

Full Length Article

Sulfur doping in multivacancy graphene systems

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ARTICLE INFO

Keywords:

Graphene

DFT

Vacancies

Sulfur

ABSTRACT

The conformational, magnetic and electronic study of one and two sulfur atoms doping on multivacancy graphene systems, using first principles calculations is presented. The location for the addition of the sulfur atoms is ruled by the presence of pentagonal figures in the optimized multivacancy graphene system or, in case of the absence of such figures, by the concave four membered structures in the vacancy. The electronic structure and the magnetism in these systems are strongly affected by the cancellation of dangling bonds due to the inclusion of sulfur atoms. Finally, it was possible to demonstrate that the inclusion of one and even a second sulfur atoms in the multivacancy graphene systems is favorable.

1. Introduction

In the last years carbon nanomaterials attracted the interest of the scientific community, first with the discovery of fullerenes [1], later with the synthesis of carbon nanotubes [2] and finally with the isolation of graphene [3].

The study of graphene has been considered as a high impact topic, due to the unique properties that have been found, for example, thermal and electrical conductivity, and mechanical properties [4,5].

In spite of these properties, very soon the scientific community started to focus on defected graphene systems in the pursuit of the applicability of these carbonaceous materials. As an example, the need to open the gap, the advantages of include tailored functionalizations or the potential that comes along when growing bottom-up hybrid materials, encourage the research in graphene systems where different approaches for including defects are attempted.

Among the defects that could occur in graphene, the presence of multivacancies is a very feasible option, since its preparation is based in oxidation and reduction processes. Due to the importance of such defected materials, systematic studies about magnetism [6] and stability [7] of these multivacancy graphene systems were performed, where the configuration of the vacancy was described using the complementary figure concept, i.e. the figure formed by the carbon atoms extracted.

Apart from the vacancy formation, and after it is created in the

material, the interaction with metal atoms or clusters is possible [8,9], not due to a mere replacement but rather as atoms or clusters present as impurities, that could interact with the more reactive zone in the material, the one where the vacancy is.

This fact and the importance of sulfur in carbonaceous materials [10], an element closely related to oxygen, makes a study of the interaction of sulfur atoms and multivacancy graphene systems worthwhile, with potential results that could contribute to the understanding of novel sulfur-carbon materials, where applications could be achieved.

For these reasons, this manuscript shows a first-principles DFT study of the interaction of one and two sulfur atoms with multivacancy graphene systems with different configurations.

2. Computational methods

We constructed 6×6 graphene supercells with a 3, 4, 6, 7 and 8-order vacancy system with sulfur, named as gv x Sy, being x the order vacancy and y the sulfur doping degree. In the case of the hexa-vacancy system the names are gv6Sy-a and gv6Sy-b, depending on the vacancy configuration employed. In order to avoid interferences between periodical images a vacuum distance was kept at $c \sim 30 \text{ \AA}$.

We use the Density Functional Theory (DFT) [11,12] as implemented in the VASP code [13–16] (Vienna *ab initio* simulation package). Pseudopotentials were applied with a plane-wave basis set

