Origin of the magnetic reorientation transition in Fe/Cu₃Au(001)

S. Gallego,[1] L. Szunyogh,[2,3] P. Weinberger,[3] and M. C. Muñoz[1]

[1]*Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, 28049 Madrid, Spain*
[2]*Department of Theoretical Physics and Center for Applied Mathematics and Computational Physics,*
Budapest University of Technology and Economics, Budafoki út. 8, 1521 Budapest, Hungary
[3]*Center for Computational Materials Science, TU Vienna, Getreidemarkt 9/134, A-1060 Vienna, Austria*

The origin of the magnetic reorientation transition in ultrathin Fe films on Cu₃Au(001) is investigated in terms of *ab-initio* calculations of the magnetic anisotropy energy of the system. We find that this reorientation transition is mainly determined by two factors, namely (1) segregation of Au into the Fe film, and (2) relaxation of the interlayer distances with respect to the semi-infinite substrate, whereby the balance between these two effects crucially depends on the thickness of the Fe slab.

I. INTRODUCTION

The controlled deposition of ultrathin Fe films on different substrates allows one to stabilize phases different from the ferromagnetic bcc bulk system. A high-spin state ferromagnetic fcc Fe phase has been stabilized at lattice constants exceeding a critical value which is close to the Cu lattice parameter.[1–4] In particular, such a phase can be formed by depositing a few monolayers (ML's) of Fe on a Cu₃Au(001) substrate; a ferromagnetic Fe phase is obtained for coverages over 1 ML.[5] The Fe/Cu₃Au(001) system is characterized by a complicated behavior of magnetic and structural properties as a function of the thickness of the Fe slab: initially the magnetization is aligned perpendicular to the surface, a magnetic reorientation (MRO) transition to the in-plane direction occurs then at coverages between 2.5–3.5 ML's, depending on the deposition temperature.[5–7]

There exists some controversy about the structure of the Fe film: at the initial stages of growth Fe adopts the two-dimensional lattice of the substrate, although with different interlayer spacing. For Fe thicknesses under 4 ML's, this phase has been identified as a pseudomorphic fcc,[5,6,8] or, as a strained bcc structure.[7] There is agreement, however, about a structural phase transition at coverages of 4–5 ML's towards a bct phase, which evolves into a bcc lattice for Fe films of more than 20 ML's.[5,7,8] The interlayer distances reported for Fe films of less than 4 ML's coverage comprise a wide range of values, depending mostly on the growth conditions and the thickness of the film. Interlayer distances from 1.53 to 2.00 Å, i.e., from approximately −20% to +10% of the substrate spacing ($d_\perp = 1.85$ Å) and a two-dimensional lattice parameter corresponding to the underlying substrate ($a_{2D} = 2.65$ Å) were reported.[5–7]

The magnetic phase transition in Fe/Cu(001) has been correlated to the structural transformation from a fct to a fcc lattice.[1] Due to the different critical thickness associated with the magnetic and structural transitions this does not apply for Fe/Cu₃Au(001). An alternative source for the MRO in the Fe/Cu₃Au(001) system can arise from intermixing of the Fe overlayers with the substrate, since chemical disorder can have a direct influence on the preferred orientation of the magnetization as already has been reported for surface alloys.[9] Although segregation of Cu can be ruled out,[7] there are hints of the existence of Au–Fe intermixing at the Fe/Cu₃Au interface.[5,8] In addition, evidence has been found of the presence of limited amounts of Au (less than 0.1 ML's) in the topmost surface layer, and lower concentrations in the underlying layers.[8] This trend has also been reported for Fe/Au(001) films, where disordered Au has been observed in the outermost surface plane.[2]

Based on *ab-initio* calculations within the density functional theory (DFT), in here we study the dependence of the magnetic anisotropy of the system nFe/Cu₃Au(001) with respect to three different factors: (1) the number of Fe layers (n), (2) the segregation of Au, and (3) the interlayer distances in the Fe slab. It should be noted that the present study follows a previous one in which we demonstrated the dominating influence of the segregation of 0.1 ML's of Au at the surface of the Fe slab on the MRO.[10]

