Effect of pressure on the magnetism of bilayer graphene

Eduardo V. Castro,[1,2] María P. López-Sancho,[1] and María A. H. Vozmediano[1]
[1]*Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain*
[2]*Centro de Física do Porto, Rua do Campo Alegre 687, P-4169-007 Porto, Portugal*
(Received 9 May 2011; revised manuscript received 17 July 2011; published 8 August 2011)

We study the effect of pressure on the localized magnetic moments induced by vacancies in bilayer graphene in the presence of topological defects breaking the bipartite nature of the lattice. By using a mean-field Hubbard model, we address the two inequivalent types of vacancies that appear in the Bernal stacking bilayer graphene. We find that by applying pressure in the direction perpendicular to the layers the critical value of the Hubbard interaction needed to polarize the system decreases. When combined with an external electric field applied perpendicularly to bilayer graphene the effect becomes sizable and can be detected experimentally. The effect is particularly enhanced for one type of vacancies, and admits straightforward generalization to multilayer graphene in Bernal stacking and graphite. The results clearly demonstrate that the magnetic behavior of multilayer graphene can be affected by mechanical transverse deformation.

DOI: 10.1103/PhysRevB.84.075432 PACS number(s): 75.70.Ak, 75.30.−m

I. INTRODUCTION

The magnetic properties of graphene and its multilayer compounds remain one of the most interesting topics in the system that still awaits experimental confirmation. The improved experimental capabilities to produce and manipulate large samples has given rise to a renewed interest in the issue.[1] It is known that vacancies, edges, and other defects that lead to dangling bonds in the graphene system induce localized magnetic moments that might give rise to interesting applications. The theoretical paradigm around the magnetism in graphene is the Lieb theorem[2] that fixes the spin of the ground state of the bipartite system to be half the number of the unpaired atoms in the lattice. Although the theorem is demonstrated only for the Hubbard model in bipartite lattices, the result has proven to be very robust and to hold in more general calculations based on *ab initio* or density functional methods.[3,4] While the interactions can be extended, it has been recently proven that the ground-state magnetization is very sensitive to the presence of local topological defects such as five or seven rings breaking the bipartite character of the lattice.[5,6] In particular it has been shown that when one of the vacancies inducing magnetic moments is reconstructed to form a pentagon, the critical value of the Hubbard interaction needed to reach a finite polarization increases significantly.[7]

Bilayer graphene (BLG) is even more interesting than single-layer graphene (SLG) under many points of view,[8] in particular for the magnetic properties. In Bernal stacking, BLG can support two types of vacancies giving rise to unpaired atoms: those produced by removing a site having a neighbor in the adjacent layer are named β, and those coming from sites that are not connected to the other layer are called α vacancies. In a bipartite lattice, unpaired atoms give rise to zero-energy states and the physics underlying the magnetic properties of the system is that of the electronic interactions in the manifold of zero-energy states. It has been recently shown[9,10] that the significant differences between the wave functions of the zero modes associated with the α and β vacancies in BLG give rise to different physical behaviors. In particular when the system is gapped by an external gate, the vacancies of type α generate fully localized states inside the gap.

Recent experimental progress in production and manipulation of graphene samples has broadened the possibilities of tailoring the properties of SLG and BLG. Pressure is known to play an important role in the stability of the gate-induced gap in BLG[11] and on the impurity states.[12]

In this work we analyze the effect of pressure on the behavior of the localized magnetic moments coming from the two types of vacancies in the presence of a topological defect. We show that the critical interaction value U_c needed to polarize the system decreases for increasing pressure. The effect is particularly enhanced for vacancies of type α. We clarify the physical mechanism leading to this behavior and propose pressure as a way to improve the magnetism of the samples.

We work with the tight-binding (TB) model, including a Hubbard interaction. The results are obtained by a self-consistent computation within the unrestricted Hartree-Fock approximation. A further analytical analysis using degenerate first-order perturbation theory explains the results in terms of the different energy lifting that occurs in the subspace of the zero modes under the perturbations originated by the pentagonal hopping. We argue that the physical result will remain when going beyond the simple calculation performed in this work and extend the results to other graphene multilayers.

