Spin-Flop Ordering from Frustrated Ferro- and Antiferromagnetic Interactions: A Combined Theoretical and Experimental Study of a Mn/Fe(100) Monolayer

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The occurrence of a noncollinear magnetic structure at a Mn monolayer grown epitaxially on Fe(100) is predicted theoretically, using spinor density-functional theory, and observed experimentally, using x-ray magnetic circular dichroism (XMCD) and linear dichroism (XMLD) spectroscopies. The combined use of XMCD and XMLD at the Mn-absorption edge allows us to assess the existence of ferromagnetic and antiferromagnetic order at the interface, and also to determine the moment orientations with element specificity. The experimental results thus obtained are in excellent agreement with the magnetic structure determined theoretically.

The magnetic structure of ultrathin antiferromagnetic (AFM) overlayers on ferromagnetic (FM) substrates determines the properties of ferromagnetic and antiferromagnetic multilayers that are key constituents of devices such as exchange-bias or tunneling magnetoresistance recording systems. Complex, noncollinear, magnetic structures are expected at these interfaces, for spin canting minimizes the exchange energy between a ferromagnet and an antiferromagnet that exposes a plane with antiparallel spins [1]. The resulting *spin-flop* alignment of the moments in the antiferromagnet, perpendicular to the magnetization in the ferromagnet, is the microscopic basis of the large coercive field in exchange-bias devices [2,3]. In spite of the great interest in these systems, the understanding gained so far on the basis of semiempirical models has not been validated by accurate first-principles calculations, nor by a direct experimental observation of the noncollinear magnetic order at the interface. In fact, on one hand, accurate, fully unconstrained, methods based on density-functional theory (DFT) for studying noncollinear magnetic structures have become available only recently [4–6]; on the other hand, the simultaneous access to both antiferromagnetic and ferromagnetic ordering, not possible by usual experimental methods, has become possible by magnetic circular and linear dichroism methods, using advanced synchrotron sources.

Thin films of Mn on Fe(100) represent an interesting case where unusual magnetic structures can occur. For Mn coverages larger than 2 monolayers (ML), an antiferromagnetic coupling between adjacent Mn layers was found by spin-polarized electron energy loss spectroscopy [7] and by spin-polarized scanning tunneling spectroscopy and microscopy [8,9]. In the monolayer and submonolayer regimes the magnetic structure is expected to be dominated by the frustration arising between competing ferromagnetic and antiferromagnetic interactions. DFT calculations indicate that Mn-Mn interactions in the overlayer evolve from FM in the diluted (low-coverage) limit [10] to AFM at a coverage of 1 ML [11]. This behavior was observed experimentally using spin-resolved core level photoemission [12] and confirmed by x-ray magnetic circular dichroism [13]. The possible occurrence of a noncollinear spin order at the interface was suggested on the basis of simplified DFT calculations [14].

The aim of this work is to determine the magnetic structure of Mn deposited on Fe(100) in the monolayer regime, using state-of-the-art theoretical and experimental techniques. Mn/Fe(100) has been simulated using fully unconstrained spinor density-functional theory (SDFT), which allows for a proper account of noncollinear magnetic structures [4–6]. This same system has then been investigated experimentally by means of a combination of x-ray magnetic circular dichroism (XMCD) and x-ray magnetic linear dichroism (XMLD) spectroscopies, which allows for a direct assessment of ferromagnetic and antiferromagnetic ordering, and also for a determination of the moment orientations with chemical sensitivity.

Our SDFT calculations have been performed within the local density approximation [15] and neglecting spin-orbit interactions. The latter approximation makes the calculated magnetic structures degenerate with respect to an arbitrary overall rotation of the magnetization field. At low pressure and temperature iron has a ferromagnetic body-centered-cubic structure, while manganese is orthorhombic with a complex antiferromagnetic order. It turns out that the equilibrium structure of a Mn monolayer is also

antiferromagnetic. By constraining all the magnetic moments to be collinear (which amounts to performing a conventional local spin-density calculation) a Mn overlayer on Fe can assume one of three distinct configurations: in the *ferromagnetic* structure all the Mn magnetic moments are parallel to each other and to the magnetization of the ferromagnetic iron substrate; in the second, *antiferromagnetic,* structure the Mn magnetic moments are antiparallel with respect to the substrate magnetization; the third, *ferrimagnetic* (FI), structure is finally characterized by an antiferromagnetic arrangement of atomic moments in the overlayer, which result alternatively parallel or antiparallel to the substrate magnetization. It is interesting to notice that the inequivalence of spin-up and spin-down atoms in the overlayer may determine some buckling in the surface.