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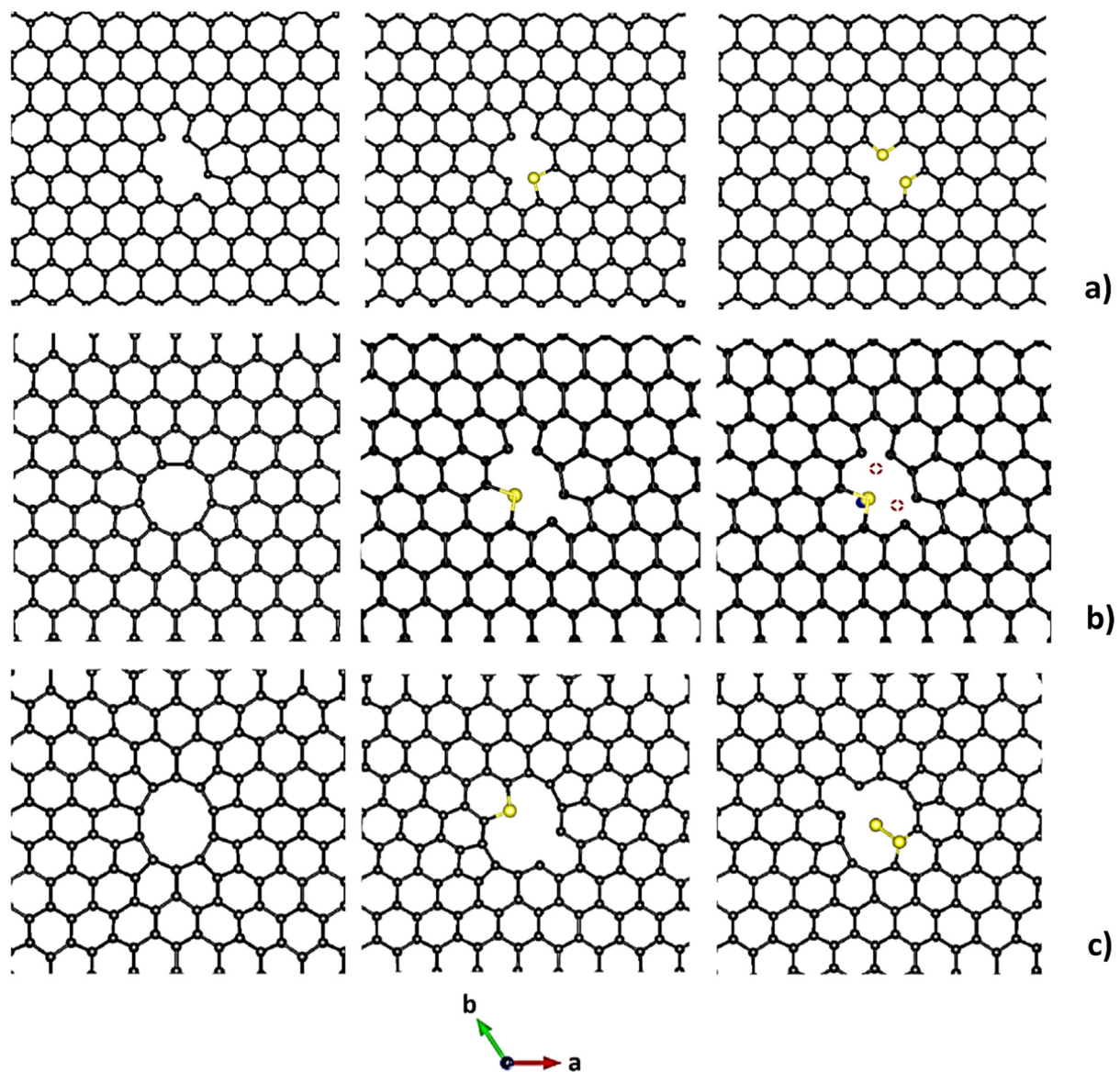


Fig. 1. Top view for (a) gv3Sy, (b) gv4Sy and (c) gv6Sy-a, with $y = 0, 1$ and 2 in the – left, middle and right, respectively. For the gv4S2 case that could not be achieved and corresponds to the third column in (b) row, the position of the equivalent carbon atom in gv3S0 is shown in blue color, and the potential position for the addition of a second sulfur atom can be seen as red dash circles [22]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

utilizing projector augmented wave (PAW) method [17], using generalized gradient approximation (GGA) as the exchange-correlation functional according to Perdew-Burke-Ernzerhof (PBE) [18,19]. An energy cutoff of 300 eV was used to expand the Kohn-Sham orbitals into plane wave basis sets, and the k-point mesh was taken equivalent to $4 \times 4 \times 1$ for the full (reducible) Brillouin Zone.

3. Results and discussion

The strategy followed in this manuscript was to perform the addition of sulfur atoms to already optimized multivacancy graphene systems. This would be the process that experimentally could happen: first the vacancy is created due to chemical or physical methods and then

