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Ab initio study of the Fe/NiO interface: Structural and magnetic properties

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The structural and magnetic properties of the Fe/NiO(100) interface have been theoretically studied by density-functional theory within generalized gradient approximation (GGA) and, in selected cases, GGA+U methods. By total energy calculation, we find that Fe atoms adsorb preferentially on O sites and that a chemical reduction of NiO occurs, giving rise, for adsorption of more than one monolayer, to an interface of complex chemical and structural compositions, characterized by oxygen migration toward the surface. The magnetic moments at the interface and their alignment in a ferromagnetic and/or antiferromagnetic ordering are deeply influenced by the geometrical configuration of the atoms, pointing out to an important interplay between structure and magnetic configuration. This mechanism, at small oxidation level, leads quite naturally to the appearance of uncompensated spins at the interface.

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I. INTRODUCTION

Ferromagnet (FM)-antiferromagnet (AFM) bilayers belong to the new class of artificial materials exhibiting the phenomenon of exchange bias;[1] these materials have recently attracted much attention for various applications in the new generation of spin based nano technologies. Despite extensive studies, the microscopic understanding of exchange bias has been hindered up to now by the lack of information about the structural and chemical rearrangements that may occur at the interface and that may influence the interface magnetic structure. Several experiments performed by spectroscopic techniques such as standard magnetization measurement,[2] x-ray magnetic circular and/or linear dichroism,[3–7] and spin-polarized scanning electron microscopy[8] in conjunction with x-ray photoemission electron microscopy[9] have investigated the magnetic interfacial structure, revealing a full spectrum of different magnetic scenarios, with parallel or antiparallel collinear or perpendicular coupling between the uncompensated spins at the FM/AFM interface and the FM magnetization axis, depending on the chosen FM and AFM materials, on the method by which the samples are grown, and on the thickness of the FM and AFM layers.

Among the exchange-bias interfaces composed by a FM metal and AFM oxides, the Fe/NiO interface has probably been the most studied, due to the ease of characterizing good single crystals or thin films of NiO and to the possibility of an epitaxial growth of Fe bcc layers on NiO(100). The structural properties of the M/NiO interface, where M=Fe or Co, have been investigated by means of experimental techniques such as x-ray absorption,[10,11] photoemission electron microscopy,[12] low energy electron diffraction,[13,14] soft x-ray resonant magnetic reflectivity,[15] surface x-ray diffraction,[16] and primary beam diffraction modulated electron emission.[17] As a general trend, an intermediate interface region is found where different reactions take place, leading to partially oxidized and reduced layers in the metal and the oxide sublattice, respectively; these phenomena are now widely recognized to be one of the main sources of the uncompensated magnetic moments in this system.

In a recent paper,[11] we have reported a combined experimental and theoretical analysis that shows clear evidence of this oxidation and/or reduction mechanism, and focused on the structural properties at this interface. Here, we will concentrate on the interplay between the structural and magnetic properties of the Fe/NiO bilayer system. There have recently been different observations on the type of magnetic coupling (collinear or noncollinear) at this interface, and what is clear now is that the type and level of the oxidation play a key role.[3] Magnetization and Mössbauer experiments have revealed very recently how ferromagnetic order is possible in Fe-doped NiO bulk systems;[18] concerning interfaces, systematic investigations by Finazzi *et al.*[19–21] have evidenced that the level of oxidation and the collinear-noncollinear coupling depend on the growth modality, with the AFM layer as a substrate for the FM layer, or vice versa. In particular, the deposition of Fe onto NiO seems to favor a collinear arrangement.[19] We will focus here on collinear magnetic states and postpone the discussion of possible noncollinear states to a future work.[22]

We have studied the ground state properties of Fe/NiO heterostructures within the density-functional theory, assuming various atomic geometries, magnetic configurations, and chemical compositions of the interface, to get information on the most stable structural and magnetic configurations. Even for single or double layer deposition, we have to deal with many degrees of freedom that involve site adsorption, oxygen migration, geometrical rearrangement of the substrate upon adsorption, and magnetic order. More specifically, we will address the following questions: Which are the adsorption sites of Fe on NiO? How much of the constituents are mixed at the interface? Does any geometrical rearrangement occur and what are the effects on the magnetic configuration of the interface? Do these effects depend on the thickness of the adsorbed layer? In order to answer these questions, we have considered different Fe/NiO interfaces, namely, a

NiO(100) surface with a different number of Fe overlayers; for each of them, we have allowed oxygen to migrate from the interface into the iron overlayer and studied the effect of geometrical rearrangement, allowing atoms to relax to their equilibrium position.

The work is organized as follows: after some computational details described in Sec. II, we discuss the results for a single Fe adlayer [within generalized gradient approximation (GGA) and GGA+U schemes] in Sec. III A, and the results from two to four Fe adlayers in Sec. III B on the NiO(100) substrate, focusing the discussion on the interplay between the magnetic properties and the chemical structure at the Fe/NiO interface. We will then summarize our results and present our conclusion in Sec. IV.

