Doping and the unique role of vacancies in promoting the magnetic ground state in carbon nanotubes and C_{60} polymers

Antonis N. Andriotis[*]

Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, Heraklio, Crete, Greece 71110

R. Michael Sheetz[†]

Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045, USA

Madhu Menon[‡]

Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055, USA
and Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045, USA

The role of various types of defects in establishing the magnetic properties of the C_{60}-based polymers and the single-wall carbon nanotubes is investigated. Comparing the role of carbon vacancies, and that of substitutional impurity atoms X (X=N, B, O, Si, P, and S) in establishing a magnetic ground state it is found that the impurity X atoms promote the spin density delocalization, whereas its localization appears as one of the primary effects of the carbon vacancies.

PACS number(s): 73.50.−h, 73.23.Hk, 73.61.Wp

Magnetism in nonmetallic systems is a fascinating phenomenon from both scientific and technological perspective. The discovery of spontaneous magnetization in two-dimensional (2D) polymeric C_{60} at room temperature by Makarova *et al.*[1] provided a theoretical challenge since this exotic *s-p* magnetism appeared to be different in nature from that of the traditional *d* ferromagnets (e.g., Fe, Co, Ni). The origin of this magnetism is still being debated. According to some recent reports, the defect induced magnetism appears to be one of the most probable scenarios for the origin of the observed carbon magnetism.[2,3] Strong evidence supporting this scenario comes from recent experiments which demonstrated the development of induced magnetism in proton-irradiated originally nonmagnetic graphite samples[4] and in nanosized diamond particles irradiated by ^{15}N and ^{12}C. On the one hand, carbon vacancies and/or C-(H-H) or C-(C*-H) complexes (C* indicating a carbon adatom) produced at C atoms around the vacancy sites by proton irradiation appear to be magnetic with a magnetic moment of approximately $1\mu_B$ per vacancy or complex unit. The magnetic configuration of single hydrogen adsorption on C atoms around the vacancy is not yet conclusive.[3,5] On the other hand, low irradiation dosages with ^{15}N and ^{12}C lead to saturation magnetization that is independent of doped species while higher doses of irradiation by ^{15}N leads to higher magnetization values than those obtained by ^{12}C irradiation.[6] The proposed rationale for the differentiation in the action of ^{15}N and ^{12}C at high dosages is probably the annealing of defects and the extensive graphitization caused by ^{12}C.

The creation of a vacancy by removing one carbon atom in a C_{60} monomer generates a dangling bond (DB) (an unpaired electron) on each of the three C atoms surrounding the site of the vacancy. In the ground state (triplet) of the C_{60} dimer with two vacancies (one per each C_{60} molecule), it is found that two of the three DBs are healed in each C_{60} molecule by the formation of an extended C-C bond (also known as a banana bond) across the vacancy site leaving just one

DB at each vacancy site. Therefore, one may mimic the effect of a C vacancy in a C_{60} molecule by substituting the vacancy with a column V element in the Periodic Table (such as an N or P atom) since each of these carries one lone electron in such a substitution.

The effects of N substitution in graphite, C_{60} and single-wall carbon nanotubes (SWCNs) have been extensively investigated recently.[3–11] These investigations reveal that substituting one C atom by a N atom in these systems does not lead to a noticeable disturbance of the graphene lattice. This is in agreement with both theory and experiment which assure that a N-concentration (N/C ratio) larger than 20% is necessary to destroy the planarity of the doped graphene sheet.[10]

In the case of azafullerene C_{59}N, theoretical investigations have shown that the impurity state lies in the middle of the gap of the undoped system.[7] The unpaired electron is in an orbital with almost *p*-like symmetry and exhibits significant delocalization,[7,8] while the corresponding spin density is found to oscillate with distance from the N atom.[8] On the other hand, the measured isotropic ^{14}N and ^{13}C hyperfine coupling constants of C_{59}N by electron spin resonance (ESR), lead to the conclusion that the spin density does not decrease monotonically with the distance from N, while the extra spin density (due to the lone orbital) is not well localized to the nearest C neighbors of N.[12] In the $(C_{59}N)_2$ dimer, the N atoms are found to be *trans* (Fig. 1) to each other.[13] Experimentally, $(C_{59}N)_2$ is found to be diamagnetic insulating solid. In N-doped SWCNs, the spin density localizes in a fairly large region around the impurity N atom.[9] However, this spin localization appears to be a feature of semiconducting (zig zag) SWCNs.