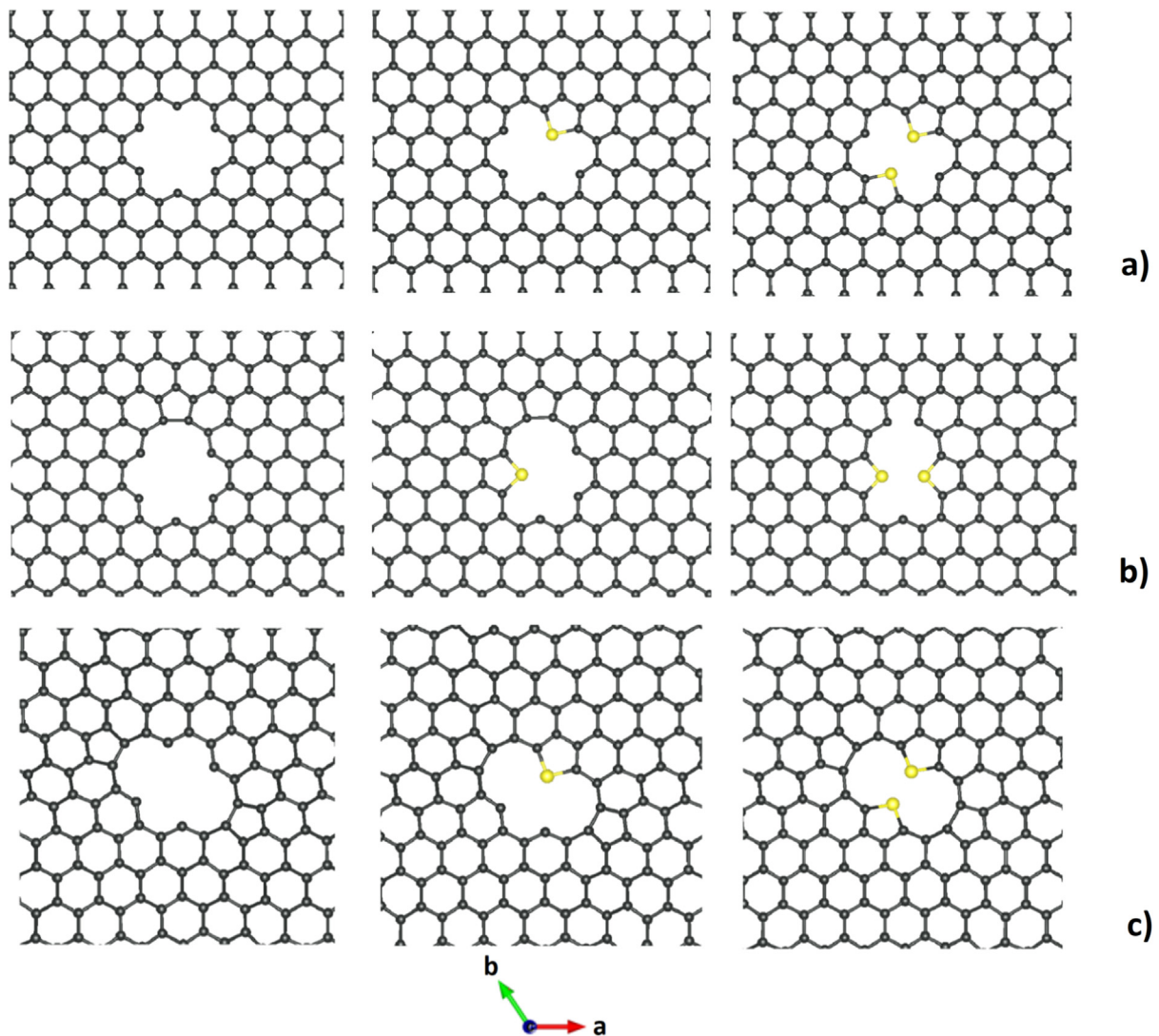


Fig. 2. Top view for (a) gv6Sy-b, (b) gv7Sy and (c) gv8Sy, with $y = 0, 1$ and 2 in the left, middle and right, respectively [22].

the sulfur atoms are added. It is more realistic to follow a sequential process than to assume that the extraction of carbon atoms can be simultaneous to the sulfur atom addition – i.e. a direct atom replacement.

Top and side view for all vacancy and sulfur doped structures are shown in Figs. 1, 2 and 3, respectively. While for the case of the simple 3-order vacancy structure system, two pentagonal figures per vacancy can be seen, as predicted by rules previously reported [6] – i.e. where the terminal carbon atoms in the complementary figure are present,

the inclusion of a single sulfur atom in the gv3S1 case, shows two pentagonal figures per vacancy are evident, but with a rearrangement that yields to a different configuration: one of the pentagonal figures transformed in an hexagonal structure with the inclusion of the sulfur atom, and a second pentagonal figure was built opposite to the first one. When two sulfur atoms are present, as for the gv3S2 structure, both of them are located in order that the original pentagonal figures transform into hexagonal ones. After this action, two pseudo pentagonal figures



Fig. 3. Side view for gvXSy structures, with $x =$ (a) 3, (b) 4, (c) 6-a, (d) 6-b, (e) 7 and (f) 8, and $y = 0, 1$ and 2 , left, middle and right [22].

