

# Magnetism in thin Cr films grown on Fe(001)-*p*(1×1)O: a spin-resolved investigation of single and multi-layers

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## ABSTRACT

We present a combined experimental and theoretical investigation of the magnetic behavior of ultra-thin Cr films grown on oxygen-passivated Fe(001)-*p*(1×1)O substrates. In all cases, oxygen floats on the metal/vacuum interface, where a monolayer-range oxide with peculiar electronic and structural characteristics is formed. Significant differences with previous experimental realizations of the Cr/Fe(001) heterostructure are thus introduced by the presence of oxygen. However, we show here that the magnetic behavior of our system is characterized by the same AF stacking at the Cr-Fe interface and by a layer-wise AF order in the Cr layer. In addition, we are able to circumvent the issue of chemical mixing at the Cr-Fe interface, characteristic of standard preparations.

**Keywords:** Chromium, Iron, antiferromagnetism, spin-polarized photoemission, density functional theory.

## 1. INTRODUCTION

The magnetic properties of 3*d* transition metals and their surfaces are a classical topic of surface science. Thin Cr layers grown on Fe(001), in particular, are considered as model systems for the study of the magnetic interactions involved in the coupling between antiferromagnetic (AF) and ferromagnetic (FM) materials.<sup>1,2</sup> Specific phenomena related to such systems are the strong exchange coupling at the Cr/Fe interface (exploited, for instance, in spin valves)<sup>3,4</sup> and the development of giant magneto-resistance in Cr/Fe tri- and multi-layers (reading heads in hard disk drives).<sup>5,6</sup> Ultra-thin films can be realized with atomic precision by means of today's state-of-the-art technologies, such as molecular beam epitaxy (MBE), performed in ultra-high vacuum. However, also in these well-controlled conditions a number of kinetic and thermodynamic limitations might prevent the growth of such metallic systems in a perfect layer-by-layer mode, resulting in a rough morphology and chemically diffuse interfaces, and altering their magnetic response. In the case of Cr, the growth mode changes from islands formation to layer-by-layer within a relatively small temperature range,<sup>7</sup> namely by increasing the temperature of the substrate during deposition from room temperature (RT) to about 600 K. High temperature (HT) growth promotes, at the same time, Cr-Fe mixing and the formation of a diffuse (about 2-3 Cr layers) interface whose magnetic behavior is not precisely known.<sup>8</sup>

Our recent contributions to the field range from the study of different AF materials, such as 3*d* metal oxides,<sup>9</sup> to the addition of controlled amounts of oxygen to the growth recipes of a large number of magnetic heterostructures.<sup>10-13</sup> Regardless of its actual composition (either Fe or Cr), the presence of a passivating layer of oxygen induces deep modifications in the structural equilibrium of the surface, which usually relaxes by increasing the distance between the topmost layer and the subsurface ones.<sup>14</sup> On the bare Fe(001) substrate, a wurzite FeO-like structure is formed [hereinafter referred to as the Fe(001)-*p*(1×1)O surface], with O atoms occupying the fourfold hollow sites in between the surface Fe atoms.<sup>15</sup> On Cr, we detected a more complex surface reorganization, leading to the formation of an highly ordered network of Cr vacancies which creates a ( $\sqrt{5} \times \sqrt{5}$ )*R*27° superstructure in an otherwise perfectly square CrO lattice<sup>16</sup>. During HT Cr deposition on Fe(001)-*p*(1×1)O, Cr inclusion in the Fe matrix is limited to the relaxed FeO layer.<sup>17</sup> Oxygen binds to the Cr atoms and floats on the metal/vacuum interface<sup>18</sup> where a Cr oxide layer is eventually formed. Incidentally, due to a reduced kinetic barrier for ad-atom incorporation at surface steps and island edges during

Cr deposition, oxygen promotes a smoother morphology also at a lower substrate temperature (oxygen “surfactant” effect).<sup>12</sup>

According to first principles calculations,<sup>19</sup> the ideal (oxygen-free) Cr/Fe(001) interface is characterized by an AF alignment of the bottom Cr layer with the Fe substrate, and by layer-wise AF order within the Cr film.<sup>20</sup> In the following, we will illustrate the results of our recent photoemission experiment<sup>21</sup> showing that under specific growth conditions (involving the oxidation of the topmost Cr layer) it is indeed possible to observe an immediate onset of Cr magnetization oscillations at the Fe interface. The O/Cr(*N*)/Fe(001) system, with *N* ranging from 1 to 4 Cr layers, is then investigated by means of first-principles calculations. Information is provided about (i) the optimized equilibrium crystal structure and (ii) the electronic and magnetic properties.

