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Origin of dead magnetic Fe overlayers on V(110)

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Recent *in situ* polarized neutron-reflectometry and magneto-optical Kerr effect measurements have displayed a few magnetically dead Fe layers deposited on V(110). We have performed *ab initio* density-functional theory calculations in order to explain the *a priori* unexpected results. An ideal layer-by-layer growth of Fe on the V(110) surface leads to the ferromagnetic solution for every Fe thickness. However, if alloying is present at the interface, a strong decrease in the Fe magnetization is found. We discuss the different magnetic configurations and the possible mechanisms that can produce the observed magnetically dead Fe layers.

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Nawrath *et al.*[1,2] have investigated the magnetic properties of thin Fe layers epitaxially grown on a V(110) substrate using *in situ* polarized neutron reflectivity[1,2] (PNR) complemented with in-plane magneto-optical Kerr effect (MOKE) measurements.[2] The samples were produced using both electron beam evaporation[1,3] and molecular-beam epitaxy,[2] characterizing the structural quality of the samples by Auger electron spectroscopy and low-energy electron diffraction. For a Fe film thickness of 6 Å ($\simeq$3 ML) the authors[3] found nearly negligible in-plane magnetic moment in the samples. For thicker Fe coverages ($>$20 Å) they always measured valuable magnetic moment in the Fe film, almost constant for a wide range of temperature. These are unexpected results,[1–3] because Fe is a ferromagnetic material so that magnetic ordering was expected even for very low coverages on V(110). As an explanation for the presence of those ''dead magnetic Fe layers,'' the authors[1] proposed that their experimental techniques (PNR and in-plane MOKE) were not able to detect the component of the magnetization perpendicular to the surface. Anisotropy effects could fix the orientation of the magnetization perpendicular to the surface hiding the spin polarization in the measurements. Indeed, an increase of the Fe coverage on V(110) could turn the magnetization to in-plane orientation so that it can be detected with the techniques employed. Very recently the same authors performed additional polar MOKE measurements on the same samples[4] finding also no out-of-plane magnetic response, thus confirming the presence of Fe dead magnetic layers at least for the first 2–3 deposited ML, and excluding the anisotropy effects as the cause of this behavior.

It is the aim of this paper to analyze the possible origin of these dead ''magnetic'' Fe layers deposited on V(110), by means of an *ab initio* study. For this purpose we have simulated different structural scenarios for the Fe/V interface, not only the perfect FeV interfaces, but also possible phenomena of intermixing and interfacial roughness. Our calculations are performed using a scalar-relativistic version of the tight-binding linear muffin-tin orbitals method (LMTO) with the atomic-sphere approximation. Detailed information about the method can be found elsewhere.[5,6] This *ab initio* method is based on the density-functional theory.[7] For the exchange and correlation functional we use the local-density approximation (LDA) in the formulation of von Barth–Hedin[8] because with the generalized gradient approximation (GGA) we obtained a strong overestimation of the V magnetization in some FeV systems,[9] and the LDA have been used successfully in previous calculations for Fe/V interfaces.[10]

We modeled the structure of the samples using a seven-layer V film in the (110) orientation to mimic the V substrate. This is an appropriate approximation because these results are not affected by the V thickness when considering thicker V slabs in our calculations. The lattice parameters of both Fe ($a_{\mathrm{Fe}}=5.29$ a.u.) and V ($a_{\mathrm{V}}=5.61$ a.u.) bcc bulks have been obtained by total energy minimization. Assuming pseudomorphic growth, the in-plane interatomic distances (V-V and Fe-Fe) are chosen to be the same as the calculated lattice parameter of bcc V, whereas the Fe-Fe out-of-plane interatomic distance is determined according to the constant volume approximation due to the lattice mismatch between Fe and V. This approximation is recommended by experimental observations, and consists in maintaining for Fe and V atoms of the samples the same volume as they have in their respective bulks. The Fe-V interface distance is chosen as the arithmetic mean value of the calculated Fe and V lattice parameters. We model the LMTO supercell by considering enough layers of empty spheres to assure that there is no interaction between the Fe surfaces of adjacent supercells[11] (5 ML of empty spheres were enough). The calculations are performed using an increasing number of k points until final convergence is obtained for at least 135 k points in the irreducible Brillouin zone. For all Fe thicknesses, we have considered the ferromagnetic (FM) and the layered antiferromagnetic configurations (with the parallel and antiparallel couplings between Fe and V at the interface), and also more complicated configurations like the $C(2\times2)$ solution.