II. COMPUTATIONAL DETAILS

All calculations are performed by using the fully relativistic Screened Korringa–Kohn–Rostoker (SKKR) method; details thereof can be found elsewhere.[11] The self-consistent effective potentials and fields are first determined for a magnetic orientation normal to the surface and then, based on the magnetic force theorem, the magnetic anisotropy energy (MAE) is calculated as the sum of the band energy (ΔE_b) and the magnetic dipole–dipole energy (ΔE_{dd}) contributions.[3,12] Reliable convergence of the MAE is obtained with 30 energy points and more than 900 $k_\parallel$-points in the irreducible surface Brillouin Zone. The MAE is defined as the difference between the energy of the system with a uniform in-plane magnetization and with the magnetization perpendicular to the surface. Thus, a positive (negative) value of the MAE indicates an easy magnetization axis normal (parallel) to the surface. It should be noted that one of the advantages of this method is that it naturally provides one with the contribution of each layer (component) to ΔE_b.

The Cu₃Au substrate is modeled as a statistically disordered Cu₀.₇₅Au₀.₂₅ alloy as described within the coherent po-
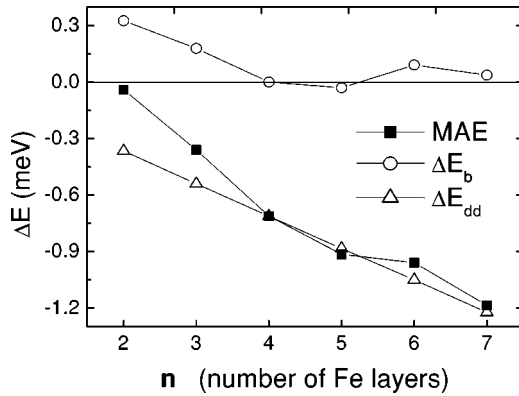
FIG. 1. Calculated MAE and its components, ΔE_b and ΔE_{dd}, as a function of the number n of Fe layers for the films nFe/Cu$_3$Au(001).

tential approximation (CPA),[13] using however the lattice parameters of the Cu$_3$Au lattice. As compared to the ordered lattice of the substrate which corresponds to four sublattices, this set-up considerably reduces the size of the matrices involved in the calculations, thus facilitating a more extensive analysis of the chemical and structural variations of the Fe film.

Different numbers of Fe layers are placed on top of the substrate assuming the ferromagnetic configuration observed experimentally. First, a pseudomorphic structure for the Fe slab is assumed; then we study variations of the interlayer distances within the experimental range, that is, from 1.55 Å (16% contraction) to 2.00 Å (8% expansion). Different amounts of segregated Au atoms in each Fe layer are considered, treated within the CPA. At the interface with the substrate a wide range of concentrations, i.e., a Fe$_x$Au$_{1-x}$ interface layer for $1 \geqslant x \geqslant 0.1$, is considered, while Au concentrations of less than 25% ($x=0.75$) are allowed at the topmost surface according to the experimental evidence.

III. RESULTS

A. Dependence on Fe thickness

We first investigated the unrelaxed system nFe/Cu$_3$Au(001) considering different Fe thicknesses (2

$\leqslant n \leqslant 7$). In all cases, there is a limited charge transfer of ~ 0.03 electrons from the Fe film to the adjacent Cu$_3$Au layer at the interface, and a significant spillover of 0.3 electrons towards the vacuum from the surface plane. The Fe atoms show a uniform spin-polarization of about $2.6\mu_B$, being slightly enhanced at the interface ($2.7\mu_B$) and in the surface ($2.9\mu_B$) planes. Only Cu and Au atoms closest to the Fe film are moderately spin-polarized and carry a magnetic moment of 0.01 to 0.02 μ_B; the rest of the substrate layers remain unpolarized. Except otherwise stated, these trends are preserved for all compositional and structural variations of the system presented here.

In Fig. 1 the MAE and its decomposition into ΔE_b and ΔE_{dd} are shown. Of the two contributions, ΔE_{dd} decreases linearly with n, while ΔE_b displays a more complicated dependence on the number of Fe layers. The balance between ΔE_b and ΔE_{dd} is governed by ΔE_{dd}, resulting in an increasing dominance of ΔE_{dd} as the thickness of the Fe film increases. This leads to a negative MAE for all Fe thicknesses that of course cannot explain the experimentally observed MRO.

