Charge transfer and magnetization of a MoS₂ monolayer at the Co(0001)/MoS₂ interface

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Abstract. The Co/MoS₂ system may constitute a fundamental building block for future spintronic devices based on a single MoS₂ transition metal dichalcogenide monolayer. Here, the hcp Co(0001)/MoS₂ interface electronic structure as well as magnetic properties are investigated by first principles calculations based on the density functional theory. The charge transfer due to covalent bonding between S and Co atoms at the interface has been calculated for the lowest energy configuration obtained after optimization of the atomic coordinates. This charge transfer is different for majority and minority spin electrons, which induces a magnetization of the MoS₂ layer below the Cobalt contact. The connection between the charge transfers at the interface and the modification of the magnetic properties is discussed.

1. Introduction

In the past five years, two-dimensional (2D) semiconductor materials based on transition metal dichalcogenide monolayers (MoS₂, WSe₂...) have encountered a large interest [1], due to their original properties [2] that could be used in nano-electronics, optoelectronics and spintronics. In view of future devices based on spintronics, electrical spin-injection into these 2D semiconducting single layers is a strong requirement. The more efficient way to realize such an injection at room temperature is to use a ferromagnetic metallic electrode, provided that the possible conductivity mismatch problem has been circumvented [3]. The understanding of the electronic and magnetic properties of MoS₂ at the interface is thus a key step to optimize such an injection. Here we focus on the Co(0001)/MoS₂ interface, and we analyze by first principles calculations based on the density functional theory the magnetic properties induced in the MoS₂ single layer at this interface. For realistic calculations, we considered supercells built from 5x5 Co(0001) atomic layers with the hcp stacking and a 4x4 MoS₂ single layer. These stacking would correspond to the very small lattice mismatch of 0.8%.

2. First principles methods and atomic structure of the Co(0001)/MoS₂ interface

The atomic and electronic structures of the interface have been calculated from first principles, using the code Wien2k [4] based on the density functional theory. This code uses a basis of Linearized Augmented Plane Waves+local orbitals (LAPW+lo) and the Perdew, Burke and Ernzerhof exchange-correlation potential to solve the Kohn-Sham equation, atomic sphere radii of 1.8, 1.8 and 2.0 atomic units, respectively for Co, S and Mo atoms, 24 different Bloch vectors for sampling the irreducible wedge of the two-dimensional Brillouin zone and a basis size corresponding to an energy cut-off of 151
eV ($R_{\text{min}}K_{\text{max}}=6.0$, with $R_{\text{min}}=1.8$ atomic units). The lowest energy atomic configuration has been selected from several symmetric slabs, which correspond to different possible interface atomic structures and different ways of superimposing the 4x4 MoS$_2$ single layer on the top of the 5x5 Co(0001) surface. Each slab contains a Co layer with a thickness of 5 Co(0001) monolayers, surrounded on each of its sides by a MoS$_2$ monolayer. The vacuum between periodically repeated MoS$_2$ monolayers has a thickness larger than 1 nm.

The lowest energy configuration, obtained after minimizing atomic forces, corresponds to the case where one of the S atoms of the 4x4 MoS$_2$ cell is located exactly in front of one of the hollow sites of the Co surface. The average distance between the Co and S atomic layers at the interface is of 0.205 nm, which means that these two layers are covalently bonded. The resulting Co(0001)/MoS$_2$ interface contains 25 Co and 16 S atoms. Its atomic structure can be described as follows: Each interface Co atom is bonded to a single interface S atom. One of the 16 S atoms (labelled S$_1$) is covalently bonded to 3 different equivalent Co atoms with an interatomic distance $d_{\text{CoS}}=0.236$ nm; 3 of the interface S atoms (labelled S$_2$) are each bonded to 2 equivalent Co atoms with an interatomic distance $d_{\text{CoS}}=0.234$ nm; all the other interface S atoms are only bonded to one interface Co atom ($d_{\text{CoS}}$ between 0.221 and 0.222 nm). The bonded MoS$_2$ layer is slightly corrugated.

