Noncollinear magnetism of thin Cr films deposited on a stepped Fe (001) surface

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A theoretical study of the noncollinear magnetic moments distribution of Cr films with thicknesses between one and two monolayers deposited on a semi-infinite Fe(001) substrate with terraces of monoatomic height is reported. The spin-polarized electronic structure is calculated with a self-consistent real space *spd* tight-binding model, parametrized to *ab initio* tight binding linear muffin tin orbital results in which we have implemented the possibility that the orientation of the spin-quantization axis changes from site to site, thus allowing noncollinear magnetic calculations in complex systems with a large number of inequivalent sites without symmetry requirements while preserving a high degree of accuracy. The calculated magnetic moment distributions are discussed in connection with the magnetic frustrations associated with structural defects.

I. INTRODUCTION

One of the main challenges for the scientific community is the understanding of phenomena at the atomic scale, not only for the fundamental knowledge, but also for technological purposes. For instance, magnetic memory bit sizes approach the superparamagnetic limit with sub-10 nanometer characteristic lengths. The increasing interest in nanostructures makes this aspect particularly interesting and useful for the potential design of new materials. Important advances have taken place in the field of structural characterization. The STM stands as one of the prototypical tools in this context. However, other fields such as magnetic characterization have been up to now mainly based on average measurements. Recently, a new experimental setup spin-polarized scanning tunneling microscopy (SP-STM)[1–3] has demonstrated its potential to unravel complex magnetic superstructures with atomic resolution. For instance, magnetic hysteresis on a nanometer scale has been studied on an array of Fe nanowires of two atomic layers thick grown on a stepped (110) tungsten substrate.[3]

From the theoretical side, quantum mechanical spin-polarized calculations in low-dimensional systems are possible at present, but they have generally been confined to a global quantization axis. This approximation has provided and provides successful results since many materials exhibit collinear magnetic order, particularly those composed of strong ferromagnetic elements or adopting ideal structural configurations that prevent magnetic frustrations. However, there exist a variety of systems where the collinear magnetic arrangement cannot be the ground state due to the particular morphology of the system or where the collinear solution does not provide a satisfactory agreement with the experiments. Typical examples are frustrated systems having competing ferromagnetic and antiferromagnetic interactions between neighbor magnetic moments. Other candidates to noncollinear ground-state configurations are clusters of transition metal elements from the middle of the series, such as Cr and Mn. Consequently, in recent years much interest has been directed toward the implementation of codes able to

deal with noncollinear magnetism in both density functional theory (DFT) and semiempirical tight-binding (TB) methods.

Within the DFT formalism the magnetic noncollinear degree of freedom has been implemented in the all-electron[4–6] and pseudopotential[7] approaches. These methods provide a detailed description of the phenomena, being able to deal even with intra-atomic noncollinear magnetism.[8] However, a high computational cost has to be paid and therefore, these calculations are limited at present to systems with very few nonequivalent sites, such as small free-standing transition metal (TM) clusters.[6,7] The calculation of extended systems with broken symmetries is a formidable task within these methods, which usually take advantage of a transformation in the reciprocal space, so a three dimensional periodicity is required. Moreover, in these kind of systems, even having such periodicity from the structural point of view, the consideration of noncollinear magnetic configuration can impose much larger periods (magnetic periodicity), as we will see in the present work. Therefore the unit cell to be considered is even larger.

The semiempirical real-space TB method has been widely used so far in the collinear framework with successful results for the study of complex TM nanostructures such as clusters, surfaces, and interfaces. In the noncollinear context, Stoeffler and Cornea[9,10] have performed TB calculations for TM multilayers for studying interlayer magnetic couplings. However, their work was focused on extended periodic systems (without surfaces), where the bulk magnetic orders are only slightly altered by interfacial interactions even when interfacial imperfections are taken into account.

The aim of the present work is to present a semiempirical self-consistent real-space TB method in the noncollinear framework without symmetry restrictions and providing at the same time a good degree of accuracy, thus able to deal with three-dimensional complex nanostructures, as those characterized experimentally. The Hamiltonian is parametrized to DFT results and the recursion method is used for determining self-consistently the electronic structure.

