxations) will be assessed. The calculations include SO effects as well as OP term proposed by Brooks[6–8] on the orbital and dipolar contributions to the HFF's.

## II. DETAILS OF THE CALCULATIONS

Calculations have been performed using density-functional theory and the generalized gradient approximation[18] for the exchange and correlation functional as implemented in the all-electron full-potential linear-augmented plane wave method (FP-LAPW).[19,20] This implementation includes total energies and atomic-force calculations, which allows for a full structure optimization via a damped molecular-dynamics approach.[21] Within this method the unit cell is divided into nonoverlapping atomic spheres and an interstitial space. The potential is expanded into spherical harmonics inside the atomic spheres and in plane waves in the interstitial space. A similar expansion is used for the basis functions. The spin-orbit coupling is included using a second-variational approach,[22] using the spherical part of the potential. This means, that first the Hamiltonian without the spin-orbit coupling term is diagonalized. Next, an energy cutoff is selected and only the states under this spin-orbit cutoff energy are used as a basis for diagonalization of the Hamiltonian including the spin-orbit coupling. This procedure is faster compared to the direct inclusion of the spin-orbit coupling into the Hamiltonian. The accuracy of these approaches is the same for high-enough energy cutoff but the second-variational-step approach is several times faster.[20]

For this calculation we used muffin-tin sphere radii $R_{\mathrm{MT}}=2.2$ bohr for Fe, Ag, and Cd. Fe has semicore $3p$ and valence $3d$, and $4s$ states, Ag and Cd have semicore $4p$ and valence $4d$, and $5s$ states. The FP-LAPW wave functions in the interstitial region are represented using a plane-wave expansion up to an energy cutoff of $E_{cut}=15$ Ry. In order to represent the potential plane waves up to 100 Ry are considered. Inside the muffin-tin spheres the wave functions are expanded in spherical harmonics with $l$ up to 10. A maximum of $l=4$ is considered for the wave functions entering in the evaluation of nonspherical matrix elements. For the expansion of the density and potential inside the spheres a maximum of $l=6$ is used. The Brillouin-zone integrations have been performed using a $(5\times5\times1)$ Monkhorst-Pack grid for the $(2\times2)$ surface unit cell. These are 48 **k** points in the full-surface Brillouin zone, which do not include the $\bar{\Gamma}$ point. A temperature broadening with a Fermi function is used with a broadening parameter $T^{el}=0.007$ Ry in order to reduce the number of **k** points that are necessary to calculate the total energy of the metallic systems. Convergence tests have been performed that guarantee the accuracy of the numerical approximations made within the present calculational approach.

The Fe/Ag(100) interface is modeled using the supercell approach. We compose our supercells out of a vertical stacking of a *n*-layer $(n=5,7)$ (100) fcc Ag slab and a *n*-layer (100) bcc Fe slab, with the [100] direction of the iron slab corresponding to the [110] direction of the silver slab. In the horizontal direction we confine the system to the GGA lattice constant of Ag, $a_{\mathrm{Ag}}=7.83$ bohr. The interlayer spacings of both the Fe and Ag slabs are chosen according to the GGA bulk lattice constants, respectively (Fe: $a_{\mathrm{Fe}}=5.38$ bohr). The interface separation $d_i=3.5$ bohr was determined by calculating the minimum total energy as a function of this distance. Atoms $\mathrm{Ag}_1$, $\mathrm{Ag}_2$, $\mathrm{Ag}_3$, and $\mathrm{Ag}_4$ in our figures denote the Ag atoms in the $7+7$ cell. $\mathrm{Ag}_4$ are the Ag atoms at the interface and $\mathrm{Ag}_1$ can be considered as representing Ag bulklike atoms. Similarly, $\mathrm{Fe}_1$, $\mathrm{Fe}_2$, $\mathrm{Fe}_3$, and $\mathrm{Fe}_4$ denote Fe atoms and $\mathrm{Fe}_4$ those atoms at the interface.

In PAC measurements, experimentalists insert $^{111}$In probe atoms that then decay to $^{111}$Cd during layer-by-layer growth producing *three* samples, namely, with the atom probes embedded in the Fe bulk, in the Fe/Ag interface, or in the second layer of Ag from the interface. For the second type of samples, probe atoms were deposited at room temperature onto a well-prepared Ag(100) surface and then covered with 26 ML of Fe.