II. COMPUTATION DETAILS

We have performed density-functional theory (DFT) calculations for a slab of five and/or seven (depending on the number of Fe overlayers) NiO(100) layers with one, two, and four Fe monolayers (MLs) adsorbed on each side. The lattice constants of bulk NiO and Fe have been determined by structure minimization as $a_{\mathrm{NiO}}=4.15$ Å and $a_{\mathrm{Fe}}=2.88$ Å, respectively. The in-plane lattice constant has been kept fixed to a_{NiO} in all the structures; as a consequence, the in-plane lattice parameter of epitaxially stacked Fe layers $(=\sqrt{2}/2a_{\mathrm{NiO}}=2.93$ Å) turns out to be 2.1% smaller than the calculated lattice constant of bulk Fe, in qualitative agreement with the experimental finding that indicates a 3% contraction of the Fe-Fe distances in the epitaxially grown thin films on NiO.[17] The thickness of the NiO slab (five NiO layers) and the amount of vacuum (8–10 Å depending on the system) between NiO slabs are enough to recover, in the case of a sharp Fe/NiO interface, both a NiO bulk character in the central layer of the NiO slab and to avoid spurious interactions between the two Fe overlayers; in the presence of Fe oxidation, the NiO slab is composed of only three NiO layers, and a small deviation in the central NiO layer from the NiO bulk behavior is observed. In all the structures, the NiO substrate is kept in its bulk AF2 AFM ordering,[23] where the magnetic moments align antiferromagnetically along the [111] direction; as depicted in Fig. 1, the in-plane cell has two inequivalent Ni atoms with opposite moments.

DFT calculations have been performed by the all-electron linearized augmented plane wave (LAPW) method as implemented in the WIEN2K package.[24] Following the basis concept of the LAPW method, where the wave function is expanded onto the product of spherical harmonics and radial functions inside atom-centered muffin-tin (MT) spheres and onto plane waves outside, we have set the MT sphere radii to 1.65, 1.9, and 2.0 a.u. for oxygen, iron, and nickel, respectively. States 1s of O and 1s, 2s, 2p, and 3s of Fe and Ni are treated as core states, i.e., states whose charge is entirely confined inside the corresponding atomic sphere. A 13 Ry plane wave cutoff and 28 k points in the irreducible part of the Brillouin zone have been used. These values give well converged values for total energy differences and Hellmann-Feynmann forces. When explicitly stated, we have carried out a full structural optimization, by allowing the atoms to relax toward their equilibrium positions, with remanent forces of the order of 1 mRy per a.u.

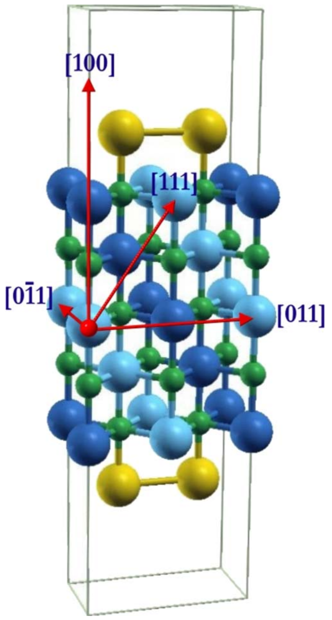

FIG. 1. (Color online) Primitive cell for the 1 ML Fe/NiO(100) system. Atomic species and magnetic moments are indicated with different colors (gray levels). The different colors (gray levels) in the NiO layers indicate the sign of the magnetic moments of Ni atoms in the AFM order, assumed for the NiO substrate throughout the paper. Crystal directions are also shown for clarity.

Spin-polarized calculations have been carried out, neglecting spin-orbit coupling and adopting the GGA to the exchange and correlation potential.[25] GGA only partially corrects the well known inadequacy of the local density approximation (LDA) in describing transition metal oxides: it provides accurate lattice constants, i.e., $a_{GGA}=7.86$ a.u. compared with the experimental value of 7.88 a.u.,[26] reproducing the insulating character of bulk NiO, although underestimating the value of the gap (around 1 eV compared with the experimental one[27] of around 4 eV) and its antiferromagnetic order,[28] as well as values of the magnetic moments $(\pm 1.37\mu_B)$, in better agreement with experiments $[\pm 1.7\mu_B$ (Ref. 29)] than LDA $(\simeq 1\mu_B)$.[30]

In order to check the influence of on-site electron-electron (e-e) interactions on structural and magnetic configurations, we have also performed GGA+U calculations[31] for two representative systems, in the case of a single Fe ML adsorbed on NiO. It is well known that for transition metal oxides, standard local approximations to the exchange and correlation potential fail to describe correctly the electron localization on the d orbitals and the nature of the p-d hybridization. Several methods have been proposed to overcome this shortcoming, from hybrid functionals[32,33] to self-interaction corrections,[34–36] and from on-site Hubbard-type static corrections in the LDA+U method,[31,37–40] to nonlocal self-energy corrections as in dynamical mean field theory.[41] We will show that for one Fe ML on NiO, the additional localization induced by U does not affect structural properties and does not qualitatively modify the magnetic configuration.

TABLE I. Total energy differences (with respect to the ground state) for 1Fe/NiO and 1FeO/1Ni/NiO in the ideal and relaxed geometries, with Fe deposited either on top of Ni or O atoms (see text for details). A label (α-δ) identifies the several structures.

