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Magnetism of Fe atoms deposited on W(001) and W(110): a theoretical study of the role of the interplanar relaxation

L. Pizzagalli *, D. Stoeffler, F. Gautier

IPCMS–GEMME, C.N.R.S, 23 rue du Loess, BP 20 CR, 67037 Strasbourg Cedex, France

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Abstract

We have investigated the stability of several magnetic configurations of Fe adatoms deposited on W(001) and W(110) surfaces. We used a tight binding model and the real-space recursion technique to investigate several cluster configurations such as dimers, chains and islands. We have determined the variation of the magnetic moments and of the magnetic order as a function of the interplanar Fe–W distance, considered here as a parameter. We show that there is a competition between the Fe–Fe direct interaction favoring parallel (P) moments, and the coupling via the W substrate favoring antiparallel (AP) moments. The AP solution on the (001) open surface and the P solution on the (110) closed surface are found to be the most stable states.

1. Introduction

The magnetic properties of deposited clusters, nanostructures and overlayers are now being extensively studied both for fundamental and applied purposes. It is now possible to elaborate well characterized ultrathin films, and to relate their morphology and structure to their magnetic properties (magnetization and magnetic order versus temperature, anisotropy, etc.) both experimentally and theoretically. For example, a recent study has shown that iron deposited on tungsten can present either superparamagnetic or ferromagnetic properties according to the film growth temperature and the corresponding film morphology. In this paper, we study the salient features of such ultrathin nanostructures in the framework of itinerant magnetism, this system being highly interesting from both theoretical and experimental points of view, as shown by the brief summary presented here.

Despite the large mismatch between Fe and W bulk lattice parameters (9.4%), several experimental studies have shown that Fe grows pseudomorphically in a layer-by-layer mode on both W(110) [1,2] and W(001) [3–5] surfaces. Fe ultrathin films on W(110) were found to be ferromagnetic with $T_C = 210$ K [2]. This is in agreement with an ab initio theoretical study at 0 K [6] which found that the ground state is ferromagnetic with a magnetic moment of $2.18\,\mu_B$ per atom.

However, experimental studies of iron deposited on W(001) substrates showed that the growth mode and the magnetic properties are quite different [3–5,7]. From a theoretical point of view, Freeman and co-workers [8] predicted in such a case a $c2 \times 2$ in-plane antiferromagnetic state for a Fe monolayer adsorbed and a ferromagnetic state for a bilayer.

So far, few experimental and theoretical studies

* Corresponding author.

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have been devoted to the magnetism of deposited iron clusters on both tungsten surfaces. From a theoretical point of view, such studies are difficult to perform using ab initio methods from the large number of inequivalent atoms on which self-consistency must be achieved. However, semi-empirical calculations based on a tight binding method are sufficient to obtain the general features for the interdependence between the magnetic order and the geometry of such clusters. A preliminary study of Fe 2D clusters on W(001) [9] has shown that the strong dependence of the magnetic order upon the configurations of the clusters can be explained in terms of an interplay between the direct adatom–adatom and adatom–substrate interactions.

This paper is devoted to a systematic study of the magnetic order of iron on W(001) and W(110) surfaces going from single adatoms and dimers to chains, 2D clusters and complete monolayers of iron. The aim of the study has been to understand the respective roles of the adatom–adatom and adatom–substrate interactions on the distribution of the magnetic moment in the overlayer and its extension in the substrate.

2. Method of calculation

Freeman and co-workers [6,8] made ab initio calculations with the FLAPW method and investigated magnetic properties of Fe complete layers adsorbed on a W substrate. This method and other first principles techniques are not still well suited to studies of deposited small clusters, because of the cost in terms of the computing time needed to consider large numbers of inequivalent atoms. This is why we use here a simplified scheme, the electronic structure being determined in the tight binding approximation (TBA).

