**Ab initio** study of the influence of adsorbed atoms on vacancy-induced magnetic moments in graphene sheets

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We present **ab initio** calculations for single-atom vacancies in graphene. In agreement with earlier work, we find that vacancies are responsible for the magnetism recently observed experimentally, creating a center with net spin. For small supercells, there is a strong symmetry breaking in the supercell with respect to the perfect graphene structure, and this symmetry breaking is much smaller for larger supercells. The influence of adsorption of H, O and N atoms on the spin center of the bare single-atom vacancy and its influence on the magnetism induced in these samples is investigated. A rich variety of mechanisms is found for the generation of magnetic moments in this system.

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Macroscopic magnetic ordering phenomena in organic materials has been one of the most exciting and interesting subjects in physics, chemistry and materials science. Organic magnetic materials have attracted the interest of scientists not only because of their fundamental properties, but mainly because of their potential applications in high-tech devices. Among them, we have to mention applications in medicine and biology, where organic magnetic materials would be highly desirable due to inherent biocompatibility.

Magnetism has been observed recently in graphite samples and its origin is attributed to the creation of vacancies in the material, which would lead to the appearance of unpaired spins and consequent magnetic moments. Previous studies have confirmed that single-atom vacancies indeed lead to the appearance of a center with a magnetic moment. A recent study has shown that the existence of magnetism in vacancies induced by the removal of more than one atom can lead to non-magnetic states, as well as magnetic ones.

Vacancy creation in graphite samples can be achieved either by ion irradiation or chemical modification. After almost two years of the production of magnetic graphite samples by some of the present authors using the chemical modification method, its magnetism remains just as strong as before, at room temperature and air exposure. It is natural, then, to ask what happens when a foreign species is adsorbed on the magnetic center. In this Letter, we analyze how the magnetic moment induced by single-atom vacancies in graphene (SAV-g) changes when a single atom of H, N or O is adsorbed on the magnetic center. As will be shown, the adsorption of these atomic species changes the fundamental mechanisms through which the magnetic moment is created in very different and surprising ways.

Our calculations have been performed in the framework of Density Functional Theory using the program SIESTA. We have used Troullier-Martins pseudopotentials, including nonlinear core corrections for N, the PBE-GGA exchange-correlation functional, and a split-valence double-zeta basis set with polarization orbitals (DZP) for all atoms. Because the Fermi surface of graphene is a single point, Monkhorst-Pack grids of 9x9x1 and 5x5x1 points were used for atomic relaxations in the small (4x4x1, SSC) and large (8x8x1, LSC) supercells, respectively, which amount to equivalent k-point samplings of 36x36x1 and 40x40x1 in the Brillouin Zone of a unit cell of graphene. Densities of states were calculated with denser grids, equivalent to BZ samplings of 96x96x3 and a gaussian smearing of 0.08 eV. The height of the supercells was fixed to c/a = 4.2 in the case of SSC, and c/a = 8.2 for LSC. All forces on atoms were smaller than 0.02 eV/Å, and cell relaxations included an additional constraint requiring that pressures be smaller than 0.05 GPa. Throughout the text, all net spin charges, δσ = σ↑ − σ↓, are referred to in units of the electron spin, that is, σe = 1.28, and net spin densities, δρσ(⃗r) = ρσ(⃗r) − ρσ(⃗r) are in units of e/Bohr³.

For both SSCs and LSCs, simple relaxation of atomic coordinates with of bare SAV-g, simple relaxation of atomic coordinates with supercell vectors parallel to those of a unit cell of perfect graphene yields stress ten-
sors with non-zero $xy$ and $yx$ elements with magnitude comparable to that of the $xx$ component; furthermore, the $xx$ and $yy$ components have very different magnitudes. Therefore, there is room for further relaxation of the supercell. Variable-cell relaxation yields lattice vectors with $|\vec{a}_1| \neq |\vec{a}_2|$ and $\theta = 61.5^\circ$ for a bare SAV-g SSC. For the bare SAV-g LSC, we have $|\vec{a}_1| = |\vec{a}_2|$ and $\theta = 59.5^\circ$, which shows that the in-plane interaction between vacancies plays an important role in the process of changes of supercell symmetry. The spin-dependent total density of states (TDOS) per C atom has two peaks close to the Fermi level, as shown in Figs. 1(a) and (b), but it is clear that the peaks for the SSC TDOS are higher and farther from each other than the ones in the LSC TDOS. It can also be seen from the 2p projected density of states (PDOS) per C atom (Fig. 1(c)) that the TDOS features are predominantly determined by those states. Therefore, in agreement with earlier DFT calculations [9], we find 2p states to be the responsible by the observed magnetism in bare SAV-g.