Label	System	Fe adsorption site	ΔE (mRy/atom) Unrelaxed	Relaxed
α	1Fe/NiO	On Ni	+170.0	
β	1Fe/NiO	On O	+77.5	+105.7
γ	1FeO/Ni/NiO	On Ni	+39.7	+57.5
δ	1FeO/Ni/NiO	On O	0.0	0.0

III. RESULTS AND DISCUSSION

A. One Fe monolayer on NiO(100)

Our first concern is to find out the preferred adsorption site for Fe on NiO(100). We compare total energies obtained for a slab of five NiO layers with one Fe ML adsorbed at both sides of the slab; we consider different adsorption sites (Fe on top of either Ni or O sites) and assume either a perfect clean interface (Fig. 1) or the creation of a full FeO ML with the consequent formation of a Ni reduced layer at the interface. In this last case, Fe atoms can adsorb either on top of Ni atoms or on "hollow" oxygen sites.

As a first step, all the atoms (including Fe atoms) have been kept fixed in the bulk fcc positions and we have assumed a FM (AFM) order in the overlayer (substrate) even in the presence of an oxidation-reduction reaction. The results are listed in the first column of Table I. We see that the preferred configuration is obtained by adsorbing Fe on oxygen sites. Moreover, the formation of an FeO overlayer is favored; as discussed in Ref. 3, standard Gibbs free energy of formation for FeO (−58.1 kJ/mol) is larger than that for NiO (−50.6 kJ/mol) and a gain of about 57 mRy/atom is expected whenever an iron atom is oxidized in place of a Ni atom. This energy gain compares well with the values reported in Table I, where for the unrelaxed structures, the energy difference between configurations β and δ, respectively, without and with Fe oxidation, is around 77 mRy/atom. Even if our calculations do not treat temperature effects involved in the process of growth, the energy differences reported in Table I are much larger than the energies provided to the system under typical growing temperatures (some hundreds of kelvins); for this reason, we may conclude that the oxidation-reduction mechanism is quite robust and the creation of an oxidized Fe interface layer occurs whenever an Fe layer is epitaxially grown on the NiO(100) substrate.

We now focus on the most stable configuration, that is, one FeO ML on Ni/NiO with Fe on top of the "hollow" oxygen site (system δ in Table I), and investigate the differences in energy involved when the magnetic ordering at the interface is varied. Table II shows the results for several possible magnetic configurations obtained by varying the ordering in the FeO layer and in the reduced Ni interface layer, while keeping the AFM order fixed in the rest of the slab. Although it has been evidenced that in FM/AFM interfaces spin frustration might lead to noncollinear coupling,[42] we will address in the following only collinear magnetic solutions and postpone the study of noncollinear states to a future work.[22] The magnetic ground state is found when both the FeO and Ni layers at the interface attain an AFM order, continuing the magnetic structure of the underlying NiO bulk layers. No constraint is imposed on the magnetic moments, setting them free to relax and, in case, to invert sign during the electronic self-consistency iteration. As expected, changes in the spin degrees of freedom lead to very small total energy differences, 1 or 2 orders of magnitude smaller than the ones associated with the variation in the chemical structure (see Table I).

TABLE II. Stability vs magnetic ordering at the FeO/Ni/NiO interface with Fe adsorbed on O hollow site, for the unrelaxed and relaxed geometries. The letter δ identifies the same configuration of Table I; the number beside δ identifies the different magnetic configurations.

Label	Magnetic order Fe	Ni	ΔE (mRy/atom) Unrelaxed	Relaxed
$\delta 1$	FM (up)	FM (down)	+2.8	
$\delta 2$	FM (up)	FM (up)	+1.2	0
$\delta 3$	FM	AFM	+1.1	
$\delta 4$	AFM	FM	+0.9	
$\delta 5$	AFM	AFM	0.0	+0.3

The analysis has then been refined by allowing the relaxation of the atomic coordinates for the three most stable cases, namely, β, γ, and δ. As evident from the comparison of the two columns in Table I, atomic relaxations increase the total energy differences and strengthen the stability of the structure δ with a fully oxidized Fe (and fully reduced Ni) layer.

In Table III, we give a list of the relaxed atomic coordinates for systems β, γ, $\delta 2$, and $\delta 5$ calculated by averaging the vertical position (measured from the central layer of the slab) of the inequivalent atoms at each plane; labels [I] and [I-1] indicate the interface and subinterface NiO layers, re-

TABLE III. Averaged (over the two inequivalent sites) atomic coordinates (in Å) along the vertical direction $\langle Z \rangle$, with respect to the central NiO layer, for the relaxed β, γ, $\delta 2$, and $\delta 5$ systems defined in Tables I and II. Labels [I] and [I-1] indicate the interface and subinterface layers, respectively.