## 2. EXPERIMENTAL AND COMPUTATIONAL METHODS

The Fe(001) substrate was prepared by growing a thick (about 100 nm) Fe film on insulating MgO(001).<sup>22</sup> The *p*(1×1)O surface was realized by dosing 30 L (1 L =  $1.33 \times 10^{-4}$  Pa · s) of O<sub>2</sub> on the Fe substrate kept at 700 K. The substrate was then flash heated to 900 K to desorb O in excess of 1 monolayer (ML), defined as the amount of atoms required to fully saturate the fourfold hollow sites of the square Fe(001) surface. The Fe and Cr layers were grown by metal sublimation from high purity rods with a deposition rate of about 0.05 Cr ML per minute, checked by means of a quartz microbalance. The pressure was kept in the low  $10^{-8}$  Pa during the metal deposition. After Cr deposition, the samples were magnetized *in-situ* along the Fe(100) direction by means of a coil. The photoemission spectroscopy (PES) measurements were then performed at RT in magnetic remanence. The PES apparatus includes a 150 mm hemispherical analyzer coupled to a micro-Mott detector for spin-resolved measurements.<sup>23</sup> A He discharge lamp was used as the photon source (He I photons at 21.22 eV). The photoemission spectra were acquired at normal photoelectron emission with an angular acceptance of  $\pm 6^\circ$  and a pass energy of 7 eV, yielding an overall resolution of about 300 meV full width at half maximum (FWHM).

Our calculations are based on density functional theory (DFT) in the generalized gradient approximation framework, as proposed by Perdew, Burke and Ernzerhof (GGA-PBE).<sup>24</sup> Specifically, we used the plane-wave code Quantum ESPRESSO<sup>25</sup> and ultrasoft pseudopotentials,<sup>26</sup> with the approach reviewed in Ref. 27. Pseudopotentials are generated starting from scalar-relativistic all-electron calculations with non-linear core corrections. In addition to *4s* and *3d* orbitals, also semi-core *3s* and *3p* orbitals are included in the calculations for Cr. Energy cutoffs are: 55 Ry for the wave functions and 280 Ry for the effective potential and the charge density. The Fe substrate is modeled by a four-layers slab, where the bottom two layers are fixed to the bulk positions with the computed lattice constant of bcc Fe ( $a_{\text{Fe}} = 2.832$  Å). Repeated slabs are separated by a 12 Å thick vacuum layer, and Cr and O are adsorbed on the top surface only. The atomic configuration is optimized by choosing a 14×14 Monkhorst and Pack<sup>28</sup> sampling of the (1×1) Fe(001) surface Brillouin zone. The magnetic moment of the atoms in the system and atom-projected density of states (DOS) are evaluated by projections on a set of Lowdin-orthogonalized atomic orbitals.

## 3. RESULTS AND DISCUSSION

### 3.1 Experimental Results

Figure 1 shows a series of spin-polarized PES spectra acquired on the Cr/Fe(001)-*p*(1×1)O surface for increasing Cr coverage. Generally speaking, features related to photoemission from *3d* states are expected to arise in a rather narrow energy region close to the Fermi energy ( $E_F$ ). While Fe and Cr features almost completely overlap within 1 eV from  $E_F$ , the peak located at a binding energy (BE) of 1.6 eV (marked with arrows in Figure 1) is not present on the bare substrate (bottom spectrum) and is therefore representative of photoemission from the sole Cr layer. Our spin polarized analysis (see Berti *et al.*<sup>23</sup> for more details) clearly shows an oscillating behavior of its spin character: the peak appears within the minority states at 1 ML and mainly within the majority states at about 2 ML, where the labels “majority” and “minority” refer to the substrate magnetization.