Denoting the SAV-g with a certain adsorbed atomic species $X$ by $X$-SAV-g, we start by analyzing H adsorption on the magnetic center of a SAV-g cell. Both the SSC and the LSC are allowed for complete relaxation, undergoing a similar symmetry breaking of the unit cell as in the case for SAV-g. The net magnetic moment is zero, in agreement with the results of Lehtinen et al [7]. The H atom undergoes an out-of-plane displacement, and for the SSC the overall distortion of the sheet is very pronounced, while it is smaller in the LSC. This suggests that relief of mechanical tensions by cell-symmetry breaking are rather important, which and for the SSC of a H-SAV-g with for supercell vectors parallel to the ones of the perfect graphene unit cell, the stress tensors also have nonzero $xy$ and $yx$ components, as well as different $xx$ and $yy$ elements. However, the surprising fact is that under applied mechanical tension, a liquid spin appears in both supercells, being $\delta \sigma = 0.94$ and 0.25 for the SSC and the LSC, respectively. This fact suggests that mechanical tension is indeed the main responsible for this different spin, because in the LSC, there is more room for tension distribution. Fig. 2 shows the relaxed structure and the net spin charge density for the H-SAV-g LSC.

While a more detailed determination of this mechanism demands a deeper investigation, an analysis of the PDOS and spin-difference charge density distribution, $\delta \rho_\sigma(\vec{r})$, shows that it involves the polarization of C atoms, while the H states contribute with no spin polarization. The spin-dependent 2p PDOS per C atom, as depicted in Fig. 3(b), clearly shows that the spin polarization is completely onto the atoms of this species, while the 1s states of the H atom, shown in Fig. 3(c), do not contribute to the magnetism in a significant way, since its contribution is about four times smaller than the average contribution of the C atoms. Moreover, in contrast to the case of bare SAV-g, in which the magnetic moment is concentrated mostly on the C atom onto which...
the foreign atom is adsorbed, large magnetic moments also on the two other atoms which approach to form a pentagon. Even more interesting is the fact that the ordering of the spin polarization on the surrounding atoms has an alternating disposition, but with decaying intensity as we move further away from the vacancy. Since the system exhibits a net magnetic moment due to the imbalance between spin up and spin down polarizations this arrangement is ferrimagnetic.

Next, we analyze the influence of N adsorption onto the magnetic center of a bare SAV-g, in the geometry depicted in Fig. 4(a). Both SSC and LSC, whether cell-relaxed or not, display $\delta \rho_\sigma = 1$, that is, the magnetic moment in N-SAV-g is independent of geometrical details. To better understand this, we plot spin-difference charge density isosurfaces with different values to check how liquid spin is distributed in the supercell. For a spin-difference of $\delta \rho_\sigma = \pm 0.01$, we can see that the positive spin charge is widely distributed around the adsorbed N atom, while the negative spin charge is narrowly distributed around the closest C atom. Isosurfaces of $\delta \rho_\sigma = 0.2$ are tightly bound to the N atom, while on C atoms $\delta \rho_\sigma = 0$. Looking at the C-N bond length, $a_{C-N} = 1.25 \text{ Å}$, we can infer that the N atom makes a double bond with the C atom. This causes the saturation of the unpaired C spin, with $\delta \sigma = 1$ coming from the N atom. Since the net spin is tightly bound to the N atom, this explains the insensitivity of the magnetism to geometrical details, in contrast with the H-SAV-g. Although according to our calculations the ground state for a N atom would be that in which it enters substitutionally, the situation depicted in Fig. 4 could be found, experimentally, in a zigzag state for a vacancy where many atoms have been removed. In these large vacancies, the N atom will not enter substitutionally and such a configuration is more likely to occur.

The case of O-adsorption is somewhat the opposite of N-adsorption. O-adsorption on the magnetic center causes the magnetic moment to completely vanish, no matter if the cell is distorted or not, for both SSC and LSC. Although this is in striking contrast with the results of Esquinazi et al \cite{6}, where the authors find that the presence of O$_2$ triggers a magnetic moment, it is important to bear in mind that the present calculations do not correspond to the experimental situation, in which the authors use molecular oxygen. Further theoretical work, with systems which approximate more realistically the experimental situation - that is, layered graphite with adsorbed and perhaps interstitial O$_2$ as well - is necessary to clarify the situation. Fig. 5 shows the TDOS, per atom of the LSC, of O-SAV-g.

