Antiferromagnetic Ordering in the Fe(001) Monolayer Mediated by the Ir Substrate

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We demonstrate, with the help of first-principle calculations, that the Fe-monomonolayer on the fcc(001) surface of iridium has a strong tendency to order antiferromagnetically in the relaxed case. On the contrary, unrelaxed Fe/Ir(001) sample has the ground state ferromagnetic. The antiferromagnetism is thus stabilized by layer-relaxations in contrast to a recently experimentally observed antiferromagnetism of Fe/W(001) system which exists also for unrelaxed geometry. The relevant part of the present study is the evaluation of pair exchange interactions between Fe-atoms in the Fe-overlayer as a function of increasing model relaxation of first interlayer distance which allows a detailed understanding of the antiferromagnetism of Fe/Ir(001) overlayer. We compare the exchange interactions in the overlayer with interactions in one Fe-monolayer embedded in the Ir crystal where the substrate influence is stronger. Our calculations indicate that in the overlayer as well as in the embedded monolayer more complex, spiral-like magnetic state can be stabilized rather than a simple $c(2\times2)$-antiferromagnetic order. [DOI: 10.1380/ejssnt.2010.152]

Keywords: Density functional calculations; Iron; Iridium; Metal-metal magnetic thin film structures

I. INTRODUCTION

There are many important features which distinguish magnetic overlayers from conventional magnetic materials. The reduced coordination on the surface induces geometry as well as chemical bonding change, the substrate can strongly modify the magnetic state and properties of the overlayer system. The position of the host Fermi level is relevant for overlayer magnetism. Magnetic overlayers are also a convenient system for a deeper understanding of the origin of magnetism in the solid. The prototypical system is a magnetic monolayer (ML) on a non-magnetic substrate which was the subject of many theoretical and experimental studies in the past [1–10]. Particularly suitable systems for detailed investigation are Fe overlayers on Ir(001) and Rh(001) surfaces. There exist reliable low energy electron diffraction (LEED) measurements (elucidating the detailed geometry) on very thin overlayers grown on Ir substrate with negligible Fe-Ir intermixing [9]. Furthermore, magneto-optical Kerr effect studies found no magnetization of iron overlayers thinner than ≈ 4 monolayers on Ir(001) [9] and ≈ 2 monolayers on Rh(001) [11]. The Fe/Ir system is a good candidate to investigate the magnetic properties of ultrathin films, since both materials grow in a two-dimensional atomic layer-by-layer growth process [12]. Because of this particular behavior it is possible to prepare iron slabs constituted of exactly one, two or another small number of atomic planes. One can prepare different multilayers of defined composition and short period superlattices of high quality [13]. Therefore also one ML of Fe embedded in the iridium substrate investigated in our contribution is a reasonable model of existing systems.

The aim of the present study is a first-principles investigation of the properties of a Fe/Ir(001) overlayer system. First-principles calculations represent a powerful tool for such studies, as they allow to determine reliably the underlying lattice structure (possible layer relaxations, surface reconstructions, etc.) which can be directly compared with experiment (LEED). They also allow to find out the underlying magnetic structure although in this respect the situation is much more complex. In addition to collinear magnetic configurations (ferromagnetic (FM) and antiferromagnetic (AFM) ones) more complex configurations may exist (e.g. recently observed chiral structures in bcc-Fe/W(001) [1], magnetism of random overlayers [2], etc.). Consequently, an estimation and discussion of exchange interactions is a useful tool to obtain a deeper understanding of properties of both overlayer and bulk magnets and magnetic alloys, including the diluted magnetic semiconductors [14]. Surprisingly and in contrast to bulk systems, studies of exchange interactions for magnetic overlayers are still very rare [3, 4] despite their obvious importance.