Fe/Cr systems have attracted the attention of the scientific community in the last decade and still today many related

works are appearing since many aspects are far from being completely understood. Apart from the interest of this interface itself in many respects, such as interlayer exchange coupling and magnetoresistance, it stands as a prototype for testing new approaches, since both elements have been largely investigated so far. The importance of noncollinear spin configurations in Cr has been recently reported in a review by Fishman.[11] We present results for Cr ultrathin layers deposited on a stepped Fe(001) substrate, that is a typical nanostructure with competing ferromagnetic and antiferromagnetic interactions, and thus a clear candidate for having noncollinear ground states. This system was studied ten years ago by Vega *et al.*[12] using a simple collinear *d*-band TB method, and a high degree of magnetic frustration together with the existence of multiple collinear arrangements were found. Experimentally, it is observed that in the first stages of the Cr growth on Fe at room temperature, interdiffussion is a probable mechanism that is strongly reduced as increasing the Cr coverage. It is not our aim to provide a complete analysis of those mechanisms as well as possible roughness at the interface, since our model is valid at low temperature ($T \to 0$) and no structural optimization is performed, taking into account that both elements have a bcc structure in their respective bulks, with a very similar lattice parameter.

II. SELF-CONSISTENT NONCOLLINEAR TB MODEL

The magnetic moment distribution within the system is determined by solving self-consistently a *spd* TB Hamiltonian. The Hamiltonian can be split into a band term H_{band} and an exchange H_{exch} term which in the orthogonal $|i\alpha\rangle$ basis of atomic site i and orbital α and with the usual notation are

$$H = H_{\text{band}} + H_{\text{exch}}, \tag{1}$$

$$H_{\text{band}} = \sum_{\substack{ij \\ \alpha,\beta}} [(\epsilon_{i\alpha}^0 + U_{i\alpha,j\beta}\langle \hat{n}_{jb}\rangle + Z_i\Omega_{i\alpha})\delta_{ij}\delta_{\alpha\beta}$$
$$+ t_{ij}^{\alpha\beta}(1-\delta_{ij})]|i\alpha\rangle\langle j\beta| \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \tag{2}$$

$$H_{\text{exch}} = \sum_{i,\alpha} \left(-\frac{1}{2}J_{i\alpha}\mu_{i_\alpha}\right)|i\alpha\rangle\langle i\alpha| \begin{bmatrix} \cos\theta_i & e^{-i\phi_i}\sin\theta_i \\ e^{i\phi_i}\sin\theta_i & -\cos\theta_i \end{bmatrix}. \tag{3}$$

The band Hamiltonian H_{band} contains both the nondiagonal matrix elements (hopping integrals $t_{ij}^{\alpha\beta}$ between orbitals α and β of different sites i and j, which are assumed to be spin independent) and the spin-independent part of the diagonal matrix elements [$\epsilon_{i\alpha}^0 + U_{i\alpha,j\beta}\langle \hat{n}_{jb}\rangle + Z_i\Omega_{i\alpha}$, being the sum of (i) the local level $\epsilon_{i\alpha}^0$, (ii) the electrostatic level shift $U_{i\alpha,j\beta}\langle \hat{n}_{jb}\rangle$ accounting for the charge variations parametrized by the Coulomb integral $U_{i\alpha,j\beta}$, and (iii) the crystal field potential $Z_i\Omega_{i\alpha}$, where Z_i is the local atomic coordination of site i]. The exchange Hamiltonian H_{exch} describes the magnetic part, through the exchange parameter $J_{i\alpha}$ multiplied by the magnitude of the local magnetic moment $\mu_{i\alpha}$

whose direction is given by the angles (θ_i, ϕ_i). In the present formalism, this direction is not restricted to a global spin-quantization axis. Therefore, the self-consistent procedure is more complicated than for purely collinear calculations since the convergence in the angles has to be required in addition to the convergence of the modulus.

The local densities of states are calculated using the recursion method in real space. This method provides the partial densities of states projected on an arbitrary local quantization axis (instead of a global one) through a rotation of the initial recursion vector in the spin space. Once the local densities of states are determined, we calculate the local electronic occupations $\langle \hat{n}_{j\beta}\rangle$ and local magnetic moments $\mu_{i\alpha}$ at each site by integrating them up to the Fermi level with the global charge neutrality condition. Self-consistency is reached when no perpendicular output component remains on all the sites. More details of the numerical procedure can be found elsewhere.[10,13]

III. PARAMETRIZATION

When using a parametrized model such as ours one may pursue two different strategies: one may seek a broadly transferable parametrization, which is pertinent when one is interested in comparing a variety of systems with different local environments, or one may seek the parametrization that is best adapted to a family of systems with rather similar local environments thus providing better accuracy in the results. In this work we have opted for the second approach.

