# Magnetic Phase Control in Monolayer Films by Substrate Tuning

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We propose tailoring exchange interactions in magnetic monolayer films by tuning the adjacent nonmagnetic substrate. As an example, we demonstrate a ferromagnetic-antiferromagnetic phase transition for one monolayer Fe on a $Ta_xW_{1-x}(001)$ surface as a function of the Ta concentration. At the critical Ta concentration, the nearest-neighbor exchange interaction is small and the magnetic phase space is dramatically broadened. Complex magnetic order such as spin spirals, multiple-$Q$, or even disordered local moment states can occur, offering the possibility of storing information in terms of ferromagnetic dots in an otherwise zero-magnetization state matrix.

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Magnetic systems play a central role in today's information technology and our ability to control and tailor their properties may open new vistas to future device concepts. Materials structured on a nanometer scale such as atomically thin films proved to be a rich field for novel magnetic properties. While our understanding of magnetic systems has tremendously increased over the past 25 years, to control magnetic order in a specific system and tailor materials with desired magnetic properties remains the grand challenge of research in magnetism.

So far the attempts to tune the magnetic state of surfaces and ultrathin films have focused on alloy formation where the concentration of the magnetic components is altered to optimize the magnetic properties [1–6]. In this Letter, we propose a completely different route. Based on the surprising observation of an antiferromagnetic (AFM) order of 1 monolayer (ML) Fe on W(001) and the prediction of the ferromagnetic (FM) order on Ta(001) [7], we suggest to tune magnetic interactions in ultrathin films by modifying only the band filling of the substrate, via the formation of a Ta-W alloy, without altering or diluting the magnetic monolayer itself.

We employ first-principles calculations to show that the nearest-neighbor exchange interaction in one ML Fe on the (001) surface of a $Ta_xW_{1-x}$ alloy can be continuously tuned from FM to AFM coupling by varying the Ta concentration $x$. At the substrate composition of small nearest-neighbor exchange interaction, we find that higher order spin interactions beyond the Heisenberg model, such as biquadratic or four-spin interactions, may stabilize complex noncollinear magnetic structures. In this case, we also consider the role of chemical disorder which might prevent any stable magnetic order due to the small energy scale involved and lead, for example, to a spin glass. The substrate turns out to be a tuner also for a magnetic order-disorder phase transition. At the corresponding Ta concentration, a highly frustrated material is formed and can be used to store information in the form of FM dots in a zero-magnetization state matrix, opening the way to a new class of material for magnetic storage devices.

While we consider a single model system, which allows to isolate magnetic effects from structural and chemical ones, depending on surface orientation, substrate element, and overlayer, a rich variety of similar systems is possible. For example, metallic magnets with small exchange coupling have been recently reported [8,9].

We have determined the electronic and magnetic properties of one ML Fe on the (001) surface of $Ta_xW_{1-x}$ by performing density-functional theory calculations in the generalized-gradient approximation to the exchange-correlation functional [10]. The substitutional $Ta_xW_{1-x}$ random alloy has been modeled in the spirit of the virtual crystal approximation (VCA) [11] by a substrate of fictitious atoms with fractional atomic numbers related to the Ta composition $x$, ranging linearly between 73 (Ta) and 74 (W). The corresponding fractional electronic charge preserves charge neutrality and accounts for the variation of the band-filling originating from alloying. Vegard's law was adopted to interpolate between the lattice constants of Ta (3.301 Å) and W (3.165 Å). A fixed surface relaxation of 18% was assumed, corresponding to the relaxation of the FM Fe monolayer on pure W(001). Based on additional studies on the effect of the lattice constant on the magnetic properties, the tiny deviations from Vegard's law [11] and the deviation of the relaxation from the adopted value [12] can be safely neglected. The calculations have been carried out with the full-potential linearized augmented plane wave (FLAPW) method in film geometry, as implemented in the FLEUR code [13]. Spin spirals have been computed in the $p(1 \times 1)$ unit cell, exploiting the generalized Bloch theorem [14]. The computational parameters were chosen according to Ref. [7].

