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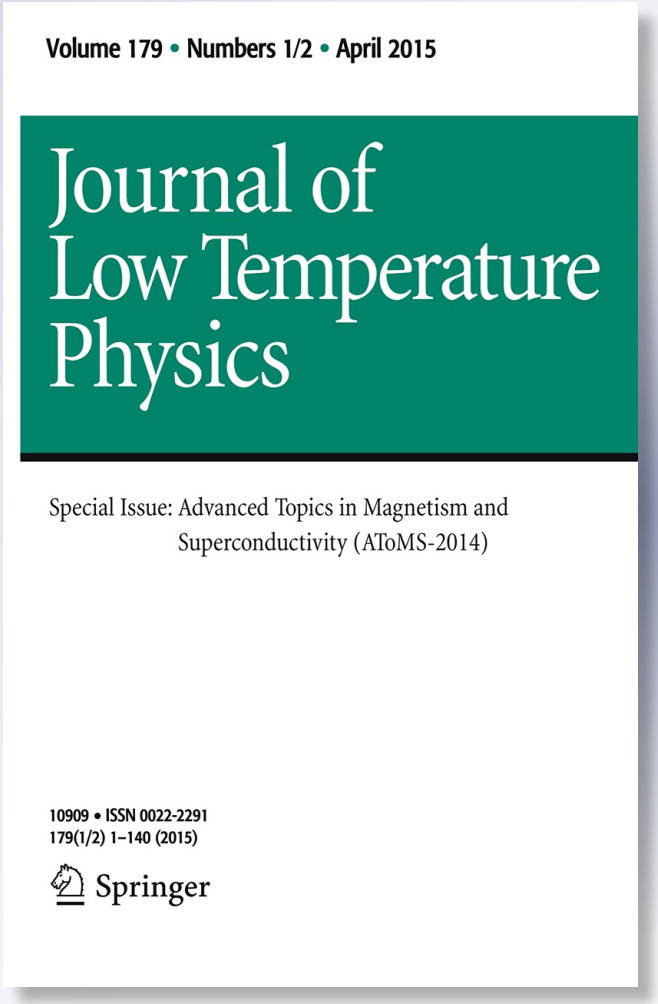

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Ab Initio Spin-Polarized calculations of Fluorine Trimers on Graphene

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Abstract We studied the magnetic states of fluorine trimers on graphene by using spin-polarized density functional calculations. We considered the absorption of fluorine atoms on one side of the graphene sheet (cis-clusters). Several possible positions of the fluorine atoms were considered to find the most energetically favorable configuration, and its different metastable magnetic states were investigated.

Keywords Graphene · Ab initio · Fluorine adatoms

1 Introduction

The chemical modification of graphene has been the subject of intense experimental and theoretical studies [1]. By attaching hydrogen, fluorine, or several other adatoms to graphene, the sp^2 hybridization of carbon atoms can be changed to sp^3. In this way, it is possible to change the electronic, magnetic, vibrational, the local structure, and in general all the properties of graphene increasing its potential applications in electronic devices.

Recently, graphene hydrogenation has been extensively studied both experimentally [2–6] and theoretically, [7–10] and hydrogen clusters are the most studied clusters on graphene. In Ref. [2], hydrogen dimers where studied in situ by Scanning Tunneling Microscopy (STM) images. A number of bright protrusions were observed which

J. Rivera-Julio · A. D. Hernández-Nieves (✉)
Centro Atomico Bariloche, 8400, San Carlos de Bariloche, Argentina
e-mail: a.d.hernandez.nieves@gmail.com