B. Influence of Au segregation

It has been observed by means of x-ray scattering measurements that Au tends to be enriched in the topmost layers of the bare Cu$_3$Au(001) surface.[14] We therefore first investigated the effect of a segregation of Au at the interface layers of the Cu$_3$Au(001) substrate on the MAE. For this purpose we modeled several concentration profiles involving the two topmost substrate layers with a maximum of the Au concentration of 50% per plane. Although significant changes in the value of ΔE_b were observed, still a negative MAE resulted for all Fe thicknesses. A similar conclusion had to be drawn when extending the Au segregation to the interface layer of the Fe slab (intermixing). As an example, the MAE of the system $(n-1)$Fe/Fe$_x$Au$_{1-x}$/Cu$_3$Au(001) is shown in Fig. 2 for the cases of $n=2$ and 3; thicker Fe films showed the same behavior of the MAE with respect to x as for $n=3$. ΔE_{dd} changes smoothly upon variations of x, while especially for $n=2$, ΔE_b shows a more remarkable dependence against x.
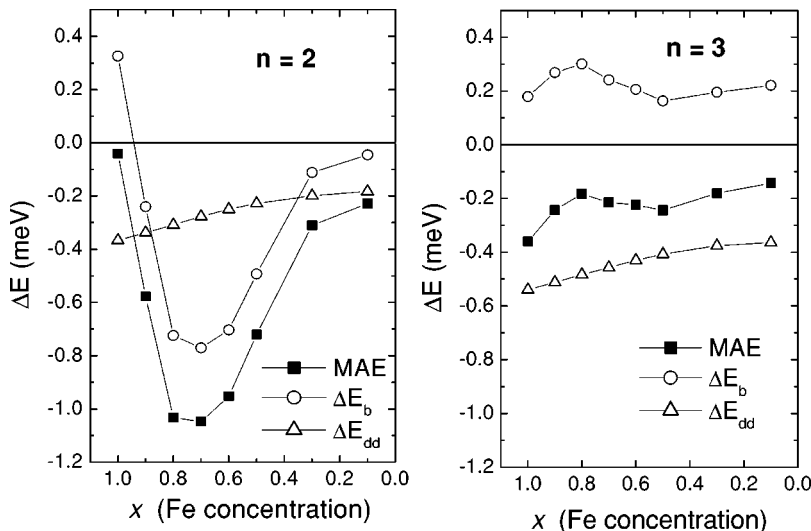

FIG. 2. Dependence of the MAE and its components, ΔE_b and ΔE_{dd}, on the concentration x for the systems $(n-1)$Fe/Fe$_x$Au$_{1-x}$/Cu$_3$Au(001) with $n=2$ and 3.
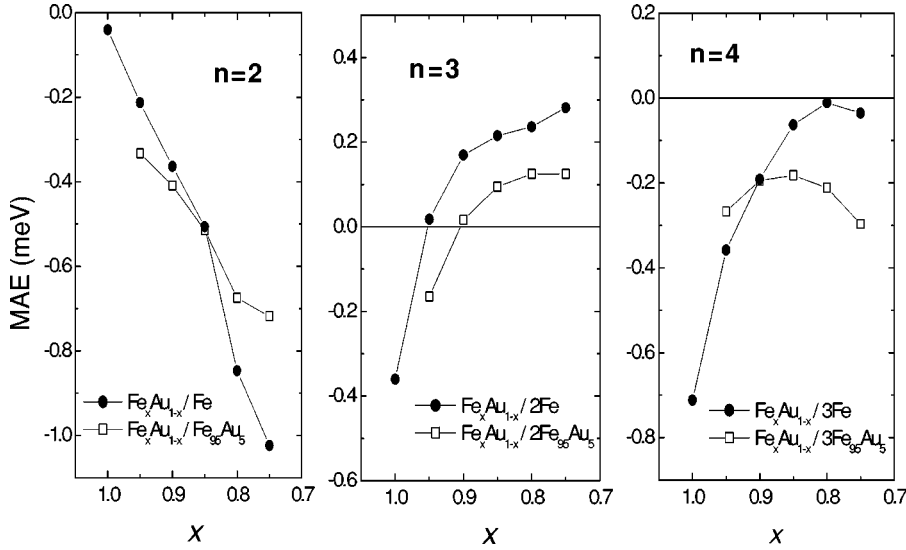
FIG. 3. Dependence of the MAE on the concentration x of the systems $Fe_xAu_{1-x}/(n-1)Fe/Cu_3Au(001)$ (solid circles) and $Fe_xAu_{1-x}/(n-1)Fe_{95}Au_5/Cu_3Au(001)$ (empty squares) for $n=2$, 3 and 4. Note that all vertical axes in the figure have a common scale, though with displaced origins.

