

Possible causes for rippling in a multivacancy graphene system

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Abstract

The occurrence of ripples in an eight-atom vacancy graphene system was analyzed through first principles calculations based on density functional theory. The study focuses on the conditions that should be considered in order that ripples could occur in the single layer defected graphene. The vacancies concentration, especially the pentagonal figures formed after relaxation of the vacant system, and the distances between neighbor pentagons, are found to be key aspects for rippling occurrence, with no charge distribution consequence. Two different configurations of rippling have been found where the position of the pentagonal figures is discussed as the driving force for any of them to occur.

KEYWORDS

density functional theory, graphene, multivacancies, rippling

1 | INTRODUCTION

Since the obtaining of graphene by Geim and Novoselov, extensive research has been performed on this material due to the extraordinary properties that it shows,^[1,2] particularly related to electronic properties, in close relationship with structural features like defects and quantum confinement.

The interest for achieving graphene materials that could be useful for applications in electronics, has led to the study of defected graphene and particularly there has been great interest in the opening up of gaps driven by the creation of vacancies.^[3–8] While single-vacancies and divacancies have been theoretically studied and experimentally created,^[9–11] multivacancies have also been studied due to the fact that they could arise using low-cost techniques, which makes them potentially more frequent to find and easier to be produced, overcoming the disadvantage of the irregularity in their conformation under less controlled conditions.^[12–17] A way to describe the configurations of multivacancies has been developed through the concept of the complementary figure, that is, the geometric figure of the atomic arrangement that has been extracted from graphene in order that the multivacancy is created. This tool is very useful to univocally relate the multivacancy configuration to the properties calculated.^[12]

However, a single graphene layer is not stable and surface effects can occur and, moreover, the presence of vacancies could affect or even enhance such effects, yielding to nonplanar structures. These situations have been addressed in the past,^[18,19] particularly when considering the oxidation of graphene with oxygen and ozone. Thus, in the cases where deviations in planarity appear, the properties of the graphene layer suffer modifications. When the deviations lead to ripples, the consequences on the properties of the graphene systems could be significant and could open new possibilities on their potential applications. In the recent years, the rippling in the graphene layer has been experimentally observed.^[20–22] However, there are many reliable simulations works where the existence of planar single layer graphene is predominant, for the case of pristine graphene as well as for defected systems, with the presence of multivacancies in different configurations. This fact shows the need for more work on this subject, to better understand the appearance of ripples in a single layer graphene and to extract conclusions about the consequences that the existence of such deviations of planarity cause in the materials properties.

This manuscript is about the electronic structure determination of an eight-order multivacant graphene system, where the complementary figure extracted from the layer is equivalent to a 1,4-dimethylphenyl moiety distributed in different concentrations in periodic supercells, with the aim to try to find possible causes for the rippling to appear.

2 | COMPUTATIONAL METHODS

We constructed 6×6 , 7×7 , 8×8 , and 9×9 graphene supercells with an eight-order vacancy system named as g66v8, g77v8, g88v8, and g99v8, respectively. A vacuum distance was kept at $c \sim 30 \text{ \AA}$ to avoid interferences between periodical images.

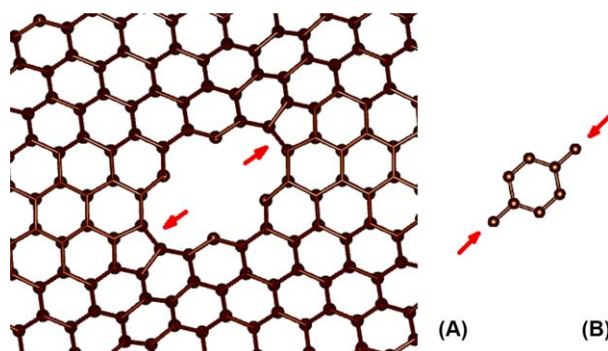


FIGURE 1 A, Eight-order multivacant system after relaxation, B, 1,4-dimethylphenyl-like complementary figure. Red arrows show pentagonal figures in A and methyl groups in B^[32]

Electronic structure calculations were performed on multivacancy graphene system with the use of the density functional theory (DFT)^[23,24] as implemented in the VASP code^[25–27] (Vienna ab initio simulation package).^[28] Pseudopotentials were applied with a plane-wave basis set utilizing projector augmented wave (PAW) method,^[29] using generalized gradient approximation (GGA) as the exchange–correlation functional according to Perdew–Burke–Ernzerhof (PBE).^[30,31] An energy cutoff of 300 eV was used to expand the Kohn–Sham orbitals into plane wave basis sets.