In Fig. 1 (top) we report the energies of the various magnetic structures relative to the energy of the FM structure. As a consequence of the stability of the antiferromagnetic order of an isolated Mn monolayer, and in agreement with previous studies [11], we find that among these three structures the FI one is the most stable. The largest stability of this structure implies that half of the Fe-Mn magnetic bonds across the interface is frustrated, whether or not these bonds are preferentially ferromagnetic or antiferromagnetic. The FM structure is actually slightly more stable than the AFM one, indicating that the exchange interaction between Mn and Fe atoms is preferentially ferromagnetic. In Fig. 1 (bottom) we report the magnitude of the calculated atomic moments, defined as the integral of the magnetization inside a sphere centered on the atoms and with a radius equal to the nearest neighbor distance. We note that in the FI structure the Mn surface layer has nearly zero total magnetization, in accordance with the experimental findings of Ref. [13].

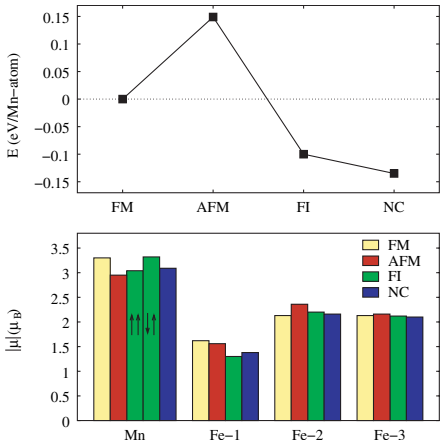

FIG. 1 (color). Top panel: total energies of the FM, AFM, FI, and NC structures relative to the FM structure. Bottom panel: magnitude of the atomic magnetic moments in the various structures. For the FI structure ↑↑ and ↑↓ indicate the Mn atom with magnetic moment parallel and antiparallel to the underlying Fe atoms, respectively.

When the constraint of spin collinearity is released, the frustration of the magnetic bonds across the interface drives a rotation of the Mn moments resulting in a chessboard arrangement where these moments form angles of $\approx \pm 80°$ with respect to those of the underlying Fe atoms [17]. This noncollinear (NC) structure is depicted in Fig. 2. We note that, with such an arrangement, the magnetic interactions between Mn and Fe are the same for all the Mn atoms, which are therefore all structurally equivalent. The almost perpendicular orientation of the Mn moments corresponds to a quasi-antiferromagnetic order in the Mn plane, still avoiding the magnetic frustration experienced in the collinear situations. We find that this NC structure is more stable by about 35 meV/atom than the FI collinear structure (see the top panel of Fig. 1), and should therefore be clearly observable also at room temperature. The departure from a 90° orientation is small, but possibly significant. In fact, as reported above, among the collinear structures the FM one is slightly more favorable than the AFM one, and this may be the cause of the small ferromagnetic bias in the NC structure.

Using XMCD and XMLD at the Mn $L_{2,3}$ edges we examined the magnetic structure of submonolayer and monolayer (0.1–1.0 ML) Mn films deposited on Fe(100). The samples were grown *in situ* in the 10^{-10} mbar range using a quartz-crystal microbalance to control the thickness. As a first step, an Fe(100) surface was epitaxially grown on a clean and ordered Ag(100) single crystal surface [18] and magnetized in remanence along the Fe[001]. The thickness of the Fe film was above 50 ML in order to suppress Ag surface segregation. A wedge of Mn in the range of 0–1.1 ML was prepared. The experiments were performed at the 4.2 beam line "Circular Polarization" at the ELETTRA storage ring, using approximately 95% linearly or 70% circularly polarized light and were collected in the total electron yield mode.

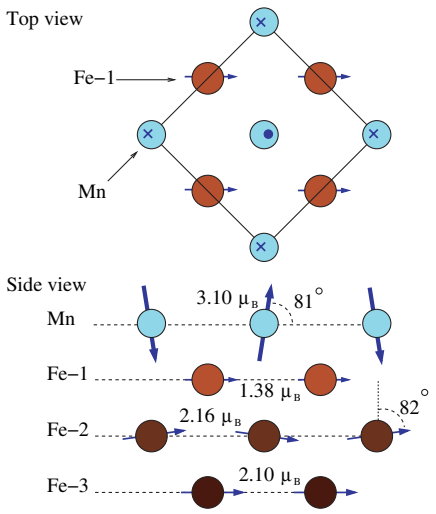

FIG. 2 (color). Schematic view of the Mn/Fe magnetic interface.

