Predicted $c(2 \times 2)$ buckling reconstruction of monolayer Mn on Fe(001) and its importance to the interfacial magnetic ordering

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The structural, electronic, and magnetic properties of a Mn monolayer on Fe(001) have been investigated using total energy and atomic forces calculated with the local density full potential linearized augmented plane wave method. A strong interplay between magnetism and atomic structure was observed. The antiparallel alignment in the Mn plane of the large (3.1 μ_B) magnetic moment is found to drive a $c(2 \times 2)$ buckling reconstruction in the Mn overlayer. Due to hybridization with the magnetic Fe(001) substrate, the valence bands of the two different Mn atoms differ substantially; however, the net magnetic circular dichroism signal for the Mn overlayer is predicted to be almost zero.

Cr/Fe(001) (Refs. 1 and 2) and Mn/Fe(001) (Refs. 3 and 4) overlayer systems have attracted increasing attention very recently, due to their importance in understanding the magnetic coupling between Fe thin films through Cr and Mn intervening layers.[5] For thicker films, Cr and Mn magnetic moments are found to align antiferromagnetically along the (001) direction with a period of 2 ML at temperatures both below and above their bulk Néel temperatures.[1,2] In the (001) plane, ferromagnetic (FM) ordering between Cr or Mn atoms forms, because of the strong magnetism in the Fe(001) substrate. However, when the thickness of the overlayer decreases down to the single monolayer regime, in-plane antiferromagnetic (AFM) coupling is expected, since this mode has been found to be much more stable energetically than the FM one in free standing Cr and Mn monolayers and even in the Cr/Ag(001) and Cr/Pd(001) overlayer and sandwich systems.[6] Indeed, recent spin-polarized core level spectroscopy[7] and magnetic circular dichroism (MCD) measurements[8] for monolayer Cr/Fe(001) found that the Cr magnetic moment is significantly smaller than the calculated value (0.6-1.0μ_B vs 3.6μ_B) using a model with FM Cr sheets[9]—indicating a possible in-plane AFM coupling.

In this paper, we demonstrate that a strong interplay exists between the in-plane AFM coupling and a $c(2 \times 2)$ buckling reconstruction for the monolayer Mn/Fe(001) system, using the atomic force approach based on the local spin density full potential linearized augmented plane wave (FLAPW) method.[10] A well-optimized interfacial structure, especially the unusual overlayer buckling, is found to be essential for the determination of the magnetic ground state. Interestingly, although the net magnetic moment in the Mn overlayer is very small ($\sim$ 0.08μ_B/atom), considerable energy band splitting (e.g., 0.8 eV for the unoccupied minority spin states) can be found between the two kinds of Mn atoms due to the hybridization with the magnetic Fe(001) substrate. Nevertheless, there is almost no net MCD signal from the Mn overlayer since their core levels undergo the same energy shifts.

The Kohn-Sham equations are solved self-consistently in the FLAPW approach for a nine layer slab geometry [with a seven layer Fe(001) and a pseudomorphic Mn monolayer on each side of the slab]. While the lattice constant in the lateral plane is chosen from experiment (a = 5.416 a.u.), the vertical positions of all the atoms are optimized according to their atomic forces.[11] To consider the possible buckling reconstruction, a $c(2 \times 2)$ supercell is used throughout the calculations for the three magnetic configurations sketched in Fig. 1. An energy cutoff of 12 Ry is used for the variational plane wave basis set. Within the muffin-tin (MT) spheres (r_{MT} =2.15 a.u.), lattice harmonics with an angular momentum l up to 8 are employed to expand the charge density, potential, and wave functions. Summations over 15 k points in the irreducible 2D Brillouin zone are employed for k-space integrations. As used in almost all of our previous calculations,[6] these parameters have been proved to be