In the 6×6 graphene supercell, the k -point mesh was taken equivalent to $4 \times 4 \times 1$, while for 7×7 , 8×8 , and 9×9 graphene supercell the $2 \times 2 \times 1$ k -point mesh was taken for the full (reducible) Brillouin Zone, allowing the convergence of stress components, total energy and atomic forces down to 1 kbar, 0.01 eV and 0.02 eV/Å, respectively.

3 | DISCUSSION AND RESULTS

The single layer graphene multivacant system studied is an eight-carbon atom vacancy, with complementary figure corresponding to 1,4-dimethylphenyl carbon structure; it is represented in Figure 1. All structures were allowed to relax, and as a consequence, the occurrence of two pentagons per multivacancy has been observed, one in the place of the methyl group of the complementary figure, as the rules previously established.^[12] As it can be seen in Figure 2, g88v8 and g99v8 single layers are planar, while the g66v8 structure clearly exhibited the arising of rippling in the lamellar structure. In the meantime, g77v8 shows an incipient rippling in the layer, with an intermediate planarity with respect to the other vacant graphene systems mentioned. This particular behavior could be associated with the concentration of the vacancy in the graphene system and could be attributed to the increment stress provoked by the proximity of the pentagonal figures when concentration of the vacancy increases. In a more rigorous and quantitative analysis, the maximum difference between the z coordinates of carbon atoms belonging to the same graphene layer—it could be considered as a rippling parameter—yielded to the values 1.97, 0.61, 0.048, and 0.0008 Å, for g66v8, g77v8, g88v8, and g99v8, respectively, suggesting that even in g88v8, a very smooth rippling could be present. The asymptotic trend of this rippling parameter with the distances between neighboring vacancies (two, one for each direction) is shown in Figure 3. The fits follow the equation $\Delta z = A - B \cdot C^x$, where A , B , and C are just fitting parameters and x the distance between figures ($R^2 = 0.9903$ and 0.9880). Since the discovery of fullerenes,^[33] the key role of the pentagonal figures in pure carbon structures in the arising of curvature has been well established. Due to this, the evolution of the rippling parameter just defined with the area of the supercell per pentagonal figure is plotted in the inset of Figure 3 (the red curve is a fit with the same equation already defined). The hollow symbol shown in this inset, stands for a system previously studied by the authors, g66v7, with a methylphenyl like complementary figure, with just one pentagonal figure per supercell. The agreement of this case with the other ones here studied is evident.

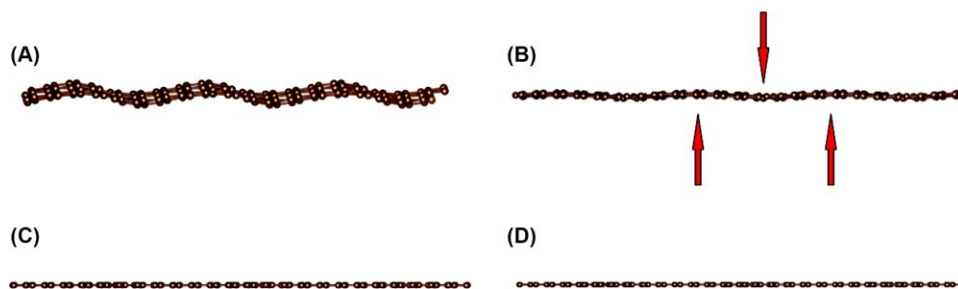


FIGURE 2 View along the a -axis of the single layer graphene eight-order multivacant systems A, g66v8, B, g77v8, C, g88v8, and D, g99v9. Arrows in B show the features in the ripple for this system