Despite the many structural and electronic configurations of graphite, C_{60} or SWCNs containing various types of defects reported, their role in inducing magnetic moments is far from clear. A detailed understanding of the magnetic contribution of different types of defects and dopants in these sys-
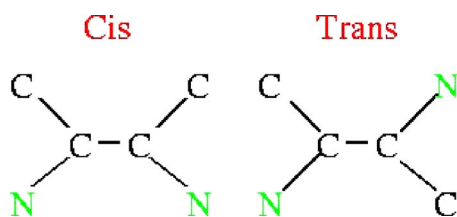
FIG. 1. (Color online) Figure showing "cis" (on the same side) and "trans" (on the opposite sides) configurations of substitutional N on the C_{60} dimer.

tems is very essential for their applications in the magnetic device technology of the future. In this paper, we attempt a systematic investigation in which we compare the effect of various defects, namely, that of vacancies and that of substitutional impurity atoms X (X=N, B, O, Si, P, and S) on the electronic and magnetic properties of C_{60}-based materials and SWCNs. We accomplish this using accurate *ab initio* calculations. We consider defects in the form of vacancies, adatoms as well as substitutional impurities on C_{60} polymers and SWCNs. In particular, we consider the cases of (i) two vacancies, (ii) one vacancy replaced by a substitutional or adsorbed impurity-atom X, and (iii) both vacancies replaced by a substitutional or adsorbed impurity atoms X. The *ab initio* molecular orbital calculations were carried out with the GAUSSIAN 03 program package using the UB3LYP density functional theory (DFT) method with the 6-311G** basis set.[14] All structures were fully relaxed with no symmetry constraints prior to the investigation of charge and spin distributions. For the charge distribution study we use both Mulliken population as well as natural bond orbital[15] (NBO) analysis (within the GAUSSIAN 03 version[14]).

We first consider defects in the form of vacancies and substitutional N atoms in C_{60} dimers. We then repeat the calculations with other substitutional atoms (P, B, O, Si, and S). Singlet and triplet multiplicities were examined and our results were further tested by DFT stabilization of the triplet states using the UMPW1PW91 hybrid functional, with the latter confirming the B3LYP results. The defects (vacancies and/or impurity atoms) were studied for various positions. In particular, defects at *cis* and *trans* positions (see Fig. 1) as well as at 90°(on a cross section perpendicular to the tube axis) to each other were studied. In all these cases the triplet states were found to be much more stable than the singlet ones with the *trans* configuration among the most stable. Finally, the same calculations were repeated by replacing the C_{60} dimer with a capped (5,5)-SWCN.

Defects in $[C_{60}]_2$. The case of two symmetric vacancies in the C_{60} dimer has already been reported by us earlier.[2,11] In it was shown that the carbon vacancies in the rhombohedral-C_{60} polymer promote significant charge and spin density transfers, resulting in the accumulation of excess negative charge on the atoms forming the inter-C_{60} link accompanied by an almost equal and opposite charge accumulation on the atoms surrounding the vacancies (see Fig. 2, top right panel). This gives rise to a rather large electric dipole moment (EDM), establishing the ferromagnetic coupling of the lone electron orbitals. This mechanism was shown to be in analogy to the McConnell-II model.[11,16] This is facilitated
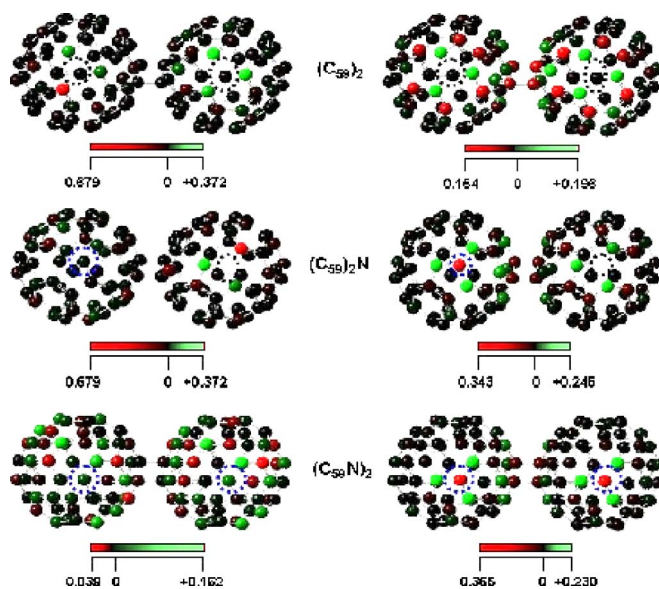

FIG. 2. (Color online) Results for the spin density (left) and charge distribution (right) in the case of a C_{60} dimer in the presence of defects in the form of; two vacancies (top panel), one vacancy and one substitutional N (middle panel), and two substitutional N atoms (bottom panel). The location of each vacancy is indicated by the dashed circle and the substitutional N atoms are indicated by dashed circles outlined in blue.