According to the preliminary work of Stoeffler and Gautier [9], we consider a bcc bulk band-width equal to 5.3 eV for Fe and 12.7 eV for W, from which we determine the Slater–Köster parameter $dd\delta$, then $dd\sigma = 6dd\delta < 0$ and $dd\pi = -4dd\delta$. We use a power law d^{-q} for the variation of these hopping integrals versus the interatomic distance d, with $q = 3$ for W and $q = 5$ for Fe [10,11]. The Fe–W hopping integrals are calculated within the Shiba [12] approximation, e.g. from the geometrical mean of the Fe and W Slater–Köster parameters.

We used the real-space recursion method to get the LDOS on each atom. The continuous fractions are expanded up to the eighth level. They are terminated by a square root within the Beer–Pettifor method [13]. This approximation is sufficient to reproduce the major features of the LDOS [14]. Self-consistent calculations have been made in the mean-field approximation, requiring local neutrality and assuming that the exchange parameters I are constants ($I_{Fe} = 0.618$ eV and $I_W = 0.576$ eV) determined from the work of Christensen et al. [15].

In this paper we do not determine self-consistently the displacements of the W atoms induced by the iron atoms. Such displacements are small and would introduce small changes in the magnetic moments which are not relevant for the present study. This is why we assume that the substrate is rigid. However, the magnetism of iron is relatively sensitive to the W–Fe distance, which determines the importance of the substrate adsorbate hybridization, so we consider this distance as a parameter in the present calculations. We assume that all the adatoms are adsorbed on hollow sites and are at the same distance d from the surface, and we determine the relative stability of the various magnetic configurations for each d value. Therefore, the relaxation is characterized by $\rho = d/d_0$ where d_0 is the interplanar distance of the bulk W planes which are parallel to the surface. The variations of the magnetic moments and of the magnetic order with d or ρ allow to determine the sensitivity of such quantities to the relaxation and to understand their physical origin. The validity of such a scheme has been proved for monolayers. A direct comparison of such semi-empirical calculations and the ab initio results showed that all the qualitative features are reproduced by this semi-empirical model.

We verified that the magnetic perturbation induced by the adsorbed atoms is strongly localized in the vicinity of the W surface. This is in agreement with previous calculations [6,8]. The comparison between the W moments with and without deposited clusters allows to determine the range of perturbation. This allows us to define the perturbation domain in the substrate for which the self-consistent procedure is achieved. The energy levels of the other

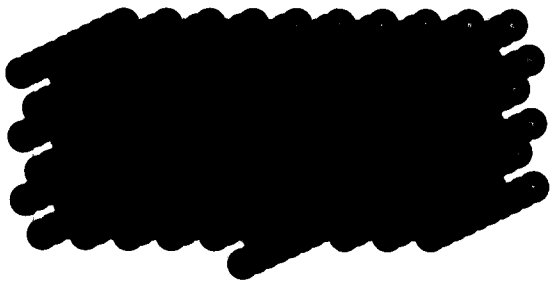

Fig. 1. Fe infinite row (black spheres) adsorbed on a W(001) surface. Some W atoms (dark grey spheres) are treated self-consistently, whereas others (light grey spheres) are assumed to be non-perturbed.

W atoms are kept equal to those determined without overlayer. For example, the infinite Fe row on the (001) surface requires a self-consistent calculation on 11 inequivalent atoms in a 'ferromagnetic' configuration, and on 16 atoms in an 'antiferromagnetic' one (see Fig. 1).

3. Magnetism of iron clusters on the (001) plane

Although the growth mode and the corresponding magnetic properties are not well known [3–5,7], all experimental studies are in agreement with a c2 × 2 antiferromagnetic configuration for the Fe monolayer adsorbed on a W(001) substrate. First-principles calculations by Wu and Freeman [8] found the same result and predicted an Fe moment equal to $0.93\mu_B$. This moment corresponds to a Fe–W relaxation of $\rho = 0.77$ in our calculations. In this paper we choose this value of the relaxation as a reference for comparing the values of the iron moment for all the clusters we consider. We assume that the most stable states correspond to this relaxation value $\rho = 0.77$. This approximation is consistent with the fact that the effect of the Fe–Fe interactions on the relaxation is very small compared with that of the Fe–W interactions.