The sum of both, however, results in a negative value of the MAE.

Next, we considered the segregation of Au into the outermost surface planes. As only limited amounts of Au of up to 0.1 ML have been detected for the $Fe/Cu_3Au(001)$ system, we restricted our study to a maximum of the Au concentrations of 25%. The values and layerwise distribution of the Fe magnetic moments are similar to those for the pure Fe slab, but—independent of x—the segregated Au atoms exhibit now enhanced moments of $0.07-0.09$ μ_B for all Fe thicknesses. As can be seen from Fig. 3 there is now a significant change at $n=3$: only at this thickness the MAE attains a positive value. This would explain a MRO for a Fe coverage between 3 and 4 layers provided there is more than 5% of segregated Au in the topmost layer. The additional existence of limited amounts of Au throughout the Fe slab does not alter this picture, as shown in Fig. 3: although the variation of the MAE with respect to x is slightly reduced, the change of sign between $n=3$ and $n=4$ persists at similar Au concentrations.

In the particular case of a surface segregation of Au atoms, it is interesting to point out that this change of sign of the MAE is caused by contributions from the inner layers of the Fe slab. This dominant role of the interface anisotropy has been previously observed in other transition metals multilayers and interfaces.[15] In Table I the layerwise contributions to ΔE_b are shown for the film systems $Fe_xAu_{1-x}/(n-1)Fe/Cu_3Au(001)$ for $n=3$ and 5 at different values of x. The case of $n=5$ serves to illustrate the evolution of ΔE_b within the film for all Fe thicknesses above 3 layers: in the absence of Au segregation ($x=1$) the surface plane has the smallest contribution in magnitude to ΔE_b, and at the inner layers ΔE_b is negative. Only in the interface layer closest to the substrate ΔE_b assumes a large positive value which however cannot compensate for all negative terms, including ΔE_{dd}. When Au atoms are present in the surface plane, the total ΔE_b is governed by contributions from the layers at both interfaces of the Fe slab: in the surface plane ΔE_b is increasingly more negative as the Au concentration is increased. The negative contribution from the surface layer is

compensated by a high positive contribution to ΔE_b from the adjacent Fe layer which with increasing Au concentration in the surface layer overweights the negative contribution from that layer. As a result, the Fe-like contributions to ΔE_b summed over the layers increase as more Au is added at the surface plane. For $n>3$ the negative values of MAE are caused by the dominating magnetic dipole–dipole interaction, ΔE_{dd}, which increases as the thickness of the Fe film increases. The case of $n=3$ is quite similar, except that Fe-like contribution to ΔE_b from the surface layer pertains its small value even in the presence of segregated Au, while in the interface plane ΔE_b increases with the surface concentration of Au. This causes a larger Fe-like contribution to the total ΔE_b, thus leading to a positive MAE, since ΔE_{dd} is smaller than for thicker Fe films. The case of $n=2$ must be considered separately, since the ratio of the Fe-like contributions to ΔE_b of the surface layer and of the interface layer differs from that of thicker films. In particular, for $n=2$ we obtain an increasingly negative MAE as the amount of surface Au increases.

In summary, segregation of Au to the surface gives rise to a MRO when increasing the thickness of the Fe slab from 3

TABLE I. Layer- and component-resolved ΔE_b and total ΔE_{dd} contributions (in meV) for the structures $Fe_xAu_{1-x}/(n-1)Fe/Cu_3Au(001)$ with $n=5$ and 3 and for $x=1$, 0.9, and 0.8. The layers are numbered from the surface ($L1$) to the bulk; negligible contributions of the Cu_3Au planes have been omitted.

