Disorder-Induced Antiferromagnetic to Ferromagnetic Transition in Magnetic Overlayers: (Fe,Mn)/W(001) as a Case Study*

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The magnetic phase stability of the random FeₓMn₁₋ₓ monolayer on the bcc-W(001) substrate is studied from first-principles. The exchange interactions among two-types of magnetic atoms in the overlayer are estimated in the framework of the adiabatic approximation and used to construct the random classical two-dimensional Heisenberg Hamiltonian. The stability of such effective Hamiltonian is then studied with respect to a broad class of magnetic arrangements which include also possible spin-spiral structures. This allows to investigate a broader class of systems than in a conventional total energy search. We have found that exchange interactions between Fe-spin are antiferromagnetic while those between Mn-spins are ferromagnetic over the whole concentration range. This pronounced frustration leads to a complex behavior in which the c(2 × 2) antiferromagnetic state for Fe-monolayer goes over to complex incommensurate spin-spiral magnetic structures with increasing Mn-content. A spin-spiral state with a large period was found also for the Mn-monolayer case in agreement with a recent experimental and theoretical study. [DOI: 10.1380/ejssnt.2010.184]

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I. INTRODUCTION

Magnetic phenomena at surfaces and interfaces have been studied extensively in recent years stimulated by the needs of both the technology (magnetic storage media, spintronics) and the development of experimental tools for research in this field (e.g., the spin-polarized scanning tunnelling microscope). This experimental effort was paralleled by the development of corresponding theoretical tools. The first-principles approaches, in particular, strongly profited from the increasing speed and memory capacity of computers.

Reduced number of nearest neighbors at surfaces and lowering of the crystal symmetry due to the presence of the surface has a strong impact on magnetic properties, e.g., the enhancement of local magnetic moments at the surface as compared to the bulk magnetic moments or the occurrence of magnetism for nonmagnetic elements when placed on the surface.

An interesting example of the interplay between the chemical properties and geometry of the surface and its effect on magnetic properties of adsorbates is an experiment which has indicated that iron monolayers on the (001) tungsten surface had zero net magnetization (see [1] and references therein). This observation is in contrast with the ferromagnetism observed for iron monolayers on the W(110) surface [2]. This puzzle was resolved recently in Ref. 3 in which the authors observed the c(2 × 2) antiferromagnetic (AFM) arrangement of Fe on the W(001) surface.

A theoretical study by Ferriani et al. showed that iron and cobalt monolayers tend to be antiferromagnetic on the W(001) surface while V, Cr and Mn monolayers exhibit the ferromagnetic (FM) order [4]. This is just the opposite trend as found for the W(110) surface, on which V, Cr, and Mn monolayers are c(2 × 2) antiferromagnets while Fe and Co order ferromagnetically.

In a subsequent theoretical study, Ferriani et al. [5] demonstrated a strong dependence of the magnetic state of a Fe-monolayer on the substrate by studying its stability on the (001)-face of bcc-TaₓW₁₋ₓ random substrates in the framework of the total energy calculations. It was found that the ground state of the Fe-monolayer on Ta(001) is the FM rather than the AFM one and there thus exists a crossover between these two magnetic configurations at a certain critical alloy substrate composition. Results of Ref. 5 has also confirmed the robustness of such behavior - even the unrelaxed system behaved similarly although large inward relaxations of about 18% exist between the Fe monolayer and the first substrate W-layer, which can influence, e.g., the critical substrate composition for the FM to AFM crossover.

Based on results of Ref. 4, namely that the Mn monolayer on the W(001) substrate is ferromagnetic, the authors of Ref. 6 predicted on the basis of total energy calculations a possible crossover between the AFM and FM states at an intermediate overlayer composition.
motivation for this study was also the fact that Fe and Mn atoms alloy easily in their bulk phase. The crossover between the AFM and FM configurations due to alloying with Mn-atoms represents a complex process which is very difficult to investigate only by conventional total energy calculations because of additional complications due to disorder and, first of all, due to a large number of possible magnetic configurations which need to be considered. It was demonstrated by Ferriani et al. [7] in a recent experimental and theoretical study that a ground state of Mn/W(001) system is in fact more complex than the originally proposed FM state, namely authors propose spin-spiral state stabilized by the Dzyaloshinskii-Moriya interaction.