3.1. Single adatom

The iron magnetic moment is equal to $1.7\mu_B$ for the assumed ground state at $\rho = 0.77$. Moreover the moment is found to vanish for $\rho \leq 0.675$ with a power variation law very close to a square root one. Note that in another context Bouarab et al. [16] found such a variation in other magnetic thin films as a function of the exchange parameter. The induced moments are very small on the subsurface layers W atoms and their DOS are bulk-like. This shows that there is a strong screening effect of the substrate.

3.2. Interaction between two iron adatoms

The first attempt to evaluate theoretically the interaction between two adatoms was made in the 1970s [17,18]. Burke [18] investigated W adatoms on a W(001) substrate and found a strong sensitivity of the interaction energy to the Fermi level value, with either an attractive or a repulsive interaction. These features can provide important insights on the nucleation on the surface and the growth mode of W on a W substrate. Here, we want to characterize the Fe magnetic coupling via the W substrate. We consider only three cases according to the distance r between the two adatoms: (A) $r = 2a_0$ (a_0 is the lattice parameter), (B) $r = \sqrt{2}\,a_0$, and (C) $r = a_0$. The interaction energies are very small for larger distances.

(A) Examination of the variation of the magnetic moment versus the relaxation reveals the lack of coupling between the two adatoms. The three curves corresponding to the P (moments in the same direction) and AP (opposite moments) configurations and to the single adatom merge together, and AP and P configurations are energetically equivalent. The induced moment on the W surface atoms between the two Fe adatoms is either small ($0.05\mu_B$ max) and parallel to the Fe moment (P situation) or negligible (AP situation). This calculation shows the short-range of the Fe–Fe interactions and of the magnetic coupling in this case.

(B) The Fe magnetic moments versus ρ are presented in Fig. 2 for both the P and AP configurations. The P and AP curves are different from each other only when $\rho < 0.9$, indicating a weak Fe–Fe coupling. The magnetic moment is $1.6\mu_B$ at $\rho = 0.77$ (AP) and vanishes for $\rho \approx 0.675$ (AP) and for $\rho \approx 0.7$ (P). The AP configuration is always the most stable one. For this dimer geometry, one W atom is in direct interaction with the two Fe adatoms. In the AP state its moment is exactly zero because of the

frustration. In contrast, in the P state, its moment is first parallel to the Fe moment for small relaxations ($0.918 < \rho < 1$) and then antiparallel ($0.7 < \rho < 0.918$) when ρ decreases. The LDOS of this W atom is strongly modified when Fe atoms are fully relaxed ($\rho = 0.77$). In conclusion, for the P configuration, there is a competition between two effects: the direct interaction between Fe adatoms inducing a P coupling (W moment parallel to the Fe moments), and the indirect interaction via the W atoms inducing an AP coupling (W moment antiparallel to the Fe moments). When ρ decreases, the indirect interaction becomes dominant.

(C) In Fig. 3, the AP and P curves are now completely different, like in a situation of strong coupling. The magnetic moment is $1.6\mu_B$ ($1.35\mu_B$) at $\rho = 0.77$ in the AP (P) configuration. As expected, the AP state is still the ground state. Note that in this case ($\rho = 0.77$), the Fe LDOS is perturbed and modified below the Fermi level, because the two Fe adatoms are second neighbors and are directly related by nonzero transfer integrals. The W atoms between them present the same trends as those observed in case B.