II. MODEL

The lattice structure of AB Bernal-stacking BLG is schematically represented in Fig. 1(a). The atoms of the A sublattice in the top layer are connected by $t_\perp$ to these of the B sublattice of the bottom layer. We will consider the minimal model for the BLG with only intralayer t and interlayer $t_\perp$ couplings. The estimated values of these parameters in the system are $t \approx 3$ eV, and $t_\perp \approx 0.3$–0.4 eV $\sim t/10$.[8]

The two different types of vacancies are also shown in Fig. 1(a). The α vacancy where the removed atom in the top layer (B_1 in the figure) is not connected to the second layer is represented in the left-hand side. The right-hand side represents a β vacancy (A_1 in the figure). Figure 1(b) shows the reconstructed pentagonal link named t_p in this work. t_p represents the hopping integral between two atoms belonging

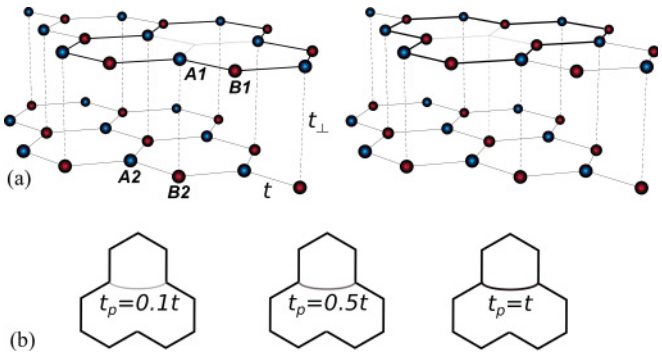

FIG. 1. (Color online) (a) Bilayer lattice structure and main tight-binding parameters. Left: α vacancy. Right: β vacancy. (b) Reconstructed vacancies modeled by a pentagonal link.

to the same sublattice in the reconstructed vacancy. The formation and dynamics of topological defects in graphene have been experimentally observed with transmission electron microscopy.[13] Defects consisting of multiple five- and seven-membered rings of C atoms spontaneously appeared. Moreover the formation of pentagonal rings is identified as the first stage of vacancy reconstruction in the honeycomb lattice.[14]

The non-interacting TB Hamiltonian for the π electrons of the bilayer system is[15–17]

$$H_{\rm TB} = \sum_{i=1}^{2} H_i - t_\perp \sum_{\mathbf{R},\sigma} [a^\dagger_{1\sigma}(\mathbf{R}) b_{2\sigma}(\mathbf{R}) + \text{H.c.}], \qquad (1)$$

where H_i corresponds to the SLG Hamiltonian:

$$H_i = -t \sum_{\mathbf{R},\sigma} a^\dagger_{i\sigma}(\mathbf{R}) [b_{i\sigma}(\mathbf{R}) + b_{i\sigma}(\mathbf{R}-\mathbf{a}_1) + b_{i\sigma}(\mathbf{R}-\mathbf{a}_2)] + \text{H.c.}\,, \qquad (2)$$

and $a_{i\sigma}(\mathbf{R})$ [$b_{i\sigma}(\mathbf{R})$] are the annihilation operators for electrons at position $\mathbf{R}$ in the sublattice A_i (B_i) of the layer i ($i = 1,2$) with spin polarization σ. The basis vectors can be chosen as $\mathbf{a}_1 = a\,\hat{\mathrm{e}}_\mathrm{x}$ and $\mathbf{a}_2 = a(\hat{\mathrm{e}}_\mathrm{x} - \sqrt{3}\,\hat{\mathrm{e}}_\mathrm{y})/2$, with $a = 0.246$ nm being the lattice spacing.