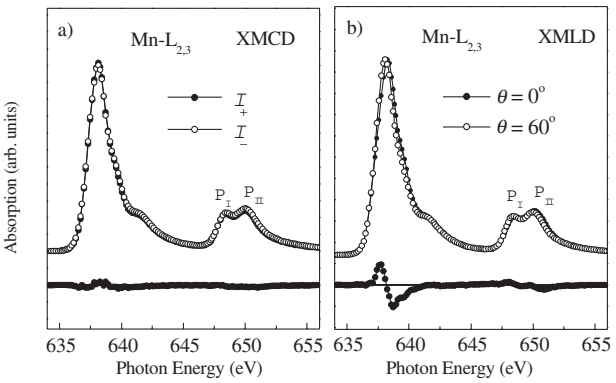

FIG. 3. (a) XMCD data at the $L_{2,3}$ edges for 1 ML of Mn. (b) Mn $L_{2,3}$ x-ray-absorption spectroscopy for 1 ML of Mn as a function of the angle θ between $\boldsymbol{E}$ and the surface normal. The difference spectra are plotted at the bottom.

The magnetization of Mn was investigated by circular dichroism. The XMCD data measurements performed at different Mn thicknesses for the submonolayer regime (not shown here) are in accordance with Rader *et al.* [13] and Dresselhaus *et al.* [19]. For less than 1 ML we observe an XMCD effect of the Mn adlayer opposite to that of Fe, which is a proof of long-range ferromagnetic order of the adlayer aligned antiparallel to the magnetization in the Fe substrate. The net magnetization of Mn decreases with increasing thickness and approaches zero for 1 ML, thus pointing out a rather smooth transition from a ferromagnetic to an antiferromagnetic arrangement. The XMCD data measured on 1 ML are reported in Fig. 3(a).

The XMLD was obtained by keeping the direction of the electric vector $\boldsymbol{E}$ of the incident linearly polarized light fixed in space and rotating the sample as illustrated schematically in Fig. 4. Since the XMLD effect is maximized when the magnetization is switched between parallel and perpendicular to the photon polarization, the sample was rotated in the polar geometry [Fig. 4(a)]. Finally, the sample was rotated in the azimuthal geometry [Fig. 4(b)]. The absorption edges recorded for in-plane and for out-of-plane polarization (polar rotation) are shown in Fig. 3(b). The features of these spectra can be identified with multiplet structures in a high-spin state with predominant Mn-$3d^5$ configuration, suggesting a local magnetic moment larger than $3.5\mu_B$. We note that DFT calculations may underestimate the magnetic moment in the case of Mn [20].

The intensity ratio between the L_2 well defined double peak structures (labeled as P_{I} and P_{II}) turns out to be well suited to detect the spectral changes. The intensity ratios for the two rotation geometries, reported in Fig. 4, show that the polar measurement has a regular dependence as a function of the angle, while the azimuthal one is much less pronounced. This indicates that the magnetic moments have preferential alignment with respect to the surface plane. The analysis of the $P_{\mathrm{I}}/P_{\mathrm{II}}$ intensity ratios, as discussed below, supports the idea that the orientation is perpendicular to the surface [21].

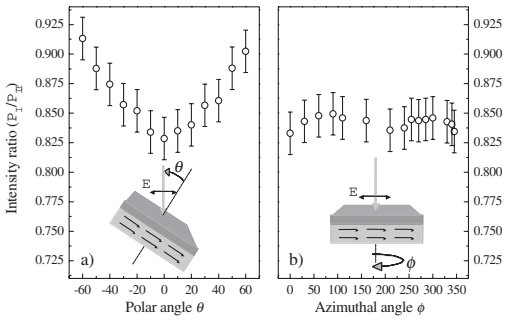

FIG. 4. XMLD effect (a) for the polar and (b) for the azimuthal rotations. The intensity ratio of the Mn L_2 double peak structures is used to measure the intensity of the effect.

We have simulated the spectral line shapes by exact diagonalization of an atomic many-body Hamiltonian, based on a fully coherent spectral function given by

$$I_q(\omega) = \Sigma_n |\Sigma_{v,c} \langle \Psi_f^n(N) | a_v^\dagger a_c | \Psi_G(N) \rangle \langle v | r C_q^{(1)} | c \rangle|^2 \times \delta(\hbar\omega - [E_f^n(N) - E_g(N)]).$$

The irreducible components of the dipole operator are defined as $T_q^{(1)} = rC_q^{(1)}$, where $q = 0, +1, -1$ correspond to z linearly polarized, right circularly polarized, and left circularly polarized light, respectively, and $C_q^{(1)}$ are normalized spherical harmonics [22,23].