Two important aspects should be noted. First, the

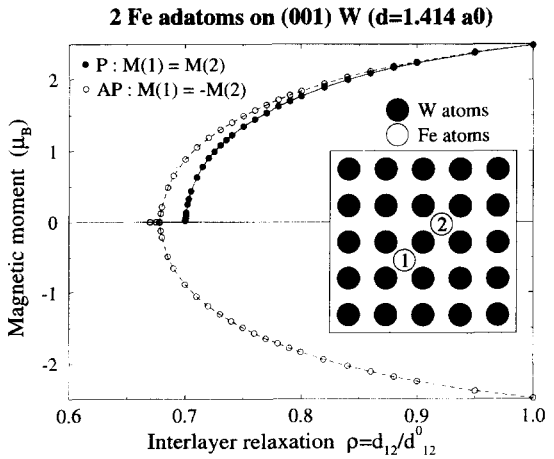

Fig. 2. Magnetic moments of two Fe adatoms deposited on W(001) versus the relaxation $\rho = d_{12}/d_{12}^0$ where d_{12} is the distance between Fe adatoms holding plane and first W plane and d_{12}^0 is the interplanar distance in W bulk. Open circles, the antiparallel solution (AP); filled circles, the parallel solution (P). The inset shows the system geometry and the inequivalent sites. Note that the distance between Fe adatoms is $\sqrt{2}a_0$, where a_0 is the W lattice parameter.

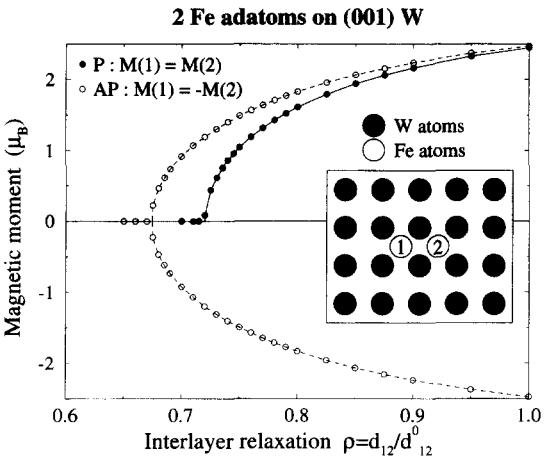

Fig. 3. Magnetic moments of two Fe adatoms on W(001) versus the relaxation ρ in the P (filled circles) and AP (open circles) cases. The distance between the Fe adatoms is a_0.

interaction via the W substrate is short-range within our model so that significant modifications of the LDOS for both the Fe adatoms and W atoms occur only if the adatoms are very near from each other. Second, there is a competition between the antiparallel coupling via the W substrate and the parallel coupling which occurs from the direct interaction between the Fe atoms. As we will see below, in the case of an Fe dimer on a W(110) surface, the most stable solution is obtained when the two Fe spins are parallel. We think that we obtain an antiferromagnetic solution for iron adatoms deposited on the W(001) because these atoms are too far away from each other. We investigated both parallel and antiparallel solutions for two Fe adatoms that we have brought closer together, separated by a distance $d = \sqrt{3}/2\,a_0$ (first-neighbor distance). Note that now the two adatoms are no longer adsorbed on the hollow sites. As expected, we found that the parallel solution is now clearly the most stable state.

3.3. Chains

Several experimental studies [19,20] have shown that for some anisotropic substrates the stable nanostructures are 1D chains [21–23] in the cases of certain transition metals adsorbed on transition or noble metals. Theoretical studies using the embedded atom method (EAM) [21,23,24] predicted such stable

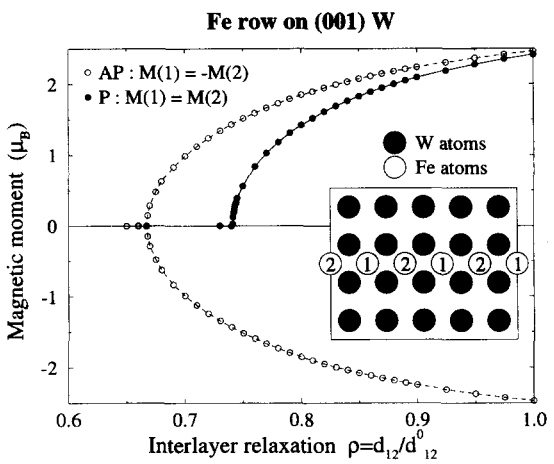

Fig. 4. Magnetic moments of an Fe infinite chain deposited on W(001) versus the relaxation ρ in the P (filled circles) and AP (open circles) cases.

configurations. Here, we investigate the magnetism of an infinite Fe chain, which we can compare with the one of a finite long chain.