Finally, a strong tendency of the Fe-monolayer on the fcc-Ir(001) surface to order antiferromagnetically for the true relaxed geometry was demonstrated in a very recent study [8]. On the contrary an unrelaxed Fe/Ir(001) samples have the FM ground state. There are thus three ways in which the magnetic ground state of the Fe-monolayer on the nonmagnetic substrate can be changed by varying either the geometry [8] or the chemical composition of the substrate [5] and/or the overlayer [6].

The main aim of the present study is to further extend our previous work [6] by characterizing the AFM to FM crossover in the (Fe,Mn)/W(001) system on the basis of calculated exchange interactions. The usefulness of such study for a deeper understanding of phenomena was illustrated in recent papers [5, 8]. In these studies exchange interactions existed only between Fe-spins in a nonrandom monolayer and the crossover between the FM and AFM magnetic states was mediated either by alloy disorder in the substrate [4] or by layer relaxations [8]. In the present case the crossover is mediated by the disorder in the monolayer in which three kinds of exchange integrals between Fe and Mn spins are present.

II. FORMALISM

The electronic properties of the random (Fe,Mn)-monolayer on the nonrandom W(001) substrate will be studied in the framework of the tight-binding linear muffin-tin orbital (TB-LMTO) method combined with the coherent potential approximation (CPA) to treat alloy disorder in the monolayer. The effect of the surface is included in the framework of the surface Green function (SGF) approach [9] which employs a realistic semiinfinite sample geometry (no slabs or periodic supercells). The one-electron potential is treated within the atomic sphere approximation, but the dipole barrier due to the redistribution of electrons in the vicinity of the surface is included in the formalism. The TB-LMTO-SGF method can include the effect of layer relaxations approximately provided that they are known either from the full-potential calculations or from the experiment. The layer relaxations are rather large for Fe/W(001) being about 18 % while for Mn/W(001) they are significantly smaller (about 5 %) and they also depend on the magnetic state, for example, they can be different for the FM- and AFM-phases [5]. It should be noted that layer relaxations do not change the magnetic phase as compared to the unrelaxed case, e.g., the ground state of Fe/W(001) is AFM for both unrelaxed and relaxed cases and the same is true for the FM ground state of Mn/W(001). To simplify the present study we shall neglect here possible layer relaxations keeping in mind that this approximation can influence results quantitatively.

An important advantage of the TB-LMTO-SGF approach is a possibility to estimate exchange interactions between magnetic atoms in the overlayer. We will describe such magnetic interactions in terms of the two-dimensional classical random Heisenberg Hamiltonian,

$$H = -\sum_{Q,Q'} \sum_{i \neq j} \eta_{ij}^{Q} J_{ij}^{Q,Q'} \mathbf{e}_{i} \cdot \mathbf{e}_{j} \eta_{ij}^{Q'}. \quad (1)$$

Here, $J_{ij}^{Q,Q'}$ denotes the exchange integral between spins of the $Q$-atom at the site $i$ and the $Q'$-atom at the site $j$ in the magnetic monolayer $(Q,Q' = \text{Fe}, \text{Mn})$, and $\mathbf{e}_{i}$ and $\mathbf{e}_{j}$ are unit vectors in the directions of local magnetic moments on sites $i$ and $j$, respectively. The quantity $\eta_{ij}^{Q}$ is the occupation index which takes randomly the value one (if the site $i$ is occupied by an atom of the type $Q$) and the value zero otherwise. The randomness thus enters the problem via occupation indices. It should be noted that we have neglected small induced moments in the W-substrate.