For the calculations reported here, we construct *four* different supercells, i.e., we distinguish between Cd at either side of the Fe/Ag interface. To describe the substitutional Cd impurity, we have performed self-consistent electronic structure calculations using a $(2\times2)$ supercell in the interface plane, in order to have the Cd impurity surrounded by Fe and Ag nearest-neighbor (NN) atoms. For the four different systems, a self-consistent calculation of the electronic structure and hyperfine fields for the unrelaxed supercell at the interface separation of $d_i=3.5$ bohr is performed first. That is, lattice relaxations about the impurity are neglected. The forces resulting from those calculations give a good guideline to the amount of lattice expansion expected in the optimal structures. Accordingly, for the cell describing the Cd impurity in the second Ag layer from the Fe/Ag interface $(\mathrm{Ag}_3)$, the positions of the nearest-neighbor atoms of the Cd impurity are not allowed to relax. However, for Cd at either side of the interface (Cd:Ag side and Cd:Fe side), we allow for relaxations (buckling) of the layer containing the impurity, in the direction parallel to the [001] (growth) direction, namely, $\mathrm{Ag}_4$ and $\mathrm{Fe}_4$ for Cd in the Ag and Fe side, respectively. Additional relaxations parallel to the growth direction as well as perpendicular (in-plane, i.e., in the Fe planes) relaxations of the $\mathrm{Fe}_4$ atoms are considered for Cd:Ag side, whereas the $\mathrm{Fe}_3$ atoms are allowed to move only parallel. Moreover, for Cd in the Fe-side parallel and in-plane relaxations for atoms on both sides ($\mathrm{Ag}_3$ and $\mathrm{Fe}_3$) of the interface layer are also taken into account.

We calculated the Cd-induced changes in the interlayer spacings and lateral displacements at the interface in a $5+5$, $(2\times2)$ supercell. Then, these relaxed coordinates are transferred to a $7+7$ cell, where two unrelaxed Fe and Ag layers are added inside the Fe and Ag slab, respectively. The resultant forces were negligible and therefore a readjustment of the atomic positions in the $7+7$ cells not necessary. In the following, the values for the contact-term contribution to the HFF's (see below) reported in this paper refer to calculations within these $7+7$ cells. For the Cd buried in bulk Fe $(\mathrm{Fe}_1)$, we have not performed a self-consistent structural optimization but just added the changes in the calculated HFF due to the lattice relaxation of the nearest Fe neighbors to the oversized Cd impurity as calculated by Cottenier and Haas[13] to the result for the unrelaxed cell.

The relativistic expressions for the $B_{\mathrm{hf}}$ in a pertubative approach have been derived by several groups.[23–25] In the lowest order, $B_{\mathrm{hf}}$ is given by

$$B_{\mathrm{hf}}=B_{\mathrm{hf}}^{\mathrm{ct}}+B_{\mathrm{hf}}^{\mathrm{o}}+B_{\mathrm{hf}}^{\mathrm{d}}, \tag{1}$$

which consists of the conventional contact term $B_{\mathrm{hf}}^{\mathrm{ct}}$, and the orbital and dipolar contributions $B_{\mathrm{hf}}^{\mathrm{o}}+B_{\mathrm{hf}}^{\mathrm{d}}$. The latter are usually called the non-*s* contribution to the hyperfine field: $B_{\mathrm{hf}}^{\mathrm{ns}}$. Further decomposition of $B_{\mathrm{hf}}^{\mathrm{ct}}$ is made as a sum of $B_{\mathrm{hf}}^{\mathrm{cv}}$ (contact valence) and $B_{\mathrm{hf}}^{\mathrm{cc}}$ (contact core). In our scalar-relativistic approach an expression derived by Blügel *et al.*[25] and $5+5$, $(2\times2)$ supercells have been used in order to calculate the non-*s* contributions to the HFF's (see Table I) to be added to the calculated conventional contact term $B_{\mathrm{hf}}^{\mathrm{ct}}$ as indicated above. In all results presented here, we have only considered the intra-atomic hyperfine fields and, for simplicity, have neglected those contributions from the spin moments on the other atoms. This interatomic field comes only from the magnetic dipole and orbital terms, and therefore is small. For cubic systems, this effect is zero and for hcp Co has been estimated to be less than 0.05 kG.[16] Its detailed evaluation for the Cd:Fe/Ag interface problem is outside the purpose of our study but we expect it to be small compared to the intra-atomic contributions.

