

Influence of iron impurities on defected graphene



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ABSTRACT

The aim of this work is to study the interaction of selected iron cluster impurities and a multivacancy graphene system, in terms of the structural distortion that the impurities cause as well as their magnetic response. While originally, the interaction has been limited to vacancies and isolated metallic atoms, in this case, we consider small iron clusters. This study was undertaken using Density Functional Theory (DFT) calculations. The influence of the iron impurities in the electronic structure of the vacant graphene system is discussed. The main conclusion of this work is that the presence of iron impurities acts lowering the magnetic signal due to the occurrence of spin pairing between carbon and iron, instead of enhancing the possible intrinsic carbon magnetism.

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1. Introduction

The emergence of intensive research in carbon nanomaterials started with the discovery of fullerenes [1] and the preparation of carbon nanotubes [2], due to the novel properties found in them.

Later, graphite [3–8] and especially graphene [9,10] have been the focus of research in the pursuit of new materials with advanced properties, particularly referred to electronic properties, such as magnetism and electronic transport, in close relationship with structural features like defects and quantum confinement.

Although magnetism in carbon materials has been a matter of controversy a few years ago, there were many articles reporting about this field [3,4,11–14] until this phenomenon was unambiguously demonstrated [15]. Recently, some studies have undertaken the attempt to explain theoretically this phenomenon [16–26], being the origin of this behavior the existence of unpaired electrons, which could arise from defects, impurities and other local structural perturbations. In particular, the occurrence of magnetism as a function of the order and shape of a multivacancy graphene system has been studied with the focus on the role of the dangling bonds and their relative configurations [18].

Multivacancies in graphene can adopt different configurations as reported in experimental studies [27–30]. This fact has been

used in other simulation works and it is widely accepted [31,32], even for more complex configurations [33,34].

The complementary figure – i.e. the geometric figure of the atomic arrangement that is extracted from graphene when the multivacancy is created – is a concept that has been very useful to describe the influence of the structural configuration of the vacancy with respect to the removed carbon atoms and the resulting magnetic arrangement [18,19].

The predictive usefulness of such a concept to determine the magnetic properties of a defected graphene material will become more important when more advanced technologies to build multivacancy graphene systems of specific configurations will be available in the future [27,28].

These multivacancy systems could be suitable for testing the interaction between a magnetic impurity – i.e. a metal atom or cluster – and a defected graphene layer. The presence of impurities is usual in most real-life carbon samples and the absence of impurities is the exception, mostly very high quality HOPG-highly oriented pyrolytic graphite – [15]. These metallic impurities and the difficulty to get rid of them has been the fact that has slowed this field for years, because the real nature of the observed magnetic signal in nanostructured carbon materials was often confused by these metals. Even if the occurrence of magnetism in pure carbon samples has been already accepted [15], the interaction between the magnetic impurities and an already intrinsic magnetic carbon material still remains open.

In relation to the interaction of vacancies with metallic impurities, several works have addressed this issue but limited to interactions of small vacancies with isolated metallic atoms [35]. While

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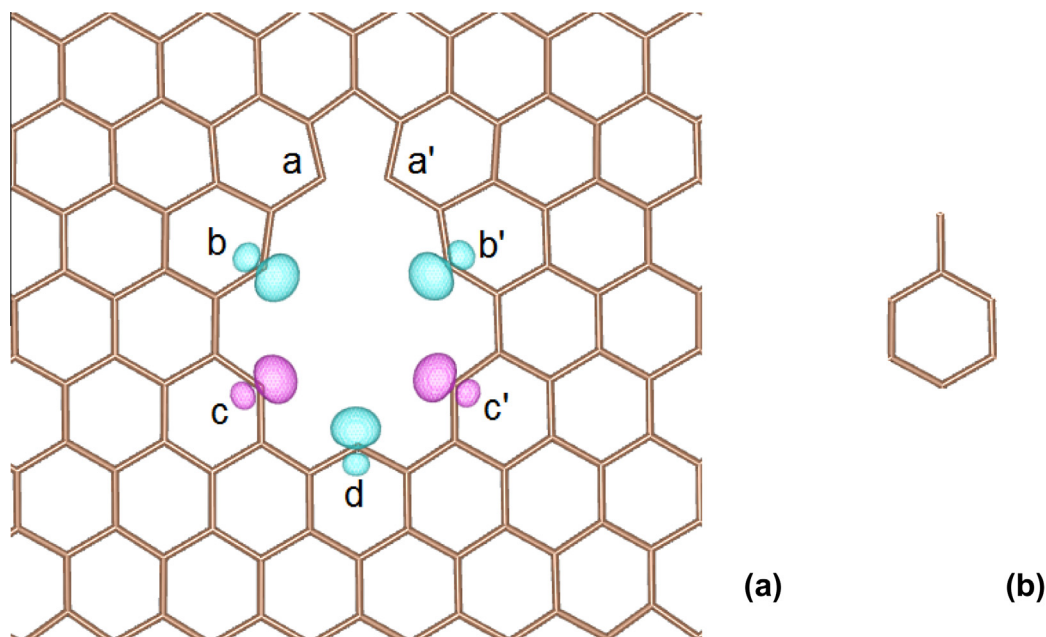


Fig. 1. (a) Scheme of the 7-order graphene multivacancy system studied in this report. The dangling bonds are shown. (b) The complementary figure that gave place the vacancy after its removal. Note: Spin-up and spin-down isosurfaces at 50% of maximum value is presented in cyan and violet, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

many of them are just focused in the graphene/metal interaction for catalysis purposes, or for graphene healing purposes, in our case the focus is on the magnetic interaction between them.