		$\langle Z \rangle$ Ideal	β	γ	$\delta 2$	$\delta 5$
	Fe	6.23	6.10	6.21	5.54	5.53
	O	6.23		6.44	5.94	5.95
I	Ni	4.16	4.38	3.97	4.03	4.03
	O	4.16	4.18			
I-1	Ni	2.08	2.09	2.26	2.27	2.38
	O	2.08	2.08	2.07	2.13	2.14

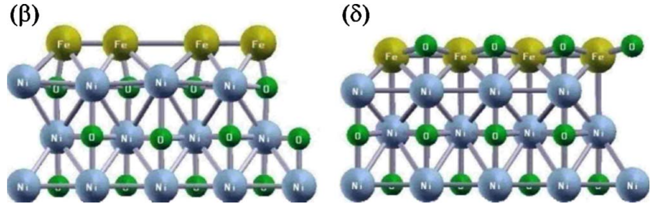

FIG. 2. (Color online) 1Fe deposited layer systems after structural relaxation: nonoxidized Fe on NiO (β) and 1FeO/1Ni/NiO (δ).

spectively. The relaxed structures for systems β and $\delta5$ are depicted in Fig. 2. We notice that the average distance between the overlayer and the substrate is reduced by relaxations except for the 1FeO/Ni/NiO interface, with Fe adsorbed on Ni (case γ). At the surface of structures $\delta2$ and $\delta5$, Fe and O atoms show an appreciable buckling of 0.4 Å, about 10% the NiO lattice constant; this buckling, even if less prominent, is seen also at the NiO interface layer (see Table III and Fig. 2). In-plane relaxations are negligible, except for system β, where a "dimerization" in the Fe plane arises due to the different exchange interactions exerted by the Ni atoms. More precisely, a contraction (expansion) of the in-plane Fe-Fe distances along the [011] direction (see Fig. 1) is observed when the Fe magnetic moments are parallel (antiparallel) to those of the Ni atoms below, due to Fe-Ni distances of 2.61 and 2.81 Å, respectively, for parallel and antiparallel orientations of the Fe and Ni magnetic moments.

We now turn to the effects of the atomic relaxations on the magnetic interactions of the ground state interface structure, i.e., FeO/Ni/NiO. As evidenced in Table II, the AFM and FM orderings in the FeO overlayer (cases $\delta2$ and $\delta5$) are equally favored, with an energy difference of only 0.3 mRy /atom in favor of the FM one ($\delta2$). All the other solutions are not stable upon structural-electronic minimization. In fact, in the configuration $\delta4$, the Ni[I] magnetic moments undertake a spin flip and the system converges to the configuration $\delta5$. Similarly, $\delta3$ and $\delta1$, during the structural optimization, fall back onto the $\delta2$ configuration. We then conclude that for realistic (minimized) atomic coordinates at the FeO/Ni/NiO interface, the magnetic interaction between the FeO and Ni interface layer is dominant, and the magnetic order in the Ni layer reflects the one assumed by the above FeO layer.

Recalling that GGA (or LDA) calculations are known to overestimate the magnetic interactions in magnetic oxides, we see how, in the case of a single FeO monolayer, the FM and AFM orders might be considered almost degenerate. This situation is similar to the case of a freestanding FeO ML, where the AFM and FM magnetic configurations, within GGA, differ in energy by 2.2 mRy/atom only. We will come back to this issue later when the case of two FeO monolayers will be investigated.

The calculated magnetic moments reported in Table IV deserve several considerations. First, we observe an enhancement of the Fe magnetic moments upon oxidation, increasing from $m=3.00\mu_B$ to $m=3.37\mu_B$ (for $\delta2$) and $m=\pm 3.23\mu_B$ (for $\delta5$). This is found also for the case of the unsupported Fe (FeO) monolayer (results in parentheses), and it is in agreement with the experimental observations obtained by the spin-resolved inverse photoemission technique[43] in the case of an oxidized Fe(100) surface. From the analysis of the orbital character of the Fe d states with and without oxidation, we see that orbitals of d_{z^2}, $d_{x^2-y^2}$, and d_{xy} symmetries—with a nonzero component in the xy plane—contribute most to the increase of the Fe magnetic moment, while d_{xz} and d_{yz} orbitals tend to reduce such an increase. Small magnetic moments, $\simeq 0.2\mu_B$, are induced on the O atoms in the FeO plane for FM ordering ($\delta2$), while for AFM ordering ($\delta5$), there is an almost exact cancellation with a net zero magnetic moment on the O sites (due to the characteristic space group of the simulation cell, small deviations from perfect AFM crystal symmetry is observed in our systems, and remanent $\pm 0.005/0.001\mu_B$ are induced on the oxygen atoms, even in perfect AFM order). We also observe that in an isolated Fe ML, the Fe magnetic moment would attain a value of $3.03\mu_B$ (see values in parentheses in Table IV), which almost coin-

TABLE IV. GGA magnetic moments in (μ_B) for the relaxed β, γ, $\delta2$, and $\delta5$ systems defined in Tables I and II. Labels [I], [I-1], and [C] indicate the interface, subinterface, and central NiO layers, respectively. In parentheses, the results for Fe and FeO unsupported monolayers are also listed. For systems β and $\delta2$, results of GGA+U calculations are also reported.