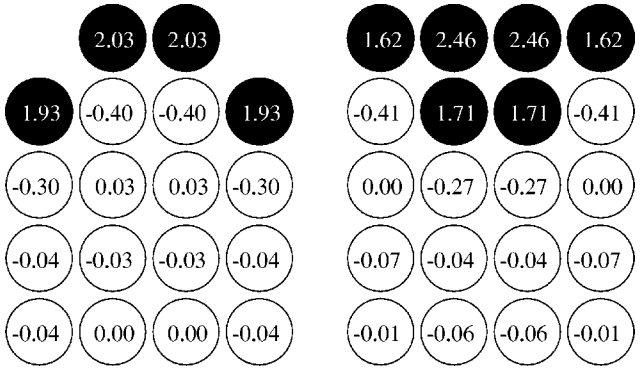

FIG. 1. Simplified modeling of some structural defects at the interface formed when Fe is deposited on V(110) substrate. Black and open balls correspond to Fe and V atoms, respectively. The magnetic moment at each atom of the sample is reported in the figure. Only a portion of the semi-infinite system is illustrated.

In our first attempt to study the system we considered a perfect FeV interface, analyzing the magnetic properties of 1 and 2 ML of Fe deposited pseudomorphically on the V(110) substrate. Only the ferromagnetic configuration is obtained as a stable solution (all the other configurations tested converge to the FM one in the self-consistent cycle). For the Fe overlayer on V(110) the Fe magnetic moment is a little bit reduced ($1.95\mu_B$) as compared to the magnetic moment of the bulk ($2.10\mu_B$ within our model for the calculated lattice distance). In this system the surface effect that enhances the Fe magnetization is competing with the interaction with the V substrate that reduces the magnetic moment of the Fe overlayer.[10] The V interface atoms exhibit an induced magnetic moment of $0.20\mu_B$ antiferromagnetically coupled with the Fe interface atoms. Similarly, for 2 Fe monolayers on V(110), the ground state corresponds to a FM configuration for Fe, whereas the $C(2\times2)$ input always converges to the FM solution. The magnetic moments at the Fe surface are now higher ($2.25\mu_B$) than in the case of the Fe overlayer, due to the larger number of Fe neighbors (less interaction with the V substrate). Notice that the loss of coordination at the surface favoring the increase of the magnetization is also present in this case. These results are clearly at odds with the experimental observations of Nawrath *et al.*[1,2] displaying a nearly negligible magnetic moment (dead layers) for this thickness range.

After excluding the anisotropy effects[12] as the cause of the experimentally observed behavior, as discussed in the introduction, we went beyond the perfect layer-by-layer growth by considering the effect of a possible intermixing[13] and roughness at the Fe/V interface (experimentally reported by Nawrath *et al.*[1,2]). We simulate first the roughness at the Fe/V interface by introducing in our calculation a simplified modeling of the structural defects. Some of the calculated configurations are shown in Fig. 1. For all the configurations tested, we obtain ferromagnetic order at the Fe atoms with high magnetic moments. These magnetic solutions are clearly more stable than the nonmagnetic solutions. Even if our modeling for the surface defects is very simple, from these results it can be inferred that the effect of these type of roughness at the interface would not change significantly the magnetic ordering of the samples, and therefore it cannot be the origin of a quasinonmagnetic configuration consistent with the magnetically dead layers.