If we compare Figs. 4 and 3 for the dimer (C), it is easy to see that there are only slight differences between the AP configurations, whereas the Fe magnetic moment vanishes more rapidly with the relaxation ($\rho \approx 0.745$) and decreases to $1.05\mu_B$ at $\rho = 0.77$ for the P configuration. Examination of the Fe LDOS in this case reveals a broadening due to the hybridization, and so a reduction of the moment. The AP configuration is still the most stable one, with the band energy difference between the AP and P states increasing in comparison with the (C) dimer.

3.4. Small clusters

Our main results can be briefly summarized as follows: (i) The AP c2 × 2 configuration is always the most stable state. (ii) The larger the number of adatoms, the more quickly the magnetism vanishes with the relaxation for the P state. (iii) The moment for a 4-adatom cluster is $1.5\mu_B$ at $\rho = 0.77$ in the AP configuration. (iv) First-order transitions occur in the P case for 5- and 12-adatom clusters.

3.5. Monolayer

We now present the results for the Fe perfect monolayer adsorbed on the W(001) substrate. The c2 × 2 antiferromagnetic configuration found both experimentally and theoretically (see refs. cited above) is energetically favored with respect to the ferromagnetic solution. The moment vanishes at $\rho \approx 0.82$ for the P configuration, so that a ferromagnetic solution cannot be obtained ($\rho \approx 0.77$). The magnetic moments induced in the substrate oscillate from plane to plane in the sublayers, the plane-to-plane antiferromagnetic order being favored in the W substrate.

4. Magnetism of iron clusters on the (110) plane

An Fe monolayer adsorbed on a W (110) surface has been found to be clearly ferromagnetically ordered, both experimentally [2] and theoretically [6]. Hong et al. found a ferromagnetic ground state with an Fe moment equal to $2.18\mu_B$, corresponding to a Fe–W relaxation $\rho = 0.835$ in our case (see Fig. 11). This value of the relaxation was used as a reference for all the clusters we investigated.

4.1. Single adatom

The magnetic moment decreases versus ρ with a square root variation law, as found for the W(001) substrate, but it vanishes for a smaller relaxation value ($\rho_{110} \sim 0.76 > \rho_{001}$), the hybridization Fe–W being stronger for smaller Fe–W distances. In the reference state ($\rho = 0.835$), the magnetic moment is equal to $1.84\mu_B$. Note that the W sublayers LDOS are bulk-like. Moreover, the induced moments on the W surface atoms are smaller ($< 0.1\mu_B$) than in Section 3; the (110) face is a compact surface, whereas the (001) is a more open one.

4.2. Magnetic interaction between two iron adatoms

Here, we investigate the direct or indirect coupling between two Fe adatoms on the (110) W surface. We consider three cases, according to the distance between adatoms: (A) the (110) dimers (Fig. 5); (B) the (001) dimers (Fig. 6); and (C) the (111) dimers (Fig. 7).