Based on the fact that our systems are characterized by a Cr/Fe interface and surface, and with the aim of incorporating into the parametrization the related Cr-Fe hybridization effects as well as the reduced coordination effects, instead of fitting our parameters to the respective bulks as usual, we have determined the homonuclear hopping integrals and the exchange integrals of Cr and Fe from a fit to *ab initio* TB-LMTO results for an ideal Cr monolayer deposited on Fe(001). In order to perform the fit, the procedure described by Andersen *et al.*[14] for the bulk has been extended to other environments. This procedure has been used in our previous works on embedded clusters.[15,16] The *d*-electron exchange integrals of Fe and Cr are determined to yield the magnetic moment distribution of a single Cr overlayer deposited on the stepped substrate. Exchange integrals involving *sp* electrons as well as interatomic Coulomb integrals are, as usual, neglected. For the direct Coulomb integrals, our choice is the same as in a previous work of Vega *et al.*[17] for Fe_N clusters embedded on a Cr matrix, and we refer the reader to this reference for more details. The crystal field parameters $\Omega_{i\alpha}$ are element and orbital dependent, and have to be determined with the requirement of being valid for Fe and Cr systems with different local coordinations. Thus, we have performed a series of TB-LMTO calculations of Fe and Cr systems with different coordinations and the crystal field parameters have been elected in order to obtain a good agreement for all these systems.

Although our aim was to obtain a parametrization adapted to our Cr/Fe systems, we have tested it for ideal Fe and
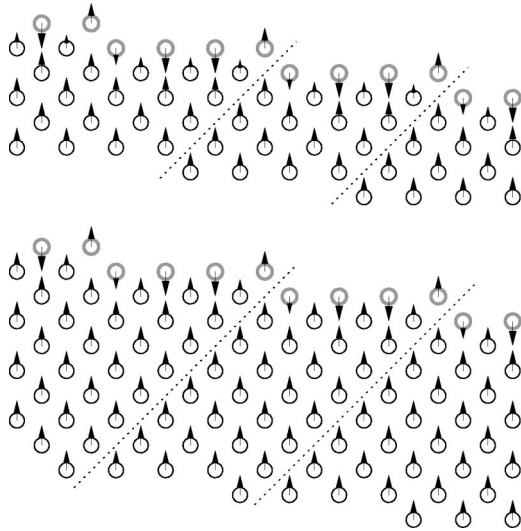
FIG. 1. Most stable collinear solution obtained by means of the TBLMTO method (upper panel) and our *ab initio* parametrized TB model (lower panel). Circle in gray line represent Cr atoms while circles in black line represent Fe ones. The sizes of the arrows are proportional to its modulus. The dotted lines define the unit cell considered in the calculation.

Cr(001) surface. The results have been compared to those of the TB-LMTO method and they are satisfactory.

IV. RESULTS AND DISCUSSION

In order to check our parameterization, we have first calculated the collinear magnetic solutions (there is not an unique solution) for the Cr monolayer deposited on the stepped Fe (001) substrate using both the parametrized TB model and the *ab initio* all-electron TB-LMTO. They are interesting not only for the sake of comparison between both theoretical methods, but also in order to get insight into the frustration mechanism driving the noncollinear configuration. The collinear solutions are expected to be metastable relative to the noncollinear ones. We will come back to this point. Figure 1 illustrates the most stable collinear arrangement that we have obtained by means of the TB-LMTO method and with our parametrized TB approach. The good qualitative agreement obtained give us confidence in our model. In addition, the absolute values of the magnetic moments obtained with both methods are similar (with differences smaller than 1%) except at some interfacial Fe atoms, for which in average we overestimate the magnetic moment in about 17%. Both calculations confirm the existence of magnetic frustration associated to the structural defect in these Fe-Cr systems and the resulting competing ferromagnetic and antiferromagnetic interactions: it is not possible, within the collinear restriction, to have at the same time all Fe-Fe nearest neighbors moments coupled ferromagnetically and all Cr-Cr and Fe-Cr ones coupled antiferromagnetically, which is the natural coupling of Fe-Cr systems. There are necessarily some nearest neighbors moments that are not coupled with their natural relative orientation. The system minimizes the magnetic frustration by leading to the most

stable collinear solution illustrated in Fig. 1, where only the moment of the Cr atoms at the edge of the step is ferromagnetically coupled to the moments of their nearest neighbor Fe atoms. Other collinear solutions of higher energy differ from this one in the degree of frustration, that in all cases is associated to the step at the interface.

