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].

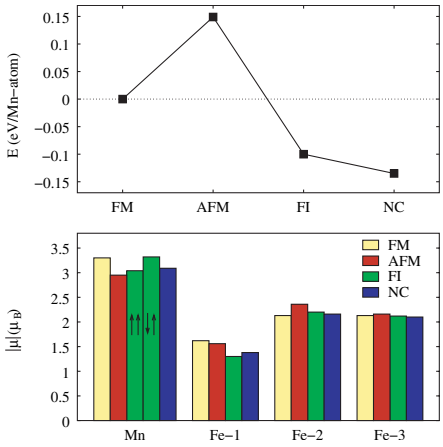

FIG. 1 (color). Top panel: total energies of the FM, AFM, FI, and NC structures relative to the FM structure. Bottom panel: magnitude of the atomic magnetic moments in the various structures. For the FI structure ↑↑ and ↑↓ indicate the Mn atom with magnetic moment parallel and antiparallel to the underlying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

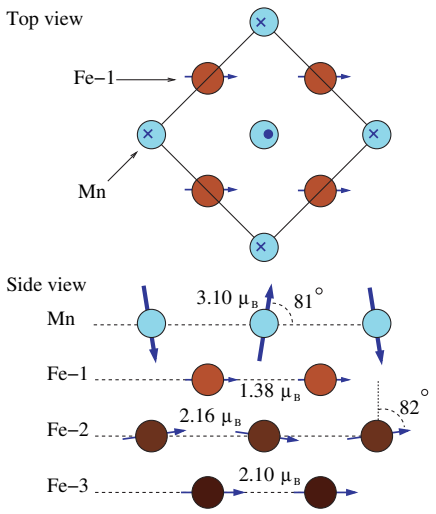

FIG. 2 (color). Schematic view of the Mn/Fe magnetic interface.