Although for some configurations the stability of multivacancies could be low and coalescence could happen, it is important not to forget that in normal samples, iron is present in the specimen before the defect is created – either using a sophisticated method such as irradiation [28] or through a simpler and less controlled technique, as the redox etching [3,4]. The iron impurities such as atoms or clusters are already in the specimen and available to interact with the vacancy as soon as it is created, thus increasing the probability of the embedding of iron cluster (or atom) in the vacant graphene to occur.

For these reasons, the iron doped vacant graphene systems are potentially realistic, even in the 7-order multivacancy system, chosen for this work, due to the intrinsically magnetic behavior that it shows because of the dangling bonds odd number.

A 7-order vacancy, corresponding to the removal of 7 carbon-atom cluster on graphene based on the extraction of a methyl-phenyl-like segment, was previously predicted and reported from our group, in which a ferrimagnetic arrangement with 5 dangling bonds with a magnetic moment $1.50 \mu_B$ is observed [18].

We have chosen this system because it has a ferrimagnetic ordering based on the dangling bonds and the vacancy formed after the removal of the toluene-like moiety of carbon atoms (i.e. the complementary figure).

As previously stated, there are many examples of vacancies in graphene and graphite where many dangling bonds could be exposed. There are experimental reports that show the formation of nano- and even micropores with rather circular shapes [4], and also with dendritic growth [27] and some experimental studies have concluded that not always there is evidence that hydrogen terminates the edge carbon atoms in nanoholes [30]. These manuscripts show the possible existence of vacancies where dangling bonds could exist long enough to participate in temporal events.

This background and the fast availability of iron atoms due to their previous presence in the samples, supports the realistic view

of this article and the interest to undertake this work is based in the presence of different iron impurities of most carbon sources and the need to further understand the interaction of these two substructures.

This manuscript undertakes the study of iron and a defected graphene layer using *First Principles* through Density Functional Theory (DFT) [36,37], to study the interaction between an impurity and a carbon material in a different size approximation. The iron impurity in this study is an atom and small tetrahedral and octahedral clusters and the carbon material is the 7-order vacancy graphene layer that was previously established to be ferrimagnetic with $1.50 \mu_B$ as magnetic moment.

2. Computational methods

Periodic spin-polarized band structure calculations were performed on graphene multivacancies systems with the use of Density Function Theory within the Kohn–Sham Framework [36,37] using GGA as the exchange correlation functional [38]. We used the VASP code (Vienna *ab initio* simulation package) [39]; where pseudopotentials were applied with a plane-wave basis set utilizing projector augmented wave (PAW) method [40,41]. In order to validate the methodology two further cases were evaluated selecting PBEsol [42] and HSE06 [43]. An energy cutoff of 500 eV was used to expand the Kohn–Sham orbitals into plane wave basis sets. In all of the calculations reported here the k-point mesh was taken equivalent to $4 \times 4 \times 1$ for the full (reducible) Brillouin Zone, allowing the convergence of total energy, stress components and ionic forces. We constructed 6×6 graphene supercell in order to include the vacancy and the iron impurity – atom or cluster, the c-axis was kept at 15 Å in order to avoid interferences between periodical images. Both supercell dimensions and ions positions were allowed to optimize, until residual forces and stress tensor components were positioned down to 0.02 eV/Å and 5 kBar respectively. In order to confirm the local minima for all the structural geometries, the corresponding vibrational frequencies and phononic density of states were obtained using the PHONOPY code