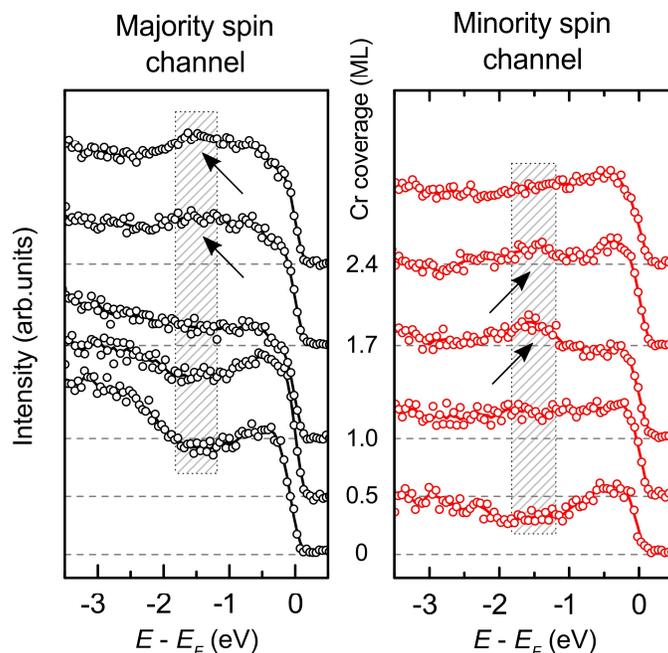


Figure 1. Spin resolved valence band spectra taken on the Fe(001)- $p(1\times 1)$ O substrate (bottom spectra) and on the Cr/Fe(001)- $p(1\times 1)$ O system for increasing Cr coverage (from the bottom to the top). Arrows mark the position of the feature at a binding energy of 1.6 eV (equivalent to an energy difference  $E-E_F$  of -1.6 eV) discussed in the text.

We define the spin polarization  $P$  of photoelectrons as  $P = \frac{I^+ - I^-}{I^+ + I^-}$ , where  $I^{+(-)}$  is the photoemission intensity measured in the majority (minority) spin channel of Figure 1. The polarization ( $P_s$ ) of the photoelectrons coming from the topmost surface layer is shown in Figure 2 for a BE of 1.6 eV. The Cr coverage is increased in steps of 0.1 ML, starting from the Fe substrate.  $P_s$  is obtained from the measured polarization  $P$ , by subtracting the polarization bias given by the Fe substrate and the subsurface Cr layers, according to the procedure explained by Berti *et al.*<sup>21</sup>

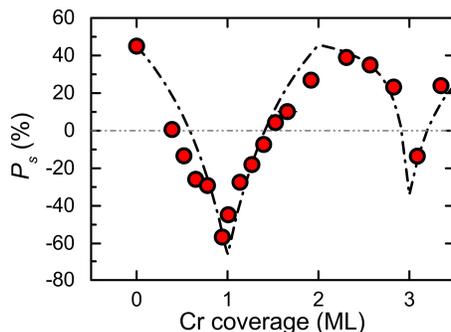


Figure 2. Polarization  $P_s$  of the electrons emitted from the topmost Cr layer with a binding energy of about 1.6 eV. Dot-dashed black line: expected behavior of  $P_s$  for fractional Cr coverages.

The extrapolated polarization rapidly decreases, reaching a clear minimum at 1 ML. Then an oscillation is established with minima/maxima at the ML completion. For larger coverages (not shown), the oscillations are smaller and the intensity of the polarization is not centered at zero, due to deviations from a perfect layer-by-layer growth in the Cr/Fe(001)- $p(1\times 1)$ O system.<sup>12</sup> According to the literature and within our experimental conditions the polarization of electrons photoemitted from the Fe(001)- $p(1\times 1)$ O surface at normal emission is parallel to the bulk magnetization.<sup>23,29</sup> For antiferromagnetic Cr, and in particular for the O-covered Cr surface, the same information is not available but we can reasonably assume that the extrapolated electron polarization at 1.6 eV is indeed parallel to the Cr surface magnetization. Following this assumption, we conclude that the topmost Cr layer is ferromagnetically ordered in-plane, with a relative orientation of its magnetization which depends on the number of Cr layer being even (parallel orientation with the substrate magnetization) or odd (antiparallel orientation). This result is consistent with our previous finding of

an antiparallel orientation of Cr magnetic moments with respect to the substrate magnetization up to a coverage of 1 ML on Fe(001)-*p*(1×1)O obtained by means of X-ray magnetic circular dichroism (XMCD).<sup>17</sup> Intermixing is expected to produce a Cr enriched interfacial region<sup>8</sup> AF coupled with the substrate, while surface roughening produces a reduced magnetization signal. A monotonic decay of the polarization signal was indeed observed in a number of past photoemission studies on the Cr/Fe(001) system,<sup>30,31</sup> and only very faint oscillations were detected in those cases where Fe-Cr intermixing was likely quenched.<sup>32</sup> In the present case, the clear onset of AF oscillations starting from the very interface (Figure 2) strongly supports an almost ideal layer-by-layer growth of the first Cr layers, enabled by the presence of oxygen.