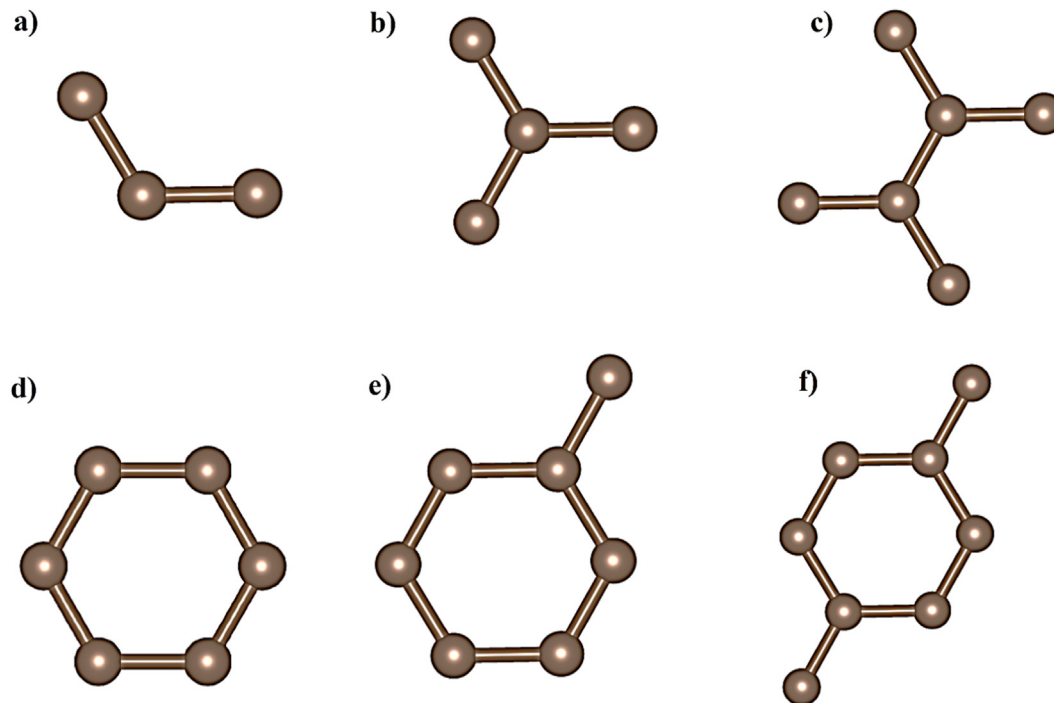


Fig. 4. Complementary figures for (a) 3-, (b) 4-, (c) and (d) 6- (6v-a and 6v-b, respectively), (e) 7- and (f) 8-orders vacancy systems [22].

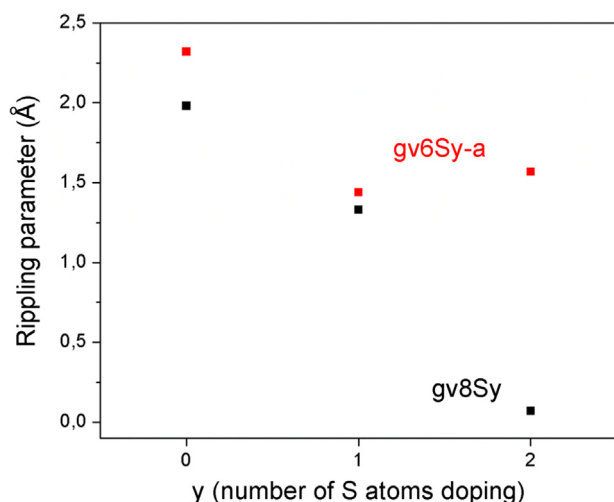


Fig. 5. Rippling parameter vs. number of S atoms doping for the 6-order (-a) and 8-order vacancy graphene systems.

occur, but neither the S–C (2.2 Å) nor the S–S (2.6 Å) distances, indicate that real bonds are formed. Although these considerations are based on the top view images, the high planarity level in both structures, as seen in Fig. 3, allows the extraction of these conclusions with reliability.

A planar structure for the 3-order vacancy system is observed in the side view (Fig. 3), and with the increase of sulfur doping the layer shows stress in the c-axis, which can be seen through the shift of z coordinate for sulfur atoms with respect to the graphene plane. The 4-order vacancy system with the complementary figure shown in Fig. 4b, exhibited three pentagonal figures in the structure and a planar layer. When one atom of sulfur is doping, the resulting system adopts the 3-order vacancy graphene structure, since the sulfur atom adopts a similar position to one of the terminal carbon removed. In this case and similarly to the previous one, a stress caused by the larger size of sulfur atom, yields to a shift of its z coordinate from the graphene plane. Although the inclusion of a second atom of sulfur was intended as for the other vacant systems, it was not possible to achieve a convergence. The possible explanation is that in the 3-order vacant graphene – the homologous structural system to the gv4S1 – offers a vacant space enough to locate a sulfur atom, but in this gv4S1 case, the space is not enough for a second sulfur one, because the first sulfur atom size yielded to a steric hindrance. The first sulfur atom centered angle is 101.0°, far from the 120° typical for hexagonal, symmetric, pure carbon polygon and also from the actual equivalent angle in gv3S0, 128.4°. This fact is shown in the third column of Fig. 1b. The 6-order vacancy structure labeled as gv6Sy-a, with the complementary figure shown in Fig. 4c, is characterized with the presence of four pentagonal figures as previously described [6]. When the first sulfur atom is added, two