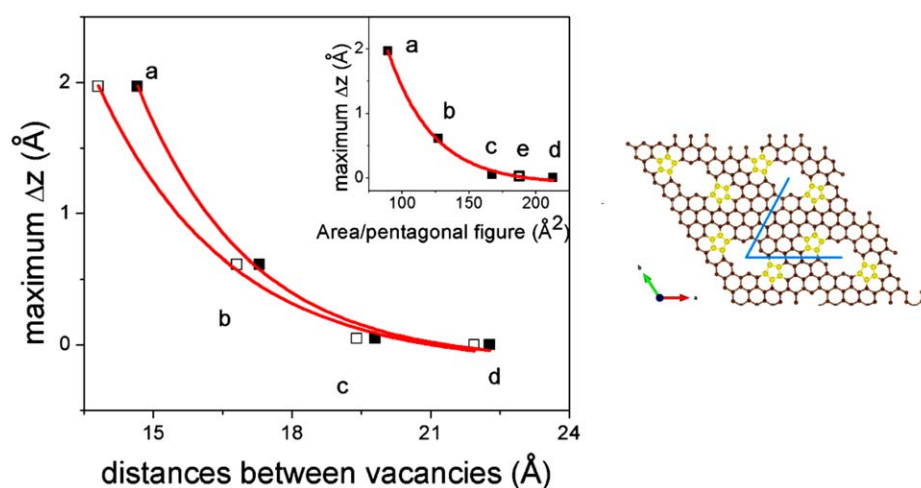


FIGURE 3 Evolution of the rippling parameter (maximum difference between z coordinates for carbon atoms in the same graphene layer) as a function of the distances between the vacancies in the two possible directions. The red curves are fits following the equation $y = A - B \cdot x^x$, showing an asymptotic behavior. The inset shows the variation of this parameter with the area of the supercell per pentagonal figure present after relaxation of the structure. The red curve fits the same function as main figure. A, B, C, and D, stand for g66v8, g77v8, g88v8, and g99v8, respectively. In the inset, E is g66v7, where the seven-order vacancy has only one pentagonal figure.^[14] The blue lines in the scheme show the two distances considered

Moreover, if we define two interpentagonal distances as in Figure 4A, among a longitudinal and a transversal distance (labeled B and C, respectively in that Figure) and we plot the rippling parameter as a function of their ratio (Figure 4B), we achieve a trend that could be fitted with a second-order polynomial equation.

This evidence could lead to the idea that the mere presence of pentagons in the carbon lamellar structure is enough to produce ripples and that only the concentration effect is important for the occurrence of such feature. A closer inspection of the g66v8 and g77v8 cases along the a -axis gives evidence that perhaps this idea could be an oversimplification. As it can be seen in Figure 5, while for the g66v8 case the pentagonal figures occupy locations in the crests and the troughs of the ripple, the situation for g77v8 is not the same—carbon atoms belonging to pentagonal figures are shown in this figure as larger and yellow for the sake of clarity. In this case, the pentagonal figures belonging to the same vacancy occupy symmetrical positions close to the trough, which is sharper, and not any of these figures can be seen close to the crest. As it is suggested by the schemes