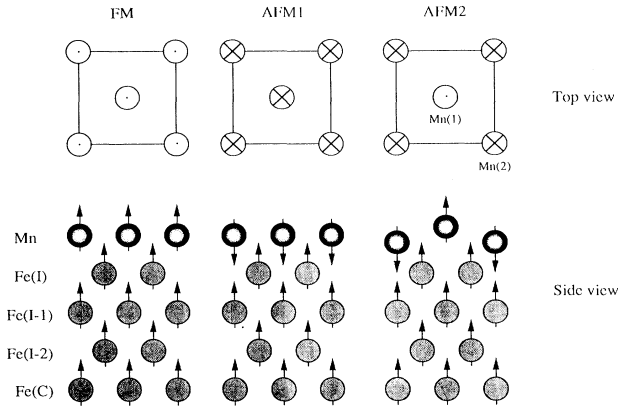

FIG. 1. Model and notation for the structural parameters for (a) FM, (b) AFM1, and (c) AFM2 configurations of Mn/Fe(001).

sufficient for three-dimensional (3D) transition metal systems.

The Mn monolayer is known to be AFM with a giant magnetic moment of $4.32\mu_B$.[6] It is thus expected that the magnetic moments in the Mn overlayer align antiparallel when it is far from the Fe(001) substrate. Indeed, we found that the AFM2 state lies lower in energy than the FM and AFM1 states when the interatomic distance $d_{\mathrm{Mn-Fe}}$ is larger than 4.4 a.u. By including the effects of multilayer relaxation and reconstruction, as listed in Table I, the total energy minimum of the AFM2 state is about 23 mRy/cell (or 78 meV per Mn atom) lower than those for the FM and AFM1 states. This large energy difference indicates unambiguously that the AFM2 state is the ground state for Mn/Fe(001).

Significantly, we predicted a detectable buckling reconstruction in the Mn overlayer by 0.12 a.u. and a small induced buckling (0.03 a.u.) in the Fe(I-1) layer for the AFM2 ground state. The driving force for this reconstruction is obviously from the AFM coupling in the Mn overlayer, since the Mn-Fe bond length changes when different magnetic alignment is adopted. This can be clearly seen from Table I, where the Mn-Fe interlayer distance in the AFM1 state (in which the Mn and Fe couple antiferromagnetically) is about 0.13 a.u. shorter than that in the FM state. Physically, following Oguchi and Freeman,[12] a shorter bond length increases the exchange splitting for the AFM coupling, which reduces the band energy in cases with a less than half-filled d band. For the FM case, the shorter bond length increases the bandwidth that has a smaller effect on the band energy. [It may be interesting to note that a similar buckling driven by the magnetic alignment was also found in the Mn/Cu(001) $c(2\times 2)$ surface alloy layer,[13] which releases an energy of as much as 0.1 eV per Mn atom].

On the other hand, we found that almost all the Fe atoms are displaced from their ideal bcc positions. Even the interlayer distance between Fe(C)-Fe(I-2) layers, $d_Fe(C) - \mathrm{Fe(I-2)} \approx 2.60$ a.u., exhibits a 4.4% contraction compared to that in bcc bulk Fe, d=2.708 a.u. This may be due in part to lattice strain imposed through the use of the experimental lattice constant (5.41 a.u.) in the lateral plane, instead of that optimized in LDA calculations (5.21 a.u.).[14] Interestingly, the equilibrium Fe(I)-Fe(I-1) distance is about 2.52–2.55 a.u., which is smaller than the distances between the interior layers (2.60 a.u.), but is larger than that on the clean Fe(001) surface (2.40 a.u.). This means that, as expected, the Mn overlayer partially restores the surface relaxation on Fe(001).