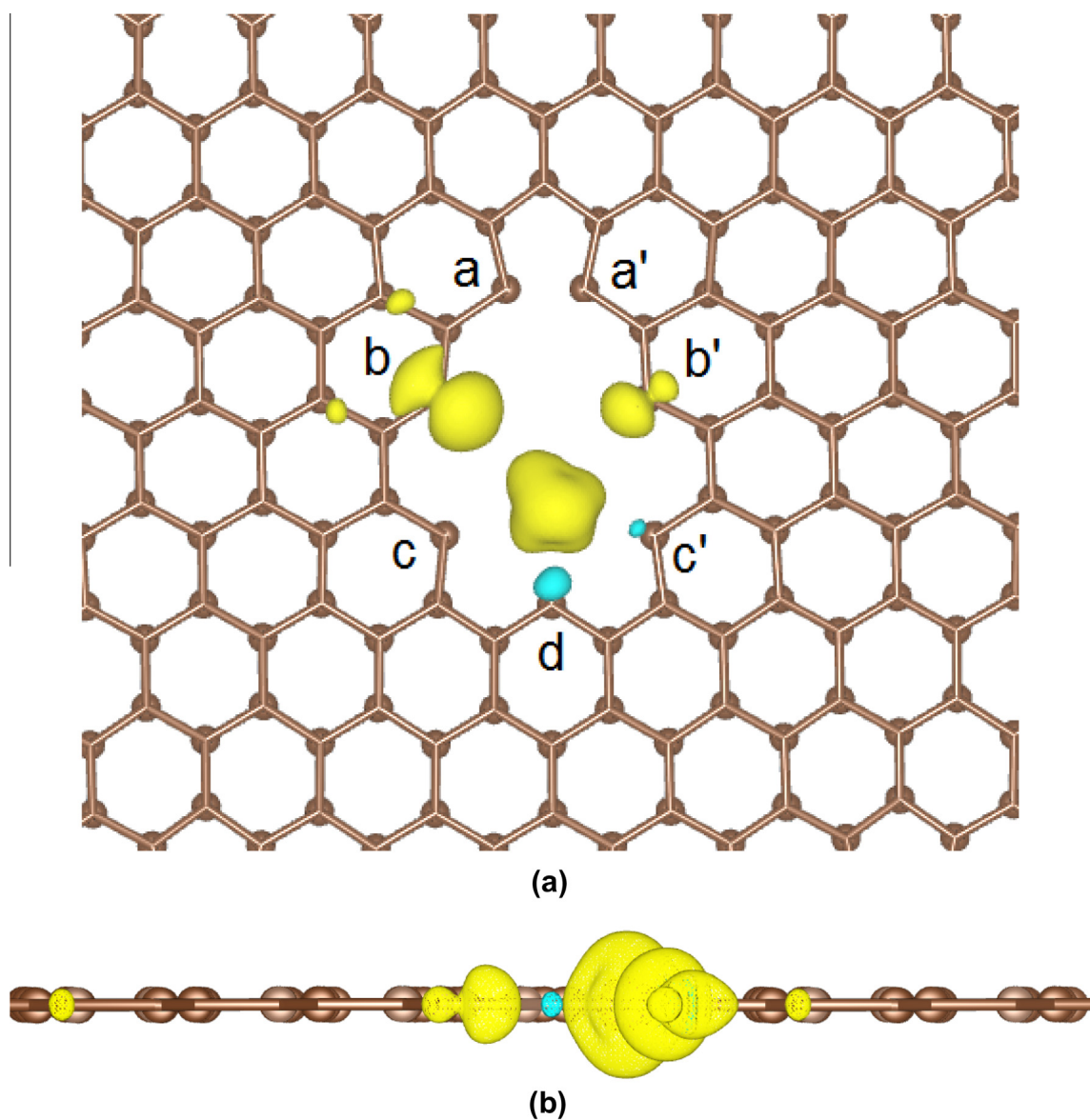


Fig. 2. One iron atom impurity in the 7-order graphene multivacancy system. (a) [001] and (b) [100] directions. Note: Spin-up and spin-down isosurfaces at 50% of maximum value is presented in yellow and cyan, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[44], which can directly use the force constants calculated by Density Functional Perturbation Theory, DFPT [45].

3. Discussion and results

The first step of our work consisted in the evaluation of the effect of different exchange–correlation functionals, particularly focused in the effect over the net magnetic moment. The bibliography shows extensive work in which GGA-PBE was selected for the full structural optimization and to get the electronic properties associated to the observed magnetism. In our case we followed the same procedure, but after performing the full structural optimization we considered PBEsol [42] and the recent hybrid functional HSE06 [43]. In the case of PBEsol we obtained a magnetic moment of $1.47 \mu_B$, which is in close agreement with the value $1.50 \mu_B$ obtained with PBE. When HSE06 is considered, the magnetic moment increases up to $2.0 \mu_B$ giving place to an enhancement of the magnetic contribution from π -states, which increases from $0.5 \mu_B$ to $1.0 \mu_B$ when changing from PBE to

HSE06. Since we are focusing in getting trends in the magnetic moment, we selected PBE as the exchange correlation functional, since it can be considered as a lower bound in terms of the obtained net magnetic moment.

Fig. 1 shows a scheme of the 7-order graphene multivacancy system, which is the focus of this report. The spin density map for the three systems containing iron, can be seen in Figs. 2–4, for Fe atom, and the tetrahedral and octahedral clusters, respectively.

Before any consideration we present a vibrational analysis in order to confirm that all the selected structures actually correspond to local minima. As mentioned in the methodology, we performed DFPT in order to get phonons, and then we used PHONOPY for getting the phononic density of states. Fig. 5 presents the four cases: 7-order graphene vacancy, Fe-monoatomic and Fe-tetrahedral and Fe-octahedral clusters. As it can be observed, there are similarities among them, with the major differences localized in two ranges: $0\text{--}400 \text{ cm}^{-1}$ and $1300\text{--}1700 \text{ cm}^{-1}$. The first range of $0\text{--}400 \text{ cm}^{-1}$ phononic is mainly the contribution from iron atoms, as can be seen from the partial phononic density of states. It