Great emphasis, both theoretical and experimental, has been put recently on the study of the magnetic properties of Fe-overlayers on the (001) and (110) faces of bcc...
tungsten. An unusual AFM state was predicted theoretically [5, 6] and confirmed experimentally for the bcc-Fe/W(001) system [6]. For the Mn on the W(001) surface a chiral state was found [1]. There is also evidence from theory that the ground state of the Co/W(001) overlayer is AFM, whereas Mn and Cr overlayers have a FM ground state [7]. This means that a (Fe,Mn)-alloy overlayer on the bcc-W(001) should exhibit a crossover from an AFM to a FM ground state [2]. Finally, a similar AFM- to FM-crossover was predicted for the bcc-Fe/(Ta,W)(001) alloy substrate system [8], where the ground state of the bcc-Fe/Ta(001) is FM while that of bcc-Fe/Ir(001) is AFM.

The clean Ir(001) surface undergoes the (5 × 1) quasi-hexagonal reconstruction. The finite Fe-coverages (larger than 0.25 monolayer) lifts the reconstruction [9]. In order to avoid possible corrugation and Fe-Ir intermixing the metastable unreconstructed (1 × 1)-Ir(001) surface was prepared which is, however, stable at room temperature and below (for details see Ref. 9).

We performed [15] a structural study of Fe/Ir(001) by using two highly accurate DFT methods, namely, the full potential linearized plane wave method (WIEN2k [16] code) and a sophisticated pseudopotential approach (VASP [17] code). We investigated magnetic stability of this system by comparing total energies of different magnetic configurations. In this approach the main problem is the large number of possible magnetic configurations (the non-magnetic (NM), FM-, and AFM-configurations (c(2×2)-AFM), non-collinear structures) to be considered. Instead of a brute-force search, we can evaluate the total energy of the disordered local moment (DLM) state similarly to Ref. 8. The DLM state [18] is a model state with zero total magnetic moment which results from the disorder of spin orientations of otherwise non-zero local magnetic moments. A strong indicator for a more complex magnetic state of the system under consideration is a lower total energy of the DLM state as compared to the NM and FM states. One should note, however, that if some specific magnetic state is the ground state, e.g., the c(2×2)-AFM, its total energy is usually lower than that of the DLM state. The usefulness of the DLM concept was demonstrated recently for both overlayer studies [8] and disordered magnetic semiconductors [19]. The DLM picture may be straightforwardly implemented in the framework of the coherent-potential approximation (CPA) [19]. We therefore perform studies based on the Green’s function implementation of the TB-LMTO-CPA method [20] in the framework of the surface Green’s function (SGF) approach, in addition to the above mentioned collinear DFT calculations. The TB-LMTO-SGF approach employs a realistic semiinfinite sample geometry (no slabs or periodic supercells) and allows us to implement the DLM model. The one-electron potentials are treated within the atomic sphere approximation and the dipole barrier due to the sample electrons in the vacuum is included in the formalism. TB-LMTO-SGF approach allows to include the effect of layer relaxations [8] provided they are known either from full-potential calculations or from experiment. An important advantage of the TB-LMTO-SGF approach is the possibility to estimate exchange interactions between magnetic atoms in the overlayer by a straightforward generalization of the well-approved bulk concept [14, 21].

II. THEORETICAL MODELS

In TB-LMTO-SGF calculations we used the local density approximation (LDA), the vacuum above the overlayer was simulated as usual by empty spheres (ES). Electronic relaxations were allowed in four empty spheres adjoining the overlayer, the overlayer itself, and in five adjoining Ir substrate layers. Similarly in the embedded layer geometry we allow charge changes only in a slab consisting from the iron monolayer and its 5 neighboring layers on both sides. This finite system was sandwiched selfconsistently between the frozen semiinfinite fcc-Ir(001) bulk and the ES vacuum-space including the dipole surface barrier or two semiinfinite fcc-Ir(001) bulks in the case of embedded layer. We have studied NM-, FM- and c(2×2)-AFM configurations as well as DLM-arrangement.