pentagonal figures subsist, the third one distorts enough to not consider it as a pentagon no longer (the C–C bond length is 2.44 Å) and following the same trend as the cases described in the previous lines, the fourth pentagon turns to a hexagon due to the inclusion of the sulfur atom, which occupies the vacant site. The sulfur atom centered angle is 105.3° for this case. In the double doped case for this system, the first sulfur atom centered angle is 95.9°. Although Fig. 1c shows an angle larger than 120°, the smaller value is explained because it is a projection, and the whole picture is seen through the ripple structure that this system has, as shown in Fig. 3c. The rest of the structure is completed by a disulfide bond rising from the ripple, with an S–S bond length 1.93 Å. While the inclusion with the first sulfur atom decreases the rippling parameter, the second one has not much effect on it, even yielding to a slight increase – rippling parameter defined as in [20], the maximum difference between z coordinates for carbon atoms in the same graphene layer.

On the other hand, the other 6-order vacancy structure named as gv6Sy-b with the complementary figure represented in Fig. 4d, is shown in Fig. 2a. When a single sulfur atom dopes this system, occupies a site where a pentagonal figure is created and when a second sulfur atom is added, it is located opposite to the first one, and no di-sulphide structure is formed, since the S–S bond length in this case is 2.90 Å. This structure remains planar in all cases. The 7-order vacancy system, with the complementary figure showed in Fig. 4e, presents one pentagon, and with one and two sulfur atoms doping, one and two pentagonal figures are added, respectively. In the case of the two sulfur atoms doping, there is no di-sulphide bond created, since the S–S bond length is 2.75 Å. This system is planar in all cases. In the 8-order vacancy system – previously reported as a potential porphyrin emulator [21] – show two pentagons per vacancy in the layer, and with one and two sulfur doping, three and four pentagons are presented in the structure, respectively. No disulfide bond has been formed for the double doped case, since the S–S bond length is 2.79 Å. A significant decrease of the rippling parameter can be observed for the first and the second doping as well – see Fig. 5. As a matter of fact, the top view for gv6S1-b, gv7S1 and gv8S1, and also for gv6S2-b, gv7S2 and gv8S2, exhibit similar structures, where the side views of gv8S1 and gv8S2, show the rippling that slightly makes a difference for the 8-order multivacancy systems with respect to the other two cases. However, density of states (DOS) for these structures represented in Fig. 6, show very different features. This fact is due to the existence of dangling bonds with different configurations in gv6S0-b, gv7S0 and gv8S0, that present six, five and four dangling bonds, respectively, as previously reported [6,8]. In all cases it is evident that the electronic structures for all cases change when sulfur atoms act as dopants.

The formation energies were calculated as follows:

$$E_{\text{form}} = E_{\text{gvxSy}} - (E_{\text{gvxS0}} + yE_{\text{S}}),$$

with $x = 3, 4, 6$ (a and b), 7 and 8, and $y = 1$ or 2, according to Table 1, where E_{gvxSy} is the total energy of the graphene doped system, E_{gvxS0} the total energy of the non-doped system and E_{S} the total energy of the