In the ground state, as also listed in Table I, the magnetic moment of the interfacial Fe(I) atom is substantially diminished to only $1.35\mu_B$, due to the strong overlayer-substrate exchange interaction. This is also obvious from the density of states plotted in Fig. 2 for the Fe(I) atom, where a considerable amount of majority spin states is seen to have been shifted above E_F. On the other hand, the cancellation between the antiparallel aligned magnetic moments of Mn(1) ($3.10\mu_B$) and Mn(2) ($-3.26\mu_B$) results in a very small net magnetic moment in the Mn overlayer ($\sim 0.08\mu_B$ per Mn atom). Unlike the case of nonmagnetic substrates,[6] however, the valence bands for Mn(1) and Mn(2) in Fig. 2 still differ remarkably, due to hybridization with the magnetic Fe substrate. Specifically, their unoccupied minority spin peaks separate in energy by 0.8 eV, which should be easily detected using inverse photoemission. This "magnetic signal" in the AFM Mn overlayer is of great interest, because it shows that very different conclusions may be drawn from experiments that use different techniques.

To resolve the signals for the Mn overlayer from that of the Fe(001) substrate, the newly developed magnetic circular dichroism (MCD) technique is the natural choice, because of its high element selectivity.[15] In Fig. 3(a), the calculated MCD spectra at the L edges (represented by the difference of the cross sections for left- and right-circularly polarized incident light beams) are presented for the buckled AFM2 Mn/Fe(001). Corresponding to the high peaks above E_F in Fig. 2, strong separate MCD signals σ_m are obtained for Mn(1) (dashed line) and Mn(2) (solid line). The energy separation between the L_3 and L_2 peaks, 10.4 eV, corresponds to the spin-orbit coupling induced splitting between $2p_{\frac{1}{2}}$ and $2p_{\frac{3}{2}}$ levels. As was also found for bulk Fe,[16] the presence of majority spin holes in Fig. 2 results in blips with opposite sign to the corresponding main peaks at the onsets

TABLE I. Calculated equilibrium vertical position (z, in a.u., measured from the center plane) and spin magnetic moment (M, in μ_B) of each atom and the total energies of the FM, AFM1, and AFM2 states for Mn/Fe(001). Data in parentheses for Fe(I-1) in the AFM state denote the results for the atom under Mn(2).

Atom	Fe(C)	Fe(I-2)	Fe(I-1)	Fe(I)	Mn(1)	Mn(2)
FM			$E = -44826.144$ Ry			
z	0.00	2.59	5.19	7.71	10.31	10.31
M	2.26	2.21	2.17	1.64	3.30	3.30
AFM1			$E = -44826.143$ Ry			
z	0.00	2.59	5.19	7.71	10.18	10.18
M	2.17	2.18	2.31	1.46	−3.21	−3.21
AFM2			$E = -44826.167$ Ry			
z	0.00	2.60	5.23(5.20)	7.77	10.32	10.20
M	2.26	2.20	2.24(2.28)	1.35	3.10	−3.26

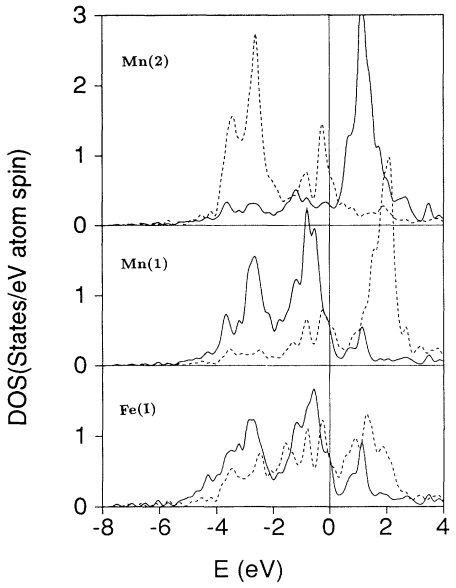

FIG. 2. The projected density of states in the Mn(2), Mn(1), and Fe(I) muffin-tin spheres for the buckled AFM2 state of Mn/Fe(001). Solid (dashed) lines represent the majority (minority) spin.

