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Tuning electronic and magnetic properties of ultrathin and bulk magnetic oxides by adsorption of organic molecules

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Summary. — By using the Hubbard-corrected density functional theory (DFT+U), we investigate the surface of bulk transition metal monooxides, studying the interaction with adsorbed molecules with/without intrinsic magnetic character. For the paradigmatic case of pentacene/NiO(001), we see that interaction only moderately affects the surface ground state magnetization. Conversely, ultrathin magnetic layers appear controllable by the adsorption of an organic layer, as we see by our DFT investigation for the interface formed by a C_{60} molecular layer on a two-dimensional Cr_4O_5 layer supported on Fe(001). There, the local hybridization between the electronic states of C_{60} and Cr_4O_5 is able to modify the magnetic coupling of the Cr atoms: molecules turn the ferromagnetic intra-layer coupling into an antiferromagnetic one; further patterning of the substrate spin polarization can be achieved by controlling the molecular adsorption site.

1. – Introduction

The possibility of using organic molecules in spintronic devices fostered the development of the so-called spinterfaces [1], *i.e.*, interfaces between a magnetic layer and an organic semiconductor (OS). New electronic states in such devices may arise as a result of the hybridization between the d-band of the magnetic layer and the molecular orbitals of the OS. The OS may also influence the magnetic character of the substrate [2], possibly inducing non-magnetic to magnetic transitions [3]. On the substrate point of view, spintronics based on antiferromagnetic insulators (such as some transition-metal oxides) may offer various advantages [4].

Here we analyse by first-principles the molecule/oxide spinterface in terms of the possibility of the OS to modify the substrate magnetic properties. We consider two

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prototype cases of organic molecules on a bulk magnetic oxide and an ultrathin oxide layer, namely: pentacene molecules on NiO(001), which is characterized by alternating magnetic moments for atoms belonging to subsequent (111) planes; C_{60} at a Cr_4O_5 atom-thick layer supported on Fe(001) [5], which is antiferromagnetic with respect to the support [6].

2. – Computational methods

We performed *ab initio* calculations within Density Functional Theory (DFT), as implemented in the Quantum ESPRESSO distribution (`www.quantum-espresso.org`) with plane waves and ultrasoft pseudopotentials. We treat the DFT exchange-correlation term by using the vdW-DF-c09x functional [7,8], also including van der Waals molecule-surface interaction. The substrates are modelled by a slab approach, including 3–5 NiO(001) layers or the Cr_4O_5 layer plus 4 Fe(001) ones. On-site correlations at Ni atoms are approximated by the DFT+U method, with $U = 4.0\,\text{eV}$.

3. – Results and discussion

3˙1. *Bulk magnetic oxide.* – We investigate the adsorption of pentacene on the (001) surface of bulk nickel oxide. While extensive structural search for the optimal configuration is in progress both theoretically and experimentally, we simulate planar molecules (as suggested by orbital tomography and similar to the case of pentacene on MgO(100) [9]) with a surface unit cell (see fig. 1) suggested by electron diffraction (LEED) measurements. We point out that the main outcomes do not depend on the specific pentacene configuration. We consider four possible types of absorption sites for pentacene as shown in fig. 1. Among these configurations, the one with the two pentacene molecules in the unit cell both adsorbed on bridge sites between pairs of Ni atoms with the same magnetization (leftmost in the figure) is slightly energetically favored.

We computed the modifications to the surface magnetic moments and the magnetic moments induced on the molecule upon molecule adsorption. Figure 2 shows them for the most stable configuration, finding overall weak effects. In particular, the magnetic moments of surface Ni atoms below the molecule (right panel) slightly reduce their absolute values, while the molecule (left panel) retains a zero net magnetization, with C

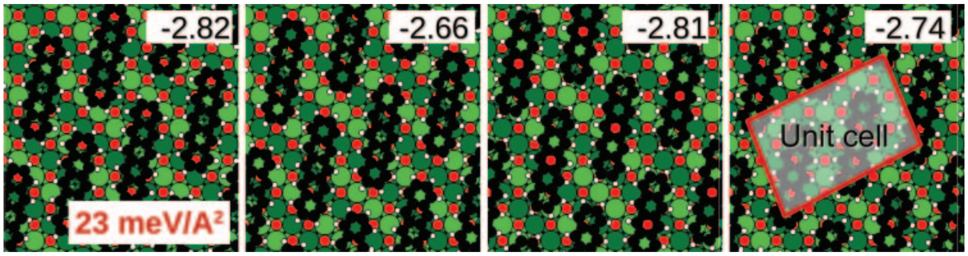

Fig. 1. – The four investigated adsorption configurations of pentacene on NiO(001), and their adsorption energies in eV per molecule, all with a surface unit cell (shown in the rightmost panel) based on electron diffraction measurements. Color codes: Ni, green (with alternating colors for AF atoms); O, red; C, black; H, white. For the energetically most favored configuration (left), the adsorption energy per unit area is also shown.