TABLE I. Orbital ($B_{\mathrm{hf}}^{\mathrm{o}}$) and dipolar ($B_{hf}^{d}$) contributions to the hyperfine field ($B_{\mathrm{hf}}$) in kG in a Cd impurity in the Fe/Ag(100) multilayer. **M** is either parallel or perpendicular to the epitaxial layers (**M**∥ and **M**⊥, respectively). A $5+5$ $(2\times2)$ supercell was used. Cd:Fe bulk, Cd:Fe side, and Cd:Ag side, indicate the position of the Cd impurity within the multilayer. SO means that spin-orbit has been included and SO+OP that the orbital polarization term from Brook[6] has been also included.

| | | Spin orbit (SO) | | | |
|---|---|---|---|---|---|
| | | Cd:Fe side | | Cd:Ag side | |
| | Cd:Fe bulk | **M**∥ | **M**⊥ | **M**∥ | **M**⊥ |
| $B_{\mathrm{hf}}^{\mathrm{o}}$ | −7.2 | −2.3 | −3.7 | −0.91 | −1.4 |
| $B_{\mathrm{hf}}^{\mathrm{d}}$ | 0.0 | 2.7 | −6.7 | −1.2 | 0.56 |
| | | Spin orbit +Orbital polarization (SO+OP) | | | |
| $B_{\mathrm{hf}}^{\mathrm{o}}$ | −6.9 | −2.6 | −3.3 | −2.4 | −1.6 |
| $B_{\mathrm{hf}}^{\mathrm{d}}$ | 0.0 | 2.7 | −6.5 | −1.2 | 0.65 |

Effects due to OP term has been considered as proposed by Brooks and co-workers.[6–8]. In our computational scheme OP is treated using the second-variational method as recently reported.[17]

## III. RESULTS

In the following we first present results for the contact term $B_{\mathrm{hf}}^{\mathrm{ct}}$ and then results for the non-*s* contributions to the $B_{\mathrm{hf}}$ [see Eq. (1)] obtained from DFT-GGA that included spin-orbit interaction. The effect of considering the orbital-polarization correction will also be discussed.

Before examining the results of introducing the Cd impurity in the Fe/Ag interface we reviewed previously reported results for the host Fe/Ag system by Rodriguez *et al.*[17] In Fig. 1 the layered-resolved values for the contact contribution to the hyperfine field $B_{\mathrm{hf}}^{\mathrm{ct}}$ at the interface separation $d_i=3.5$ bohr, are shown as open circles. We note that these values differ slightly from those of Ref. 17 for a $5+5$ $(1\times1)$ calculation at the same $d_i$ value, which was determined by minimizing the total energy within a $7+7$ $(1\times1)$ supercell. The dependence of the magnitude $|B_{\mathrm{hf}}^{\mathrm{ct}}|$ on $d_i$ at the Ag side, and across the Fe/Ag(100) interface (i.e., the difference between its value for atoms $\mathrm{Fe}_4$ and $\mathrm{Ag}_4$), is pronounced. For example, at the Ag side ranges from zero at $d_i=\infty$ to 400 kG at $d_i=2.5$ bohr and across the interface varies from 140 kG to 0 at $d_i=2.5$ and 3.7 bohr, respectively. The GGA-calculated interlayer spacing of (100) planes in bulk fcc Ag and bcc Fe are 3.915 and 2.690 bohr, respectively. The sizeable $B_{\mathrm{hf}}^{\mathrm{ct}}$ at the side of the nonmagnetic Ag is of "transferred" origin, meaning it comes from the polarization of the *sp*