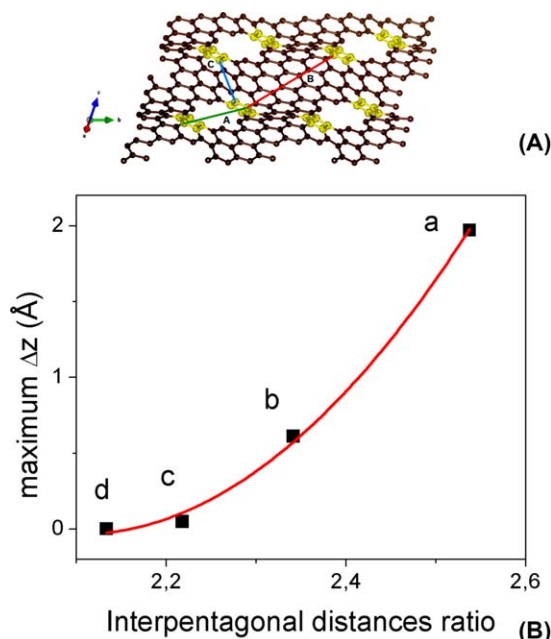


FIGURE 4 A, View of the three interpentagonal distances, two longitudinal and one transversal. B, Maximum Δz in each single layer multivacancy systems (eight-order vacancy), that is, the here defined rippling parameter-, as a function of the interpentagonal distances ratio, longitudinal distance/transversal distance, B/C. The red curve is a second-order polynomial fit. Letters A to D, have the same meaning as in Figure 3

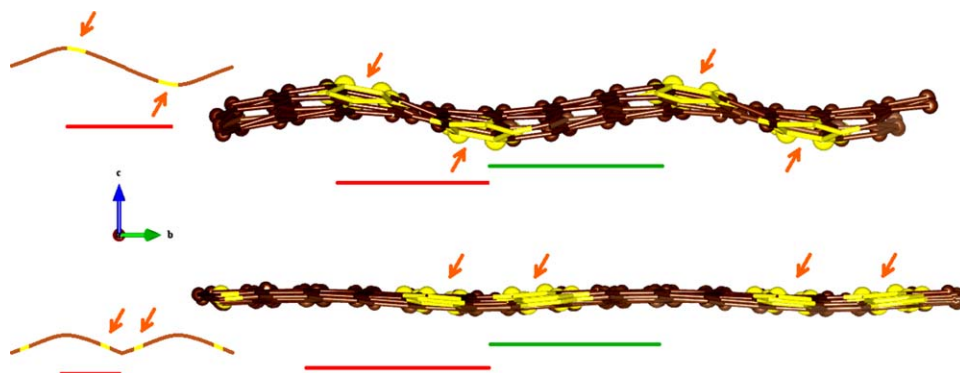


FIGURE 5 View of the ripples along the a -axis for $g66v8$ and $g77v8$ (upper and lower figures, respectively). For the sake of clarity, carbon atoms belonging to pentagonal figures are shown as larger and yellow. Red and green lines show the distances between crests and troughs. In the left side schemes of ripples are shown for both cases, where the pentagonal figures location and the red line are shown

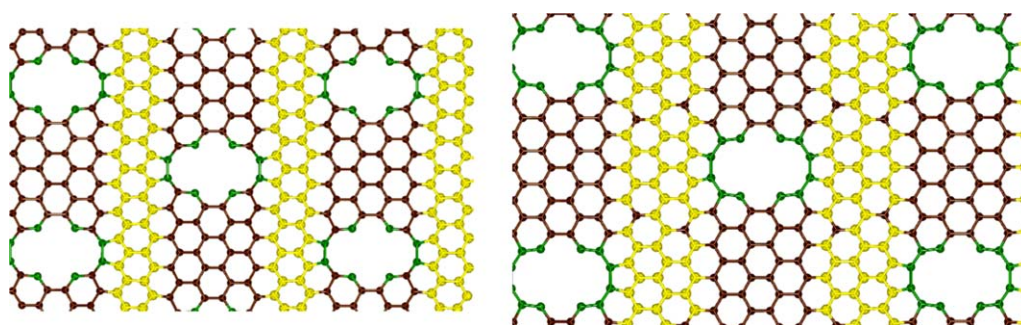


FIGURE 6 View of $g66v8$ and $g77v8$ along the c -axis (left and right side, respectively). Carbon atoms with charge lower than $2.55 e^-$ and higher than $2.65 e^-$ are shown with green and yellow color, respectively

in the left side of this Figure, while the ripple in $g66v8$ can be seen as a sinusoidal function—with different crest-to-trough distances, that is, the red and the green lines—the one in $g77v8$ resembles more as a squared sinusoidal function. This description reinforces the idea that the pentagonal figures are not sufficient to explain the rippling of graphene multivacant systems. Figure 6 shows the c -axis view for $g66v8$ and $g77v8$, with the two different types of rippings. In this Figure the carbon atoms with charge defect are shown with green color and the ones with charge excess with