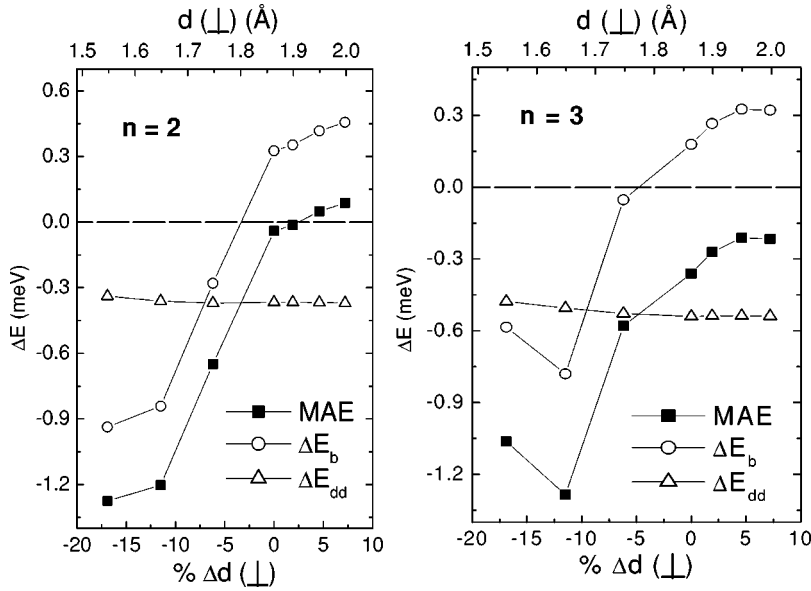| n	5			3		
x	1.00	0.90	0.80	1.00	0.90	0.80
$\Delta E_b(Au)_{L1}$		−0.015	−0.034		−0.015	−0.032
$\Delta E_b(Fe)_{L1}$	0.035	−0.023	−0.166	0.059	0.110	0.072
$\Delta E_b(Fe)_{L2}$	−0.059	0.300	0.487	−0.024	0.318	0.392
$\Delta E_b(Fe)_{L3}$	−0.087	0.026	0.075	0.194	0.269	0.275
$\Delta E_b(Fe)_{L4}$	−0.041	−0.013	0.008			
$\Delta E_b(Fe)_{L5}$	0.180	0.198	0.210			
ΔE_{dd}	−0.884	−0.846	−0.815	−0.540	−0.510	−0.478

FIG. 4. Calculated MAE as a function of uniform interlayer distances in the Fe slab $(d_\perp)$ for the structures $n\mathrm{Fe}/\mathrm{Cu_3Au}(001)$ with $n=2$ and 3. The ΔE_b and ΔE_{dd} contributions are also shown.

to 4 layers. However, the failure for $n=2$ in obtaining a positive MAE indicates that additional factors have to be taken into account to explain the experimental results.

C. Influence of interlayer relaxations

In order to explore the differences between the cases of $n=2$ and $n=3$, we analyzed the effect of uniform variations of the interlayer spacing in the Fe slab on the MAE. As can be seen from Fig. 4, in changing the interlayer distance ΔE_{dd} remains almost unchanged, since a reduction in the interlayer distance is compensated by an increase of the magnetic moments. In fact, the magnetic moments in the inner layers of the Fe slab are strongly affected by $d_\perp$, mainly in the case of compression. For $n=2$, e.g., as compared to the unrelaxed system the magnetic moment of the surface Fe layer is by 0.7% larger for the case of the maximum expansion ($\Delta d_\perp=8\%$) and by 5.2% smaller for the case of the maximum compression ($\Delta d_\perp=-16\%$), while in the interface Fe layer the enhancement of the magnetic moment amounts 2.5% for $\Delta d_\perp=8\%$ and is reduced by 12% for $\Delta d_\perp=-16\%$.