3. Spin magnetic moments at the Co(0001)/MoS$_2$ interface

The spin magnetic moment of Co atoms is on average 8% lower at the Co(0001)/MoS$_2$ interface than in bulk hcp Co, with values that depend on the kind of interface S atom to which they are covalently bonded: The interface Co atoms that show the highest spin magnetic moment (1.62 $\mu_B$) are those bonded to the S$_1$ atom, followed by the Co atoms which are bonded to the S$_2$ atoms (1.57 $\mu_B$). All the other interface Co atoms have a spin-magnetic moment between 1.48 and 1.50 $\mu_B$. The lowering of the interface Co atom spin magnetic moment is consequently more important when Co atoms exhibit a stronger covalent bond with S atoms, with a shorter Co-S bond length. All the interface S atoms have a small spin magnetic moment which has the same sign as the Co atom magnetic moments, and take values between 0.012 and 0.016 $\mu_B$ without a clear correlation with the length of the corresponding Co-S bond. The spin magnetic moment of S atoms in the external S layer is even smaller (between 0.003 and 0.004 $\mu_B$). The spin magnetic moment of Mo atoms (between -0.029 and -0.024 $\mu_B$) is antiferromagnetically coupled to the Co and S magnetic moments, except when these Mo atoms are bonded to one or to two S$_2$ atoms (Mo spin magnetic moments are in this case positive and respectively take the values of 0.008 and 0.050 $\mu_B$).

4. Charge transfers at the Co(0001)/MoS$_2$ interface

To calculate the charge transfer between atoms induced by covalent bonding at the Co(0001)/MoS$_2$ interface, we proceeded in the following way: in a first step, we calculated the majority spin electron density $n_{\uparrow}(r)$ for the lowest energy atomic structure of the whole slab. In a second step, we calculated the majority spin density $n_{\uparrow,\text{Co}}(r)$ when all the Co atoms keep exactly the same positions, but Mo and S atoms are removed. In a third step, we obtained the majority spin density $n_{\uparrow,\text{MoS}_2}(r)$, calculated when Mo and S atoms keep the same positions, but Co atoms are removed. The majority spin space-dependent charge transfer can finally be obtained from $\Delta n_{\uparrow}(r) = n_{\uparrow}(r) - \{n_{\uparrow,\text{Co}}(r) + n_{\uparrow,\text{MoS}_2}(r)\}$. The minority spin charge transfer $\Delta n_{\downarrow}(r)$ can be obtained in exactly the same way. Fig.1 shows a side view of the unit cell (we can see that the interface atoms of the same chemical species are not all equivalent) and of the calculated three-dimensional minority spin charge transfer $\Delta n_{\downarrow}(r)$. Red and green areas respectively correspond to a local excess and a local lack of minority spin electrons. We see on this figure that charge transfer between Co and S atoms at the interface are exactly along the Co-S bonds. A similar figure (not shown here) has been drawn for majority spin electrons. These figures show that the reduction of the Co magnetic moment at the interface is due to an excess of minority spin electrons concomitant with a lack of majority spin electrons on this layer. Similarly, this figure shows that the magnetic moment of Mo atoms is due to a lack of minority spin (and to an excess of majority spin) electrons for the Mo atoms.
which have a positive spin magnetic moment (right hand side of Fig.1b), and mostly to an excess of minority spin electrons for Mo atoms which have a negative magnetic moment (left hand side of Fig.1b).

Fig.1. a) Side view of the atomic structure of the unit cell used in the calculation; Co, Mo and S atoms are respectively shown with blue, green and yellow spheres. b) Side view of the calculated three-dimensional minority spin charge transfer. Red and green areas respectively correspond to a local excess and a local lack of minority spin electrons.

5. Conclusion
We interpreted the magnetic properties induced in a MoS$_2$ layer by a Co(0001) contact in terms of charge transfer. A decrease of the interface Co atom spin magnetic moment is observed, together with a small magnetization of interface S atoms. Mo atoms also hold small magnetic moments which can take positive or negative values, depending on the atomic environment of the S atoms to which they are bonded. Such Co(0001)/MoS$_2$ interface constitute an elementary block of a full spintronic device. Results on the semiconductor or metallic nature of MoS$_2$ below the Cobalt contact, as well as on the electron spin polarization at the Fermi level in the MoS$_2$ layer bonded to Co will be published elsewhere.

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