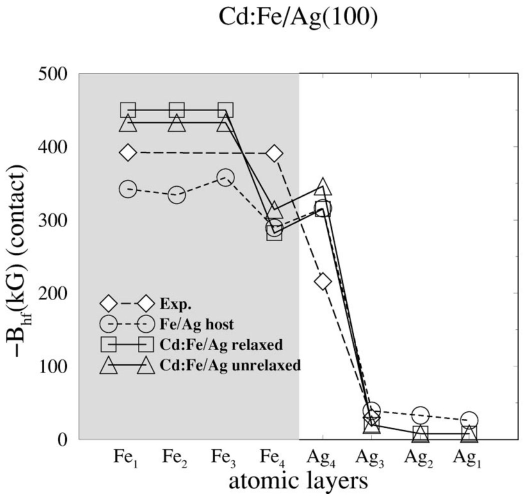

FIG. 1. Layered-resolved contact contribution to the hyperfine field $B_{hf}^{ct}$ in Cd embedded in bulk Fe ($Fe_1$), in the Fe/Ag(100) interface ($Fe_4$ and $Ag_4$), and the second Ag layer from the interface ($Ag_3$) for the unrelaxed (triangles) and relaxed (squares) supercells. The values for $B_{hf}^{ct}$ in Cd in Fe/Ag(100) at the $Fe_2$ and $Fe_3$ atomic layers are assumed to be equal to that in Fe bulk. Those for Cd in the $Ag_2$ and $Ag_1$ atomic layers are set equal to zero. The experimental data from Ref. 1.

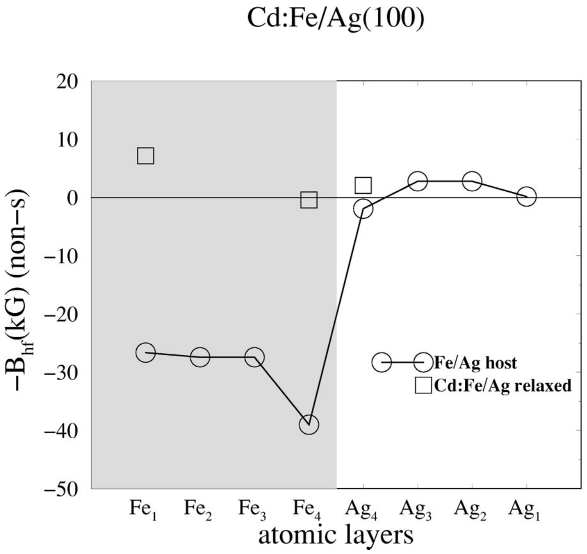

FIG. 2. Layered-resolved non-*s* contribution to the hyperfine field $B_{hf}^{ns}$ in Cd embedded in bulk Fe ($Fe_1$), in the Fe/Ag(100) interface ($Fe_4$ and $Ag_4$), and the second Ag layer from the interface ($Ag_3$) for the relaxed (squares) supercells. The values are those of Table I for **M**‖ to the interface. Theoretical data for the Fe/Ag host system (circles) are those of Ref. 17 for a $5+5$ $(1\times1)$ supercell. The values for $B_{hf}^{ns}$ at the $Fe_2$ and $Ag_2$ atomic layers are assumed to be equal to those at the $Fe_3$ and $Ag_3$ layers, respectively.

valence electrons of Ag that hybridize with the $3d$ electrons of Fe. For bulk bcc Fe, a value of $|B_{hf}^{ct}|=320$ kG at the calculated lattice constant, has been reported.[17] We note that because of the occurrence of interface-induced Friedel oscillations of magnetic moments and hyperfine fields in multilayers the corresponding computed values for the $Fe_1$ atoms of a stacking of $n+n$ layers $(n=5,7)$ are at variance with those of bulk Fe.[17] To obtain a better agreement the use of a much larger supercell would have been necessary. Nevertheless, test calculations for a $9+9$ supercell indicated that the conclusions made in this work are not affected by the size of the supercell used.

Three types of samples were produced and measured in the PAC experiments. One of these contained an embedded $^{111}$In probe in an Fe film. 25 ML of bcc Fe were epitaxially grown on the Ag(100) surface, probe atoms then deposited and covered with 10 ML of Fe. This produced a calibration sample. Although this was a thin film it could nevertheless be considered nearly bulklike with the Cd embedded within the 35 ML film. After film preparation measurements were performed and the observed frequency peaks could be attributed to a magnetic $B_{hf}=-392$ kG with $B_{hf}$ parallel to the Fe[100] axes of easy magnetization. This is in agreement with earlier work done on Fe single crystals.