It is expected that the lifting of the collinear restriction will allow the system to find a more stable magnetic moment configuration. That's what we have obtained, as seen in Fig. 2(a). The periodicity of the system in the (010) direction is reflected in the fact that only the θ_i angles are needed in the calculation. Let us point out that for the calculation of the noncollinear configurations a double cell has been used, i.e., we have taken explicitly into account in the calculations all the atoms in two adjacent steps of the terrace. This is necessary to obtain the most stable configuration of the noncollinear system, and also because when the Cr coverage is increased, the system tends to a layer by layer antiferromagnetic configuration, which can be only described within such a double cell calculation. Let us remark that no additional solutions have been found for the collinear case considering a double cell. By comparing the noncollinear magnetic solution with the most stable collinear one, one notices that the magnetic frustration of those Cr atoms at the edge of the step and their nearest neigbor Fe atoms is, as expected, partially relaxed in the noncollinear solution: they are no longer ferromagnetically coupled and the moments are tilted to form a relative angle of about 90°. This change in the moment direction of the atoms in the neighborhood of the structural defect (step) leads to a final solution that minimizes the magnetic frustration since the natural magnetic coupling among the involved nearest neighbors is approached as much as possible. One can further notice that the Cr-Cr and Fe-Fe magnetic interactions in this system dominate the Cr-Fe one (the relative moment orientations between nearest neighbor Cr-Cr and Fe-Fe atoms are close to 180° and 0°, respectively, whereas, as we have already pointed out, for Cr-Fe nearest neighbors some are close to 90°) contrary to what is obtained in multilayers.[18] This is due to the large enhancement of the Cr moment at the surface as compared to the Fe/Cr interface, and illustrate the strong influence of the local environment on the magnetic coupling. The resulting noncollinear configuration is 122 meV more stable than the most stable of the collinear solutions. This is the total energy difference for the whole unit cell, that is considering all the atoms within the dotted lines in Fig. 2. In order to evaluate this energy difference, we calculate for both magnetic configurations the band energy corrected by the double counting terms arising in our mean field approximation. Since the atomic positions are considered to be the same for the different magnetic solutions, the contribution of the ionic repulsion to the total energy difference is cancelled. Let us point out that the main part of this energy difference is located near the step. It is important to remark that without the collinear restriction, even a small perturbation of the collinear solution leads to a noncollinear one, revealing the former as unstable.