W and Ta are adjacent elements of the periodic table with similar properties. Both crystallize in the bcc structure

 

with comparable lattice constants. W has one $d$ electron more than Ta. While one ML Fe exhibits a $c(2 \times 2)$-AFM state, Fig. 1(a), if grown on W(001), it is FM on Ta(001) [7]. Hence, the magnetic configuration in the Fe layer is related to the substrate $d$-band filling that affects the position of the substrate $d$-band relative to the Fermi energy ($E_F$) and controls by hybridization the position of the Fe states at $E_F$. For $3d$ metals with large magnetic moments it is well-established that in good approximation the magnetic configuration with the lowest minority density of states at $E_F$ exhibits the lowest energy (e.g., compare Figs. 3 and 4 in Ref. [15]). By forming $Ta_xW_{1-x}$ alloys with different compositions we can adjust the $5d$-band filling or the position of the minority Fe $d$ state at $E_F$ and continuously investigate the transition between the AFM and FM state of the Fe overlayer in Fe/W(001) and Fe/Ta(001), respectively. This is expected to be experimentally feasible due to the full miscibility of W and Ta for every concentration [16].

This scenario is presented in Fig. 1. We initially focus on three collinear configurations, Fig. 1(a): $c(2 \times 2)$-AFM, $p(2 \times 1)$-AFM, also referred to as row-wise AFM (RW-AFM), and FM. The magnetic ground state is obtained from the total energy, Fig. 1(b), as a function of the Ta concentration, $x$, relative to the FM state. At small Ta concentrations up to about 25%, the Fe monolayer exhibits a $c(2 \times 2)$-AFM order, while at large $x$, roughly beyond 70%, the ground state is FM. In the intermediate range the RW-AFM state is energetically favorable [17].

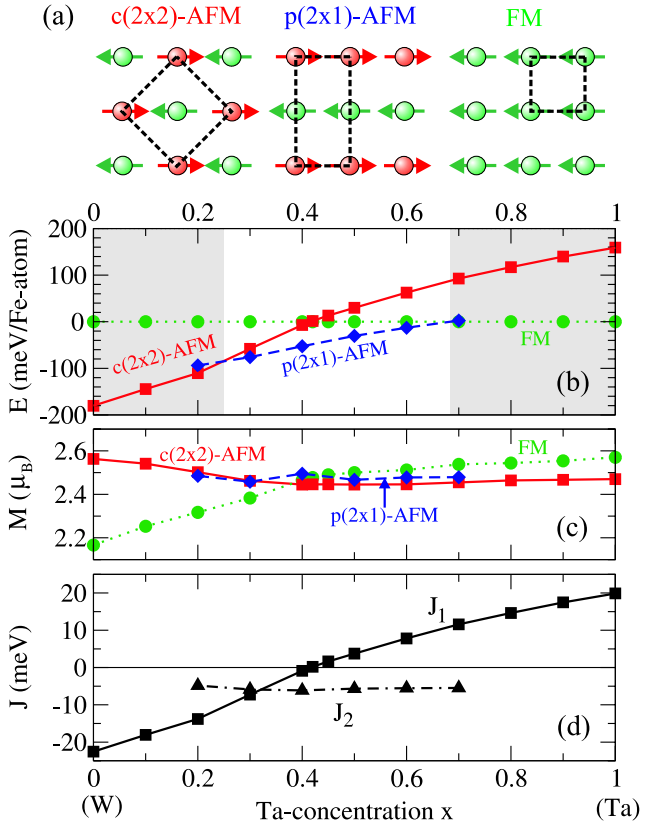


FIG. 1 (color online). (a) Unit cell sketch of the investigated magnetic configurations. (b) Total energy, (c) magnetic moment, and (d) exchange constants for 1 ML $Fe/Ta_xW_{1-x}$ as calculated by the FLAPW method.

In order to analyze these *ab initio* calculations in terms of exchange interactions, we can map the results onto a classical Heisenberg Hamiltonian, $H = -\sum_{i<j} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j$, where $J_{ij}$ is the exchange interaction between spins at lattice sites $i$ and $j$ pointing in the direction of the unit vectors $\mathbf{s}_i$ and $\mathbf{s}_j$, respectively. Such a model with fixed spin values is legitimated by the weak dependence of the magnetic moment on the Ta concentration and magnetic order, Fig. 1(c). For a monolayer on a square lattice the nearest neighbor (NN) and next-nearest neighbor (NNN) exchange constants $J_1$ and $J_2$, respectively, can be extracted from the energies of the FM, $c(2 \times 2)$-, and $p(2 \times 1)$-AFM states.