In the framework of the TB-LMTO-SGF method the exchange integrals $J_{ij}^{Fe,Fe}$ between sites $i, j$ in the magnetic overlayer may be expressed as follows [14, 21]

$$J_{ij}^{Fe,Fe} = \frac{1}{4\pi} \int \left( \frac{\Delta_{ij}^{Fe}(z) g_{i,j}(z) \Delta_{ij}^{Fe}(z)}{\left[ \Delta_{ij}^{Fe}(z) g_{i,j}(z) \right]} \right) dz. \quad (1)$$

Here, the trace extends over the spdf-basis set, the quantities $\Delta_{ij}^{Fe}$ are proportional to the calculated exchange splittings, and the Green’s function $g_{i,j}$ describes the propagation of electrons of a given spin ($\sigma = \uparrow, \downarrow$) between sites $i, j$ in the monolayer. It should be noted that both the direct propagation of electrons in the magnetic overlayer and the indirect one via the Ir-substrate are included in Eq. (1) on an equal footing. For more details see Ref. 14. Once the exchange interactions are known, we constructed a two-dimensional (2D) classical Heisenberg Hamiltonian to describe the magnetic behavior of the Fe-overlayer in contact with a non-magnetic fcc-Ir(001) substrate

$$H = - \sum_{i \neq j} J_{ij}^{Fe,Fe} \mathbf{e}_i \cdot \mathbf{e}_j. \quad (2)$$

In Eq. (2), $\mathbf{e}_i$ denotes the orientation of the Fe-magnetic moment at the site $i$. By construction, the value of the corresponding magnetic moment is included in the definition of $J_{ij}^{Fe,Fe}$, and positive (negative) values denote FM (AFM) couplings. An early study of exchange interactions in fcc-Fe,Co/Cu(001) systems can be found in Ref. 3, whereas some more recent estimates of exchange integrals for a bcc-Fe/W(001) overlayer were obtained either by a supercell approach [8, 22] or by an approach closely related to the present one [23, 24]. In the DLM state possible induced moments on Ir atoms collapse to zero.

III. RESULTS AND DISCUSSION

We first relaxed geometries [15] by ab initio force minimization procedure [16, 17]. The calculated geometries depend on the magnetic state (NM, FM, and AFM states), but the most important result is the reduction of the Fe-Ir interlayer distance as compared to the bulk value by about 12 % for the AFM order. This geometry agrees well with available experimental data [9]. A better agreement was obtained for the Fe-Ir distance using...
generalized gradient approximation rather than the LDA. Nevertheless, all values given here have been obtained in the LDA with WIEN2K code, for detailed discussion of results sensitivity to the exchange-correlation potential or calculation scheme see Ref. 15. In the magnetic stability study [15] we compared the total energies, $E_{\text{tot}}$, of selected magnetic systems for the unrelaxed geometry as well as for the realistic, relaxed case. Our calculations clearly show that the NM case can be safely excluded. All models with local magnetic moments have a substantially lower total energy. $E_{\text{NM}}$ is more as 20 mRy/Fe atom larger than total energy of other magnetic configurations. The most striking result, obtained by all methods, is the fact that while the FM is the ground state for an unrelaxed geometry ($E_{\text{AFM}} - E_{\text{FM}} = 2.2$ mRy/Fe atom), the layer relaxations stabilize the $c(2\times2)$-AFM phase ($E_{\text{AFM}} - E_{\text{FM}} = -7.8$ mRy/Fe atom). This is in a striking contrast to the closely related bcc-Fe/W(001) case [5, 6], where the antiferromagnetism of bcc-Fe/W(001) is robust with respect to structural relaxations. However, strictly speaking, the $c(2\times2)$-AFM may not be the true ground state of fcc-Fe/Ir(001). Similarly to bcc-Fe/W(001) one should consider other possibilities, e.g., the $p(2\times1)$-AFM or even some non-collinear configurations, such as spin-spirals or a chiral state [1]. To shed some light on this issue we present calculations in the framework of the TB-LMTO-SGF approach. It confirms the FM ground state for unrelaxed geometry and the AFM ground state while the total energy in the DLM state is slightly higher (2.1 for unrelaxed or 0.8 mRy/Fe atom for relaxed geometry). The sufficient reliability of the TB-LMTO-SGF approach for the present purpose is confirmed by a comparison with accurate full potential calculations for NM-, FM-, and $c(2\times2)$-AFM configurations in both the ideal and relaxed geometries. This also justifies the use of the TB-LMTO-SGF approach to obtain exchange interactions in the Fe-overlayer in the following. It is quite obvious that, if the DLM state has a lower energy than the NM- and FM-states, then a more complex, AFM-like state can exist and this conclusion can be reached without performing calculations for many possible candidates. But clearly, this fact does not render the necessity of searching for the true ground state of the system obsolete, but rather represents a reliable qualitative indicator for a more complex magnetic state of the system.