A further check of our model concerns the stability of the noncollinear solution under a slight variation of the exchange parameter. We have performed a series of calculations chang-
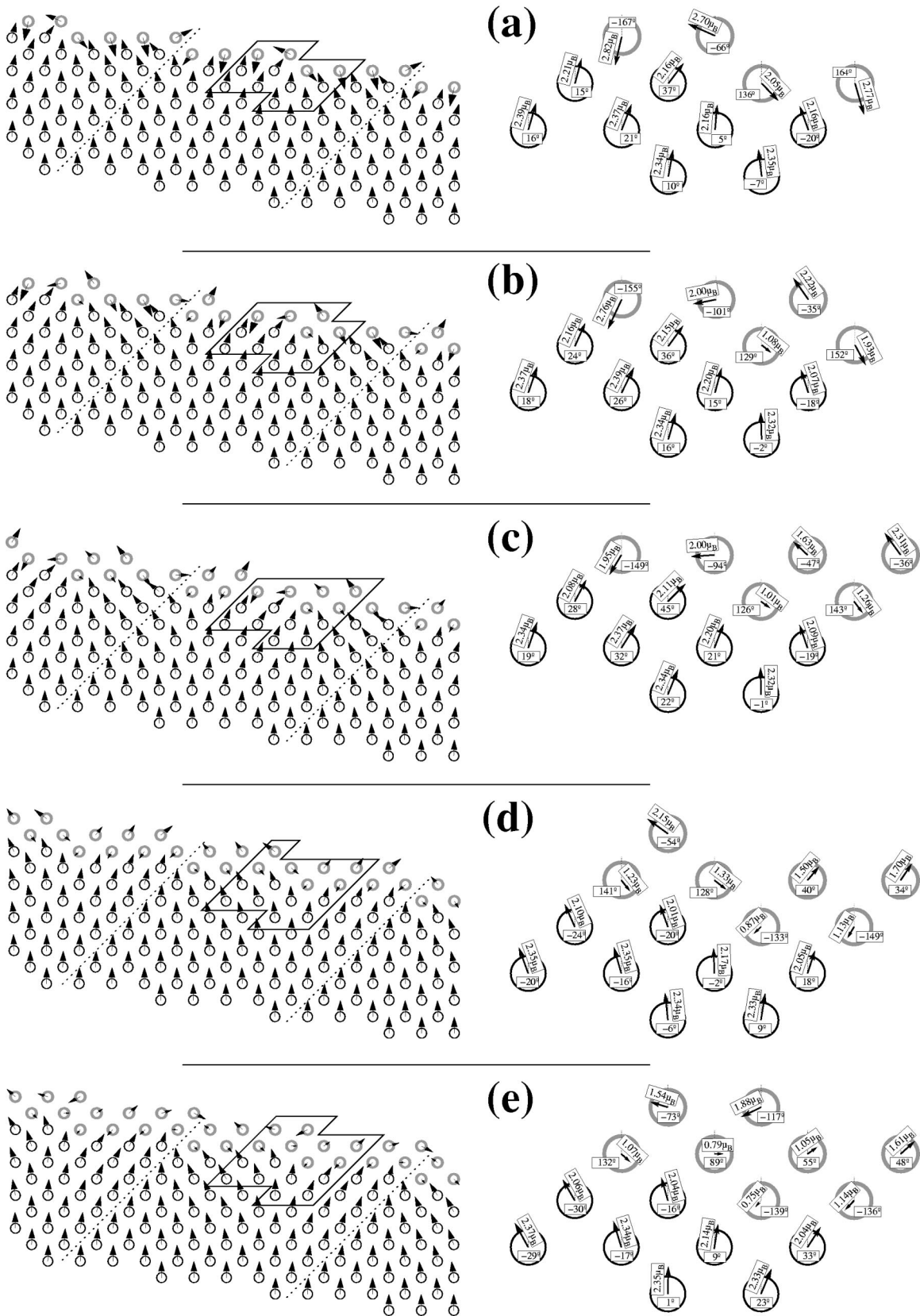
FIG. 2. Ground state magnetic configurations of our noncollinear TB model calculated considering different Cr coverages, from one (a) to two (e) full monolayers. The values for the angles and the local magnetic moments in the neighborhood of the step are shown in the right panel. The dotted lines define the unit cell considered in the calculation.

ing the exchange parameter for Cr between 0.70 and 0.90 eV (our fitted value is 0.80 eV). The variation of the relative orientation of the magnetic moments is nearly imperceptible. We have also tested the stability of the solution when increasing the number of inequivalent Fe layers (below the Cr overlayer) on which the local moments are free to rotate. We have seen that a smaller number of layers below the Cr overlayer are not sufficient for determining the direction of the local magnetic moments although their modulus is already converged. The increase within the calculation of the number of Fe underlayers different from the collinear bulk leads to slight but noticeable rearrangement of the moments direction. Therefore, the noncollinear calculation of extended systems requires one to take explicitly into account a larger environment than that typically needed in collinear calculations of the same system. This fact further limits the use of *ab initio* methods for quantitative noncollinear calculations in such systems.

A question arises at this point that is of special relevance in understanding the relation between the local environment and the magnetic behavior. How the noncollinearity evolves as increasing gradually the Cr coverage in the first stages of the growth. Variations in the relative orientation of the moments at the interface are expected as the local environment changes. In order to answer this question, we have performed calculations for Cr coverage between one and two full monolayers on the same stepped substrate. The resulting noncollinear solutions are plotted in Fig. 2. As increasing the Cr coverage, the Cr atoms at the interface gradually lose their surface character (when the full second monolayer is deposited, every Cr atom at the interface has its complete nearest-neighbor coordination). Therefore, a strong decrease of the magnetic moment of the interfacial Cr atoms takes place, leading to a reduction in the Cr-Fe magnetic coupling strength at the interface. As a consequence, as can be seen in Fig. 2, now the Fe-Fe interactions and surface Cr-Cr interactions dominate increasingly as the Cr coverage increases. Nevertheless, despite the local ferromagnetic coupling in Fe, a noticeable tilt of the Fe moments at the interface relative to those at the bulk exist, indicating a long-range order effect associated to the structural defect.