The lattice of BLG is a bipartite lattice and the TB minimal model has electron-hole symmetry. Vacancies are modeled by suppressing the corresponding lattice site. When the pentagonal reconstruction is considered, a bond between two neighboring atoms is added as explained below. We will consider the simplest topological defect modeled by first producing a vacancy and then adding a pentagonal link connecting two of the closest atoms to the vacancy as shown in Fig. 1(b). Since the two atoms belong to the same sublattice, this defect breaks the bipartite nature of the lattice.

The magnetic behavior of BLG in the presence of vacancies, edges, and other defects has been investigated using the Hubbard model in Refs. 9,18–20. The interacting TB Hamiltonian is $H = H_{\rm TB} + H_U$, with

$$H_U = U \sum_{\boldsymbol{R},\iota} [n_{a\iota\uparrow}(\boldsymbol{R}) n_{a\iota\downarrow}(\boldsymbol{R}) + n_{b\iota\uparrow}(\boldsymbol{R}) n_{b\iota\downarrow}(\boldsymbol{R})]\,, \qquad (3)$$

where $n_{x\iota\sigma}(\boldsymbol{R}) = x^\dagger_{\iota\sigma}(\boldsymbol{R}) x_{\iota\sigma}(\boldsymbol{R})$, with $x = a,b$, $\iota = 1,2$ and $\sigma = \uparrow,\downarrow$.

We use finite clusters with one electron per atom (half-filling) and impose periodic boundary conditions in order to avoid edge effects. The calculations have been performed with clusters of different number $N \times N$ of unit cells, with four C atoms per unit cell. Clusters up to 2500 atoms have been considered to explore finite size effects. We found that they are negligible in all our physical variables (energy per cell, charge distribution, spin-spin correlations) for cluster sizes above 900 atoms. The Hamiltonian is solved in the unrestricted Hartree-Fock approximation, and the mean-field spin density at each lattice site is obtained self-consistently.

It is known that a finite staggered magnetization appears in the honeycomb lattice above a critical value of the on-site Coulomb interaction which, in mean-field calculations is $U_c \approx 2.2t$.[21,22] We will keep the values of U below this value to make sure that the physics explored is due to the magnetic moments associated with the defects on the lattice. Notice that the critical values of the Hubbard repulsion obtained with a mean-field approach are smaller than those obtained with methods which take into account quantum fluctuations.[23]

Evidence of the presence of localized magnetic moments around isolated vacancies has been reported recently in scanning tunneling microscopy experiments on a graphite surface.[24] The experimental results have been fitted by using a nearest-neighbor TB model for the π electrons, showing that the π band TB Hamiltonian describes correctly the main electronic properties of the system in the presence of a vacancy.

III. VACANCY-INDUCED ZERO-ENERGY STATES

In the honeycomb lattice, a vacancy gives rise to a quasilocalized state with a continuum limit wave function

$$\Psi(x,y) \approx \frac{e^{i\mathbf{K}.\mathbf{r}}}{x+iy} + \frac{e^{i\mathbf{K}'.\mathbf{r}}}{x-iy}, \qquad (4)$$

where $\mathbf{K}$ and $\mathbf{K}'$ are the reciprocal space vectors of the two inequivalent corners of the first Brillouin zone, and (x,y) are distances from the vacancy position.[25]

An analytic expression for the vacancy-induced states in the continuum model of BLG was obtained recently in Ref. 10 following the procedure outlined in Ref. 26 for the monolayer case. By cutting the lattice into left and right regions with respect to the vacancy position, a zigzag edge to the left and a Klein edge[27,28] to the right appear. The wave function is obtained by matching surface state solutions at the zigzag edge with that localized at the Klein edge. Depending on the type of vacancy, two solutions are obtained. The β vacancy produces a zero-energy state quasilocalized on atoms of the opposite sublattice in the same layer of the vacancy, decaying as $1/r$ away from the vacancy. Assuming the vacancy to be located in layer 1, the continuum limit wave function can be written as

$$\Upsilon_1(x,y) \approx \Psi(x,y), \qquad \Upsilon_2(x,y) \approx 0\,, \qquad (5)$$