### 3.2 First-principles results

Driven by the experimental result shown in Figure 2, we adopted a collinear spin configuration where all spins are aligned within the same atomic layer. For the 1 ML case, the AF coupling between the Cr layer and the underlying substrate is preferred, while for higher Cr coverages, an alternating magnetization of the Cr layers is assumed.<sup>20</sup> As explained in the introduction, the topmost Cr surface is characterized by a complex reconstruction, involving Cr vacancies. We decided, however, to adopt a simplified atomic arrangement, characterized by the same 1×1 periodicity of the Fe substrate in order to save time and computational resources. The same strategy has been successfully applied by Eichler *et al.*<sup>33</sup> for modelling the electronic properties of the CrO patches produced by O segregation on the bare Cr(001) surface, where vacancy formation was also reported.<sup>34</sup> They found little differences in the optimized surface relaxations and magnetic moments for the *p*(1×1) and the  $(\sqrt{5} \times \sqrt{5})R27^\circ$  surfaces, consistently with our results discussed next.

Table 1 summarizes the results of our calculations.

Table 1. Computed interlayer spacing and magnetic moments for different atomic configurations. Layer 1 is the Cr layer. The interlayer spacing  $\Delta d_{ij}$  is given relative to  $\Delta d_{\text{Fe,Fe}}$ , computed for the bulk (1.416 Å, almost identical to the value of 1.424 Å computed for bulk Cr). Values in parentheses refer to literature results on the Cr/Fe(001) system by Xu *et al.*<sup>30</sup> and Victoria *et al.*<sup>34</sup> (labels *a* and *b*, respectively) and the results of Eichler *et al.*<sup>32</sup> for the oxidized Cr(001) surface (label *c*).

	1 ML Cr/Fe	1 ML Cr- <i>p</i> (1×1)O/Fe	1 ML Cr- $(\sqrt{5} \times \sqrt{5})R27^\circ$ O/Fe
$\Delta d_{12}(\%)$	-6	+24 (+19.1) <sup>c</sup>	+26 (+19.7) <sup>c</sup>
$\Delta d_{23}(\%)$	+5	+1	+2
$\mu_0(\mu_B)$	--	+0.0	+0.0 (--) <sup>c</sup>
$\mu_{\text{Cr}}(\mu_B)$	-3.3 (-3.15) <sup>a</sup> (-3.63) <sup>b</sup>	-3.1 (-2.6) <sup>c</sup>	-3.0 (-2.6) <sup>c</sup>
$\mu_{\text{Fe}}(\mu_B)$	+1.9 (+1.97) <sup>a</sup> (+1.95) <sup>b</sup>	+2.5	+2.5

On clean surfaces, bond breaking and the reinforcement of back-bonds with the subsurface layers brings to a reduction of the interlayer spacing for the topmost layer. This, in turns, lifts the second layer towards the surface of almost the same extent. The addition of oxygen completely reverses such a situation and causes instead a giant outward relaxation of the topmost layer. Interestingly, for the Cr/Fe(001)-*p*(1×1)O system, the interlayer spacing slightly increases also for the underlying Fe layer [ $\Delta d_{23}(\%)>0$ ]. Compared to the calculated magnetic moments for bulk materials ( $0.7 \mu_B$  and  $2.2 \mu_B$  for Cr and Fe, respectively),<sup>33,35</sup> the magnetic moment for 1 ML Cr/Fe(001) is increased by a factor of 5 to  $3.3 \mu_B$ , while the magnetic moment of the underlying Fe layer is reduced. An overall good agreement between our results and other first-principles studies related to 1 ML Cr/Fe(001) is observed in Table 1. The magnetic moment calculated for the oxygen-covered Cr layer is only slightly reduced with respect to the clean case, while a different behavior is observed for the magnetic properties of the underlying Fe layer. Due to the large outward relaxation of the topmost layer, the magnetic moment per Fe atom is indeed increased with respect to the bulk value.