The NN exchange constant varies as a function of the Ta concentration, Fig. 1(d), and mimics the energy of the $c(2 \times 2)$-AFM configuration, Fig. 1(b). In contrast, we observe only a weak dependence for the NNN coupling which is on the order of $J_2 \approx -5$ meV. The strength of the typically dominating NN exchange interaction in a magnetic film can therefore be tuned by selecting the proper substrate composition, without requiring structural or chemical modifications of the film. This opens the way to a dramatically broader magnetic phase space, as we will see in the following.

The possible magnetic states in a two-dimensional (2D) film on a square lattice can be studied in the magnetic phase diagrams derived within the Heisenberg model, Fig. 2. For dominating NN exchange interaction only two magnetic states can occur, either the FM ($J_1 > 0$) or the $c(2 \times 2)$-AFM ($J_1 < 0$) state; see Fig. 2(a). Even in the presence of NNN exchange, the magnetic states are still limited to collinear solutions. However, if $J_1$ is negligible or at least comparable to interactions beyond second nearest neighbors, complex noncollinear magnetic phases appear; see Fig. 2(b). For example, a considerable value of $J_3$

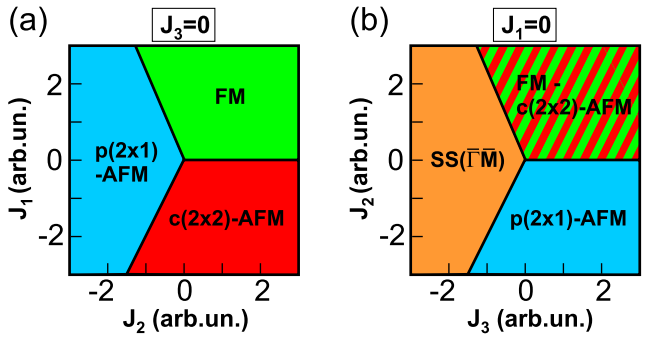


FIG. 2 (color online). Phase diagrams for 2D systems on a square lattice based on the Heisenberg model. (a) If $J_1$ and $J_2$ dominate, only collinear states are possible. (b) If $J_1$ is small compared to $J_3$, the FM and the $c(2 \times 2)$-AFM configurations are degenerate and spin spirals with $\mathbf{q}$ along $\bar{\Gamma}$-$\bar{M}$ can occur.

leads to so-called spin-spiral states. Flat spin spirals are the general solution of the Heisenberg Hamiltonian and are characterized by a wave vector $\mathbf{q}$. For a given $\mathbf{q}$, the magnetic moment of an atom at site $\mathbf{R}$ points in the direction $\hat{\mathbf{s}}(\mathbf{R}) = [\cos(\mathbf{q}\cdot\mathbf{R}), \sin(\mathbf{q}\cdot\mathbf{R}), 0]$.

Based on these phase diagrams, the Ta concentration of very small $J_1$, i.e., close to $x = 42\%$, is particularly intriguing, as interactions beyond NN will determine the magnetic ground state and noncollinear solutions are likely [8,9]. This suggests extending the calculations by including spin spirals for vectors $\mathbf{q}$ along the high-symmetry lines of the irreducible 2D Brillouin zone. The high-symmetry points represent the previously discussed collinear states: $\bar{\Gamma}$, $\bar{M}$, and $\bar{X}$ correspond to the FM, $c(2\times 2)$-AFM, and $p(2\times 1)$-AFM state, respectively.

In order to emphasize the interplay of overlayer-substrate interaction and magnetic order, we study the energy dispersion $E(\mathbf{q})$ for 1 ML Fe in different environments, Fig. 3. The unsupported monolayer (UML) of Fe(001) at the W(001) lattice constant is an example of a system dominated by $J_1$; i.e., the FM state is the ground state, the $c(2\times 2)$-AFM state is unstable, and the RW-AFM state is metastable, with large energy differences among them. From a fit based on the Heisenberg model, we obtain the exchange constants and find $J_1 = 17$ meV and $J_1 \gg J_i$, for $i > 1$, in good agreement with the frozen magnon calculation of Ref. [18]. For 1 ML Fe/W(001) the hybridization with the substrate modifies the electronic structure. The dispersion is reversed, with the minimum at the $\bar{M}$ point. This implies that $J_1$ is again the leading term, but with a negative sign: $J_1 = -26$ meV.