One can speculate about the structural origin of such an AFM order. The reduction of the Fe-Ir atom distance stabilizes the AFM-/DLM-state for this fcc(001) surface. This is a strong indication that indirect interactions of Fe-spins via the Ir-substrate play an essential role for the fcc-Fe/Ir(001) magnetism. A dominant character of indirect interactions as compared to direct ones between Fe-spins in the overlayers will result in a strong dependence of exchange interactions on the Fe-Ir interlayer distance as we shall see below. The unsupported Fe-layer is FM, the Ir substrate changes the character of effective Fe-Fe interactions in the ML.

Exchange interactions $J_{\text{Fe,Fe}}^{c}(d)$ have been determined by the TB-LMTO-SGF method for Fe/Ir(001) as a function of the interatomic Fe-Fe distance $d$ for both unrelaxed and relaxed geometries using the DLM-reference state. Additionally we present results in the DLM state for a simple model where only the Fe-Ir interlayer distance is reduced from the unrelaxed value (1.92 Å) to values of 1.82 Å, 1.72 Å, and 1.62 Å corresponding to a reduction of 5%, 10.5%, and 16%. In the case of embedded Fe-layer we found for all geometries that the antiferromagnetic ordered spin structure is preferred to ferromagnetic one. This is result of exchange interactions behavior presented in Fig. 1. The decrease of negative third neighbor interactions in comparison to overlayer situation destroys ferromagnetic order also for larger Fe-Ir interlayer distances and supports more complex ground state. We found the relaxation of Fe-Ir interlayer distance in the case of incorporation of Fe-monolayer in the iridium (001) layer sequence by a force minimization iteration procedure to be $\approx 11\%$. These results are shown in Fig. 1.

Figure 1 shows that the layer relaxation affects considerably the first two exchange interactions $J_1$ and $J_2$. $J_1$ changes its sign and it is the strongest interaction, suggesting that the transition to antiferromagnetism is governed by the large variation of the Fe-Fe nearest-neighbour exchange interaction. This variation is caused by the Fe-Ir hybridization leading to a strong modification of the electronic structure of the Fe layer. The increase of $J_2$, with negative sign, stabilizes the $c(2\times2)$ AFM configuration as compared to the $p(2\times1)$. There is large similarity to the antiferromagnetism of the Fe/W(001) system (see Ref. 10). The dominating role of indirect interactions between Fe-atoms via the Ir-substrate is obvious: the only varying quantity is the Fe-Ir distance and thus the Fe-Ir hybridization. Results for experimental layer relaxations (1.69 Å) are between model cases of 10.5%, and 16%. The fact that a strong AFM coupling in the layer-relaxed case was obtained from a reference FM state indicates the robustness of the AFM order (more precisely, of a more complex magnetic state) for the relaxed Fe/Ir(001) overlayer.