Our findings certainly will have important implications in most of the applications of carbon-based magnetic materials in nanotechnology, such as sensors, detectors, actuators, telecommunications, electronics, biosensors, magnetic materials separation, etc.. However, those implications will be particularly important for applications in medicine, specially for targeted drug delivery by use of magnetic field gradients \cite{3, 16}. Our calculations imply that, if magnetic graphene is to be used in this kind of application, one must avoid the saturation of the magnetic centers, as much as possible, by oxygen, and that a good situation might be that in which the magnetic centers have N adsorbed. Experimentally, it is known that biologically relevant molecules such as cholesterol oxidase...
attach to magnetic Fe$_3$O$_4$ nanoparticles through amino and carbodiimide-activated carboxyl groups [16], both of which contain N. This suggests that proteins could attach to magnetic graphene without the use of a ligand, which would make the use of magnetic graphene extremely attractive for biomedical applications. Our results also imply that, if graphene with vacancies should be used for any kind of application involving its magnetic properties, it should be, as much as possible, oxygen-free. If H should be present in the system, then deposition of the graphene sheet onto a substrate might provide the tension necessary for the appearance of a magnetic moment due to lattice mismatch. The use of multi-layered graphitic structures is, in principle, also not discarded: preliminary FPLAPW results show that bulk graphite with vacancies on different layers, and in different concentrations, also exhibit a net magnetic moment [17].

In summary, we have studied three very different mechanisms that lead to the appearance of a net magnetic moment on a graphene sheet with a single-atom vacancy, both bare and with foreign atomic species adsorbed on top of it, particularly H, N and O. Both small and large supercells have been studied. A strong breaking of the supercell symmetry is observed for all systems. While the magnetic moment initially present in the bare SAV-g, regardless of the geometrical details of the supercell, is completely quenched by O adsorption and is remarkably stable upon N adsorption, we find that it can be induced by tensile stress of the lattice when H is adsorbed in the system. Although we have studied only the adsorption of atomic species on the system, it is highly possible that adsorption of molecules is also capable of preserving the magnetism in the system, and its implications for device manufacturing make this a good subject for further studies.

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[1] T. L. Makarova and F. Palacio (Editors), in “Carbon-Based Magnetism”, ISBN 13:978.0.444.51947-4, Elsevier B. V., Amsterdam, The Netherlands (2006).
[2] K. Tsukagoshi, B. W. Alphenaar and H. Ago, Nature 401, 572 (1999).
[3] O. V. Salata, J. Nanobiotechnol. 2:3 (2004).
[4] A. W. Mombrú, H. Pardo, R. Faccio, O. F. de Lima, E. R. Leite, G. Zanelatto, A. J. C. Lanfredi, C. A. Cardoso, and F. M. Araújo-Moreira, Phys. Rev. B 71, 100404(R) (2005); H. Pardo, R. Faccio, A. W. Mombrú, F. M. Araújo-Moreira, and O. F. De Lima; Carbon 44, 565 (2006).
[5] P. Esquinazi, D. Spemann, R. Höhne, A. Setzer, K.-H. Han, and T. Butz, Phys. Rev. Lett. 91, 227201 (2003).
[6] P. Esquinazi, A. Setzer, R. Höhne, C. Semmelhack, Y. Kopelevich, D. Spemann, T. Butz, B. Kohlstrunk and M. Lösche, Phys. Rev. B 66, 024429 (2002).
[7] P.O. Lehtinen, A. S. Foster, Y. Ma, A.V. Krasheninnikov and R. M. Nieminen, Phys. Rev. Lett. 93, 187202 (2004).
[8] Y. Ma, P. O. Lehtinen, A. S. Foster and R. M. Nieminen, New J. Phys. 6 68 (2004).
[9] J. M. Carlsson and M. Scheffler, Phys. Rev. Lett. 96, 046806 (2006).
[10] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
[11] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[12] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, J. Phys.: Condens. Matter 14, 2745 (2002).
[13] N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
[14] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[15] H. J. Monkhorst and J. D. Pack, Phys Rev. B 13, 5188 (1976).
[16] G. K. Kouassi, J. Irudayaraj and G. McCarty, J. Nanobiotechnol. 3:1 (2005).
[17] Ricardo Faccio, Helena Pardo, Alvaro W. Mombrú, Rodrigo Yoshikawa Oeiras, Fernando M. Araújo-Moreira and Marcos Veríssimo-Alves, to be published elsewhere.