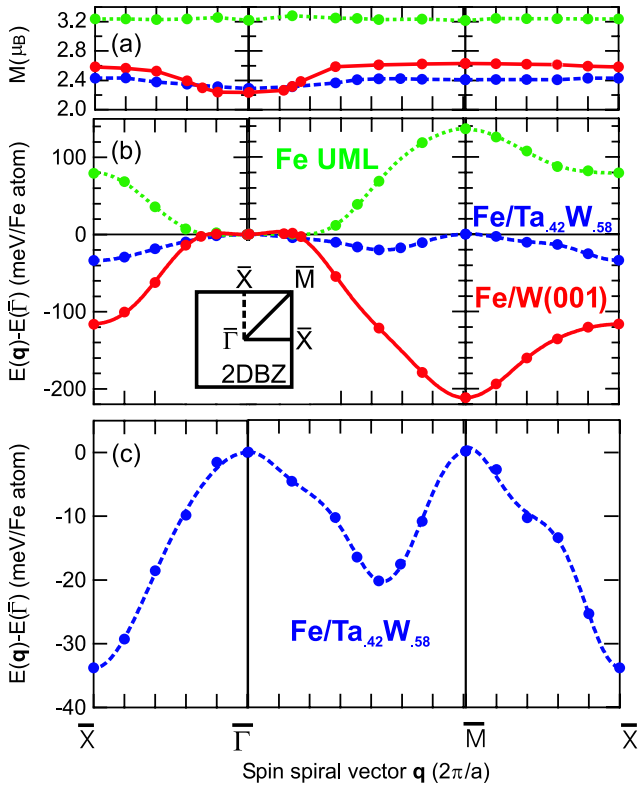


FIG. 3 (color online). (a) Magnetic moment and (b) energy dispersion for spin spirals of an Fe UML at the W(001) lattice constant (dotted green line), 1 ML Fe/W(001) (solid red line), and 1 ML Fe/$Ta_{0.42}W_{0.58}$ (001) (dashed blue line). (c) Dispersion for 1 ML Fe/$Ta_{0.42}W_{0.58}$ (001) on a larger scale. Symbols denote *ab initio* calculations and lines are Heisenberg fits.

However, for 1 ML Fe/$Ta_{0.42}W_{0.58}$(001) the dispersion is strikingly different from the two previous cases. Since $J_1 \approx 0$ for this particular substrate composition, the FM and $c(2\times 2)$-AFM states are degenerate and the energy scale is strongly reduced; see Fig. 3(b). Interestingly, a metastable spin-spiral state is found along the $\bar{\Gamma}$-$\bar{M}$ direction, 20 meV/Fe-atom lower than the FM one, Fig. 3(c). The RW-AFM state is the global energy minimum. The fit of the dispersion reveals that the leading interaction is $J_2 = -6$ meV and the system is in the lower left part of the $p(2\times 1)$ region in the phase diagram of Fig. 2(b).

Because of the surface symmetry, there are two equivalent $\bar{X}$ states in the Brillouin zone [see inset of Fig. 3(b)], corresponding to two degenerate $p(2\times 1)$-AFM configurations with perpendicular orientations of the ferromagnetically coupled rows. Any superposition of these two spin spirals, a so-called multi-$Q$ state, is a degenerate solution of the Heisenberg Hamiltonian. However, the degeneracy with the $p(2\times 1)$-AFM state can be lifted by higher order interactions beyond the Heisenberg model, such as the four-spin and the biquadratic ones [19].

Such interactions are implicitly included in the exchange-correlation potential, and we can evaluate their magnitude from first principles. We performed calculations in the $p(2\times 2)$ unit cell rotating the moments on all sites by an angle $\alpha$ as depicted in the inset of Fig. 4. $\alpha = 0°$ corresponds to the RW-AFM state while for $\alpha = 45°$ we obtain the $2Q$-state, a 2D noncollinear structure with perpendicular adjacent moments. Since all these states are degenerate within the Heisenberg model, the total energy difference depends only on higher order interactions. We find that noncollinear states gain energy on the order of 5 meV due to these interactions, the minimum being at