		Magnetic moment (μ_B)					
		β		γ	$\delta2$		$\delta5$
Vertical position	Atom	GGA	GGA+U	GGA	GGA	GGA+U	GGA
	Fe	3.00	2.98	3.16	3.37	3.60	±3.23
		(3.03)	(3.02)	(3.26)	(3.26)	(3.47)	(±3.33)
I	Ni1	−0.75	−1.63	0.70	0.71	0.68	−0.14
	Ni2	1.20	1.62	0.73	0.77	0.70	0.14
I-1	Ni1	1.40	1.73	1.02	1.24	1.67	1.15
	Ni2	−1.36	−1.72	−1.19	−0.51	−1.11	−1.15
C	Ni1	1.35	1.72	1.36	1.43	1.75	1.38
	Ni2	−1.34	−1.72	−1.40	−1.38	−1.74	−1.38

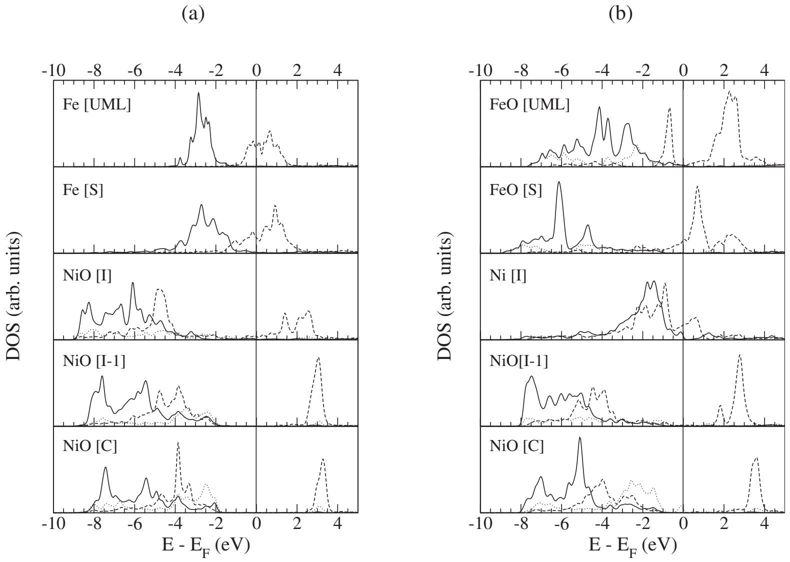

FIG. 3. DOSs for the systems (a) 1Fe/NiO and (b) 1FeO/1Ni/NiO, with Fe adsorbed on O sites. Densities of states are shown for surface (S), interface (I), subinterface (I-1), and central (C) planes and compared with (a) Fe and (b) FeO UMLs. Solid (dashed) lines refer to majority and minority Fe (Ni) densities of states; dotted lines refer to oxygen majority-spin states

cide with those of 1ML Fe deposited on NiO (system β). This would be an indication that in the absence of the oxidation-reduction mechanism, NiO would behave as MgO (see the work of Li and Freeman[44]) in supplying a very weak substrate/overlayer interaction. In spite of this, the Ni magnetic moments at such a clean interface are influenced by the presence of the Fe overlayer, reaching values of $-0.75\mu_B$ and $1.20\mu_B$ compared with $\pm 1.36\mu_B$ in the bulk. In the case of an FeO overlayer (systems $\delta 2$ and $\delta 5$), hybridization with the Ni/NiO substrate increases (FM) or decreases (AFM) the absolute values of the Fe magnetic moments depending on their magnetic order; changes are very small, anyhow, in terms of less than 3%–4% of the total value. In the oxidized interface (systems γ, $\delta 2$, and $\delta 5$), the Ni moments in the interface layer [I] vary sensibly depending on the magnetic ordering of the upper FeO layer; in the case of FM order (system $\delta 2$), sensible changes are observed also in the NiO sublayer [I-1], while for AFM order, the absolute values of the Ni magnetic moment are very small at the interface layer and retain a weak AFM order mainly induced by the upper and lower layers.

Up to now, we have considered the results obtained by GGA. In order to take into account on-site e-e interaction, we have performed GGA+U calculations for two selected configurations, namely, 1Fe/NiO(β) and 1FeO/Ni/NiO ($\delta 2$). Since Fe and Ni bulk systems are reasonably well reproduced by standard local functionals, the +U term is considered to act only on the d orbitals of the transition metal atoms when they are in an oxidized configuration. For this reason, in the case of a sharp Fe/NiO interface, only Ni atoms are modified by a +U term; for the FeO/Ni/NiO interface, +U corrections are added on all the Fe and Ni atoms except for the Ni atoms in the Ni metallic layer where, again, the GGA is a reasonable approximation. Consistent with previous studies,[45,46] we have used U=6.8 eV and U=4.1 eV, respectively, for Ni and Fe atoms.

For the sake of completeness, we plot the densities of states for the Ni, Fe, and O atoms across the interface for the relaxed β and $\delta 2$ structures [Figs. 3(a) and 3(b), respectively]. We report in the upper panel the density of states of unsupported Fe and FeO monolayers (UMLs) calculated by assuming the same in-plane lattice constants and magnetic order as in the Fe and FeO adsorbed monolayers. First of all, we notice that in both cases, GGA+U reproduces at the central layer the correct gap value of bulk NiO (about 3.5 eV) as expected.[39,40] In system β, the presence of the Fe overlayer induces minority-spin states at the Fermi level, closing the NiO gap at the interface layer [I]. The influence of the Fe overlayer extends only one layer down through the NiO substrate, and the subinterface NiO layer [I-1] has already a bulklike character. NiO represents a quite inert substrate in this configuration as indicated by the similarity between the density of states of the Fe overlayer and the Fe UML as well as by the similar values of their magnetic moments (see Table IV). For the FeO/Ni/NiO interface (system $\delta 2$), we observe a complete metal character in the Ni reduced layer and, more surprisingly, in the FeO overlayer, due to hybridization with the Ni atoms, while the FeO unsupported monolayer has a very small density of states (DOS) at the Fermi level.