Exchange interactions $J_{ij}^{Q,Q'}$ can be evaluated in the framework of the TB-LMTO-SGF-CPA method as

$$J_{ij}^{Q,Q'} = \frac{1}{4\pi} \text{Im} \text{tr}_{L} \int_{C} \Delta_{Q}^{Q}(z) \bar{g}_{ij}^{Q,Q'}(z) \Delta_{Q}^{Q'}(z) \bar{g}_{ji}^{Q'-Q}(z) dz, \quad (2)$$

where $\Delta_{Q}^{Q}(z)$ characterizes the exchange splitting of the Q-atom at the site $i$, and $\bar{g}_{ij}^{Q,Q'}$ is the conditionally averaged Green function which describes the motion of an electron between sites $i$ and $j$ in the random magnetic monolayer and which corresponds to the spin $\sigma = (\uparrow, \downarrow)$. The integral in (2) is done over the contour $C$ in the complex energy plane $z$ which starts below the valence band and ends at the Fermi energy. Symbol $\text{tr}_{L}$ denotes the trace over the atomic orbitals $(L \equiv (l,m))$. Finally, the quantity $\Delta_{Q}^{Q}(z)$ is defined in the TB-LMTO method in terms of potential functions $P_{Q}^{Q}(z)$ as $\Delta_{Q}^{Q}(z) = P_{Q}^{Q}(z) - P_{Q'}^{Q'}(z)$. The above expression represents a straightforward generalization of the corresponding bulk expression [10, 11] since it is formulated in the real space. We refer the reader to Refs. 9, 12 for details of evaluation of the real-space configurationally averaged Green function $\bar{g}_{ij}^{Q,Q'}$ for the magnetic overlayer on a nonrandom substrate. The present approach can be considered a generalization of the method developed by one of the present authors for ordered magnetic monolayers to the case of random magnetic overlayers [13].

It should be noted that an alternative approach was used in Ref. 5 in which the total energies of the FM configuration and of few possible AFM configurations (e.g., the c(2x2) and p(2x1) Fe-overlayers on W(001)) were used to extract two effective exchange interactions. One can also apply this approach to the present (Fe,Mn)/W(001) system by choosing several configurations of the (Fe,Mn) monolayer which are chemically as well as magnetically ordered. Alternatively, a supercell version of the spin spiral approach representing few chemically ordered configur-
rations of the (Fe,Mn) monolayer can be also used to construct corresponding exchange integrals. Recently such an approach was applied to the case of the Fe/W(001) monolayer [14]. It should be noted, however, the the present real-space approach is more suitable to account for the randomness in the system.

We wish to discuss briefly an important issue of the choice of the reference state for the determination of exchange integrals in Eq. (1). A conventional choice [10] is the FM reference state. An alternative reference state is the the disordered local moment (DLM) state [15]. The DLM state is a model state with zero total magnetic moment which results from the disorder of spin orientations of otherwise non-zero local magnetic moments [16]. This reference state has an obvious advantage for the study of the magnetic phase stability of the system as it assumes no specific magnetic order from the very beginning. The lattice Fourier transform of exchange integrals can be conveniently used to search over much broader set of possible magnetic configurations as compared to the conventional total energy search which necessarily includes a limited set of ad hoc chosen FM and AFM configurations. We have recently demonstrated the usefulness of such approach [8]. We will present below an extension of this approach to a more complex case of the random (Fe,Mn) magnetic overlayer on the bcc-W(001) substrate. It should be noted that this approach allows us to find even the spin-spiral ground state starting from the collinear reference state as demonstrated e.g. for the case of bcc-Eu crystal [17].

III. RESULTS AND DISCUSSION

We wish to point out that even the bulk FeMn alloy represents a quite complex and not yet fully understood system. For example, the fcc γ-FeMn ordered alloy seems to exhibit a non-collinear spin arrangement [18] and the situation is even more complex in the disordered phase [19]. On the other hand, the two-dimensional (Fe,Mn) alloy is structurally simpler than its bulk counterpart. We assume that the (Fe,Mn) monolayer forms a surface alloy and neglect possible intermixing at the interface with the W(001) substrate. The local magnetic moments of the FM and DLM phases of the (Fe,Mn)/W(001) surface alloy were studied in detail in a previous paper [6]. Here we just mention that local Mn- and Fe-moments are almost concentration independent and quite rigid as their values evaluated in that local Mn- and Fe-moments are almost concentration phases of the (Fe,Mn)/W(001) surface alloy were studied [19]. On the other hand, the two-dimensional (Fe,Mn) alloy is structurally simpler than its bulk counterpart. We assume that the (Fe,Mn) monolayer forms a surface alloy and neglect possible intermixing at the interface with the W(001) substrate.