Let us explore now the situation when Fe/V intermixing takes place. We simulate this phenomenon by considering ordered alloyed $Fe_{50\%}V_{50\%}$ layers deposited on the V(110) substrate. We have calculated the magnetic map for the following samples with ideal ordered alloying at the Fe/V interface. We start with $n=1-6$ ML of $Fe_{50\%}V_{50\%}$ ordered alloy deposited on V(110). This system will be denoted as $V(110)/(Fe_{0.5}V_{0.5})_n$, and corresponds to a deposition of 1–3 pure Fe ML, where the experimental measurements[1,2] found no magnetization in the samples. We also considered the ordered semi-infinite alloy on the (110) orientation as the limiting situation. Then, we study $m=1-4$ ML of pure Fe on a slab of six $Fe_{50\%}V_{50\%}$ layers deposited on V(110). These systems, denoted as $V(110)/(Fe_{0.5}V_{0.5})_6/Fe_m$, correspond to Fe coverages of 4–5 ML, for which the experiments[1,2] found clear magnetic ordering. The magnetic maps obtained for the most representative samples cited above are shown in Fig. 2. Energetically, these configurations are more stable than the pseudomorphic ones.

At the initial stage of Fe-V intermixing [(i) in Fig. 2] the stable solution is nonmagnetic. In this case the strong V environment ''kills'' the magnetic moment of Fe. If we increase the alloying [(ii–v) in Fig. 2] all the samples display magnetic ordering. The magnetic moment appears due to the change in the local coordination of Fe and V in the mixed FeV layers. Now, the Fe atoms have less V and more Fe in the first-nearest-neighboring shell and this is clearly reflected in the local density of states plotted in Fig. 3. The density of states at the Fermi level of the Fe atoms is higher in the case of 2 ML of ordered FeV alloy [(ii) in Fig. 2]. This indicates, following Stoner's criterion, that this system should have a stronger tendency to display magnetic ordering than 1 ML of FeV ordered alloy on V(110) [(i) in Fig. 2].

The magnetic map obtained in our calculations for these alloyed FeV systems seems to be in disagreement with the negligible magnetic moment obtained by Nawrath *et al.*,[1–3] since, in our case, only at the beginning of the deposition, the nonmagnetic configuration is obtained as the unique solution. In Table I we show the energy differences between magnetic and nonmagnetic configurations for the different mixed FeV samples (ii)–(v) on V(110) [(i) sample is not included because only no magnetic solution is found for this case]. In the estimation of the total energy we have taken into account only the mixed Fe-V layers and the first layers of the system since below the V recovers its paramagnetic character. We have normalized by the number of Fe atoms, which are the responsible for the magnetic character of the system. The energetic contribution corresponding to room temperature is about 25 meV per atom, while the energy differences reported in Table I are smaller than this value. This means that at room temperature both solutions, magnetic and nonmagnetic, could coexist. This fact could be the origin of the magnetic behavior found for this system, but this hypothesis is not consistent with some of the experimental