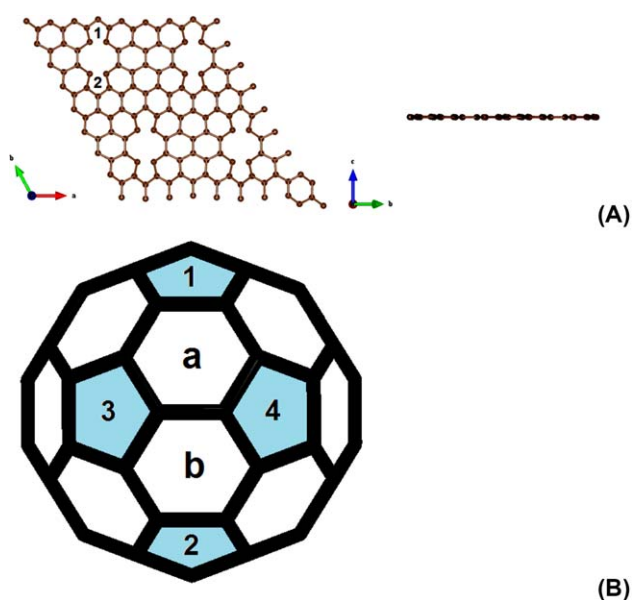


FIGURE 7 A, View of the $g44v2$ system along the c and a axes. B, Buckminsterfullerene showing the scheme of pentagonal (with number, in skyblue color) and main hexagonal figures surrounding them (with letters)

TABLE 1 Magnetic moment and formation energies for g66v8, g77v8, g88v8, and g99v8

	g66v8	g77v8	g88v8	g99v8
Magnetic moment (μ_B)	4.51	4.00	4.00	4.52
Formation energy (eV)	0.223	0.152	0.105	0.073

yellow color. It can be seen that there are no differences between both charge distributions, suggesting that the two kind of observed ripples are not based on the charge configuration surrounding the vacancies.

In the search of more evidence for an explanation for the ripple formation, we performed the structural relaxation of a simple divacant system, with a small supercell, 4×4 . Figure 7A shows the *c*- and the *a*-axes perspectives for such divacant system. No rippling is evident for this case, in spite of the fact that the area of the supercell per pentagonal figure, 40.8, suggests that rippling should be present, according to the graph shown in the inset of Figure 3. The explanation for this behavior could be found in the geometrical configuration of the truncate icosahedron, buckminsterfullerene. Figure 7B shows the main features of the C_{60} molecule. The pentagonal figures opposed by their bases (numbered 1 and 2) are separated by two hexagonal units (*a* and *b*), offering the chance that strain could overcome the stress and thus allowing curvature to exist. This condition is not necessary for pentagons connected by their vertices (numbered 3 and 4). If we return to Figure 7A, with this idea in mind, the pentagon's number 1 and 2 are too close to overcome the stress and then allow the curvature required for ripples to arise.

The formation energies were determined according to the following expression: $E_{\text{form}} = \left(\frac{E_{\text{total}}}{N_{\text{total}}} - \mu(C) \right)$, where E_{total} and N_{total} are the total energy and the total number of carbon atoms for g66v8, g77v8, g88v8, and g99v8, respectively; and $\mu(C)$ is the chemical potential of carbon determined as the total energy per atom of pristine graphene. All the results are summarized in Table 1.

A decrease in the absolute value in the formation energy is observed when concentration in the vacancy system increases, probably related with the stress produced by the rippling.

Density of states (DOS) of g66v8, g77v8, g88v8, and g99v8 were represented in Figure 3 with a detail of the Fermi zone showed in the inset. It is observed that g66v8 and g99v8 structures showed a metallic behavior; in the meantime, g77v8 and g88v8 exhibited a small gap.