The local magnetic moments of the FM and DLM phases of the (Fe,Mn)/W(001) surface alloy were studied in detail in a previous paper [6]. Here we just mention that local Mn- and Fe-moments are almost concentration independent and quite rigid as their values evaluated in the FM- and DLM-reference states are almost the same: m_{Fe} \approx 2.65 \mu_{B} and m_{Mn} \approx 3.4 \mu_{B} [20].

In Fig. 1 we plot the 1st nearest-neighbor (NN) real-space exchange interactions J^{Q,Q'}_{i,j} (Q, Q' = Fe, Fe; Mn, and Mn, Mn) over the whole concentration range. The 1st NN interactions dominate the other more distant exchange interactions (see Fig. 2 below). By construction, J^{Fe,Fe}_{1} for x_{Mn}=0 corresponds to the 1st NN exchange interaction between Fe-spins in the Fe-overlayer on the bcc-W(001) substrate, J^{Mn,Mn}_{1} corresponds to the exchange interaction between the nearest Mn-spins embedded in the Fe-overlayer, and J^{Fe,Mn}_{1} corresponds to the exchange interaction between the Mn-spin and its NN Fe-spins in the Fe-overlayer. The role of Fe- and Mn-spins is just interchanged for the case x_{Fe}=0. The dominating AFM character of the J^{Fe,Fe}_{1} interactions over the whole concentration range and their weak concentration dependence has to be noted. On the contrary, the NN Mn-Mn interactions are FM over the whole concentration range and their values decrease with the increasing Fe-content. The mixed interactions, J^{Mn,Fe}_{1}, are also AFM like the Fe-Fe interactions but their absolute values are smaller. It should be noted that calculated Fe-Fe, Fe-Mn, and Mn-Mn exchange interactions agree in signs and approximately also in their value with those found in Ref. 6.

We have also plotted the effective interactions J^{eff}_{ij} which are obtained as a weighted average of all interactions, namely

\[ J^{eff}_{ij} = \sum_{Q} J^{Q,Q'}_{ij} (Q, Q' = Fe, Fe; Mn, and Mn, Mn). \]

This is so-called averaged lattice model (ALM) and it is simply the result of the configurational average applied to the Heisenberg model, Eq. (1). In this way, the originally random problem is formally reduced to a simpler problem with non-random but concentration-dependent exchange integrals. Strictly speaking, the ALM can lead in some cases to quantitatively and even qualitatively incorrect results due to the magnetic percolation effect as shown in Ref. 21. This effect is strong for very dilute magnetic spins in a nonmagnetic host like the diluted magnetic semiconductors. In the present case there are two magnetic atoms of comparable spin moments and large

![Figure 1](http://www.sssj.org/ejssnt)
alloy concentrations. In such a case the ALM is an acceptable approximation as shown in Ref. 22 for the case of Ni-based transition metal alloys. We will assume that the ALM model is also a reasonable approximation in the present case but its approximate character has to be kept in mind. The calculated $J_{\text{eff}}$ clearly indicate the AFM to FM transition with increasing Mn-content: the AFM character of exchange interactions is changed to the FM one for less than 30% of Fe-atoms in the overlayer.