To further investigate this point we present in Fig. 2 the result of the lattice Fourier transformation of exchange integrals (1) as obtained for the DLM reference state. It should be noted that the DLM state is neither the ground state for the ideal geometry nor for the experimental layer-relaxed model. On the other hand, possible magnetic phases of the 2D-Heisenberg model (2) can be obtained by studying its stability with respect to the periodic excitations. A similar approach was successfully used in the study of the complex magnetic stability of bcc-Eu: starting from the FM reference state, a proper spin-spiral ground state was obtained in a good agreement with the experiment [25]. Due to the sign convention in equation (2) the maximum of $J(q_{\parallel})$ corresponds to the ground state (the energy minimum). It is obvious that the ground state for the unrelaxed model is the ferromagnetic state (the maximum of $J(q_{\parallel})$ is obtained for $q_{\parallel} = 2\pi/a_{1} (0, 0)$, where $a_{1}$ is the lattice constant). With reduced Fe-Ir interlayer distance we observe a quick decrease of the stability of the FM state and the ground state is found for the ordering vector $q_{\parallel} = 2\pi/a_{1} (1, 0)$ which corresponds to the $c(2\times2)$-AFM state (for the Fe-Ir interlayer distance $d = 1.82$ Å, or reduced by 5%). If the Fe-Ir interlayer distance further decreases (by 10.5% and 16%) the stability of the FM state further decreases and a new, complex spin-spiral like magnetic state becomes more stable as compared to the $c(2\times2)$-AFM state (ordering vector on the line X-M in the irreducible surface Brillouin zone).
FIG. 1: Exchange interactions among Fe-atoms in the Fe/Ir(001) overlayer (left panel) and embedded in the Ir substrate (right panel). Results for unrelaxed geometry (circles) are compared with results for different model Fe-Ir layer relaxations. Interactions are evaluated as a function of the reduced interatomic distance \((d/a)\), where \(a\) denotes the lattice constant. Numbers attached to symbols indicate the reduction of the Fe-Ir interlayer distances in % as compared to the bulk value of 1.92 Å. All results were obtained assuming the DLM-reference state.

On the other hand, the \((2\times2)\)-AFM state becomes more and more stable as compared to the FM state in accordance with the total energy calculations. Also, both for the experimental layer-relaxation model [9] and for the model with the largest reduction of the Fe-Ir interlayer distance (by 16%) the \((2\times2)\)-AFM state (the ordering vector \(q_k=\bar{X}=2\pi/a_L(1/2,0)\)) has lower energy than the FM- and \(p(2\times1)\)-AFM states.

The influence of substrate is even stronger for embedded Fe-layer in the iridium. In this case the interlayer distance relaxation plays inferior role shifting only slightly the maximum in Fig. 2, but not changing results qualitatively. The ground state in the form of more complex magnetic structure is expected.

IV. CONCLUSION

We investigated the magnetic phase stability of the system by calculating the exchange interactions between Fe atoms in the overlayer. The following conclusions can be drawn: (i) For unsupported Fe ML and for the unrelaxed geometry of Fe/Ir(001) system we found the FM ground state. (ii) The \((2\times2)\)-AFM state is more stable as compared to the NM and FM states for the correctly relaxed structure as well as for Fe-monolayer embedded in the Ir
substrate. (iii) A detailed study of the magnetic stability based on the Heisenberg Hamiltonian derived from the first-principles total energies confirms the stability of the c(2×2)-AFM state as compared to the FM one for relaxed geometry, but indicates that spin-spiral like state can be stabilized by reducing the Fe-Ir interlayer distance.

Hence, we conclude that the stability of the AFM state is induced by the substrate via layer-relaxations. The effect of substrate on exchange interaction is significant; our calculations for embedded Fe monolayer show an increasing tendency towards more complex spin spiral state. Since Ir is a heavy element, the spin-orbit interaction can have non-negligible effect on the exchange interaction, and can lead to chiral magnetic order induced by Dzyaloshinskii-Moriya interaction. Our analysis shows that disappearance of magnetization as observed by Kerr effect experiment [2] for lower coverages in Fe/Ir(001) system is not a proof that Fe on the Ir(001) surface is magnetically dead.

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