The second sample had $^{111}$In probe atoms deposited at the Fe/Ag interface. PAC spectra, were immediately obtained after the deposition of the probe atoms onto the Ag surface. An electric-field gradient was measured of $V_{zz}=7.50\times10^{21}$ V/m$^2$ and an asymmetry parameter $\eta=0.00(3)$. This field gradient corresponds to the substitutional terrace site of $^{111}$In on the first monolayer of Ag(100) surface. Therefore, we have performed self-consistent electronic structure calculations for a substitutional Cd impurity using a $(2\times2)$ 7 layer (100) Ag slab in the interface plane and obtained a $V_{zz}=7.85\times10^{21}$ V/m$^2$ close to the experimental value and an asymmetry parameter $\eta=0.00$.

The experimental sample was then covered with 26 ML of Fe for two different substrate temperatures (room temperature and 110 K) and spectra recorded at temperatures between 110 K and 400 K for different magnetization directions of the Fe film. The remnant magnetization direction was parallel to the film plane. From the analysis of the spectra recorded for the sample grown at 110 K substrate temperature, two different frequency peaks leading to magnetic HFF's $B_{hf,1}=-391$ kG and $B_{hf,2}=-216$ kG were observed. Runge *et al.*[1] assigned $B_{hf,1}$ to atom probes in the Fe layer at the interface and $B_{hf,2}$ to those in the Ag layer.

Runge *et al.* concluded that their assignment was the *only* reasonable interpretation mainly based on the similarity of the $B_{hf,1}$ with the value measured inside bulk Fe. There is experimental evidence that a certain fraction of atoms exchange places upon deposition of the Fe film, but they found that most of the probe atoms (56%) are subject to the reduced field $B_{hf,2}$. An additional argument that $B_{hf,2}$ arises from those probe atoms that remained in their Ag lattice sites.

Our calculated values for the HFF in Cd embedded in bulk Fe ($Fe_1$), in the Fe/Ag(100) interface ($Fe_4$ and $Ag_4$), and the second Ag layer from the interface ($Ag_3$) are shown in Figs. 1 and 2. Figure 1 displays the contact contribution to the HFF's for the unrelaxed and relaxed $7+7$ $(2\times2)$ supercells (see Sec. II). Figure 2 shows the non-*s* contributions for **M**‖ to the interface, as listed in Table I. In Fig. 1 the values for $B_{hf}^{ct}$ in Cd in Fe/Ag(100) at the $Fe_2$ and $Fe_3$ atomic layers are simply assumed to be equal to that in Fe bulk. Those for

TABLE II. Average interlayer spacings $d$ (in bohr) for $7+7$ $(2\times 2)$ Cd:Fe/Ag(100) with Cd in the Fe side or in the Ag side of the interface.

| $d$ | Cd:Fe side | Cd:Ag side |
|---|---|---|
| Ag-bulk | 3.915 | 3.915 |
| $Ag_4$-$Ag_3$ | 3.856 | 4.013 |
| $Fe_4$-$Ag_4$ | 3.619 | 3.554 |
| $Fe_3$-$Fe_4$ | 2.692 | 2.587 |
| Fe-bulk | 2.690 | 2.690 |

Cd in the $Ag_2$ and $Ag_1$ atomic layers are set equal to zero. Similarly, in Fig. 2 the non-*s* contributions to the HFF's for the Fe/Ag host system are those of Ref. 17 calculated for a $5+5$ $(1\times 1)$ supercell, where the values for the $Fe_2$ and $Ag_2$ layers are set equal to those for the $Fe_3$ and $Ag_3$, respectively.

As it is evident from Figs. 1 and 2, the present theoretical values of $B_{\text{hf}}$ [see Eq. (1)] for Cd in the $Fe_4$ and $Ag_4$ atomic layers give an inverted assignment to the two different values at the interface as that given by Runge *et al.*[1] The calculated fields are larger (in magnitude) at the Ag side of the interface by $\sim 40$ kG. The reason for the qualitative disagreement is not as yet completely clear. We believe that the behavior of the HFF's for the Fe/Ag host and the Cd:Fe/Ag system should be qualitatively similar, and in the reliability of our predictive methods, thus we disagree with the experimental assignment of the measured HFF's at the interface.