where Υ_i specifies the wave function component on layer i, and $\Psi(x,y)$ is the quasilocalized state given in Eq. (4). The

zero-energy states induced by a vacancy of α type has the wave function

$$\Upsilon_1(x,y) \approx \Psi(x,y),$$
$$\Upsilon_2(x,y) \approx \frac{t_\perp}{t} e^{-i2\theta} e^{i\mathbf{K}.\mathbf{r}} + \frac{t_\perp}{t} e^{i2\theta} e^{i\mathbf{K}'.\mathbf{r}}, \quad (6)$$

where $\theta = \arctan(y/x)$. This is a delocalized state, with the peculiarity of being quasilocalized in one layer (where the vacancy sits) and delocalized in the other.[10] We notice here that the wave function of the β vacancy is insensitive to $t_\perp$ while this parameter enters explicitly in the wave function of the α vacancy, a fact that will be important in the forthcoming analysis.

IV. NUMERICAL RESULTS

A. Magnetism and the pentagonal links

Since the lattice of the BLG model used in this work is bipartite, the magnetic behavior of the system follows Lieb's theorem as in SLG. Therefore in the presence of vacancies, for any repulsive value of the Hubbard interaction U, the ground state of the system at half filling has a total spin equal to half the number of unbalanced atoms $S = (N_A - N_B)/2$. We have analyzed the magnetic behavior of the two different types of vacancies that occur in the BLG in the presence of a pentagonal link. We observed that both types of vacancies have the same behavior and it coincides with what happens in SLG.[7] We first considered the simplest situation: two vacancies on the same layer and of the same sublattice, one of them reconstructed by forming a pentagonal link t_p pictorially shown in Fig. 1(b). In this situation a finite critical value of the on-site Coulomb interaction is needed to reach the ground-state polarization predicted by Lieb's theorem. For values of U below U_c, the total spin of the ground state is zero. By varying the pentagonal hopping integral from $0.1t$ to t we have verified that the critical value of U increases monotonically with t_p for both types of vacancies. This is shown in Fig. 2(a) for different values of the perpendicular hopping $t_\perp$.

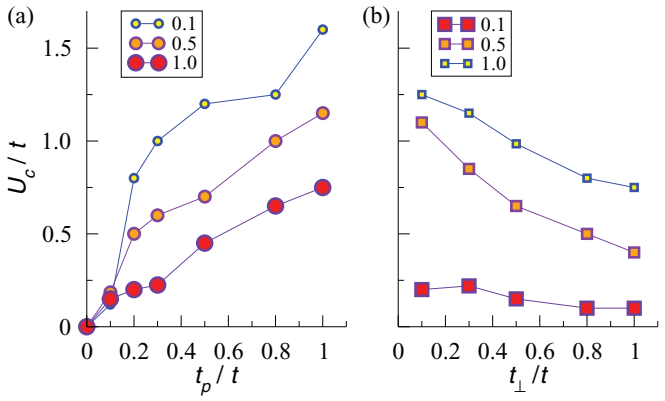

FIG. 2. (Color online) (a) Critical value of the Hubbard parameter U needed to polarize the cluster as a function of the strength of the pentagonal link t_p, for different values of the perpendicular hopping $t_\perp$ in units of t. From lower to upper curves: $t_\perp/t = 1$, 0.5, 0.1. (b) Dependence of the critical U on the perpendicular hopping $t_\perp$ for fixed values of the pentagonal link.

B. Effect of pressure

We have explored the influence of pressure on the magnetic properties of BLG. The effect of increasing pressure is modeled by increasing the hopping between atoms of different layers $t_\perp$. The most common value for $t_\perp$ considered in BLG is $t_\perp \approx 0.1t$, although recent works considering different types of stacking in few layers graphene have produced values up to $t_\perp \sim 0.502$ eV with $t = 3.16$ eV.[29]

In order to exemplify the behavior found in this work and for simplicity we will study the magnetic polarization of the system in the situation described before: two vacancies of the same sublattice, one of them reconstructed forming a pentagonal ring. We have seen that the effect of pressure is very different for the two different types of vacancies supported by BLG.