Total energy results confirm $\delta 2$ as the stable configuration, system β exhibiting a positive total energy difference ΔE=119.9 mRy/atom. Differences exist between the absolute values of the magnetic moments obtained by GGA and GGA+U as reported in Table IV: GGA+U gives rise to larger magnetic moments at oxidized Fe and Ni, recovering, for instance, at the Ni atoms of the central layer a value closer to the bulk one. Moreover, the additional electron localization induced by the GGA+U functional leads to a less reactive character of the NiO interface, as compared to the one described in GGA; if in the GGA the Ni moments depart from the bulk ones at the interface quite sensibly, the Ni GGA+U values are quite robust, with a small deviation at the interface as compared to the values in the [C] NiO layer.

Although GGA and GGA+U methods lead to a different description of the electronic states and to different absolute values of total energy and magnetic moments, the overall picture coming out from *differences* in total energies between

TABLE V. Two layer deposition. Total energy differences, with respect to the ground state, for different structures with two overlayers of iron deposited on NiO in the relaxed geometry. A letter code (A–F) identifies the configurations.

	System	ΔE (mRy)
F	2Fe/NiO	+462.5
E	2FeNi/1FeO/NiO	+317.1
D	2FeO/2Ni/NiO	+172.5
C	1FeO/2FeNi/NiO	+101.3
B	1FeO/1Fe/1Ni/NiO	+83.9
A	1FeO/2Ni/1FeO/NiO	0.0

the two structures considered and differences between the magnetic moments at various layer positions is qualitatively the same in the two approaches. For this reason—and for the intrinsic difficulties due to the dependence of U parameters on the chemical element and on the environment, number, and position of the oxygen neighbors—we will not proceed to a systematic GGA+U analysis, and the more complex structures corresponding to the adsorption of more than one Fe monolayer will be studied in GGA only.

B. Two and four Fe monolayers on NiO(100)

The deposition of two Fe layers on NiO(100) allows us to study more deeply the effects of oxygen migration from the substrate into the overlayer. We have calculated total energies for structures with two Fe layers deposited on NiO, differing both for the amount of oxygen migrated into the overlayer and for a possible mixing between Fe and Ni atoms at the interface. After a preliminary check of the relative stability of unrelaxed structures with different Fe adsorption sites, we have concluded that Fe prefers again to deposit on oxygen sites. All the configurations that we have then relaxed have Fe on O sites; moreover, we have assumed oxide layers (FeO and NiO) to be AFM ordered and each metal layer (Fe and Ni) to be FM ordered. Comparing total energies (see Table V), we observe that full oxidation of both Fe layers is preferred, and that it goes together with an oxygen migration to the surface and the formation of a double interface between FeO and Ni (system A). The formation of a 50% Fe-50% Ni alloy (system E), predicted by x-ray absorption spectroscopy,[11] appears to be not energetically favored, its total energy being as much as 317 mRy larger than the most stable one. All the same, a detailed comparison between experimental and theoretical interplanar distances[11] has recently shown that the growing process leads the system most likely to configuration E, suggesting the existence of kinetic barriers for the diffusion of oxygen atoms.

Effects of the structural relaxation are shown in Fig. 4. The optimized average layer distances are indicated beside each structure; for most of the transition metal oxide layers, a buckling between the transition metal and oxygen atoms is observed, which can be extracted by subtracting the two values given in the figure, which represent the distance between each sublayer from the lower layer. Dimpling effects of the order of 5%–10% a_{NiO} are evident in all the structures at the FM/AFM interface (i.e., Ni/NiO, Fe/FeO, and so on) between oxygens and Fe or Ni atoms. We observe an overall reduction of the distances between two metal layers or between a metal layer and the oxide substrate of the order of 20% and 4% a_{NiO}, respectively. This results in a distance between the Fe planes slightly shorter than the bcc nearest-neighbor distance characteristic of bulk Fe. Another feature common to all the structures is the increase of the distances between the oxidized layer at the interface and the NiO substrate (e.g., the distance between the FeO and NiO layers of case E), which increases on the order of 4%–5% a_{NiO}. For all the configurations, the inner NiO layers remain in the ideal fcc structure after structural relaxation. In the particular cases