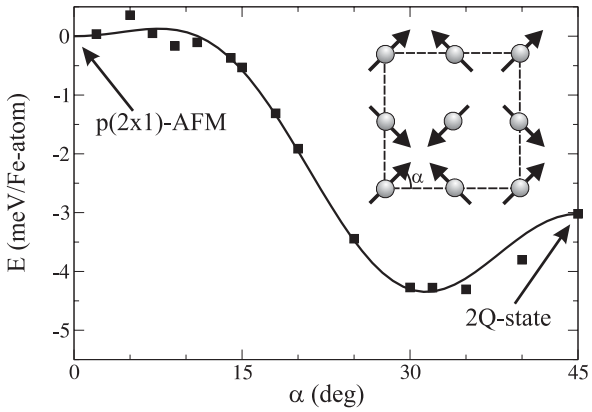


FIG. 4. Total energy of the configuration depicted in the inset for 1 ML Fe/$Ta_{0.42}W_{0.58}$ (001), as a function of the angle $\alpha$.

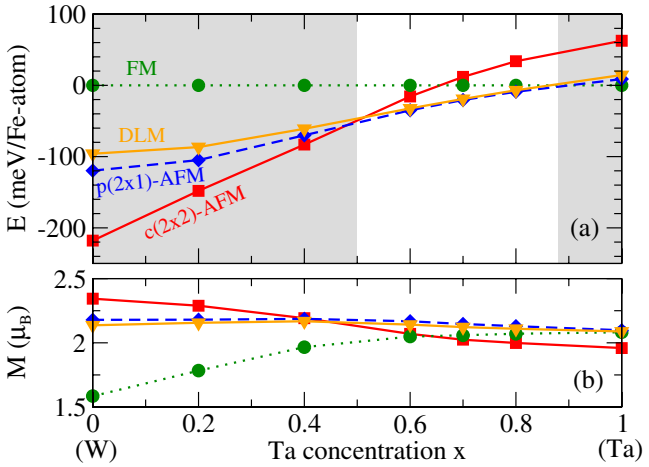


FIG. 5 (color online). (a) Total energy and (b) magnetic moment for 1 ML $Fe/Ta_xW_{1-x}$ (001) as a function of the Ta concentration $x$, as obtained with the TB-LMTO method.

$\alpha = 31°$. The fitting revealed that even terms beyond the biquadratic and four-spin interactions are present in this system. The moment arrangement can be slightly modified by the magnetocrystalline anisotropy. E.g., an out-of-plane easy axis with an anisotropy energy on the order of 2 meV, similar to that of 1 ML Fe/W(001) [7], would decrease $\alpha$ from 31° to about 20°, based on Fig. 4, but would not prevent the noncollinear order.

The small energy scale found in the spin spiral and in the $2Q$-state calculations for 1 ML $Fe/Ta_{0.42}W_{0.58}(001)$ indicates that only a small amount of energy is required to rotate the magnetic moments and that there is a competition between several magnetic interactions. This suggests a frustrated system. Under these circumstances, the disordered local moment (DLM) state with local moments pointing in random directions and zero net magnetization needs to be considered. We have evaluated its energy using the tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic sphere approximation within the framework of the coherent-potential approximation (CPA) [20,21]. Concerning the magnetically ordered states, we found that for small, intermediate, and large Ta concentrations the ground state is $c(2 \times 2)$-AFM, $p(2 \times 1)$-AFM, and FM, respectively, (Fig. 5). The qualitative agreement between FLAPW-VCA and TB-LMTO-CPA proves that the VCA is a good approximation to the CPA for the treatment of the alloy. Interestingly, for intermediate compositions the DLM and the $p(2 \times 1)$-AFM states are degenerate, within the computational accuracy. Note that the DLM state is often encountered as a spin-glass-like ground state in disordered bulk alloys, such as fcc $Ni_{0.80}Mn_{0.20}$ [22]. All important conditions for the spin-glass (SG) arrangement, namely, competing ferro- and antiferromagnetic exchange interactions accompanied by chemical and/or topological disorder [23], are fulfilled in the present case owing to the random Ta-W substrate. At around $x = 85\%$ Ta concentration, the SG, FM, and $p(2 \times 1)$-AFM states are degenerate. This offers the great perspective of imprinting magnetic information as nanoscale dots. E.g., cooling down the dot, after local heating at elevated temperatures, with or without an external magnetic field allows to select the FM or the zero-magnetization SG state.

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