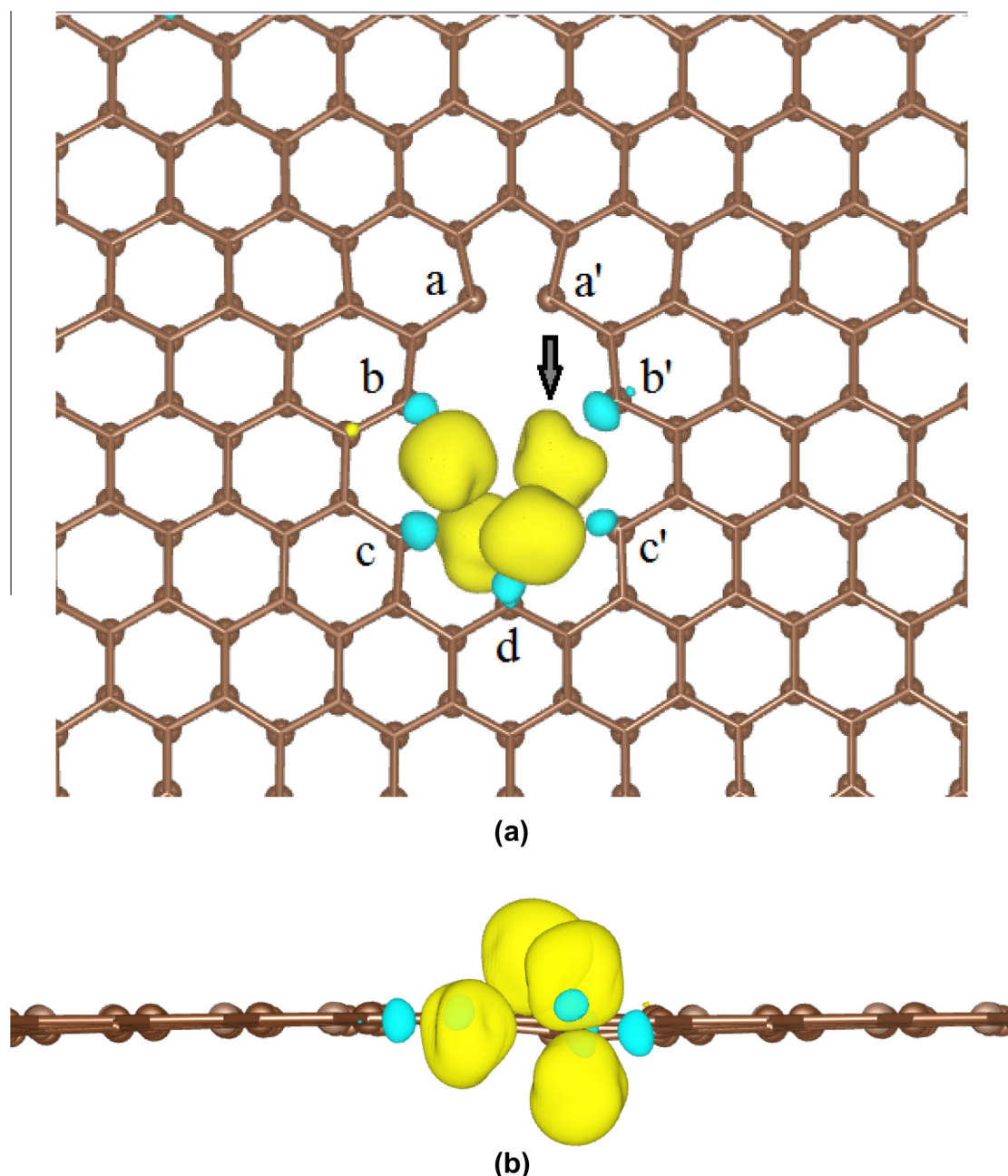


Fig. 3. Tetrahedral iron cluster in the 7-order graphene multivacancy system. (a) [001] and (b) [100] directions. Arrow shows the iron atom in the graphene plane. *Note:* Spin-up and spin-down isosurfaces at 50% of maximum value is presented in yellow and cyan, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

explains the differences observed in that region due to the differences in the iron contents. The other mentioned phonons range – $1300\text{--}1700\text{ cm}^{-1}$ – is attributed to strong carbon–carbon bonds, as a consequence of the structural reconstructions in the vicinity of the vacancy. As soon as the iron clusters starts to heal the vacancy, forming more Fe–C bonds, the shorter C–C bonds disappear, recovering the hexagonal and conventional sp^2 -hybridization. This situation approaches the pristine graphene, where the higher frequencies correspond to the G-band located 1585 cm^{-1} , as observed in Fig. 5b.

After demonstrating the local minima on all the structures we start to study the interaction of the 7-order graphene vacancy system with the monoatomic iron impurity. This iron atom was located in the centroid of the vacancy and its three coordinates

were released to optimize the structure of the total system. The final structure is shown in Fig. 2. The dangling bonds system that was responsible for the ferrimagnetism exhibited in the impurity-free 7-order vacancy is severely modified after the iron atom inclusion. While the a and a' coordination points are close enough to form a pentagon, thus leaving no dangling bonds at those points – as in the impurity-free system, the rest of the coordination points, where the dangling bonds were resident, were affected. In fact, the spin-down electronic density is non-significant – only visible at c' and d – and the spin-up electronic density is seen on the iron atom and the b and b' points, in a nonsymmetric manner. This can be seen from Fig. 1 and the bond lengths in Table 1.

The second and the third cases are iron clusters, tetrahedron and octahedron. The coordinates for all the iron atoms belonging