The concentration trend of the first five effective exchange interactions $J_{\text{eff}}^s$, $s=1−5$ is shown in Fig. 2. This plot clearly indicates the dominating character of the 1st NN effective exchange interactions over a broad concentration range with the exception of the region of $x_{\text{Fe}} \in (0.2, 0.4)$ where the 1st and 2nd NN interactions compete. The dominating 1st NN interactions exhibit a dramatic concentration behavior and clearly explain the stabilization of the robust AFM state for Fe-rich systems. On the contrary, the influence of non-negligible 2nd and 3rd NN effective interactions for the Mn-rich case is possible because they are of AFM-type and thus frustrated with 1st NN interactions. One can thus expect more complex behavior in the Mn-rich case: for example, we have the first three effective exchange interactions of comparable sizes but with different signs for $x_{\text{Fe}} \approx 0.25$.

The magnetic phase stability of the system described by the Hamiltonian (1) can be studied by evaluating the lattice Fourier transform of its configurational average, i.e., of the effective Hamiltonian

$$H = - \sum_{i \neq j} J_{ij}^{\text{eff}} \mathbf{e}_i \cdot \mathbf{e}_j ,$$

where $J_{ij}^{\text{eff}}$ are defined by Eq. (3). The result of such study is presented in Fig. 3.

We wish first to note the limitations of such study: (i) The magnetic order can depend also on the chemical order and, strictly speaking, the magnetic and chemical orders cannot be studied separately as in the present case. For example, the chemically disordered $\text{Fe}_{0.5}\text{Mn}_{0.5}$ random surface alloy and its ordered counterpart (e.g. the $c(2 \times 2)$ ordered phase) have very different local nearest-neighbor environment, which can also influence corresponding magnetic states.

Concerning the lattice Fourier transform we mention that the minimum of $-J_{ij}^{\text{eff}}(q)$ reached for a particular value of the vector $\mathbf{q}_0$ in the surface Brillouin zone indicates a tendency of the magnetic system to form a magnetic ground state characterized by this wave vector. The wave vector $\mathbf{q}_0$ corresponds to the $c(2 \times 2)$ (checkerboard-like) AFM ground state and the point $\bar{\Gamma}$ corresponds to the $p(2 \times 1)$ (row-wise) AFM ground state. The case of Fe-monolayer on the W(001) substrate gives a well pronounced minimum at the point $\bar{\Gamma}$ in a perfect agreement with previous total energy studies [4–6]. We also find that the FM state has a smaller energy as compared to the $c(2 \times 2)$ or $p(2 \times 1)$ AFM states for the Mn-monolayer on the W(001) substrate. This result is also in agreement with the total energy studies [4, 6] but our calculations indicate a possible existence of a more complex magnetic ground state (shallow energy minima on the lines $\bar{\Gamma}-\bar{M}$ or $\bar{\Gamma}-\bar{X}$ were found). This indicates a possibility of stabilization of the spin-spiral state corresponding to the above mentioned

\[\text{Fe}_{x}\text{Mn}_{1-x}/\text{W}(001)\text{ (DLM)}\]

\[\text{J}_{\text{eff}}(\mathbf{q}): \text{Fe } x \text{ Mn } 1-x/\text{W}(001)\text{ (DLM)}\]

FIG. 2: The concentration dependence of the effective nearest-neighbor exchange interactions $J_{\text{eff}}^s$, $s=1−5$ (see Eq. (3) in the text for the definition).

FIG. 3: The lattice Fourier transform of effective exchange interactions $-J_{ij}^{\text{eff}}$ (see Eq. (3)) for few chosen surface alloy compositions characterizing the stability of the system described by the effective Hamiltonian, Eq. (4), with respect to the periodic spin excitations. The symbols at the minima of corresponding curves denote possible magnetic orderings in each specific case.

http://www.sssj.org/ejsnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejsnt/)
wave-vector. The spin-spiral state was also found in a recent spin-polarized STM experiment and its origin was ascribed to the Dzyaloshinskii-Moriya interactions [7]. However, the existence of some amount of spin-disorder which is mediated by external perturbation (the presence of the Mn-W interface) is also possible. The presence of spin-disorder in the otherwise perfect Mn-sublattice in Heusler alloys (Cu,Ni)MnSb was supported by recent theoretical calculations [24].