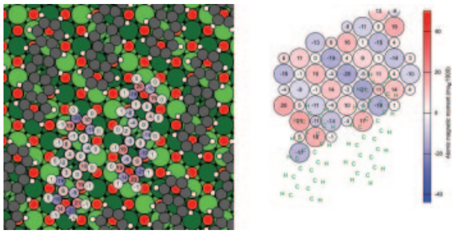

Fig. 2. – Magnetic moments (in units of $\mu_B/1000$) induced in the molecule (left) and changes in the surface magnetic moments (right) upon pentacene adsorption on NiO(001) for the most stable adsorption configuration. Left panel: same atom color codes as in fig. 1; both panels: color codes for magnetization changes as indicated in the blue to red scale on the right.

atoms attaining a rather small magnetic moment. These results depend only mildly on the adsorption configuration.

3˙2. *Ultrathin magnetic oxides.* – In order to enhance the magnetic effects induced by the adsorbed molecules on the antiferromagnetic substrate, we consider an ultrathin Cr_4O_5 layer supported by bulk iron [6, 10, 11]. Freestanding Cr_4O_5 is an antiferromagnet with alternating magnetization of Cr atoms in groups of four (see fig. 3(a), top). When adsorbed on iron, the antiferromagnetic ordering is lost, and the monolayer turns into a ferromagnet with the magnetic moments of all the Cr atoms opposite to the ones of the underlying Fe atoms [12] (see bottom panel of fig. 3(a)). The calculated energy cost to restore the antiferromagnetic configuration (AFM) is 1.2 eV, much larger than the

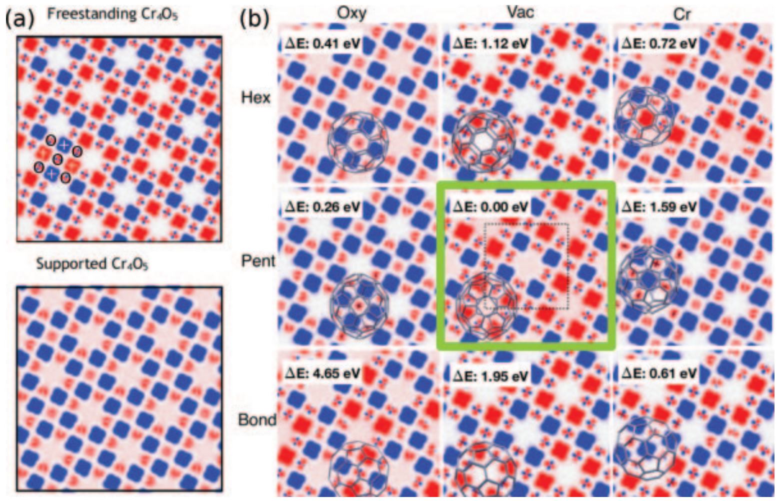

Fig. 3. – Spin density cut on a plane passing through the Cr atoms. The isosurface value is $0.02\,\text{Å}^{-3}$. Red and blue areas correspond to positive and negative values of spin polarization, respectively. (a) Without C_{60}, freestanding (top) and iron-supported (bottom) Cr_4O_5 monolayer. Cr atoms and O atoms in a surface unit cell are indicated as "+" and "O", respectively. (b) With C_{60}, for different adsorption configurations. Numbers in eV are adsorption energies with respect to the Pent/Vac case. Panel (b) is adapted from ref. [5].

energy difference between the magnetic ground state and the ferromagnetic phase in the freestanding (0.04 eV). This result highlights the strength of the magnetic interaction between the ultrathin oxide layer and the substrate that determines the spin frustration.

We evaluate the capability of C_{60} molecules to weaken the coupling between Cr_4O_5 and iron through the interaction with the organic layer. We consider a monolayer of C_{60} molecules forming a $\sqrt{2} \times \sqrt{2}R45^\circ$ superstructure of the $\sqrt{5} \times \sqrt{5}R26.6^\circ$ periodicity of Cr_4O_5/Fe. Nine possible high-symmetry adsorption configurations for the molecule have been analyzed, differing for the adsorption site and the orientation of the molecule (see fig. 3(b)). For the most stable one, namely when a pentagonal face of the molecule is adsorbed on an oxygen atom, the calculated spin density evidences an antiferromagnetic ordering of the underlying Cr atoms that is the same found for the freestanding Cr_4O_5. This indicates the possibility of restoring the original magnetic ordering by covering the surface with C_{60} molecules that reduce the magnetic coupling with the substrate, as confirmed also by the reduction of the energy cost associated to AFM to FM transition that amounts to 0.26 eV when the molecules are adsorbed. Interestingly, the other adsorption configurations at higher energy exhibit other kinds of magnetic ordering of the surface, including completely FM and completely AFM cases, or more complex magnetic patterning of the Cr atoms.

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