(A) The two adatoms are located at a distance $d = \sqrt{2}\,a_0$, so that this case is comparable to case B of Section 3.2. Fig. 5 shows the Fe magnetic mo-

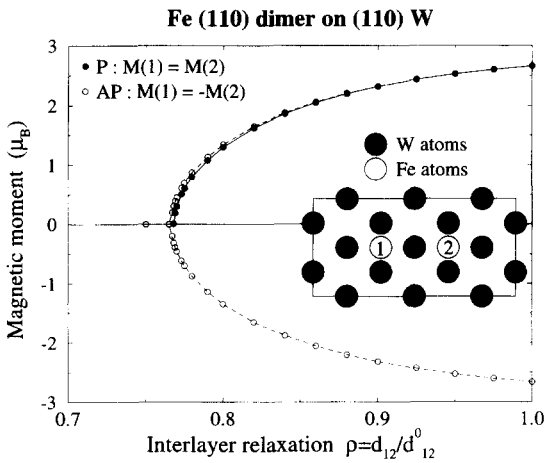

Fig. 5. Magnetic moments of two Fe adatoms on W(110) versus the relaxation ρ in the P (filled circles) and AP (open circles) cases. The distance between the Fe adatoms is $\sqrt{2}\,a_0$.

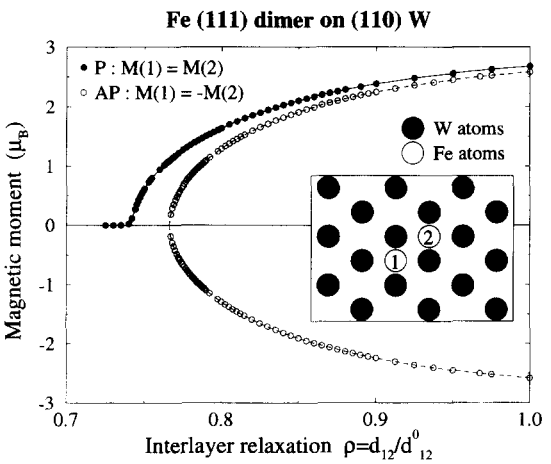

Fig. 7. Magnetic moments of two Fe adatoms on W(110) versus the relaxation ρ in the P (filled circles) and AP (open circles) cases. The distance between the Fe adatoms is $a_0\sqrt{3}/2$.

ments versus ρ in the P and AP configurations. There are only slight differences between the two curves, indicating a weak magnetic coupling. The magnetic moment is $\sim 1.95\mu_B$ at $\rho = 0.835$ and vanishes at $\rho \approx 0.765$. Surprisingly, the AP state is more stable than the P one, although an Fe monolayer on a W(110) surface is ferromagnetic. In the AP state, the induced moment on the W atom between the Fe adatoms is zero, because of the frustration, whereas it is negative in the P state.

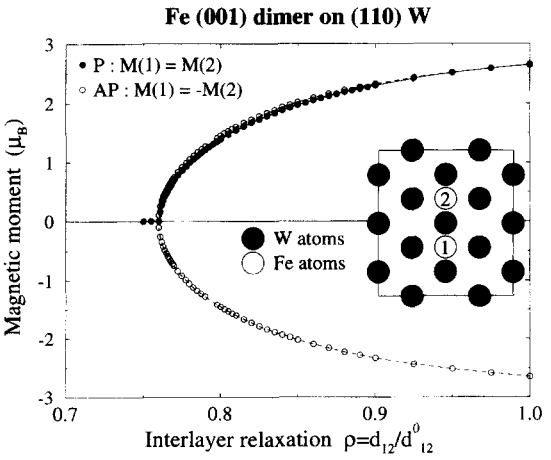

Fig. 6. Magnetic moments of two Fe adatoms on W(110) versus the relaxation ρ in the P (filled circles) and AP (open circles) cases. The distance between the Fe adatoms is a_0.

(B) This case is directly comparable with case C of Section 3.2. The main feature of Fig. 6 is the similarity of the P and AP curves, whereas we could expect some differences as observed for the Fe dimer on the W(001) surface. Moreover, the AP configuration is found to be the ground state at $\rho = 0.835$ but the energetic difference is very small. This suggests that there is a competition between the Fe–Fe ferromagnetic interaction and the coupling via the W substrate. Another important difference between the two surfaces is the induced moment on the W central atom in the P configuration. For the (001) surface, the moment is antiparallel to the Fe moment (AP coupling), whereas it is parallel (P coupling) for the (110) surface.