From the experimental point of view, an enhanced Cr magnetic moment of  $3 \mu_B$ , i.e. close to the calculated one, was measured by *in-situ* magnetometry at 1 ML Cr coverage on Fe(001).<sup>36</sup> Indirect estimates by photoemission<sup>30,31</sup> and XMCD<sup>37,38</sup> resulted in a range of magnetic moments which are smaller than the calculated ones, but nevertheless larger (up to a value of about  $1.8 \mu_B$ ) than the bulk Cr magnetic moment. In line with previous results, we obtained with XMCD a maximum value of  $1.7 \mu_B$  for the Cr/Fe(001)-*p*(1×1)O system.<sup>17</sup>

The results of Table 1 are complemented by the projected DOS calculated for the Cr/Fe(001) [Figure 3(a)] and Cr/Fe(001)- $p(1\times 1)$ O [Figure 3(b)] cases.

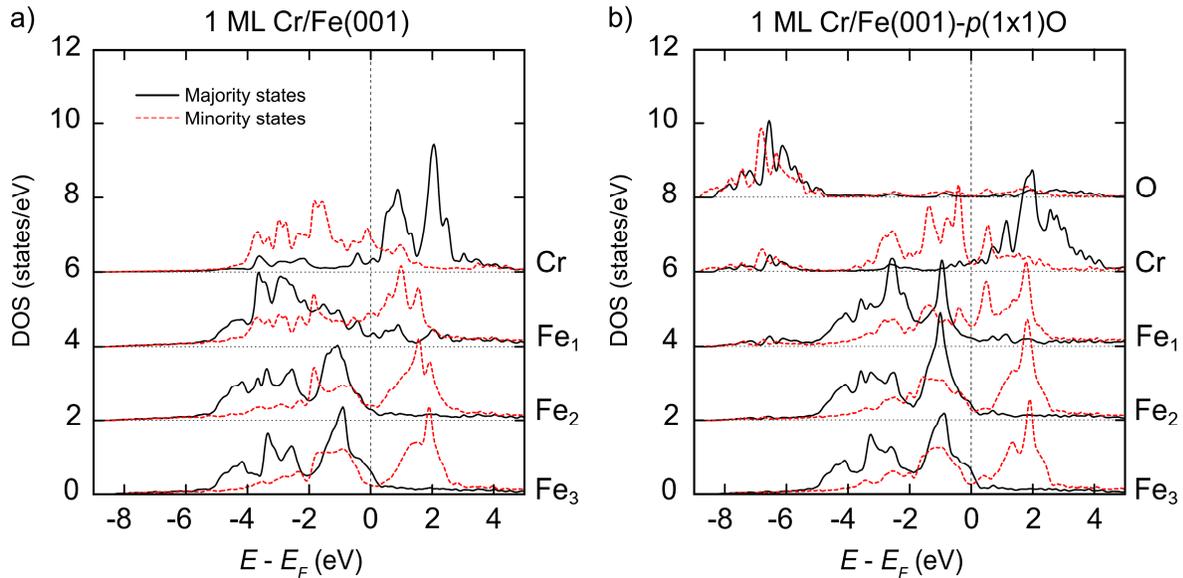


Figure 3. Projected density of states (DOS) at the adsorbate (O), the Cr layer and subsurface Fe layers for Cr grown a) on clean Fe(001) and b) Fe(001)- $p(1\times 1)$ O. This result was evaluated for a thicker Fe slab (25 layers).

Starting from 1 ML Cr/Fe(001) [Figure 3(a)], we observe (i) a clear splitting between the majority and minority Cr  $3d$  bands, reflected in the large calculated magnetic moment for the Cr layer, and (ii) sensible modifications in the DOS of the first Fe layer, compared to the DOS of layers 2 and 3 also included in Figure 3(a). The increased magnetic moment of the topmost layer is related to the reduced coordination of surface atoms, leading to the narrowing of the  $d$  band and therefore to a smaller overlap between majority and minority states within the Cr layer. Charge donation from Cr to the underlying Fe layer (about  $-0.6 e/\text{atom}$ , where  $e$  is the elementary positive charge) is detected, possibly associated to the strengthening of Cr back-bonds leading to the observed inward relaxation. This charge transfer results in a slight shift of the center of mass of Fe  $3d$  states towards higher BE, the filling of minority states and eventually in a reduced Fe magnetic moment. In the Cr/Fe(001)- $p(1\times 1)$ O system [Figure 3(b)], the large outward relaxation of the Cr layer is significant of a weaker interaction with the Fe substrate. This is reflected also in a smaller amount of electronic charge transferred to the topmost Fe layer ( $-0.2 e/\text{atom}$ ), which retains more or less the same DOS for all layers (1-3). Charges are indeed transferred from Cr to oxygen atoms ( $-0.65 e/\text{atom}$ ) as a result of a strong O  $2p - \text{Cr } 3d$  hybridization, characteristic of transition metal oxides. The localization of  $3d$  electrons in the surface layer is again reflected in an increased minority-to-majority bands separation. The observed enhancement of the Cr magnetic moment is also compatible with the larger value expected for Cr oxides.<sup>33</sup> For the interpretation of the DOS features we might refer to the work of Eichler *et al.*<sup>33</sup> At large BE (from 6 eV to 8 eV) O  $2p - \text{Cr } 3d$  bonding orbitals are found (occupied by majority and minority electrons), while at lower BE the main contribution is represented by non-bonding states together to antibonding O  $2p - \text{Cr } 3d$  orbitals close to  $E_F$ , occupied by majority electrons. The occupation of in-plane  $d_{x^2-y^2}$  hybrid anti-bonding states by majority electrons considerably weakens the O-Cr bonds and is linked to the formation of Cr vacancies in the Cr layer.