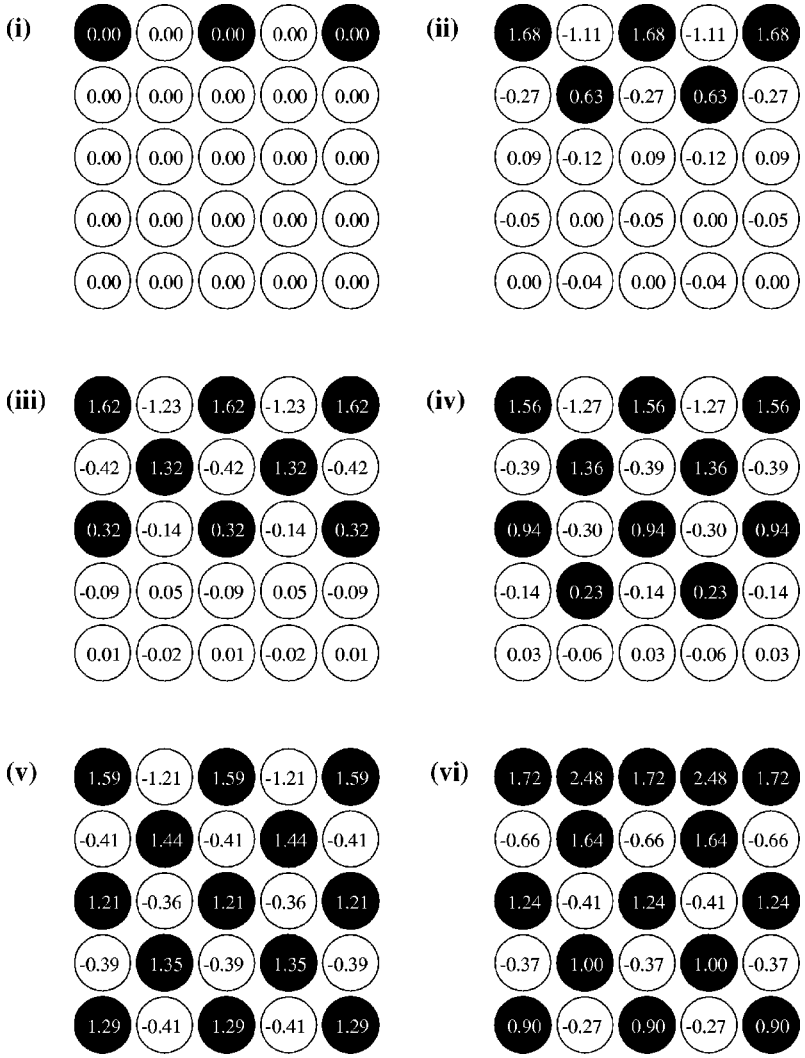

FIG. 2. Magnetic moments (in units of μ_B) at the inequivalent sites of V(110)/$(Fe_{0.5}V_{0.5})_n$ samples with $n=1,2,3,4$ [panels (i)–(iv)]; semi-infinite alloy $Fe_{50\%}V_{50\%}$ on the (110) orientation [panel (v)]; (vi) V(110)/$(Fe_{0.5}V_{0.5})_6$/Fe_m sample with $m=1$ [panel (vi)]. Black balls correspond to Fe atoms while open balls correspond to V atoms. Only a portion of the semi-infinite system is illustrated.

measurements[2] that were performed at very low temperatures (80 K) and did not show appreciable magnetization for Fe coverages of less than 3 ML.

The PNR and MOKE techniques used by Nawrath *et al.*,[1,2] to characterize the magnetic behavior of the samples account not only for the magnetization of the deposited Fe atoms but also for the contribution of V atoms (PNR measurements detect the total magnetization of the sample and MOKE measurements have a typical penetration of 20–100 Å in the sample). In Fig. 4 we have plotted the average magnetic moment per Fe atom (considering the Fe and V contributions) as a function of the Fe coverage deposited on V(110) substrate for the different systems simulated in our calculations, that is, considering both ideal or mixed Fe/V interfaces. Also the experimental data obtained by Nawrath *et al.*[1,2] are included in the figure for comparison.

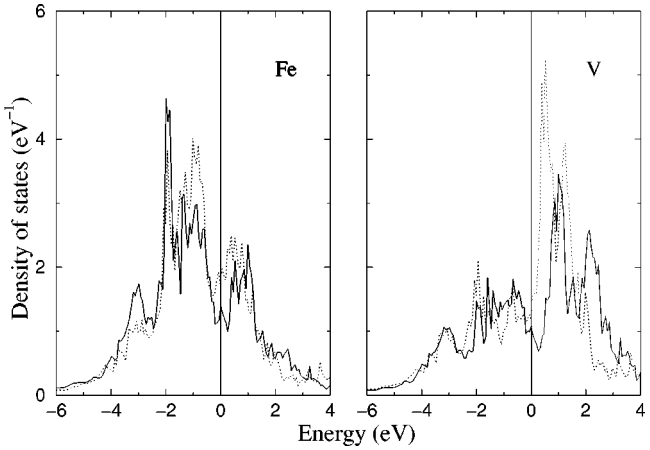

FIG. 3. Paramagnetic density of states of Fe and V surface atoms for 1 mixed FeV ML (solid line) on V(110) and 2 mixed FeV ML (dashed line) on V(110) [(i) and (ii) in Fig. 2, respectively].