J. Rivera-Julio · A. D. Hernández-Nieves
CONICET, Buenos Aires, Argentina
e-mail: jaggerio@hotmail.com

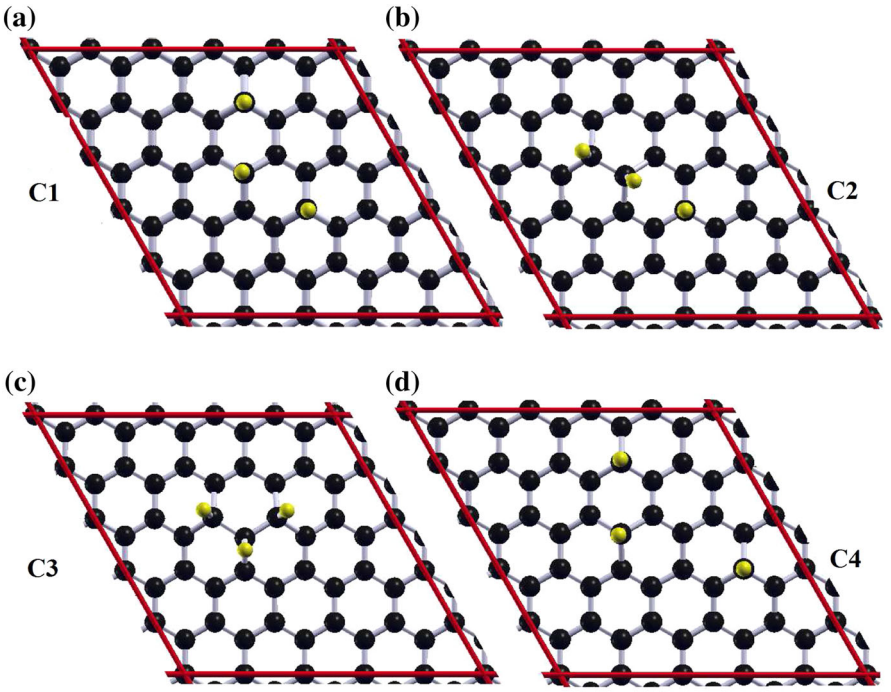

Fig. 1 *Top* view of four relaxed configurations of fluorine trimers on graphene. The *red lines* show the size of the 5×5 graphene supercell containing 50 carbon atoms (*black spheres*) and 3 fluorine adatoms (*yellow spheres*) (Color figure online)

can be attributed to hydrogen adsorbates. These experimental STM images were correlated with STM images obtained by ab initio calculations [4]. On the other hand, the experimental research of fluorine clusters on graphene is still scarce. STM images of fluorine monomers were reported for a low fluorine coverage in Ref. [11]. At these low coverages, the formation of clusters is rare but small fluorine clusters can be observed. For example, a STM image of a fluorine trimer was reported in the inset of Fig. 1 of Ref. [11].

The graphene lattice has two equivalent sublattices of carbon atoms that are usually denoted as A and B. These sublattices may become no longer equivalent after adatoms adsorption. To emphasize this point, we can use the abbreviation N_A, N_B to denote a cluster with N_A adatoms in the sublattice A and N_B adatoms in the sublattice B. In Ref. [9] by using first-principles calculations of small clusters of hydrogen adatoms, it was found that the energetically favored structures are those for which $n_I = |N_A - N_B|$ is a minimum. They also found that the electronic ground state has $|N_A - N_B|$ unpaired electrons and therefore 0, 1, 2, and 3 μB of magnetization in clusters up to four atoms, with the total spin of the system $S = n_I/2$ being also a minimum for the energetically favored structures. For three adatoms there is always an imbalance between the two graphene sublattices, and therefore all the hydrogen trimers were found to be magnetic in Ref. [9].

In this work, we analyze the magnetic behavior of four different configurations of fluorine trimers. We found that two of the fluorine trimers are magnetic, while the other two configurations are nonmagnetic. This result differs substantially from the behavior of hydrogen trimers.

2 Computational Details

The calculations were performed by using spin-polarized Density Functional Theory (DFT), as implemented in the simulation package Quantum-Expresso [12]. Exchange and correlation effects were treated within the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhoff (PBE) functional [13]. An ultrasoft pseudopotential description of the ion-electron interaction was used together with a plane-wave basis set for the electronic wave functions and the charge density, with energy cutoffs of 40 and 400 Ry, respectively. The total energy calculations were checked to be converged with a $6 \times 6 \times 1$ grid of K-points and a Gaussian smearing of 0.01 Ry. The two-dimensional behavior of graphene was simulated by adding a vacuum region of 13 Å above it. In order to obtain the most stable configuration, the fluorine trimers were studied in several configurations. All the structures were relaxed using criteria of forces and stresses on atoms of 0.01 eV/Å and 0.2 GPa, respectively. The convergence tolerance of energy in the calculations was set to 0.5 meV per atom.