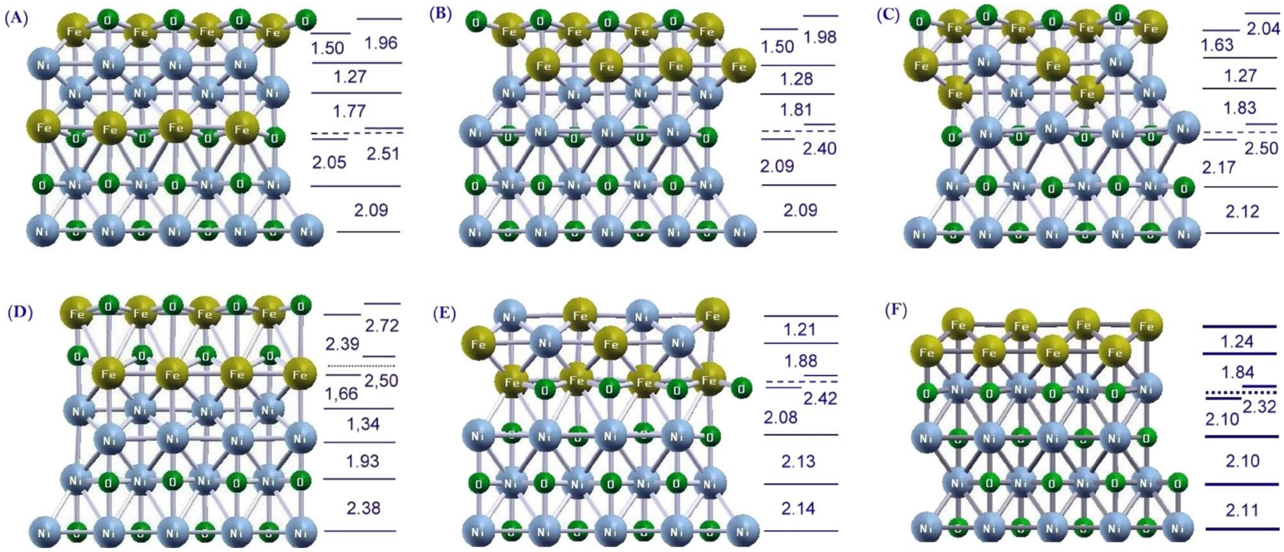

FIG. 4. (Color online) Systems with two iron layers after structural relaxation. The letter code (A–F) identifies each configuration as indicated in Table V. Beside the structures, the averaged distances between the layers (in Å) along the vertical direction are indicated.

TABLE VI. Two layer deposition. Stability vs magnetic ordering at the interface 2FeO/Ni/NiO.

	Structure	Fe	ΔE (mRy) Unrelaxed	Relaxed
D'	2FeO/2Ni/NiO	FM	+0.0	+10.0
D	2FeO/2Ni/NiO	AFM	+34.0	+0.0

C and E, a rumpling between Fe and Ni is visible at the interface region, caused by the different exchange forces between the two atomic species in the alloy. When the Fe double layer is oxidized, the mean distance $\langle Z \rangle$ between the 2FeO planes increases by 11% a_{NiO}, changing completely the fcc structure.

In Table VI, we report the comparison between two magnetic orderings, for the fully oxidized overlayer; in this case, we show the results for both relaxed and unrelaxed calculations, observing that the AFM ordering in the overlayer is preferred only when the atom relaxation is included, stressing the interplay between geometric and magnetic arrangements.

As far as the magnetic moments are concerned, we notice (Table VII) that when oxygens have moved into the Fe overlayer, Ni atoms at the interface are aligned in a FM order; this result is robust in the sense that even assuming an AFM configuration in the reduced Ni atoms at the interface as a starting point for the self-consistent density-functional procedure, one would end up with a FM alignment. Moreover, we observe that magnetic moments of Fe atoms increase significantly upon oxidation. As we discussed in the previous section, for the case of a single Fe overlayer, this result is confirmed by spin-resolved inverse photoemission experiments.[43]

We have seen that iron oxidation is energetically favored and that oxygens prefer to leave the NiO substrate to go into the Fe overlayer. We have drawn this conclusion from the comparison between total energies calculated for different structures. Obviously, this does not include any information on the true kinetics of oxygen interdiffusion that would require an explicit simulation, inclusive of energy barriers. All the same, we may try to get indications on the mechanism of oxygen migration within the Fe overlayer. To do this, we have considered a thicker Fe overlayer.

In order to explain qualitatively the underlying mechanism, we have considered the system with 4 ML of Fe on 5 ML of NiO, limiting our analysis to perfect fcc stacking without trying any structural optimization. We have considered five different structures obtained by moving oxygens from the NiO interface layer into the Fe overlayer; these structures differ for the oxygen position within the overlayer: starting from the ideal configuration of four Fe layers on NiO, we remove oxygen from the outermost NiO plane and we put it on the first, second, third, and surface Fe layers. The comparison between the total energy calculated for the sharp interface between NiO and four Fe adlayers [S1], and for the structures where oxygens removed from the interface NiO plane have been put in the first [S2], second [S3], third [S4], and fourth (surface) [S5] Fe layers, is reported in Fig. 5.

TABLE VII. Two layer deposition. Magnetic moments (in a.u.) on Fe and Ni atoms for the relaxed structures obtained by depositing 2 ML of Fe on 7 ML of NiO. Columns [F], [D], and [D'] refer to the case of 2Fe/NiO, 2FeO/2Ni/NiO(AFM), and 2FeO/2Ni/NiO(FM), respectively. OVL1 and OVL2 stand for overlayer 1 (the interfacial one) and overlayer 2 (the surface one).