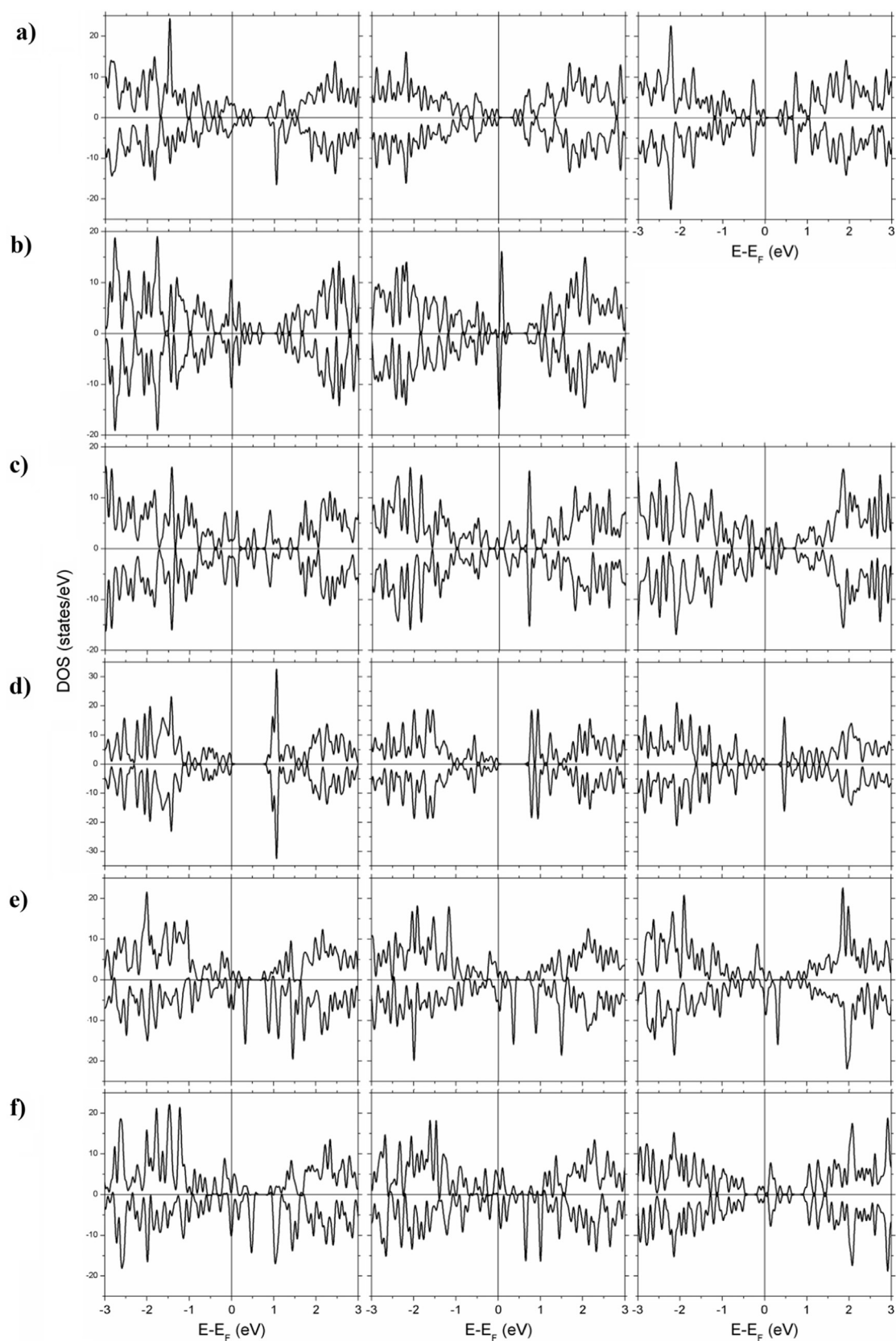


Fig. 6. Density of states (DOS) for (a) gv3Sy, (b) gv4Sy, (c) gv6Sy-a, (d) gv6Sy-b, (e) gv7Sy (f) gv8Sy. In the left $y = 1$ and in the right $y = 2$.

Table 1

Formation energy, E_{form} – eV – for sulfur-multivacancy graphene systems, and band gap – eV – where applicable.

System	E_{form} (eV)	E_{gap} (eV)
gv3S0	–	–
gv3S1	–6.23	0.34
gv3S2	–10.73	0.31
gv4S0	–	–
gv4S1	–4.58	–
gv6S0-a	–	–
gv6S1-a	–4.78	0.12
gv6S2-a	–6.05	–
gv6S0-b	–	0.82
gv6S1-b	–7.67	0.72
gv6S2-b	–14.94	0.42
gv7S0	–	–
gv7S1	–7.71	–
gv7S2	–14.40	–
gv8S0	–	–
gv8S1	–7.51	–
gv8S2	–13.55	–

Formation energy was calculated following: $E_{\text{form}} = E_{\text{gvxSy}} - (E_{\text{gvxS0}} + yE_{\text{S}})$. According to this definition E_{FORM} for gvxs0 is 0 (cases used as references).