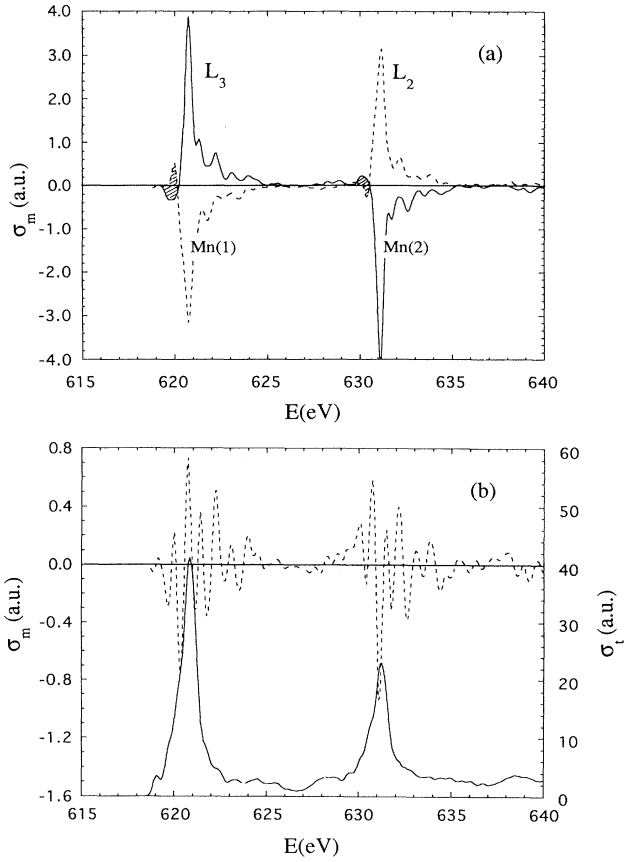

FIG. 3. The calculated (a) MCD spectra for Mn(1) (dashed curve) and Mn(2) (solid curve), and (b) the net total MCD [i.e., the sum of the two contributions in panel (a), the left scale, dashed curve], and XAS (the right scale, solid curve) for the buckled AFM2 Mn/Fe(001).

of the L_3 and L_2 edges for both Mn(1) and Mn(2) atoms [shown as shaded region in Fig. 3(a)].

Surprisingly, despite the large exchange splitting between their valence bands, the x-ray absorption edges for Mn(1) and Mn(2) shift to almost the same energy position shown in Fig. 3(a). This results from the fact that the $2p$ core levels of Mn(1) are also 0.7 eV higher than those of Mn(2). As a result, the net MCD spectrum [i.e., the sum of the separate contributions from Mn(1) and Mn(2) atoms] becomes a strong oscillatory function of the photon energy—shown as the dashed curve in Fig. 3(b). The net σ_m is only less than 4% of σ_t in magnitude, and thus is almost undetectable when Gaussian broadened for instrumentation and Lorentzian broadened for lifetime effects are included.

Finally, the magnetic properties of Mn/Fe(001) [and also Cr/Fe(001)] are expected to be very sensitive to the film thickness. In the submonolayer regime, the in-plane Mn-Mn coupling is weakened and thus the Mn-Fe interaction plays the dominant role. As a result, parallel alignment of the Mn moments (FM sheet, with an opposite orientation to that of the substrate) should prevail in the lower coverage regime and change to antiparallel near monolayer coverage. For a bilayer Mn film, we found that the AFM coupling between Mn(S)-Fe(I) [note that Mn(I) couples ferromagnetically with Fe(I)] is favored in total energy after multilayer relaxation is considered.[17] The calculated magnetic moment for the Mn(S) layer is $-2.93\ \mu_B$/atom, which agrees essentially exactly with the measured value of $-2.9\mu_B$/atom.[4] Since the magnetic moment of Mn(I) ($1.21\mu_B$) is much smaller in magnitude, a detectable net x-ray magnetic circular dichroism signal is predicted for the antiferromagnetic Mn bilayer. Thus, an experimental test of our predictions in the ultrathin regime is desired.

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