For the Fe/Ag host system the $B_{\text{hf}}^{\text{ct}}$ values of $-289$ kG $(Fe_4)$ and $-316$ kG $(Ag_4)$ deviate from the experimental assignment. Adding the non-*s* contributions of 1.9 and 39 kG, respectively (see Fig. 1), reduces the magnitude of both values but the qualitative different trend at the interface remains.

For the self-consistent calculations of the $B_{\text{hf}}^{\text{ct}}$ in the Cd impurity at either side of the interface for the unrelaxed $(2\times 2)$ $7+7$ cells, values of $-314$ kG $(Fe_4)$ and $-346$ kG $(Ag_4)$ are obtained. The effect of lattice relaxations reduces the magnitude of both values by $\sim 30$ kG so that the calculated trend at the interface remains. The displacements of the nearest-neighbor atoms around the Cd impurity are expected to be larger for Cd:Fe side than for Cd:Ag side. The interface interlayer spacing is expanded by 3.4% for Cd:Fe side and 1.5% for Cd:Ag side. Averaged interlayer spacings are given in Table II. Recently, Cottenier and Hass[13] reported a $\sim 4.4\%$ expansion of the NN distances for a Cd impurity in Fe bulk with a resultant equilibrium distance of 4.903 bohr. The Cd-Fe and Cd-Ag nearest neighbor distances for the unrelaxed Cd:Fe side are 4.750 bohr and 5.251 bohr, respectively. For the relaxed structure, an expansion of 5.2% and a contraction of 0.2% are obtained for the Cd-Fe and Cd-Ag distances, respectively. The magnitude of the expansion and the equilibrium NN distance of 4.997 bohr induced by the oversized Cd impurity in the Fe side is in agreement with those reported for Cd in Fe bulk.

As has been pointed out before, we did not self-consistently calculate the relaxation-induced change in the HFF of Cd in Fe bulk for the present study. We added the value of $-20$ kG reported in Ref. 13 to our calculated $-433$ kG. Non-*s* contributions add $\sim -7.0$ kG (see Table I). The present theoretical value for the contact contribution of $-453$ kG compares well with the results of most recent calculations of $-434$ kG and $-455$ kG (Ref. 13) and the experimental value of $-392$ kG.

For Cd in the Ag side, the NN atoms are those Fe atoms at the other side of the interface. This NN distance is slightly expanded by 1.8% when relaxations are considered. Accordingly, the calculated contact term decreases by about 30 kG as already mentioned. Non-*s* contributions are small.

The experimental estimated upper limit for the HFF in the second monolayer of Ag from the interface is $\approx 30$ kG. For the calculations we have used a $7+7$ $(2\times 2)$ supercell with a substitutional Cd impurity in the $Ag_3$ atomic layer, where atomic positions were not relaxed. The contact contribution to the HFF is calculated to be $-20$ kG and non-*s* contributions are negligible giving good agreement with experiment.

Further inspection of Table I indicates a magnetic anisotropy in the HFF's from in-plane and perpendicular magnetization. On the Cd:Fe side its magnitude amounts to $\approx 11$ kG and on the Cd:Ag side is negligible. Finally, we have considered the effect of including the orbital-polarization term as proposed by Brooks on the values for the HFF's at the interface. The values are listed in Table I. See Ref. 17 for details.

The first detailed theoretical study based on non-self consistent band-structure calculations of the microscopic origin of the the contact contribution to the HFF's for $sp$ impurities was done by Kanamori *et al.*[26] An overview on the self-consistent calculations performed later is given in Ref. 27. Accordingly, the magnetization at the nuclear position of nonmagnetic $sp$ impurities (as Cd in the present study) originates from the hybridization of the impurity *s* and the host metal *d* states. As a consequence, the impurity spin-resolved projected *s*-density of states (*s*-DOS) splits into bonding and antibonding states separated by a dip at the so-called "antiresonance" energy $E_{\text{a}}$. Majority (up) spin electrons see a different (deeper) potential than minority ones at the host site, thus the position of $E_{\text{a}}$ will be spin-dependent. Moreover, it is located within the metal host *d* band below the Fermi level and is quite independent of the specific impurity atom. The contact contribution to the HFF's is related to the difference between majority and minority spin *s*-DOS. The contributions to the HFF's from bonding states is of negative sign while antibonding states make a positive contribution. Thus, the sign of the HFF is determined by a competition between these two contributions and it varies systematically in a period of typical $sp$ elements of the periodic table. At the beginning of the period is negative as a result of the preferential filling of minority spin bonding states. When the impurity potential becomes deeper with increasing valence in a given period, the spin-resolved *s*-DOS changes so that the antibonding states are subsequently occupied and the density of states of the majority spin between $E_{\text{a}}$ and the Fermi level increases faster than that of minority spin resulting in an increase of the positive contributions.