Vertical position	Atom	Magnetic moment (in μ_B) [F]	[D]	[D']
OVL2	Fe1	2.88	3.50	3.51
	Fe2	2.84	−3.51	3.50
OVL1	Fe1	2.58	3.24	3.36
	Fe2	2.59	−3.26	3.34
I	Ni1	1.18	0.58	0.77
	Ni2	−0.83	0.23	0.71
I-1	Ni1	1.40	0.82	0.84
	Ni2	−1.38	0.59	−0.26
I-2	Ni1	1.36	1.20	1.17
	Ni2	−1.36	−1.10	−1.18

It appears that the mechanism of oxygen migration is characterized by two energy drops: the first occurs when we move the oxygens from NiO to Fe; the second, when oxygens are moved into the surface Fe layer. We notice again that O prefers to oxidize Fe due to electronegativity differences, and this explains the first energy gain. Moving O from the first to the second or to the third layer does not cause any substantial change in the total energy, and a second energy drop occurs only when oxygens are moved to the outermost layer. This energy gain may be associated with the saturation of Fe dangling bonds on the surface layer.

IV. CONCLUSIONS

The adsorption of a few (one to four) Fe monolayers on NiO has been studied by DFT methods within the GGA and GGA+U schemes. Spin-polarized calculations have been performed assuming collinear orientation and neglecting spin-orbit coupling. We find that Fe is preferentially adsorbed on the oxygen, and that the oxidization of Fe and the consequent reduction of Ni at the interface layer stabilize the structures with one Fe adlayer. From the results on the systems with two Fe layers, it turns out that the total oxidation of the irons is favored, and it is accompanied by the formation of a double interface (1FeO/2Ni/1FeO/NiO), where a structure of two oxidized Fe layers sandwiching two nickel planes lies on top of the NiO surface. The predicted stability of this structure does not take into account possible energy barriers to oxygen migration that may be responsible for other configurations observed during the real growth process. Results on the adsorption of a thicker iron film (four monolayers) indicate that the two distinct mechanisms are present during the oxygen migration within the adsorbed layer: first, the reduction of NiO due to the different oxygen affinity of

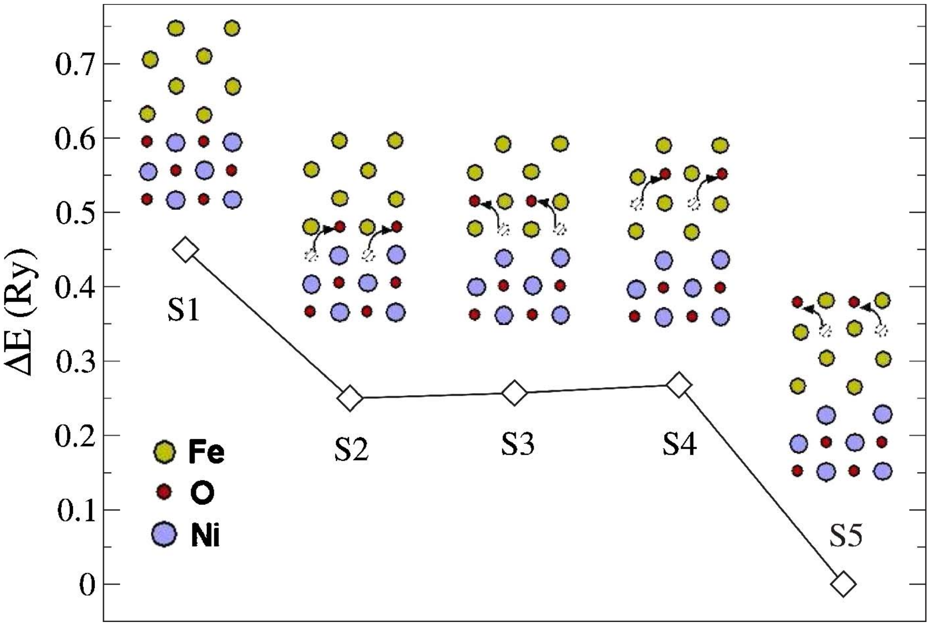

FIG. 5. (Color online) Total energy differences (with respect to the most stable system, i.e., S5) as a function of the position of the oxygens within the Fe overlayers.

the deposited metal; second, the saturation of Fe dangling bonds at the surface. For each geometrical structure, we have studied different magnetic configurations at the interface and we have verified a deep interplay between structural relaxation and magnetic configuration. We have observed that the magnetic order at the interface layers is related to the degree of oxidization (reduction) of Fe (Ni). In the special case of a single Fe monolayer, in the presence of oxidation, FM and AFM configurations of the atomic spins at the Fe/NiO interface are almost degenerate in energy. When two Fe adlayers are completely oxidized, AFM order between the Fe atoms is regained as the most stable situation, as it should in a bulk of FeO. Ni atoms in the reduced layers always prefer to align ferromagnetically. The above observations allow us to endorse the idea that oxidation at the Fe/NiO interface favors the presence of several uncompensated spins, pointed as the major cause of the exchange-bias effect at this interface.

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