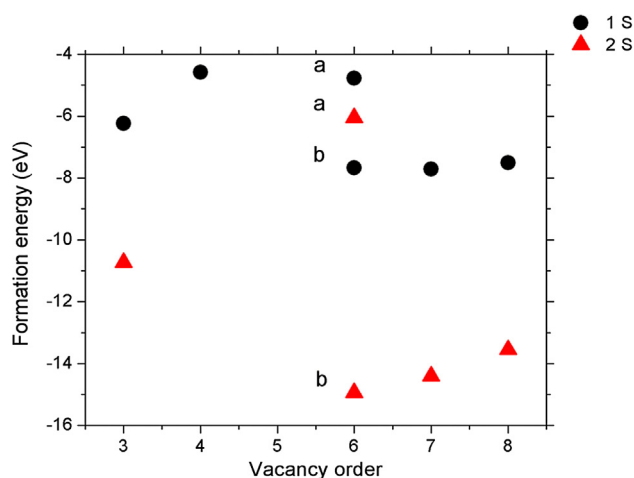


Fig. 7. Formation energy versus vacancy order for one (circles) and two (triangles) sulfur incorporation. According to the way it was calculated ($E_{\text{form}} = E_{\text{gvxSy}} - (E_{\text{gvxS0}} + yE_{\text{S}})$), the formation energy for the gvxs0 cases is zero, and correspond to a reference to the other cases.

sulfur atom. All formation energies indicate that the processes of addition of one sulfur atom to the already multivacancy systems are favorable, and that the addition of a second one yields to even more stable states. This information and the band gaps for the applicable cases are shown in Table 1.

Table 2

Magnetic moments for gvxsy (μ_{B}).

	S0	S1	S2
gv3	0.98	0.00	0.00
gv4	0.03	0.31	–
gv6-a	0.00	0.00	0.00
gv6-b	0.00	0.00	0.00
gv7v	5.51	3.52	1.75
gv8v	4.51	2.51	0.00

The magnetic moment versus vacancy order are represented in Fig. 7. A decrease in the magnetic moment is observed with the sulfur addition except for $x = 4$, as shown in Table 2. In the 3-order multivacancy system case, the magnetic moment is $0.98 \mu_{\text{B}}$, and with one sulfur atom doping the magnetic moment disappears. This fact is shown in Fig. 6a where spin-up and spin-down contributions for DOS are the same. The origin for this effect is the quenching of the magnetic signal provoked by the elimination of the dangling bonds due to the inclusion of the sulfur atoms. For gv6Sy-a and b structures the magnetic moment were not affected by the sulfur doping, with a magnetic moment of $0 \mu_{\text{B}}$ for all hexa-carbon vacancies structures. In the gv6Sy-a cases for $y = 1$ and 2, no dangling bonds are created when the sulfur atoms are included and for gv6Sy-b ($y = 1$ and 2), the sulfur atoms quench pairs of dangling bonds with opposite spin character, changing the magnetic configurations but keeping the antiferromagnetic nature of the whole structure. The symmetry between the spin-up and spin-down density of states is in agreement with this interpretation. The magnetic moment for the sulfur-free, 4-order multivacancy system was meaningless, while for gv4S1 was $0.31 \mu_{\text{B}}$. The reason for this exception is the appearance of dangling bonds when sulfur is added. This fact can be seen in Fig. 8, where top view of spin-up and spin-down isosurfaces are shown. The 7- and 8-order multivacancy systems behave similarly as the gv6Sy-b, for $y = 1$ and 2, being the dangling bonds for the free-sulfur case, quenched by the inclusion of the sulfur atoms. The spin-up and spin-down contributions for DOS are different for these cases, as shown in Fig. 6 and are in agreement with Table 2 (see Fig. 9).

4. Conclusions

In this work we studied the effect of doping with one and two sulfur atoms on multivacancy graphene systems. These free-sulfur systems were previously studied and their magnetic behavior based on the disposition of dangling bonds related to a complementary figure was previously reported [6]. The configuration of the systems yielded by the doping of one and two sulfur atoms after geometrical optimization was described. The inclusion of sulfur atoms was observed to prefer the inclusion under two circumstances: one of them is close to pentagonal figures in order to transform them into hexagonal ones. The second one is, in the absence of pentagonal figures, close to concave four membered edges in order that new pentagonal figures form. This fact has clear consequences on the electronic structure and the magnetic