We have varied the perpendicular hopping in the range $t_\perp = 0.1t$ to $t_\perp = t$ and for each value of $t_\perp$, we increased the pentagonal hopping t_p from $0.1t$ to t. In the case of the β vacancies we found that the magnetic behavior of the system is independent of $t_\perp$. The value of U_c increases with t_p but does not depend on $t_\perp$. Pressure has no effects on the spin polarization of the system in this case. This can be understood by observing that since the wave functions induced by β vacancies have amplitude only on one layer, the behavior is just that of the SLG. This behavior will change if next-nearest interlayer hoppings γ_3 and γ_4 are taken into account, with β vacancies becoming more similar to α vacancies.

Considering α vacancies we observed that for a fixed value of the pentagonal hopping t_p, U_c decreases as $t_\perp$ increases. This behavior can be appreciated in Fig. 2(b), where we show the dependence of the critical U_c on $t_\perp$ for various fixed values of t_p. This indicates that pressure could help the polarization of the BLG ground state. In Sec. VI we discuss how effective is pressure in changing $t_\perp$ in real systems, and thus how sensitive is BLG magnetism to pressure. Here we anticipate that, when used simultaneously with a perpendicular electric field,[9] the effect could be seen experimentally.

We have seen that the strength of the pentagonal hopping increases the critical U_c needed to polarize the cluster, but in the case of the α vacancies the perpendicular hopping has the opposite effect: it decreases U_c and favors the magnetization. This behavior will be explained in Sec. V by performing an analysis with degenerate perturbation theory.

We have also considered the case that the two vacancies are in different layers. To obtain a nonzero magnetization, Lieb's theorem requires that the two vacancies belong to the same sublattice, A or B. Hence, in this case to get a magnetic ground state, both types of vacancies α and β must be present. We observe that $t_\perp$ has no effect on the critical value of the Hubbard interaction needed to obtain the spin polarization of the ground state when the pentagonal link is attached to a vacancy of β type. On the contrary, when the pentagonal ring is formed by reconstructing the α vacancy, U_c decreases as $t_\perp$ increases as it occurs in the case of having both vacancies of α type. Therefore the value of $t_\perp$ affects the magnetic behavior of the bilayer system when a pentagonal hopping exists. Otherwise Lieb's theorem holds and the critical U is zero for any value of $t_\perp$. This behavior will also hold for other types of local defects breaking the sublattice symmetry as heptagons, dislocations, or clusters of defects.

V. PERTURBATIVE ANALYSIS

In the following we explain the results obtained in the previous section by studying how the zero-energy modes introduced in Sec. III are affected by the pentagonal link giving rise to the topological defect shown in Fig. 1(b). We use first-order degenerate perturbation theory. The discussion is presented on general grounds having in mind application to multilayer graphene and graphite.

A. Definitions

Let H be the noninteracting TB model Hamiltonian for some graphitic system preserving the bipartite nature of the lattice, as is the case of Eq. (1). Let us assume the system to hold n vacancies belongs to the same sublattice, with n induced zero-energy modes $|\psi_v^1\rangle \cdots |\psi_v^n\rangle$, such that

$$H\left|\psi_v^i\right\rangle = 0. \tag{7}$$

Explicitly, using localized atomic orbitals as TB basis, $\{|1\rangle, \ldots, |N\rangle\}$, where N is the number of lattice sites in the system, we can write the zero-energy modes as

$$\left|\psi_v^i\right\rangle = \sum_j a_j \left|j\right\rangle. \tag{8}$$

Without loss of generality, we assume the vacancies to belong to the A sublattice, which allows us to write

$$\left|\psi_v^i\right\rangle = \sum_{j\in B} a_j \left|j\right\rangle. \tag{9}$$

In the case of SLG, for example, the continuum limit would give $\langle \boldsymbol{r}|\psi_v^i\rangle \approx \Psi(x,y)$, with $\Psi(x,y)$ as given in Eq. (4).