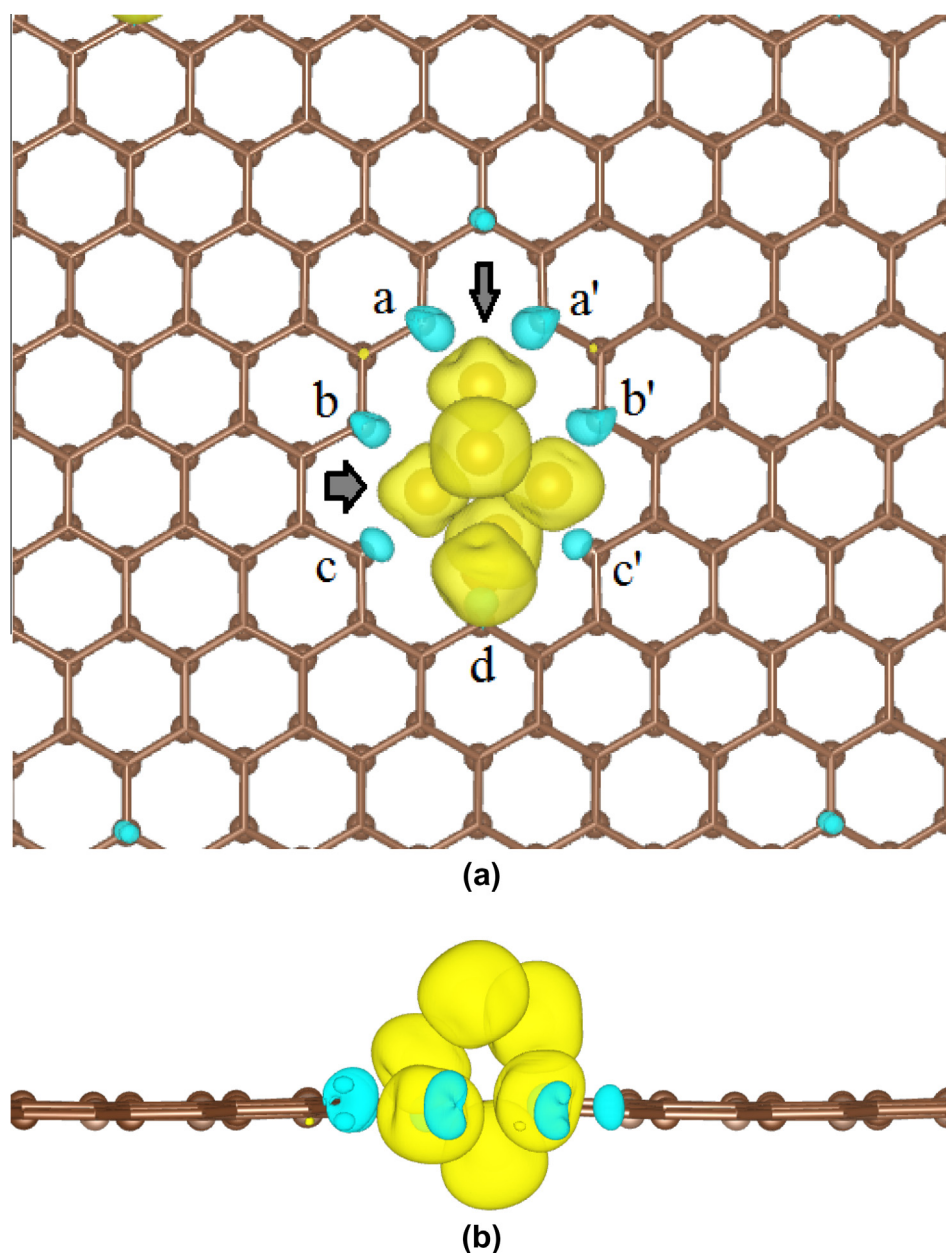


Fig. 4. Octahedral iron cluster in the 7-order graphene multivacancy system. (a) [001] and (b) [100] directions. Arrows shows the iron atoms in the graphene plane (horizontal arrow, Fe1, vertical arrow, Fe2). Note: Spin-up and spin-down isosurfaces at 50% of maximum value is presented in yellow and cyan, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to these clusters were released to optimize so that the final structures do not preserve the symmetry of the original platonic solids.

In the case of the tetrahedron, one of the iron atoms occupy a position in the plane of the defected graphene system – Fe2 according to our records. In this case almost no dangling bonds can be seen with the exception of a very small spin-down signal at b'. It can be seen in Fig. 3.

The octahedron case shows an edge in the plane of the graphene system – Fe1 and Fe2 to our records, as shown in Fig. 4. For this case it is not possible to determine any trace of spin density along the defected graphene system. The spin density is only on the iron atoms at the distorted octahedral environment.

Table 1 shows the structural distortion that the presence of the iron impurities causes when compared with the impurity-free system and pure graphene too. Some of these parameters are also graphically shown in Fig. 6. It can be seen from Table 1 and from

Figs. 2–4, that no significant distortion on the planarity of the graphene lamellar structure is evident even with the largest impurity. The largest anomaly is seen for the tetrahedral case, with a dihedral angle of 169.66° in the surroundings of the d' point. Moreover, Fig. 6 shows a better behavior from the structural point of view, for the Fe atom case than for the impurities-free one, since a–a', b–b' and c–c' distances are shorter. These distances become longer for the tetrahedral and the octahedral cases.

Another relevant observation refers to the geometrical reconstruction induced for both iron clusters, and the generated carbon-to-carbon distances and their relationship with pure graphene. The a–a' distance correspond 1.62 Å and 2.47 Å for 7-order vacancy and pure graphene respectively. When iron is embedded in the vacant graphene, the a–a' distances change to 1.62 Å, 1.68 Å and 2.57 Å for Fe-atom, Fe-tetrahedral and Fe-octahedral systems, respectively. These results indicate that the Fe-