Contrary to ΔE_{dd}, especially for $n=2$, ΔE_b is extremely sensitive to interlayer relaxation. In general a decreasing $d_\perp$ reduces ΔE_b, leading thus to a negative MAE, while in the expanded structures ΔE_b is enhanced. In the case of $n=2$ this leads to a positive MAE for increased $d_\perp$, which corresponds to the most stable structures; while for $n\geq3$ a decrease of $d_\perp$ tends to stabilize the system as expected due to a compensation of the in-plane lattice expansion with respect to the bulk Fe lattice. This argument is supported by the fact the slopes in the total energy difference with respect to $d_\perp$,

$$\frac{\delta[E_{\mathrm{tot}}(d_\perp)-E_{\mathrm{tot}}(d_\perp^0)]}{\delta d_\perp} = \begin{cases} <0; & n=2, \\ >0; & n=3, \end{cases}$$

where $d_\perp^0$ refers to the unrelaxed interlayer distance, are distinctly different in these two cases. Thus, a MRO for a thickness between 2 and 3 Fe layers occurs due to the relaxation of the interlayer spacing of the Fe slab.

D. Interlayer relaxations and Au segregation

The combined effect of segregation of Au into the topmost surface and variation of the interlayer spacing was finally studied investigating systems of the type $\mathrm{Fe}_x\mathrm{Au}_{1-x}/(n-1)\mathrm{Fe}/\mathrm{Cu_3Au}(001)$ for different values of $d_\perp$. The variation of MAE versus $d_\perp$ for the cases of $n=2$ and 3 with x ranging from 1 to 0.75 is presented in Fig. 5. For $n=2$ the segrega-
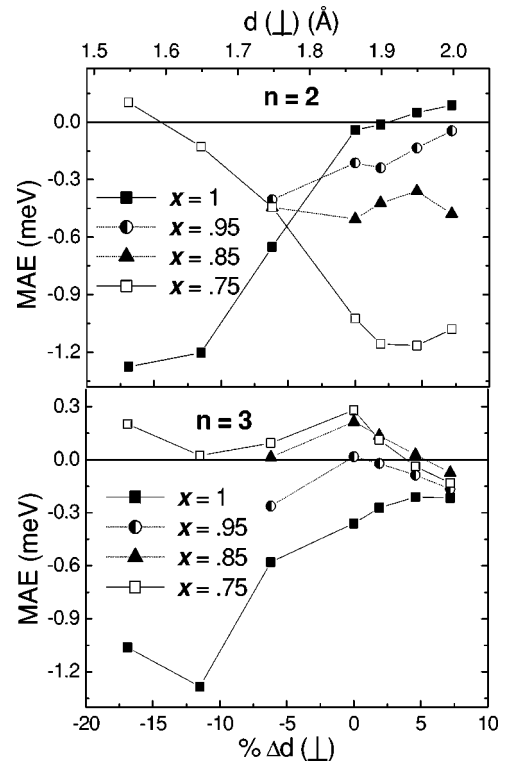

FIG. 5. Calculated MAE as a function of uniform interlayer distances in the Fe slab of the systems $\mathrm{Fe}_x\mathrm{Au}_{1-x}/(n-1)\mathrm{Fe}/\mathrm{Cu_3Au}(001)$ with $n=2$ (upper panel) and $n=3$ (lower panel) for different Fe concentrations x.

tion of Au inverts the sign of the MAE in the expanded structures. The occurrence of only 5% of Au in the surface is sufficient to cause a negative MAE. The positive values found for reduced values of $d_\perp$ at 75% Au most likely correspond to less stable structures. This implies that for $n=2$ only in the absence of Au segregation a magnetization perpendicular to the surface can occur.

For the case of $n=3$ the effect of Au segregation is opposite: the addition of Au leads to positive values of the MAE for a wide range of $\Delta d_\perp$. The different atomic volumes of Fe and Au cause a competition between expanded and contracted structures. Stable structures with positive MAE occur for a slight contraction ($\Delta d_\perp$ between -5% and -10%) with quite a large amount (25%) of segregated Au.