We want to perturb the system with a term that disrupts the bipartite nature of the lattice. The simplest such term is just an extra local hopping connecting the same sublattice,

$$H_\gamma = -t_p c_\gamma^\dagger c_{\gamma+\boldsymbol{\delta}}, \tag{10}$$

where $c_\gamma^\dagger$ creates an electron in the localized atomic orbital $|\gamma\rangle$, and $\boldsymbol{\delta}$ is a vector connecting next-nearest neighbors. The local perturbation defined by Eq. (10) provides a simple parametrization of the pentagonal link shown in Fig. 1(b).

B. First-order degenerate perturbation theory

We want to know what happens to zero-energy modes once we add the perturbation defined by Eq. (10) to the system. Here we use a perturbative analysis, and apply degenerate first-order perturbation theory within the zero-energy mode sector. This is justified, strictly speaking, if the perturbing parameter t_p is much smaller than the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), i.e., the HOMO-LUMO gap.

The new energies for $|\psi_v^i\rangle$ within first-order perturbation theory are given by the eigenvectors of the matrix

$$\mathcal{T} = \begin{pmatrix} T_{11} & T_{12} & \cdots \\ T_{21} & T_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \tag{11}$$

where

$$T_{ij} = \left\langle \psi_v^i \right| H_\gamma \left| \psi_v^j \right\rangle = \begin{cases} 0 & \gamma \in A, \\ -t_p a_\gamma^* a_{\gamma+\boldsymbol{\delta}} & \gamma \in B, \end{cases} \tag{12}$$

as we have assumed the vacancies to belong to the A sublattice.

Owing to the quasilocalized nature of vacancy-induced zero modes (in multilayer systems we assume H_γ to act on the layer where the zero mode has its quasilocalized component), we may consider the limiting case where vacancies are sufficiently far apart. In this particular case, zero modes will be almost unaffected if t_p connects two sites that are also sufficiently far apart from any vacancy. Once these two sites approach a given vacancy we will see the energy of the associated zero mode go up as

$$E \approx -t_p a_\gamma^* a_{\gamma+\boldsymbol{\delta}}, \tag{13}$$

where a_γ and $a_{\gamma+\boldsymbol{\delta}'}$ are the real amplitudes of that particular zero mode at the perturbed sites. The other zero modes being almost unaffected. This is certainly a good description for the pentagonal link shown in Fig. 1(b), when t_p connects two of the closest sites to a given vacancy.

It was shown in Ref. 7 that in SLG the pentagonal link induces a finite Hubbard interaction U_c to polarize the system. Within the present perturbative analysis this can be understood as a consequence of the energy shift of the zero mode affected by the pentagonal link: the effect of the Hubbard term has to overcome the energy scale set by the shift in Eq. (13).

Multilayer graphene, and in particular BLG, are of especial interest. There we can tune a_γ by applying pressure, since by increasing hopping between layers the amplitude of the zero mode over the layer where the vacancy resides decreases. This is apparent in Eq. (6) for the zero mode induced by the α type vacancy and explains the numerical results shown in Fig. 2. Nevertheless we must note that there is no possibility of totally suppressing U_c by applying pressure. For that, the wave function amplitude of the vacancy-induced state has to be completely transferred to the layer opposite to the vacancy.

VI. PRESSURE IN REAL SYSTEMS AND THE INFLUENCE OF AN EXTERNAL ELECTRIC FIELD

To our knowledge, no direct measure of the variation of the interlayer hopping with pressure for BLG is available. However, it is known on experimental grounds that the perpendicular hopping is sensitive to external presure.[30] In a simple parallel plate capacitor model for bilayer, a pressure variation up to several MPa can be achieved in standard electric field effect devices. Changes in the $t_\perp$ parameter above 10% are thus within experimental reach. In our model a 10% change in $t_\perp$ translates in a few percent change in U_c.