(C) For this last configuration, the two Fe adatoms are first neighbours and are strongly interacting. The two curves of Fig. 7 are quite distinct; the magnetic moment vanishes at $\rho \approx 0.74$ (P state) and $\rho \approx 0.765$ (AP state). The P configuration is clearly the most stable one and the magnetic moment is $\sim 1.95\mu_B$ at $\rho = 0.835$. In this case, the two Fe adatoms are directly coupled via large transfer integrals so that the Fe LDOS are strongly broadened by the strong hybridization between the two adatoms.

In both cases, there is a competition between a short-range Fe–Fe interaction favoring parallel magnetic moments and an interaction via the W substrate favoring antiparallel moments. On the (001) surface,

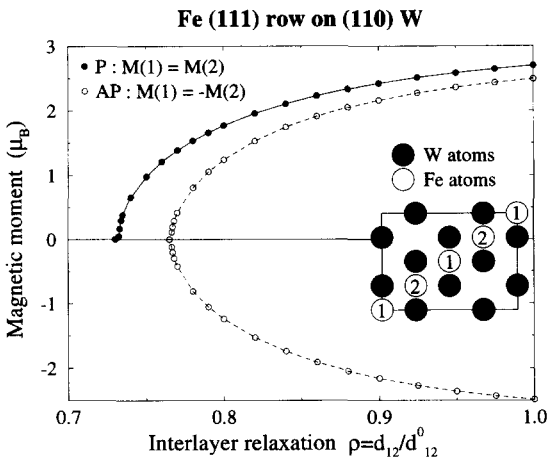

Fig. 8. Magnetic moments of an Fe infinite chain deposited on W(110) along the (111) direction versus the relaxation ρ in the P (filled circles) and AP (open circles) cases.

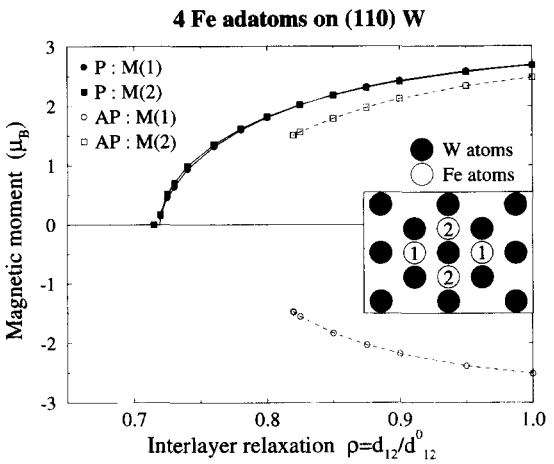

Fig. 9. Magnetic moments of a cluster of four Fe adatoms on W(110) versus the relaxation ρ in the P (filled circles) and AP (open circles) cases. Note the first-order transition for $\rho \approx 0.82$ in the AP case.

the Fe adatoms are never close enough to ensure that the P configuration is the most stable one. For the P configuration, we observe a W moment parallel to the Fe moment for the (110) surface, whereas it is antiparallel for a (001) one.

4.3. Chains on a W(110) surface

We investigate two infinite rows, the (001) and (111) (Fig. 8). The first one is very similar to the (001) dimer and is not very interesting. There are some slight differences with the dimer in the second case, and the magnetism remains for larger relaxation values (until $\rho \approx 0.73$). The strong interaction of one Fe adatom with two Fe first neighbors changes the LDOS, which is more broadened and now includes a two-peak structure below the Fermi level.

4.4. Small clusters

To relate the 1D to the monolayer electronic structure, we investigated small 2D clusters made of 4 (Fig. 9) or 5 (Fig. 10) Fe adatoms, which can occur during the first growth steps. As expected, the P solution is the ground state in both cases. First-order transitions occur versus ρ for the AP configuration at $\rho \approx 0.82$ (4 adatoms) and $\rho \approx 0.9$ (5 adatoms). Some similar behaviors are obtained for Fe clusters on a (001) surface, but for the P configuration. It is noteworthy that the ground state (AP configuration for the (001) plane and P configuration for the (110) plane) behaves more smoothly (second-order transition) versus ρ than the excited state (P configuration for the (001) plane and AP configuration for the (110) plane).