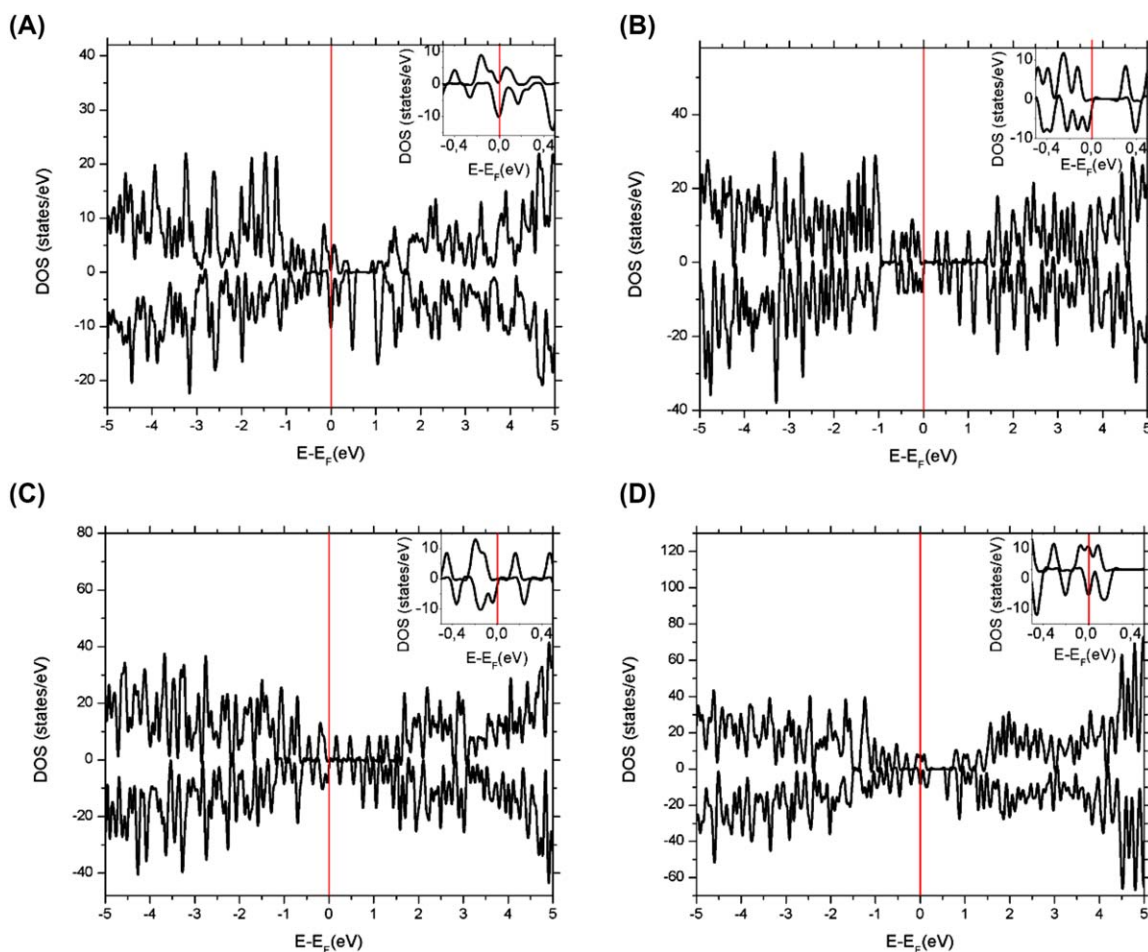


FIGURE 8 Density of states (DOS) for A, g66v8, B, g77v8, C, g88v8, and D, g99v8. A detail of the Fermi zone is shown in the inset