In BLG an external electric field applied, through a back gate, in the perpendicular direction to the planes opens a gap by making the two layers asymmetric. The electrostatic energy difference between both layers, $eE_z d$ ($d = 0.34$ nm is the interlayer distance and e the electron charge), thus can be tuned by fixing the magnitude of the electric field E_z.[9] Furthermore, the electric field introduces nonzero diagonal elements in the Hamiltonian matrix so that the bipartite nature of the lattice is lost and Lieb's theorem does not hold. The finite value of the Hubbard interaction needed to polarize the system is,

therefore, directly related to the magnitude of the E_Z applied, thus making it possible to externally manipulate the strength of U_c. The few percent sensitivity to pressure found here, in conjunction with a back gate bias, could be enough to tune magnetic moments in BLG in experiments.

VII. DISCUSSION

The role of pentagonal or heptagonal rings in the magnetic behavior of the honeycomb lattice is understood on the basis of its breaking of the bipartite nature of the lattice by linking two atoms belonging to the same sublattice. The magnetic properties of the bipartite lattice, according to Lieb's theory, depend on the midgap states induced by defects that in the case of vacancies of the same sublattice, are all degenerated at zero energy. The pentagonal hopping integral t_p lifts the degeneracy lowering the corresponding zero-energy state, henceforth a finite value of the Hubbard interaction is needed in order to polarize the system. In BLG the interlayer hopping can affect the interplay between kinetic energy and Coulomb interaction. The increase of $t_\perp$ from its estimated value $\approx 0.1t$, has just the opposite effect of t_p on the midgap states, shifting them upward in energy. Thus, there is an interesting interplay of these two parameters in multilayer materials that affects their magnetic behavior.

Since we are using a simple Hubbard model in a Hartree-Fock approximation, the results of the present work refer to the total magnetization of the ground state of the cluster and little can be said with full accuracy on the local magnetization around the defects or on the influence of the distance between the vacancies on the given results. The qualitative analysis of Sec. V permits us to envisage that if the topological defect breaking the sublattice symmetry is very far apart from the vacancies, voids, or defects contributing to the magnetism of the sample, its effects will be minimized, but a full analysis must be done with other methods to ascertain the matter. The analysis referring to the different behavior of the two types of vacancies is robust since it relies on the structure of the zero modes responsible for the magnetism in these types of lattices.

VIII. CONCLUSIONS

The possibility of tuning magnetic behavior by lattice deformation in graphitic materials is nowadays a very active development in the field. Tunable magnetism by mechanical control in graphene is a hot topic due to the broad field of applications of organic magnets and continues been a challenge from the conceptual point of view. In this work we have shown that pressure applied in the perpendicular direction to the planes can override the negative effect of topological defects breaking the sublattice symmetry in multilayer graphene.

Vacancies are the principal type of defects produced in graphitic materials by ion bombardment[31,32] and play a substantial role in material properties. Topological defects breaking the sublattice symmetry are also energetically favorable and are being considered in defect engineered devices.[13,33,34]

We have seen that the two different types of vacancies that can form in Bernal stacked multilayer graphene have different magnetic behaviors under pressure. Both of them are affected by topological defects in the sense that a larger value of the Hubbard interaction is needed to polarize the ground state. We have seen that the critical U decreases by applying pressure to the sample in the case of having a majority of α vacancies. The β vacancies are not affected by pressure. These different behaviors are due to the differences in the wave functions of the zero-energy states induced by vacancies of the two types.

ACKNOWLEDGMENTS

We thank Fernando de Juan for useful discussions. Support from MEC (Spain) through Grants No. FIS2008-00124 and No. PIB2010BZ-00512 is acknowledged.