As can be observed in Fig. 4, the only mechanism consistent with the experimental results is based on the intermixing

TABLE I. Energy differences per Fe atom between the magnetic ground states and the metastable nonmagnetic configurations for 2, 3, and 4 mixed FeV ML on V(110) substrate [corresponding to (ii–iv) in Fig. 2]. The energy difference associated with the ordered alloy $Fe_{50\%}V_{50\%}$ with the lattice parameter of bcc V bulk is also included in the table (v*).

System	ii	iii	iv	v*
ΔE (meV)	18.7	18.2	22.7	32

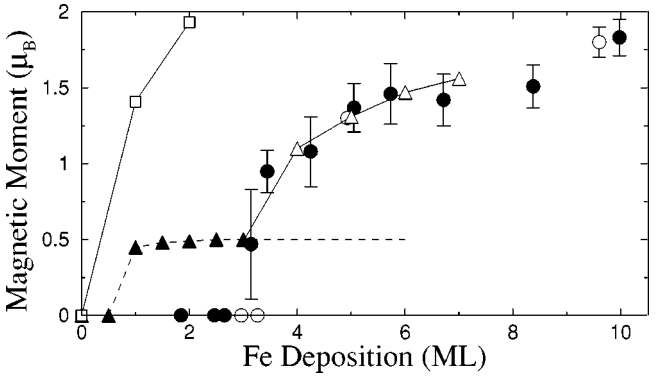

FIG. 4. Average magnetic moment per atom as a function of the Fe coverage on the V(110) substrate. Balls (open and black) correspond to the experimental PNR (open) and MOKE (black) measurements by Nawrath *et al.* (Refs. 1 and 2). Squares are the results obtained in our calculation for 1 and 2 pure Fe ML on V(110) for a perfect Fe/V interface. Triangles (open and black) correspond to the simulations including intermixing at the Fe/V interface. Black triangles are the results obtained at the beginning of the growth process: $V(110)/(Fe_{0.5}V_{0.5})_n (n=1-6)$ samples, whereas open triangles correspond to the subsequent deposition of pure Fe monolayers: $V(110)/(Fe_{0.5}V_{0.5})_6/Fe_m$ $(m=1-4)$ samples. The lines are for eye guide.

phenomena at the Fe/V interface. If we assume that Fe atoms diffuse into the V substrate up to a deposition of 3 ML of Fe (corresponding to 6 ML of mixed FeV) and for thicker coverages a pure Fe film starts to develop on top of the mixed slab, our results are in qualitative agreement with the experimental data. For low coverages we obtain a small average magnetic moment ($\sim 0.5\mu_B$ per Fe atom).[14] Although we slightly overestimate the experimental values at low coverages, it is important to take into account that in the PNR measurements the authors detected a slight asymmetry (that can be clearly seen in Fig. 6 of Ref. 2) indicating the presence of a residual magnetization of $0.15-0.20\mu_B$ per atom.[12] Taking into account this last point, our results are in qualitative agreement with the experiments even for low Fe coverages, and the intermixing at the Fe/V interface could explain the origin of the unexpected magnetic behavior found by Nawrath *et al.*[1,2] for these systems.

In summary, we have explored the magnetic behavior of Fe deposited on V(110) substrate in order to understand the unexpected experimental measurements of Nawrath *et al.*[1,2] that found a nearly negligible magnetic moment for low coverages of Fe. After performing a systematic study considering different structural approaches to the problem (perfect and mixed interfaces, and interfacial defects), we propose a mechanism consistent with the magnetic behavior reported experimentally[1,2] based on the intermixing at the Fe/V interface. For intermixed samples corresponding to low coverages of Fe, the average magnetization is low. For thicker Fe coverages where a pure Fe slab starts to develop, the samples display a high magnetic moment, as is observed experimentally. The present study gives further support to the strong relation between the structural and magnetic properties of transition metal systems. More detailed information about the structural characterization of the Fe/V interface in these systems is necessary in order to test the validity of the mechanism proposed here.

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[14] Although we have not performed a full relaxation in order to calculate the interatomic positions, we have verified that changes up to 5% in the interatomic distances do not modify this value average of $0.5\mu_B$ per atom. Therefore, we think that our conclusions would have been the same if we had performed a more refined structural optimization.