3 Results

In the present work, we analyze four configurations of fluorine trimers. These configurations are among the most stable configurations for hydrogen trimers on graphene [7], and we found that this is also the case for fluorine adatoms (An extended work that will include a larger number of configurations is under way and will be reported elsewhere). The top view of the relaxed positions of the considered fluorine trimers is shown in Fig. 1. The configurations of Fig. 1 are ordered according to their binding energy, starting with the most stable configuration represented in Fig. 1a. The fluorine atoms of the configurations (a) and (d) are located almost exactly on top the respective carbon atoms, while on the contrary in the configurations (b) and (c) the fluorine atoms are shifted from the position of the carbon atoms that are below them. This is a consequence of a stronger Coulomb repulsion between fluorine atoms due to a shorter distance between them in configurations (b) and (c). Löwding charges analysis show that each F atom is charged and acquires around 0.3 electrons from graphene.

The properties of the trimers are summarized in Table 1. The energy differences between the four configurations are smaller than 0.32 eV and the energy of the second configuration is only 0.162 eV larger than the lowest energy configuration. For hydrogen dimers on the graphite (0001) surface, several metastable configurations have been observed experimentally [4] with energy differences up to 0.8 eV with respect to the most stable configuration. It is therefore expected that all of these configurations of fluorine clusters could also be found experimentally as metastable clusters.

As we mentioned before, an interesting question is whether the fluorine trimers are magnetic. We have found that two of these configurations are magnetic while the other

Table 1 Properties of the trimer configurations considered in this work

Configuration	Energy (eV)	μ_{total} (μB/cell)	μ_{abs} (μB/cell)	ΔE (meV)
C1	0.0	0	0	–
C2	0.162	0.55	1.05	1.2
C3	0.289	0.65	1.29	3.1
C4	0.314	0	0	–

Energies (eV) are reported with respect to the energy of the most stable configuration (C1). μ_{total} and μ_{abs} are the total and absolute magnetic moments of the supercell, and ΔE is the energy differences between the magnetic and non-magnetic metastable states of each configuration

two are not magnetic as can be seen in Table 1. The total magnetic moments are close to 0.5 Bohr magneton per supercell and the absolute magnetic moments are around 1.0 (μB/cell) in both cases.

If we compare fluorine trimers with hydrogen trimers, we can note important differences. In the case of hydrogen trimers, the lowest energy configuration is (c) followed by (b), and (a) [7–9]. Then in general, the lowest energy configurations are more or less the same in both cases but the order in energy is changed. More importantly, in the case of hydrogen trimers all the configurations are magnetic and their magnetization can be inferred from the imbalance between the two graphene sublattices as explained in the introduction. Therefore, we have found that the behavior of fluorine trimers is more complicated. If we analyze the four lowest energy configurations, two of them are magnetic while the other two are nonmagnetic. This shows that the magnetic state of F trimers cannot be inferred solely from the imbalance between the two graphene sublattices.

Different types of adatoms can induce magnetism in graphene [14–18]. For the case of transition metal adatoms (for example Fe and Ti, see Ref. [15]) the magnetization is mostly concentrated at the adatom, this is also the case for N adatoms [18]. On the other hand, for the hydrogen chemisorption the hydrogen induces magnetic moments in the carbon atoms in a large region around the absorption point, [17] and an itinerant magnetism was predicted in DFT calculations [17].

The spin polarization of the two fluorine trimer configurations is shown in Fig. 2. The behavior is similar to the hydrogen adatom-induced magnetism, in the sense that the fluorine adatoms induce magnetic moments in the surrounding carbon atoms. The total magnetic moment of the supercell is in both cases close to 0.5 μB, and it is distributed in the entire supercell. Therefore, the resulting magnetic moments of each atom are small around ± 0.02 μB, and some carbon atoms have larger magnetic moments of ~ 0.1 μB. This can be appreciated qualitatively in Fig. 2a and b.

The Partial Density of States (PDOS) of the magnetic trimers shows the presence of strong spin-polarized peaks very close to the Fermi level (see Fig. 3). While these peaks have a contribution from the fluorine atoms they are mainly due to the contribution coming from the carbon atoms as can be inferred from the comparison between the total DOS and the PDOS of the individual fluorine atoms in Fig. 3a and b. It is also interesting to note that for both trimer configurations (but more clearly for Fig. 3a)