As soon as the impurity is placed in the interface either at the Fe or Ag side a doubling of the *s*-like bonding and antibonding peaks occur. The reduced symmetry at the interface positions as compared to Cd in Fe bulk sets up the possibility for the appearance of $s-p_z$ impurity hybrids. One of the hybrids will interact more strongly with the Fe *d* states due to their different spatial overlaps. Also, the reduced coordination has an effect in reducing the bonding-antibonding splitting of the impurity *s* states. The simple inspection of the spin-resolved *s*-DOS for the Cd impurity at either side of the Fe/Ag interface, however, does not obviously tell about the relative magnitude of the HFF's in Cd. Moreover, at the Ag side the situation is even more complex since now Ag $sp$ and *d* states also modify the impurity *s*-DOS. It is when one evaluates the difference of the integrated self-consistent *s*-DOS that the result of the delicate balance between host-impurity interactions manifest itself.

The above considerations allowed Mavropoulos *et al.*[11] to explain the double-peak structure observed for the HFF of $sp$ impurities as adatoms or at the surface of Ni and Fe (as a function of atomic number). It is clear from their Fig. 3 for the cases of Zn (which is isoelectronic to Cd) and Ga, that the HFF's of the adatoms are bigger (in absolute value) than those of the impurities at the surfaces by 40–100 kG similar to our calculated difference $|\Delta B_{\rm hf}^{\rm ct}|$ of 33 kG across the Fe/Ag interface. Cd in the Ag side may resemble the Cd adatom *on* the Fe(001) surface and Cd in the Fe side the substitutional surface impurity *in* the surface. The precise values of the HFF's in the Cd:Fe/Ag system will most certainly depend on system-dependent details but the qualitative behavior remains.

## IV. CONCLUSIONS

In summary, we have performed a first-principles DFT determination within the GGA approximation of the HFF's in a Cd impurity in Fe bulk, the Fe/Ag(100) interface, and the second Ag substrate layer from the interface. The lattice relaxations due to the Cd impurity were calculated self-consistently at the interface. Relaxations induced an expansion of the nearest-neighbor distances that is more pronounced at the Fe side and in both cases leads to a reduction of the magnitude of the HFF's. The calculated fields are larger (in magnitude) at the Ag-side of the interface by ~40 kG. Taken together with the similar trend for the Fe/Ag host, we suggest that perhaps the assignment of the two experimental observed frequencies is not correct.

The changes in the coordination number of the Cd impurity to magnetic Fe neighbors as one moves from the Fe bulk, to the Fe side of the interface to the Ag side results first in a decrease from the bulk to Cd:Fe side and a subsequent increase on the Cd:Ag-side. Similarly as in the comparative study of Zn in bulk Fe, in the surface layer of Fe(001), or as an adatom on the surface, a splitting of the spin-resolved *s*-DOS bonding and antibonding peaks of the impurity occurs at both sides of the interface and the precise value of the corresponding HFF's will depend on a delicate balance between competing hybridizations and filling of the states.

Finally, we have included the effect of orbital polarization as proposed by Brooks. The contributions to the HFF's in Cd at either side of the interface are negligible.

## ACKNOWLEDGMENTS

We acknowledge helpful communications with B.U. Runge, G. Schatz, M. Prandolini, E.K.U. Gross, W.D. Brewer, and M. Scheffler during the course of this work. This work was supported by a DRL-SECYT (Germany- Argentina) International Collaboration, Project No. ARG AD 45P.

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