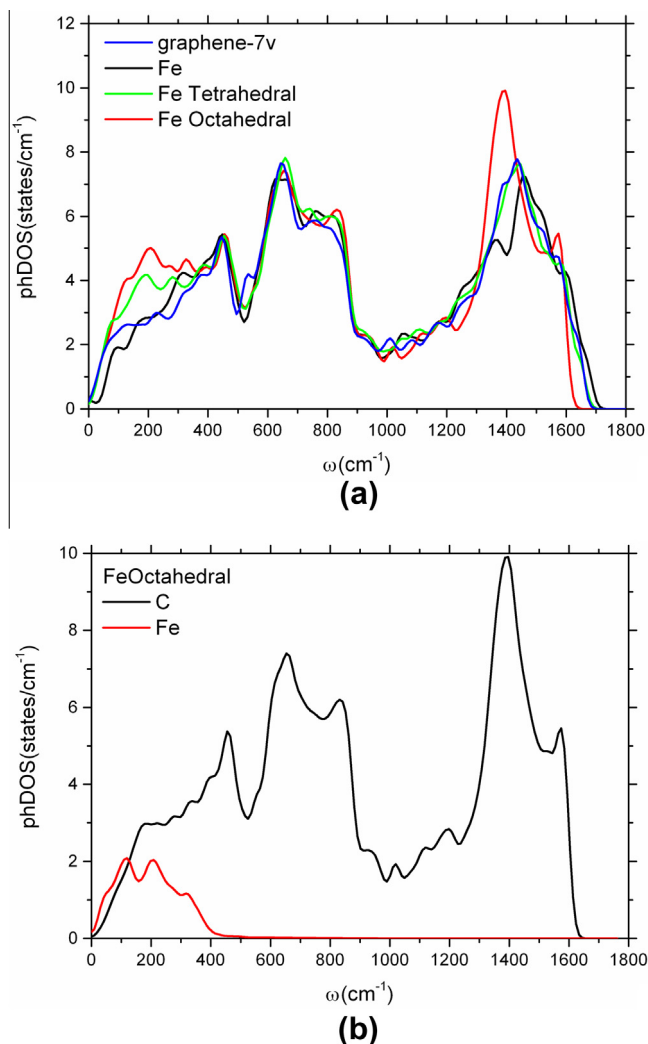


Fig. 5. (a) Phononic density of states for the four evaluated systems: graphene 7-order vacancy, graphene with Fe monoatomic, graphene with tetrahedral cluster and graphene with octahedral cluster. (b) Partial phononic density of states showing the contribution from Fe and C atoms separately.

Table 1

Structural features in the vacancy, for the pure graphene system and the ones containing impurities.

	Pure 7-order vacancy system	Fe atom	Fe tetrahedral cluster	Fe octahedral cluster	Pure graphene
a–a' distance (Å)	1.650	1.622	1.676	2.567	2.47
b–b' distance (Å)	4.648	4.301	4.474	5.021	4.94
c–c' distance (Å)	4.852	4.352	4.690	4.973	4.94
c–b'–c' dihedral angle (°)	0.07	0.00	6.09	3.91	0.00

octahedral case favors a structural reconstruction closer to the pristine graphene, and confirmed for other structural features like b–b' and c–c' distances as presented in Table 1. This fact explains the relatively favorable formation energy for the octahedral case when comparing with the other cases (see Table 2).

The presence of the single Fe atom contributes with electronic density to the vacancy, compensating the loss of charge that appears when the carbon atoms are removed. Subsequent addition of iron atoms stresses the structure in the vacancy systems, yielding to distortions that allow the clusters to fit in them. These distortions occur mainly in-plane and the more significant effect

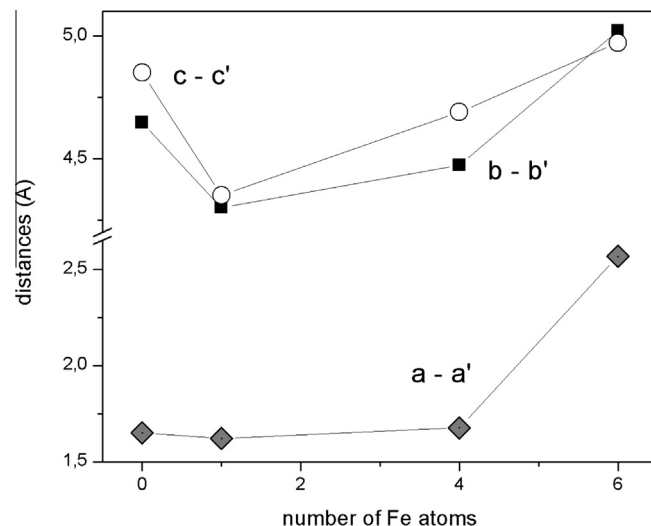


Fig. 6. According to the scheme of coordination points, distances between carbon atoms in impurity free (0), one atom (1), tetrahedral (4) and octahedral (6) cluster systems. Solid lines are just guides to the eye. Grey diamonds are a–a', solid squares are b–b' and hollow circles are c–c' distances, respectively.

Table 2

Structural features related to the iron atoms, for the pure graphene system and the ones containing impurities.

	Fe atom	Fe tetrahedral cluster	Fe octahedral cluster
Shortest Fe–C distance (Å)	1.971 (respect to d)	1.911 (Fe2 respect to b')	1.893 (Fe2 respect to a and a')
Fe–Fe distances range (Å)	N.A.	2.187–2.592	2.231–4.034
Dihedral angle related to the in-plane Fe atom(s) (°)	c–b'– Fe: 0.02	c–b'–Fe: 2.50	a–Fe2–Fe1–c': 179.68 a'–Fe2–Fe1–c: 179.06

out-of-plane can be seen for the tetrahedral cluster. Table 3 exhibits information about the magnetic moments of the pure iron and the pure carbon systems and the vacant graphene with iron impurities, as well as their stabilization energies. These results imply that the inclusion of the iron impurities is favorable and therefore the incorporation of such clusters is possible. In principle this results is reasonable, on the basis of the interaction of a system with vacancies with another small atom cluster.

In relation to the magnetism in the iron impurities containing systems, the differences in magnetic moments, as defined for Table 3, show loss of magnetic signal as compared to the separated and non-interacting systems. However, if interaction occurs among the vacant graphene and the iron cluster (or atom), it is expected that spins pairing occur with the decrease in the magnetic moment. With this in mind, if we calculate the net magnetic coupling as defined in Table 3, this result would imply the magnetic moment that the carbon structure would contribute with to pair the same (but opposite) magnetic moment in the iron cluster. In the case of the iron atom, the interaction with the vacant graphene is incipient so it is the spin pairing. When the tetrahedral and the octahedral clusters are embedded in the vacant graphene, the net magnetic coupling is greater than the magnetic moment in the pure carbon structure, which means that in these cases, a variation from the ferrimagnetic ordering observed in the pure carbon structure should take place. In fact, as can be seen in Figs. 3 and 4, a ferromagnetic arrangement stabilizes in the vacancy due to the strong

Table 3

Magnetic moment data and formation energies for the impurity free and the iron containing systems ((*) magnetic moment orbital occupancy).