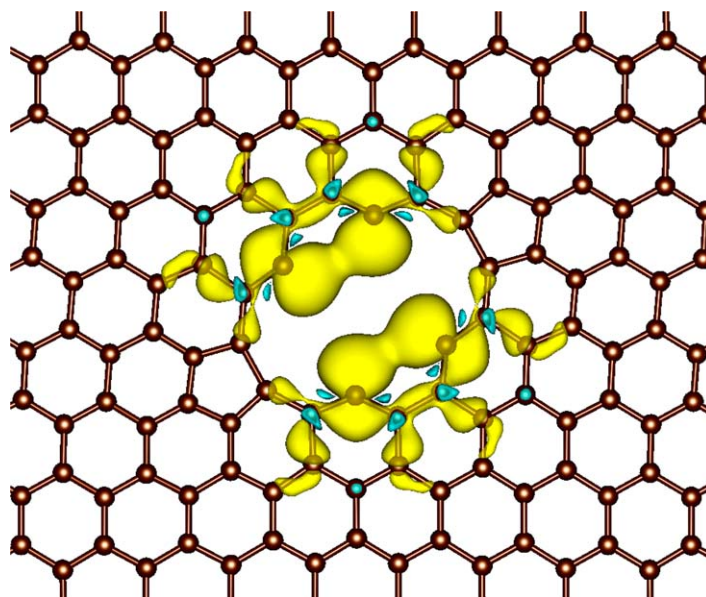


FIGURE 9 Spin-up and spin-down isosurface at 50% of maximum value for g77v8 is presented in yellow and cyan, respectively

All the studied structures present unbalanced spin density in the dangling bond scheme yielding to local ferrimagnetic, with one spin majority surrounding each vacancy. The spin polarization is influenced by the relaxed structure in the carbon backbone in the multivacancy graphene. The two pentagonal figures formed after relaxation per multivacancy in the positions where the terminal methyl groups of the complementary figure were located, block the persistence of dangling bonds leaving only four dangling bonds available. Actually, the configuration of this eight-order vacancy is a good candidate as a protoporphyrin emulator to build gas sensors. This was the origin of our interest in this particular multivacant graphene system and will be published elsewhere very soon.

The ferrimagnetic behavior of the system can be evidenced from the projected density of states, particularly in the region close to the Fermi energy, in which the difference between up- and down- states is present for all the atoms, as it can be seen in Figure 8. This effect is evident in the spin-density map for g77v8, presented in Figure 9. The obtained magnetic moments are in concordance with what is expected for metals, g66v8 and g99v8, presenting fractional magnetic moment; while for the semiconducting systems, g77v8 and g88v8, the obtained magnetic moments are integers. Thus, g77v8 and g88v8 structures showed magnetic moments $\sim 4.0\mu_B$, and g66v8 and g99v8 structures exhibited magnetic moments $\sim 4.5\mu_B$, as seen in Table 1.

4 | CONCLUSIONS

The specific eight-order vacancy graphene system studied in this manuscript yielded to a ferrimagnetic structure, locally in each vacancy, as a consequence of the configuration of this multivacancy, the formation of two pentagons in the relaxed structure, causing the occurrence of ordered magnetism in graphene. The rippling in the graphene layer arises with the vacancy concentration in the system, being smooth for the 7×7 superstructure and intense for the 6×6 one. Carefully checking the z coordinates of the carbon atoms belonging to the same multivacant graphene layer, suggests that a low degree of rippling is persistent even for the 8×8 case.

Our results suggest that the occurrence of rippling of vacant graphene systems obeys to complex reasons. On one hand, the presence of pentagonal figures are important to promote the curvature of the layer, but the relative distance among them along the vacancy itself and between the pentagons of neighboring vacancies are also relevant.

Two kind of rippling have been identified: one following a sinusoidal-like shape and another one as a squared sinusoidal form. The first one show pentagons in the crest and the trough of the ripple, allowing a more relaxed structure that could have a larger amplitude $-1.97 \text{ \AA}$ for the g66v8 case. The second one shows the trough coincident with the vacancy, with no pentagons in the crest, but instead a long curvature surrounding it, suffering a tension distributed along this intervacency space, purely formed by hexagons. This produces a less relaxed structure, what would yield to smaller amplitudes $-0.61 \text{ \AA}$ for the g77v8 case. The role of the charge distribution along the graphene single layer with the described multivacancy is ruled out, since two systems with different type of rippling show the same charge scheme.

This study could provide an explanation for the experimental evidence of rippling in the graphene layer that was previously reported.^[18–20] However, it seems clear that more work should be done to better understand the rippling occurrence in multivacant graphene systems with different configurations of the complementary figure.