IV. CONCLUSIONS

We have studied the origin of the MRO of ultrathin Fe films on $Cu_3Au(001)$ using first-principles calculations of the MAE of this system. For Fe films thicker than 4 ML's, the MAE is governed by the magnetic dipole–dipole interaction, ΔE_{dd}, thus favoring an in-plane magnetization. At very low Fe thicknesses (less than 4 ML's) the sign of the MAE is determined by an interplay between segregation of Au to the surface and relaxation of the interlayer distances in the Fe slab. This leads to a magnetization along the normal to the surface depending on the number of Fe layers and growth conditions. The slabs formed by two Fe layers correspond to expanded interlayer distances and are magnetized along the normal to the surface only in the absence of Au segregation. For systems with an Fe slab of three layers the segregation of Au into the surface favors a perpendicular magnetization, which can be stabilized within a range of interlayer relaxations from -5% to -10% with respect to the interlayer spacing of the ideal substrate.

[1] L. Szunyogh, B. Újfalussy, and P. Weinberger, Phys. Rev. B **55**, 14392 (1997); D. Peterka, A. Enders, G. Haas, and K. Kern, *ibid.* **66**, 104411 (2002); M. Kurahashi, T. Suzuki, X. Ju, and Y. Yamauchi, *ibid.* **67**, 024407 (2002).

[2] A. M. Begley, S. K. Kim, J. Quinn, F. Jona, H. Over, and P. M. Marcus, Phys. Rev. B **48**, 1779 (1993).

[3] L. Szunyogh, B. Újfalussy, and P. Weinberger, Phys. Rev. B **51**, 9552 (1995).

[4] W. A. A. Macedo, F. Sirotti, G. Panaccione, A. Schatz, W. Keuner, W. N. Rodrigues, and G. Rossi, Phys. Rev. B **58**, 11534 (1998); S. S. Kang, W. Kuch, and J. Kirschner, *ibid.* **63**, 024401 (2000).

[5] F. Bruno, S. Terreni, L. Floreano, A. Cossaro, D. Cvetko, P. Luches, L. Mattera, A. Morgante, R. Moroni, M. Repetto, A. Verdini, and M. Canepa, Phys. Rev. B **66**, 045402 (2001).

[6] M. T. Lin, J. Shen, W. Kuch, H. Jenniches, M. Klaua, C. M. Schneider, and J. Kirschner, Phys. Rev. B **55**, 5886 (1997).

[7] B. Feldmann, B. Schirmer, A. Sokoll, and M. Wuttig, Phys. Rev. B **57**, 1014 (1998).

[8] P. Luches, A. di Bona, S. Valeri, and M. Canepa, Surf. Sci. **471**, 32 (2001).

[9] S. Gallego, M. C. Muñoz, J. Zabloudil, L. Szunyogh, and P. Weinberger, Phys. Rev. B **63**, 064428 (2001).

[10] S. Gallego, L. Szunyogh, M. C. Muñoz, and P. Weinberger, J. Magn. Magn. Mater. (in press).

[11] B. Újfalussy, L. Szunyogh, and P. Weinberger, Phys. Rev. B **51**, 12836 (1995); R. Zeller, P. H. Dederichs, B. Újfalussy, L. Szunyogh, and P. Weinberger, *ibid.* **52**, 8807 (1995); C. Uiberacker, J. Zabloudil, P. Weinberger, L. Szunyogh, and C. Sommers, Phys. Rev. Lett. **82**, 1289 (1999).

[12] M. Weinert, R. E. Watson, and J. M. Davenport, Phys. Rev. B **32**, 2115 (1985); G. H. O. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, *ibid.* **41**, 11919 (1990).

[13] P. Weinberger, P. M. Levy, J. Banhart, L. Szunyogh, and B. Újfalussy, J. Phys.: Condens. Matter **8**, 7677 (1996).

[14] H. Reichter and H. Dosch, Surf. Sci. **345**, 27 (1996).

[15] G. H. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, Phys. Rev. B **50**, 9989 (1994); J. Kohlhepp and U. Gradmann, J. Magn. Magn. Mater. **139**, 347 (1995); B. Újfalussy, L. Szunyogh, P. Bruno, and P. Weinberger, Phys. Rev. Lett. **77**, 1805 (1996); J. Dorantes-Dávila, H. Dreyssé, and G. M. Pastor, *ibid.* **91**, 197206 (2003).