	Pure 7-order vacancy system [18]	Fe atom	Fe tetrahedral cluster	Fe octahedral cluster
Magnetic moment for the pure iron systems (μ_B)	N.A.	3.53	12.27	18.01
Magnetic moment for the pure vacant graphene and the impure systems (μ_B)	1.50	3.37	9.29	13.54
Difference in magnetic moment (μ_B)	N.A.	−1.66	−4.48	−5.97
Net magnetic coupling (μ_B)	N.A.	0.16	2.98	4.48
Magnetic moment, z component (μ_B) (*)	0.00	2.73	9.20	13.94
Magnetic moment in the Fe atom(s) system (μ_B)	N.A.	2.81	9.33	14.01
Magnetic moment, z component, in the Fe atom(s) system (μ_B) (*)	N.A.	2.73	9.20	13.94
Magnetic moment, xy plane component, in the Fe atom(s) system (μ_B) (*)	N.A.	0.06	0.10	0.12
Magnetic moment per Fe atom (μ_B)	N.A.	2.81	2.33	2.34
Magnetic moment in the defected graphene system – exclusively confined in the xy plane – (μ_B) (*)	0.02	0.01	0.00	−0.01
Magnetic moment in the defected graphene system per carbon atom (65 atoms) (μ_B)	0.02	0.01	0.00	−0.01
Formation energy (eV)	−584.557	−592.186	−616.350	−632.504
Formation energy for the pure iron systems (eV)		−3.255	−21.929	−36.285
Stabilization energy (eV)		−4.374	−9.864	−11.662

Stabilization energy = formation energy (impure system) – (formation energy (vacant graphene pure system) – formation energy for the pure iron systems).
 Difference in magnetic moment = magnetic moment (impure system) – (magnetic moment (vacant graphene pure system) + magnetic moment (pure iron system)).
 Net magnetic coupling = magnetic moment (pure iron system) – magnetic moment (impure system).

influence of the iron clusters. The higher value of the magnetic moment of this ferromagnetic ordering in the octahedral cluster compared to the tetrahedral cluster containing system, could be explained by the a–a' distance elongation. The distortion induced by the steric hindrance caused by the bigger octahedral cluster is enough to allow the appearance of incipient dangling bonds at a and a' carbon atoms in the vacancy.

Figs. 7 and 8 show the density of states for the Fe, Fe-tetrahedral and Fe-octahedral clusters, in a wide view and focused in the Fermi level region, exhibiting the carbon and the iron atoms contributions. The contribution at Fermi level is mainly due to C, as expected. Since there still exist dangling bonds from graphene, which contributes with non-bonding states at the Fermi level. When we consider the interaction of larger Fe atom clusters, there is an increase in the contributions from Fe and since there are less dangling bonds in graphene, the contribution of graphene at the Fermi level is small.

In all cases there is a clear asymmetry between the spin-up and the spin-down curves, confirming their magnetic nature. While for the iron atom case, the structure looks like half metal, with emphasis on the π -system of the carbon atoms, the tetrahedral and the octahedral cases are semimetals, with very low DOS at the Fermi energy level, where iron and carbon contribute similarly to this feature.