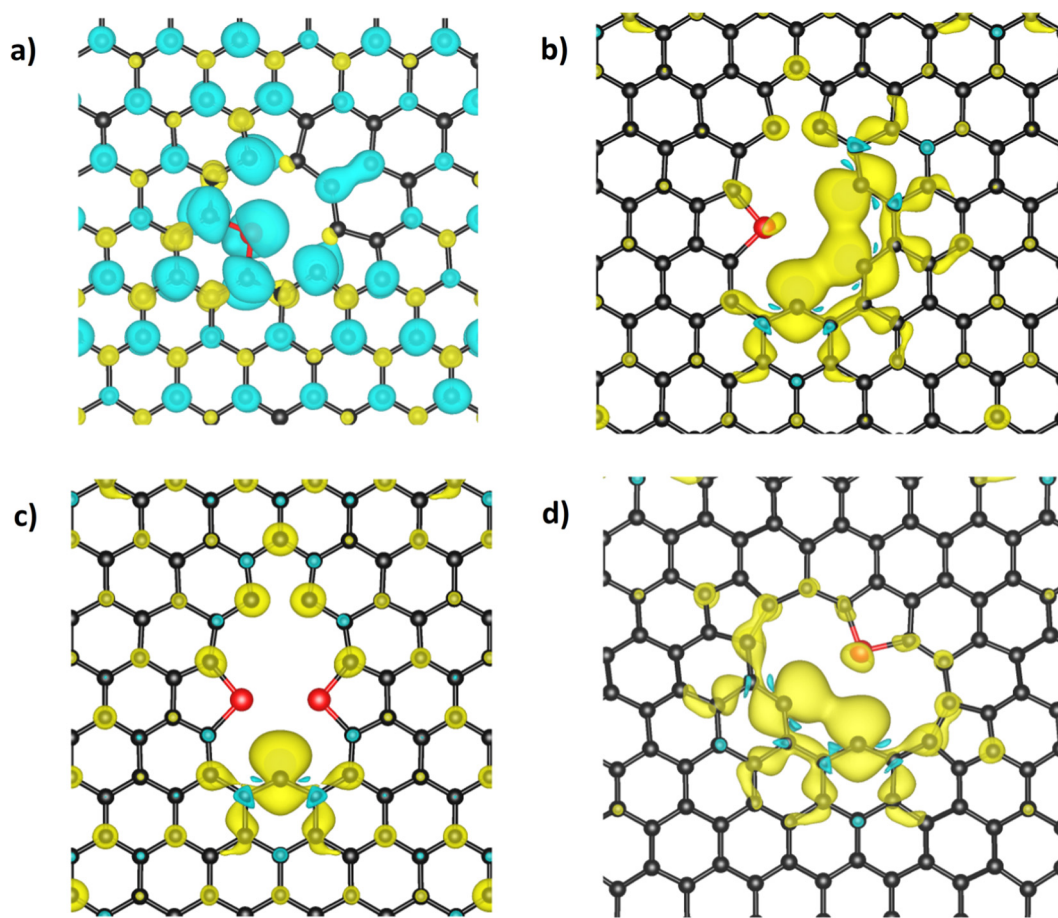


Fig. 8. Spin-up and spin-down isosurfaces at 100% of maximum value for (a) gv4S1 and (c) gv7S2 and at 50% of maximum value for (b) gv7S1 and (d) gv8S1. Spin-up and spin-down are presented in yellow and cyan, respectively. Sulfur atoms are represented in red [22]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

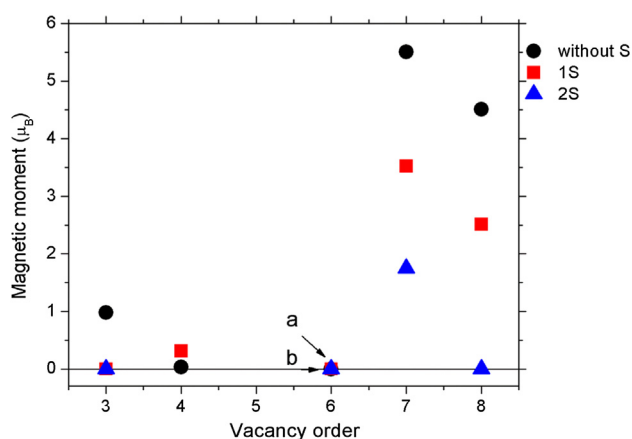


Fig. 9. Magnetic moment for all structures.

properties of the doped systems, since the inclusion of the sulfur atoms quenches the magnetism due to dangling bonds.

Since the size of sulfur is larger than carbon, these new pentagonal figures – or the hexagonal ones in the first description – are distorted, and the added sulfur atom is out-of-plane, when the room left by the vacancy is not enough to incorporate it. A trend to decrease the ripples of the free-sulfur systems when sulfur atoms are doping is observed.

Finally, it can be concluded that the doping by sulfur atoms is favorable and the addition of the second sulfur atom is favorable as well.

Acknowledgments

The authors wish to thank the Uruguayan funding institutions, CSIC, ANII and PEDECIBA.

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