[1] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, and B. H. Hong, Nature (London) **457**, 706 (2009).
[2] E. H. Lieb, Phys. Rev. Lett. **62**, 1201 (1989).
[3] Y. Ma, P. O. Lehtinen, A. S. Foster, and R. M. Nieminen, New J. Phys. **6**, 68 (2004).
[4] J. J. Palacios, J. Fernández-Rossier, and L. Brey, Phys. Rev. B **77**, 195428 (2008).
[5] A. Carpio, L. L. Bonilla, F. de Juan, and M. A. H. Vozmediano, New J. Phys. **10**, 053021 (2008).
[6] E. J. G. Santos, D. Sánchez-Portal, A. Ayuela, and S. Riikonen, (2010), e-print arXiv:1012.3304.
[7] M. P. López-Sancho, F. de Juan, and M. A. H. Vozmediano, Phys. Rev. B **79**, 075413 (2009).
[8] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. **81**, 109 (2009).
[9] E. V. Castro, M. P. López-Sancho, and M. A. H. Vozmediano, New J. Phys. **11**, 095017 (2009).
[10] E. V. Castro, M. P. López-Sancho, and M. A. H. Vozmediano, Phys. Rev. Lett. **104**, 036802 (2010).
[11] Y. Guo, W. Guo, and C. Chen, Appl. Phys. Lett. **24**, 243101 (2008).
[12] H. P. Dahal, A. V. Balatsky, and J. X. Zhu, Phys. Rev. B **77**, 115114 (2008).
[13] J. C. Meyer, C. Kisielowski, R. Erni, M. D. Rossell, M. F. Crommie, and A. Zettl, Nano Lett. **8**, 3582 (2008).
[14] V. Krasheninnikov and F. Banhart, Nat. Mater. **6**, 723 (2007).
[15] J. W. McClure, Phys. Rev. **108**, 612 (1957).
[16] J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).
[17] E. McCann and V. I. Fal'ko, Phys. Rev. Lett. **96**, 086805 (2006).
[18] E. V. Castro, N. M. R. Peres, and J. M. B. Lopes dos Santos, J. Optoelectron. Adv. Materials **10**, 1716 (2008).
[19] E. V. Castro, N. M. R. Peres, T. Stauber, and N. A. P. Silva, Phys. Rev. Lett. **100**, 186803 (2008).
[20] T. Stauber, E. V. Castro, N. A. P. Silva, and N. M. R. Peres, J. Phys. Condens. Matter **20**, 335207 (2008).

[21]M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. **65**, 1920 (1996).
[22]N. M. R. Peres, M. A. N. Araújo, and D. Bozi, Phys. Rev. B **70**, 195122 (2004).
[23] S. Sorella and E. Tossati, Europhys. Lett. **19**, 699 (1992).
[24]M. M. Ugeda, I. Brihuega, F. Guinea, and J. M. Gómez-Rodríguez, Phys. Rev. Lett. **104**, 096804 (2010).
[25]M. A. H. Vozmediano, M. P. López-Sancho, T. Stauber, and F. Guinea, Phys. Rev. B **72**, 155121 (2005).
[26]V. M. Pereira, F. Guinea, J. M. B. Lopes dos Santos, N. M. R. Peres, and A. H. Castro Neto, Phys. Rev. Lett. **96**, 036801 (2006).
[27]E. V. Castro, N. M. R. Peres, J. M. B. Lopes dos Santos, A. H. Castro Neto, and F. Guinea, Phys. Rev. Lett. **100**, 026802 (2008).
[28]E. V. Castro, N. M. R. Peres, and J. M. B. Lopes dos Santos, Europhys. Lett. **84**, 17001 (2008).
[29]F. Zhang, B. Sahu, H. Min, and A. H. MacDonald, Phys. Rev. B **82**, 035409 (2010).
[30]T. Otha, A. Botswick, T. Seyller, K. Horn, and E. Rotenberg, Science **313**, 951 (2006).
[31]L. Tapaszto, G. Dobrik, P. Nemes Incze, G. Vertesy, P. Lambin, and L. P. Biro, Phys. Rev. B **78**, 233407 (2008).
[32]D. Teweldebrhan and A. Balandin, Appl. Phys. Lett. **94**, 013101 (2009).
[33]A. Hashimoto, K. Suenaga, A. Gloter, K. Urita, and S. Iijima, Nature (London) **430**, 870 (2004).
[34]O. V. Yazyev and S. G. Louie, Nat. Mater. **9**, 806 (2010).