In all the considered cases, the noncollinear solutions always lead to lower average magnetic moments than the collinear ones. However, it is important to notice that the local magnetic moments in the noncollinear solution are, in general, higher than in the collinear one, particularly in those atoms where the magnetic frustration is relaxed. This is particularly evident in the Cr atoms. It is interesting to notice also that the magnetic moment of the nonfrustrated Cr atoms is considerably enhanced compared to their bulk value of $0.8\mu_B$ for a commensurate spin density wave,[19] whereas frustrated Cr atoms display a lower moment than in the bulk, despite the fact of having a low coordination. In Fig. 3 we illustrate this situation for different Cr coverages. When using a global spin quantization axes, the only way for the system to reduce the magnetic frustration is lowering the modulus of the magnetic moment, whereas when allowing the noncollinear situation, additional degrees of freedom are present and the system can relax the magnetic frustration
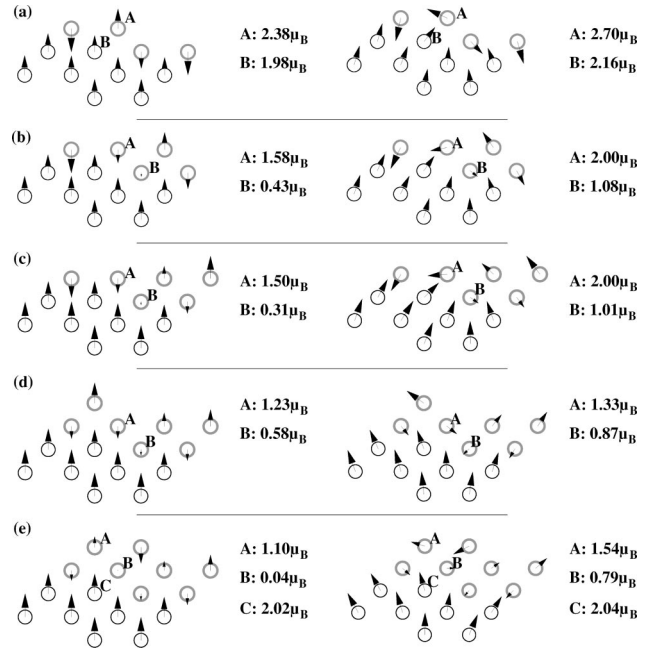

FIG. 3. Magnetic configurations in the neighborhood of the step for the collinear (left panel) and the noncollinear (right panel) solutions. The modulus of the local magnetic moments is shown for those atoms not having their natural magnetic coupling in the collinear solution. Notice the increase of the modulus of the local moment when the collinear restriction is lifted.

without the need of reducing the modulus of the magnetic moment.

V. CONCLUSIONS AND PERSPECTIVES

Using a self-consistent real space tight binding model parametrized to DFT calculations and without collinear restriction for the spin direction we have studied the magnetic moment distribution of a Cr film varying gradually from one to two monolayers deposited on a semi-infinite Fe(001) substrate with terraces of monoatomic height. We have seen that in the noncollinear ground state solution, the magnetic frustration associated to the structural defects (steps) is relaxed as compared with the collinear one. The natural magnetic coupling among the nearest neighbors is approached as much as possible when the collinear restriction is not imposed. The noncollinear calculation of extended systems requires, for a quantitative description, to have explicitly taken into account a larger environment than that typically used in collinear calculations of the same system and that the noncollinearity imposes a magnetic periodicity over the structural one. We also expect that the potential of the recently developed SP-STM technique for the magnetic characterization at the atomic scale will allow to confirm our predictions in the near future. Our theoretical approach allow the noncollinear study of complex magnetic nanostructures like supported or embedded clusters, surfaces and interfaces with defects for which a lot of experimental work is currently in progress. Work in this line will be reported in the near future.

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