In Figs. 5(a) and 5(b) we show the results of the spectral simulations. By using different combinations of the irreducible components of the dipole operator $T_q^{(1)}$, we are able to simulate the Mn $L_{2,3}$ spectra as a function of the orientation between the magnetic moment on Mn and $\boldsymbol{E}$: I_0 for $\boldsymbol{E} \parallel \boldsymbol{\mu}$ and $\frac{1}{2}(I_+ + I_-)$ for $\boldsymbol{E} \perp \boldsymbol{\mu}$. In terms of the line shape, the agreement with the experimental spectra of

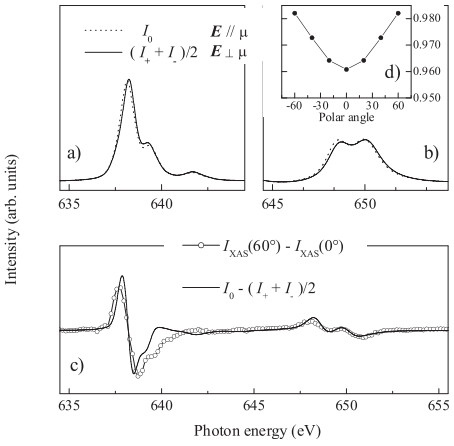

FIG. 5. (a),(b) Simulation of the absorption spectra for the two polarization directions after suitable broadening. (c) Comparison between the simulated and the experimental XMLD. (d) Simulated $P_{\mathrm{I}}/P_{\mathrm{II}}$ intensity ratio.

Fig. 3(b) is very good. Remarkably, also the calculated spectra display the line shape modifications (changes in the relative peak intensities and relative peak energy positions) that have been detected experimentally. As shown in Fig. 5(c), the XMLD spectrum, which carries all information about the line shape changes, is well reproduced by the simulated XMLD line shape calculated as $I_0 - \frac{1}{2} \times (I_+ + I_-)$. The calculated $P_{\mathrm{I}}/P_{\mathrm{II}}$ intensity ratio, assuming perpendicular orientation of the Mn moments with respect to the surface plane, also simulates the angular dependence of the experimental results. We can conclude that the magnetic moments of Mn are aligned out of the surface plane, perpendicular to the Fe magnetization.

It is known from the experimental works in Refs. [8,9] that in thicker Mn(100) films the layers are coupled antiferromagnetically to each other. The growth of Mn over a step edge of the substrate gives rise to a topological frustration among adjacent layers with opposite magnetization direction [8]. The magnetic frustration is, in such a case, relaxed through the formation of a narrow and magnetically noncollinear structure, similar to a 180° domain wall, with a lateral extension of the order of a few nanometers. In the present case, instead, the noncollinear magnetism of the system intrinsically derives from the competing exchange interactions between the monolayer and the substrate moments, and therefore uniformly extends over a macroscopic area. This mechanism may also lead to the development of similar spin-flop structures in other monolayer systems, where the exchange interaction within the antiferromagnetic monolayers prevails, but does not overwhelm, the coupling with the ferromagnetic substrate.

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[15] Our calculations have been performed using ultrasoft Vanderbilt pseudopotentials [16] and plane waves with a cutoff of 408 eV. Surfaces have been modeled using symmetric slab geometry, with 7 atomic layers of Fe and Mn adsorbates on both sides of the slab, and a vacuum region corresponding to 6 atomic layers. The primitive cell used in our calculations contained two surface atoms, with $c(2 \times 2)$ geometry. Integration inside the Brillouin zone has been performed by summation over 18 uniformly spaced surface **k** points, and/or a smearing function of 0.068 eV affected the magnitude of the calculated magnetic moments by $\sim 0.02 \mu_B$ and their directions by a fraction of a degree. Calculations have been performed using the PWSCF code, distributed with the Quantum ESPRESSO package (www.pwscf.org and www.quantum-espresso.org).

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[17] We have performed several calculations starting from different initial magnetic configurations. All these calculations finally converged to either one of the three collinear magnetic structures described in the text, or to a noncollinear structure in which the Mn adlayer has an almost antiferromagnetic arrangement, as described in the text.

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[22] The atomic many-body Hamiltonian involves the on-site energies of the Mn $2p$ and $3d$ levels, full multiplet Coulomb interaction within the Mn $3d$ manifold and between the Mn $2p$ and $3d$ manifolds and spin-orbit interaction in the Mn $3d$ and $2p$ levels [23]. Additionally, we have used a Zeeman field (coupling to both the spin and orbital moments) of 7 Tesla and an exchange (spin-only) field of 10 meV or 173 Tesla to simulate the exchange coupling between the magnetic ions in the system. The average Mn $3d$-$3d$ multiplet interaction (U_{dd}) was chosen to be 4.0 eV. The Slater-Condon multiplet parameters used in the calculation were taken from Ref. [24] and were scaled to 75% of their atomic values to take into account screening effects of the metallic host. As is customary, the Mn $2p$-$3d$ average multiplet interaction (U_{pd}) was chosen to be $1.1 U_{dd} = 4.4$ eV.

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