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REFERENCES

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, 306, 666.
- [2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature* **2005**, 438, 197.
- [3] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, S. Roth, *Nature* **2007**, 446, 60.
- [4] C. D. Latham, M. I. Heggie, M. Alatalo, S. Öberg, P. R. Briddon, *J. Phys. Condens. Matter* **2013**, 25, 135403.
- [5] R. R. Nair, M. Sepioni, I. L. Tsai, O. Lehtinen, J. Keinonen, A. V. Krasheninnikov, T. Thomson, A. K. Geim, I. V. Grigorieva, *Nat. Phys.* **2012**, 8, 199.
- [6] J. J. Palacios, F. Ynduráin, *Phys. Rev. B* **2012**, 85, 245443.
- [7] R. Faccio, L. Fernández-Werner, H. Pardo, C. Goyenola, O. N. Ventura, Á. W. Mombrú, *J. Phys. Chem. C* **2010**, 114, 18961.
- [8] H. Tachikawa, Y. Nagoya, H. Kawabata, *J. Chem. Theory Comput.* **2009**, 5, 2101.
- [9] A. W. Robertson, C. S. Allen, Y. A. Wu, K. He, J. Olivier, J. Neethling, A. I. Kirkland, J. H. Warner, *Nat. Commun.* **2012**, 3, 1144.
- [10] J. E. Padilha, R. G. Amorim, A. R. Rocha, A. J. R. da Silva, A. Fazzio, *Solid State Commun.* **2011**, 151, 482.
- [11] R. G. Amorim, A. Fazzio, A. Antonelli, F. D. Novaes, A. J. R. da Silva, *Nano Lett.* **2007**, 7, 2459.
- [12] R. Faccio, A. W. Mombrú, *J. Phys. Condens. Matter* **2012**, 24, 375304.
- [13] R. Faccio, A. W. Mombrú, *Comput. Mater. Sci.* **2015**, 97, 193.
- [14] R. Faccio, H. Pardo, F. M. Araújo-Moreira, A. W. Mombrú, *Chem. Phys.* **2015**, 449, 14.
- [15] A. W. Mombrú, H. Pardo, R. Faccio, O. F. de Lima, E. R. Leite, G. Zanelatto, A. J. C. Lanfredi, C. A. Cardoso, F. M. Araújo-Moreira, *Phys. Rev. B* **2005**, 71, 100404.
- [16] H. Pardo, R. Faccio, F. M. Araújo-Moreira, O. F. de Lima, A. W. Mombrú, *Carbon* **2006**, 44, 565.
- [17] R. Faccio, H. Pardo, P. A. Denis, R. Y. Oeiras, F. M. Araújo-Moreira, M. Veríssimo-Alves, A. W. Mombrú, *Phys. Rev. B* **2008**, 77, 035416.
- [18] Y. C. Cheng, T. P. Kaloni, Z. Y. Zhu, U. Schwingenschlögl, *Appl. Phys. Lett.* **2012**, 101, 073110.
- [19] T. P. Kaloni, Y. C. Cheng, R. Faccio, U. Schwingenschlögl, *J. Mater. Chem.* **2011**, 21, 18284.
- [20] T. M. Paronyan, E. M. Pigos, G. Chen, A. R. Harutyunyan, *ACS Nano*. **2011**, 5, 9619.
- [21] J. H. Warner, Y. Fan, A. W. Robertson, K. He, E. Yoon, G. D. Lee, *Nano Lett.* **2013**, 13, 4937.
- [22] U. Monteverde, J. Pal, M. A. Migliorato, M. Missous, U. Bangert, R. Zan, R. Kashtiban, D. Powell, *Carbon*. **2015**, 91, 266.
- [23] P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**, 136, B864.
- [24] W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, 140, A1133.
- [25] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, 6, 15.
- [26] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, 47, 558.
- [27] G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, 49, 14251.
- [28] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, 59, 1758.
- [29] P. E. Blöchl, *Phys. Rev. B* **1994**, 50, 17953.
- [30] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865.
- [31] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, 78, 1396.
- [32] K. Momma, F. Izumi, *J. Appl. Crystallogr.* **2008**, 41, 653.
- [33] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, 318, 162.

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