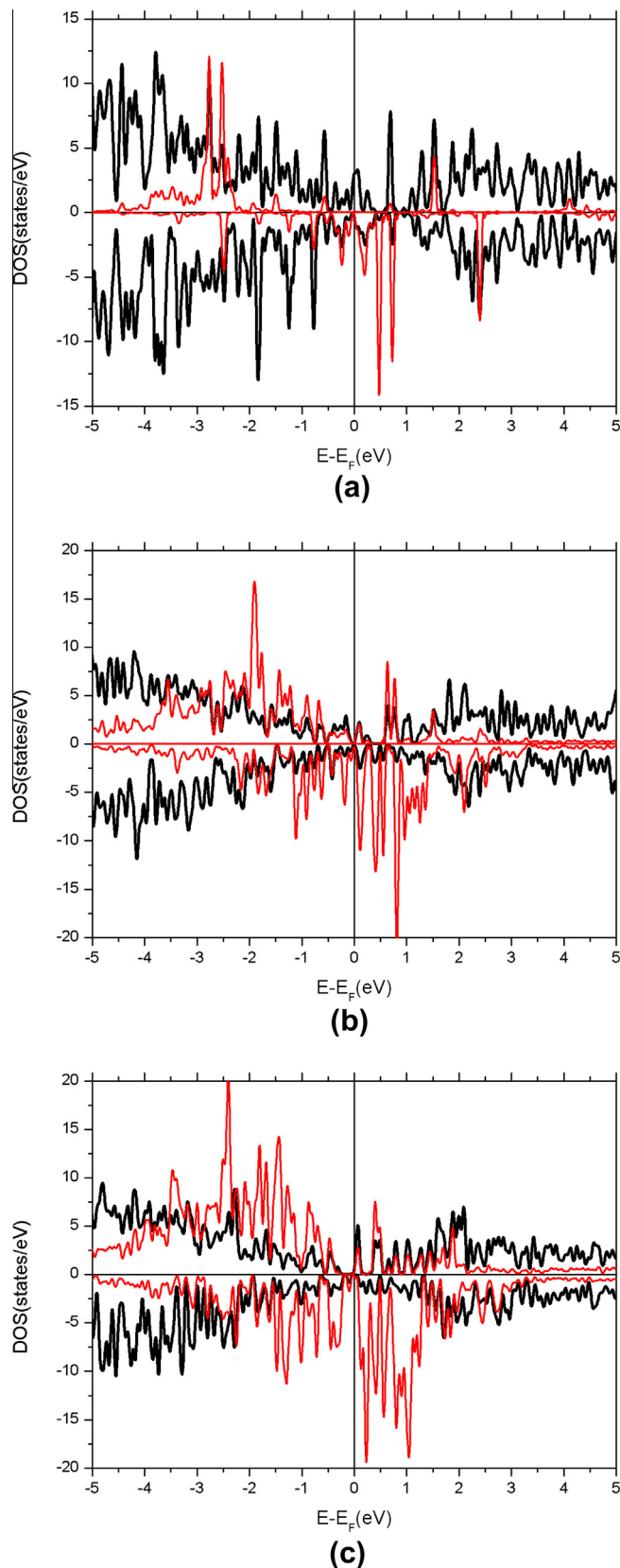


Fig. 7. Density of states for (a) Fe atom, (b) Fe tetrahedral and (c) Fe octahedral clusters, in a 7-order graphene multivacancy system – black thick and red thin lines corresponds to C and Fe atoms contributions, respectively.

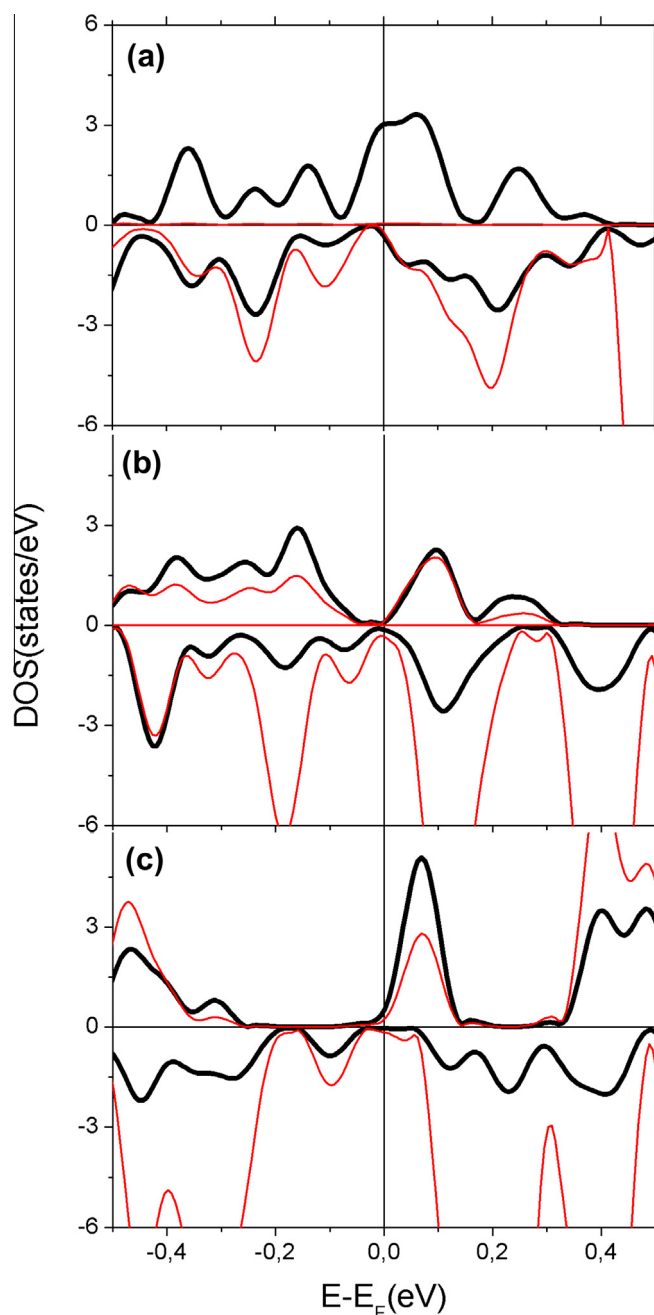


Fig. 8. Density of states for (a) Fe atom, (b) Fe tetrahedral and (c) Fe octahedral clusters, in the vicinity of the Fermi energy level in a 7-order graphene multivacancy system – black thick and red thin lines corresponds to C and Fe atoms contributions, respectively.

4. Conclusions

From the structural point of view, the inclusion of iron impurities in the 7-order vacancy graphene system shows an evolution, first fitting in the vacancy as is the case of the iron atom, then affecting the atomic structure with a slight distortion, as for the tetrahedral cluster and finally with a distortion that opens the vacancy for the octahedral cluster case. In all the studied cases, the incorporation of the iron clusters (or atom) is favorable according to the formation energies. The magnetic response of the vacant graphene structure when the iron clusters are embedded is to switch from ferri- to ferromagnetic arrangement in the dangling

bonds at the vacancy edge, in order to stabilize structures by promoting spin pairing between iron and carbon. For this reason the magnetic moment of the overall structure is lower than the ones of the iron clusters when isolated. Previous experiments using MFM (magnetic force microscopy) in a defected graphitic structure, obtained after a process that chemically created nanostructural vacancies [3], showed the occurrence of magnetic domains along the whole graphitic material. Instead of enhancing the possible intrinsic magnetism in defected graphitic specimens, the presence of iron impurities lowers the magnetic signal due to the occurrence of spin pairing between carbon and iron.

The results obtained in this manuscript suggest that the signals obtained by MFM, observed along the lamellar structures, are produced by the presence of defects – vacancies – in the structure at the nanoscale level, rather than the iron impurity nanoparticles that could be present contaminating intrinsically the original unprocessed graphitic material.

Finally, the existence of magnetic nanoparticles affects the electronic structure of the graphitic material, leading in some cases to half metal or semimetallic behavior.

Conflict of interest

The authors declare that there is no conflict of interest in this article.

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