We complete our theoretical overview of the Cr/Fe(001)- $p(1\times 1)$ O system by showing the results of first-principles calculations pertaining to higher coverages (from 2 to 4 ML Cr).

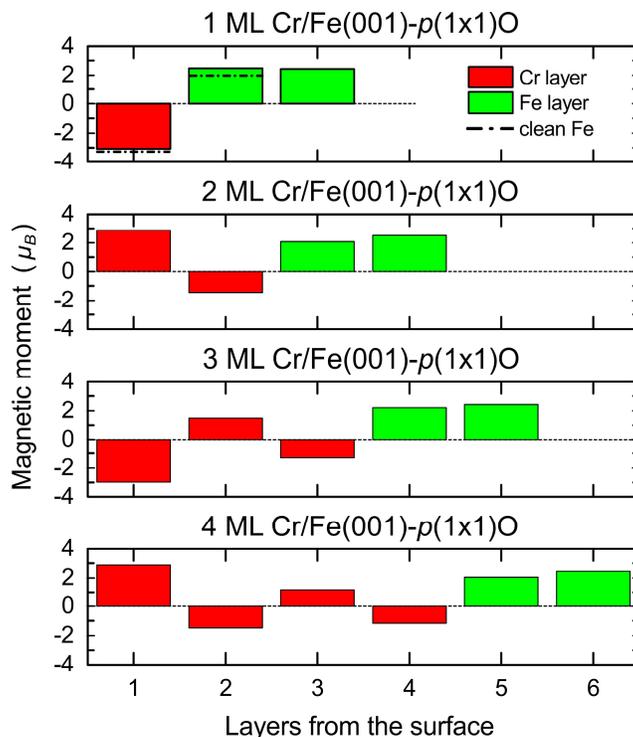


Figure 4. Layer dependent magnetic moment per atom for increasing Cr coverage on Fe(001)- $p(1\times 1)$ O. From 1 ML (top) to 4 ML (bottom).

A clear oscillating behavior of the topmost layer magnetization (settling to  $2.9 \mu_B$  for Cr coverages  $\geq 2$  ML) is observed in Figure 4, in good agreement with the experimental results shown in the previous section. The layer-resolved magnetic moment of sub-surface Cr atoms is sensibly larger than the bulk one and decreases with increasing Cr layer index, in analogy with previous results on the clean Cr(001) surface (see, for instance, Ref. 33 for a brief review). Such deviations from the Cr bulk magnetization are governed by boundary conditions (i.e. the proximity to the surface and to the Fe substrate), while intrinsic modulations related to specific details of the Cr electronic structure (i.e. Fermi surface nesting) are expected to play a role only for thicker Cr films.<sup>1</sup> Similar to the 1 ML Cr/Fe(001) case, as soon as a metallic Cr layer is formed in contact with the Fe substrate (i.e. for Cr coverages  $\geq 2$  ML), charge back-donation towards the substrate occurs (about  $-0.4 e$  per Fe atom) and the Fe magnetization at the interface drops below its bulk value.

#### 4. CONCLUSIONS

We have demonstrated a viable strategy for the realization of a chemically sharp AF Cr/Fe interface and ultra-thin Cr films showing an AF stacking in the direction perpendicular to the surface. This result is obtained by keeping a high substrate temperature during Cr growth and passivating the Fe-surface with a layer of oxygen prior to Cr deposition. First principles calculations provide a detailed picture of the spin structure of the topmost Cr oxide layer, which is found to be ferromagnetic with an enhanced magnetic moment of about  $3 \mu_B$ , as well as of buried Cr layers and the Fe interface.

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