4.5. Monolayer

For the Fe monolayer adsorbed on the W(110) surface (Fig. 11), the ferromagnetic configuration is

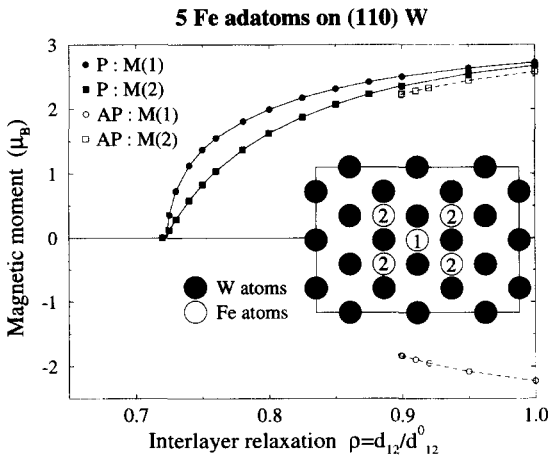

Fig. 10. Magnetic moments of a cluster of five Fe adatoms on W(110) versus the relaxation ρ in the P (filled circles) and AP (open circles) cases. Note the first-order transition for $\rho \approx 0.89$ in the AP case.

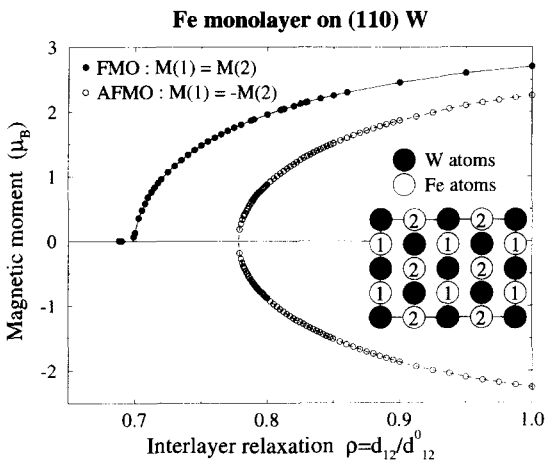

Fig. 11. Magnetic moments of a Fe monolayer on W(110) versus the relaxation ρ. Filled circles, the ferromagnetic solution; open circles, the antiferromagnetic solution.

found to be the ground state one, in agreement with experimental results [2] and other theoretical studies [6]. We found the AP solution to be a metastable one with a Fe moment $\sim 1.3\mu_B$.

5. Conclusions

The AP solution is always the ground state for all the Fe clusters adsorbed on a W(001) substrate. The magnetism of Fe clusters on the W(110) surface can be more complex. The AP solution is the most stable one if the Fe adatoms are separated by a distance larger than the first-neighbour one. However, when the Fe atoms are first-neighbours, the P solution becomes the most stable state. This is consistent with the fact that the ferromagnetic state is the most stable one for an Fe monolayer deposited on the W(110) substrate. On the other hand, the W(001) and W(110) surfaces react differently to the Fe polarization. For example, for two second-neighbor Fe adatoms with parallel moments (case C in Section 3.2 and case B in Section 4.2), the W atoms in their neighbourhood carry a magnetic moment parallel to the Fe ones for a (110) surface, and an antiparallel one for a (001) surface.

As a general rule, the W substrate is hard to polarize. An antiferromagnetic state is associated with a (001) surface because Fe adatoms are too far away from each other to induce large W polarizations. In this case it is energetically better to frustrate the substrate. In contrast, for the compact (110) surface for which the Fe atoms can be first neighbours, the interactions are strong enough to polarize the W atoms.

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