Between these two limits we observe quite complex behavior which is due to the combination of magnetic frustration (various signs of system exchange interactions \( J_{Q,Q^2} \), \( Q, Q^2 = \text{Fe, Mn} \)) and the alloy disorder in the overlayer. It should be noted that the ALM model can mask to a certain extent even more complex behavior which can be additionally modified by possible chemical ordering effects in the surface alloy (see Ref. 23 for more details). In each case the \( c(2 \times 2) \) antiferromagnetism of the Fe/W(001) system is strongly reduced by alloying with Mn-atoms until the FM state or even a more complex spin-spiral state with relatively large period of oscillations is stabilized (the FM state can be considered a spin-spiral state with the infinite period).

The present results are also compatible with our previous study of this system which was based on the total energy search for the ground state [6]. The main conclusions of both approaches agree to each other. The main disadvantage of the total energy search is a limited choice of possible magnetic configurations used in the search which, in addition, are chosen in an \emph{ad hoc} manner. A much broader class of possible configurations can be investigated by the present approach although also this approach has its limitations as mentioned below.

We wish to point out that the study of possible phases in random magnetic overlayer in which the transition between the AFM-like and FM-like configurations can be expected is of current interest. A related system is, for example, the fcc-(Fe,Co)/Ir(001) system where the AFM state exists for fcc-Fe/Ir(001) [8] while the system fcc-Co/Ir(001) seems to prefer the FM configuration. Clearly, the ALM model represents an approximation whose validity has to be further tested. The relativistic effects like, e.g., the magnetic anisotropy and/or the Dzyaloshinskii-Moriya interaction can also influence the magnetic phase stability. We have also neglected possible local environment effects and other space inhomogeneities. The relevance of such effects increases in the concentration region where several of the effective exchange interactions drop to zero. This can influence e.g. the value of the critical concentration for which the transition from the AFM to FM state occurs. Probably the best approach will be the direct search for the minimum of the random Heisenberg model (1) which will allow the search among the more general non-collinear magnetic configurations. Such study goes beyond the scope of the present paper.

IV. CONCLUSION

We have presented a new approach how to studying a magnetic phase stability of magnetic surface alloy on non-magnetic non-random substrates. As a case study we have considered a random (Fe,Mn) monolayer on the bcc-W(001) substrate. The key elements in the present approach are exchange interactions between alloy species which were estimated from the reference DLM state. The exchange interactions between Fe-spins are AFM over the whole concentration range while the Mn-Mn interactions are FM. The mixed interactions are weakly AFM. This inherent frustration leads to the cross-over between the \( c(2 \times 2) \)-AFM state for a pure Fe-monolayer and the FM state for a pure Mn-overlayer in agreement with previous conventional total energy studies [4, 6]. The magnetic ground state was found to be the one which minimizes the corresponding random Heisenberg Hamiltonian. Due to the randomness and possible chemical ordering in the surface alloys this is quite a difficult problem and we have presented a simplified solution in which the disorder in the Heisenberg Hamiltonian was treated in the virtual-crystal approximation which formally converts a complex random problem to the nonrandom one with the effective concentration-dependent exchange integrals (the average lattice model). We have studied the magnetic stability of this simplified model which has lead to a complex magnetic configuration for the random overlayer. For example, we have found that the ground state of Mn-overlayer is not the FM state but a related more complex spin-spiral although with a large period (the FM state corresponds to a spin-spiral with the infinite period). This spin-spiral state was observed recently by the spin-polarized STM experiment [7]. Calculations clearly demonstrate the loss of stability of the \( c(2 \times 2) \)-AFM state for pure Fe-monolayer with increasing Mn-content. On the other hand, the neglect of spin-orbit interaction in the W-substrate, the simplified treatment of alloy disorder in the Heisenberg Hamiltonian in the framework of the ALM, the neglect of the influence of possible chemical order and layer relaxations can modify conclusions of the present paper quantitatively. A more complex study goes beyond the scope of the present paper and will be the subject of future papers.

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[20] Calculated local magnetic moments are slightly smaller as those given in Ref. 6. The difference is due to different basis sets used, namely the $spdf$-basis in the present study as compared to the $spd$-basis adopted in the previous study.