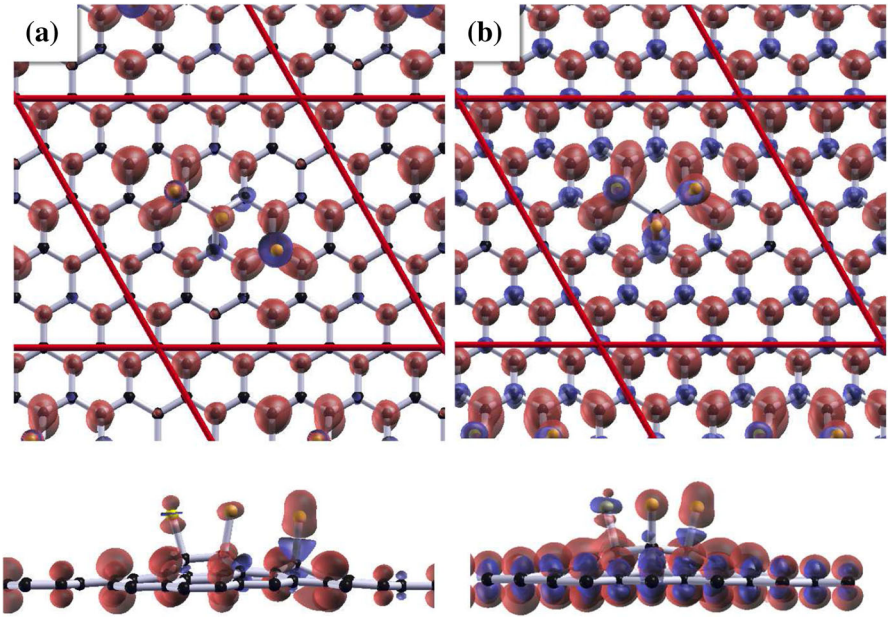

Fig. 2 *Top* and *side* views of spin density corresponding to **a** C2 and **b** C3 configurations. Regions with positive spin density are represented in *red* (*dark gray*) and regions with a negative spin density are shown in *light blue* (*light gray*). Isosurfaces correspond to $\rho_{\uparrow} - \rho_{\downarrow} = 1.3 \times 10^{-6}$ e/ Å^3 (Color figure online)

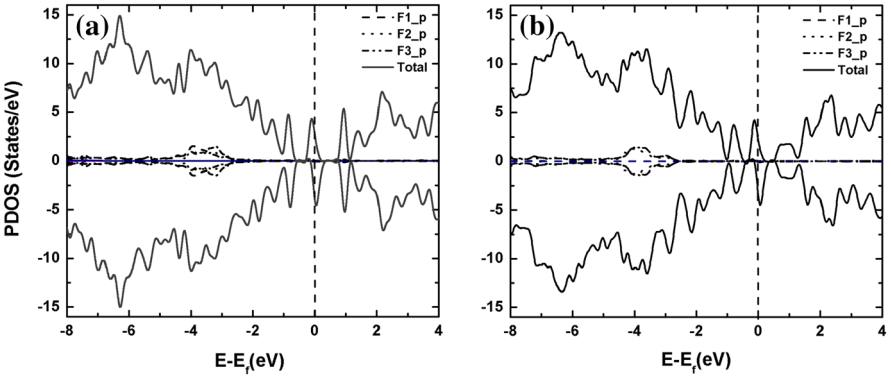

Fig. 3 Partial Density of States (PDOS) of the two magnetic configurations corresponding to **a** C2 and **b** C3 configurations of Fig. 1

the peak at the Fermi level is isolated, i.e., has two gap regions above and below the Fermi level. It is worth to mention that in our case we have periodic boundary conditions and our results correspond to a periodic array of trimers. Figure 3 also shows that spin polarization is mainly due to the shifting of the peaks at the Fermi level.

4 Conclusions

The magnetic properties of fluorine trimers on graphene show a rich behavior. We have shown that for fluorine trimers the total spin (S) is not determined by the imbalance between the two sublattices ($S = |N_A - N_B|/2$) as is the case for hydrogen clusters. Some of the analyzed F trimers are not magnetic even when the graphene sublattices are not balanced. This is also the case for an isolated fluorine atom [19].

The spin density plots show that the fluorine adatoms also induce small magnetic moments on the surrounding carbon sublattices at distances given by the analyzed 5×5 graphene superlattice, containing 50 carbon atoms. A behavior that in this case is similar to the behavior of small hydrogen clusters on graphene.

The energy differences between the magnetic states and the metastable non-magnetic states of the fluorine clusters are small, of the order of 3 meV ($\sim$35 K).

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