by the vacancy-induced extensive molecular orbital remote delocalization which may be considered as the means for the ferromagnetic coupling among the lone electron spins. In the top left panel of Fig. 2, it is observed that the spin density is localized on the C atoms surrounding the two vacancy sites (the latter shown by the dashed circle outlined in black). No carbon atoms outside of the immediate vicinity of the vacancy site possess any significant spin density. It is noteworthy that in addition to these results, our calculations for vacancies in a graphene layer and in SWCNs also revealed an accumulation of positive charge around the vacancies. These results are at odds with the results reported in Ref. 3 where a negative charge accumulation around the vacancies in graphene sheets was reported. The above described picture is not altered in a qualitative way, if the relative position of the vacancies is changed. However, from a quantitative point of view, we find a noticeable anisotropy in the value of the exchange coupling constant J.[17] In particular, for vacancies at *cis* and *trans* positions J=0.79 eV, while for vacancies at perpendicular positions J=0.62 eV. These values of J are consistent with the observed high Curie temperatures T_C for the tetragonal and rhombohedral C_{60} polymers.[1]

When a vacancy is healed in one of the monomers of $[C_{59}]_2$ by a substitution of a single N atom (shown by the dashed circle outlined in blue, middle panel of Fig. 2), spin density becomes localized on the C atoms neighboring the remaining vacancy on the second monomer with essentially no spin density present on the monomer containing the dopant N atom. As illustrated in the middle-left panel of Fig. 2, two of these C atoms in $[C_{59}]_2$N possess positive spin density, whereas one of these carbons possesses negative spin density, identical to the pattern exhibited by the correspond-
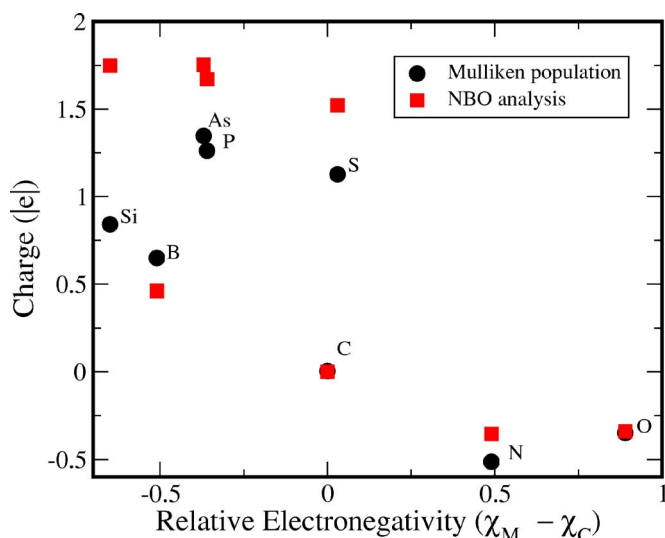
FIG. 3. (Color online) The calculated charge accumulation around an impurity atom X=B, N, O, Si, P, and S, as a function of its relative electronegativity with respect to that of the C atom obtained using both Mulliken population and NBO analysis.
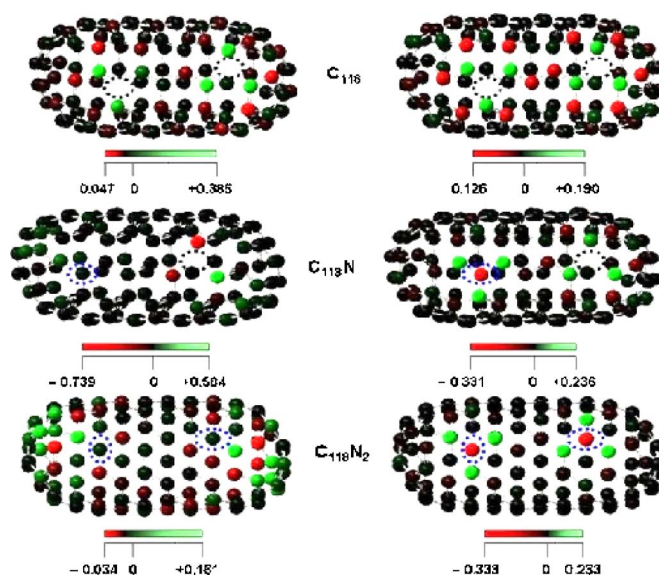

FIG. 4. (Color online) Results for the spin density and charge distribution in the case of SWCN in the presence of defects in the form of two vacancies (top panel), one vacancy, and one substitutional N (middle panel) and two substitutional N atoms (bottom panel). As in Fig. 2, the location of each vacancy is indicated by the dashed circle and the substitutional N atoms are indicated by dashed circles outlined in blue.

ing atoms in the left monomer in the unsubstituted $[C_{59}]_2$ molecule. The dopant N atom develops a significant negative charge with positive charge accumulating on the C atoms neighboring both the dopant in one monomer and the vacancy in the second monomer. However, a tendency for charge delocalization is found in the monomer with the vacancy as compared to the case of two vacancies. At the same time, a significant reduction is observed in the accumulated negative charge on the cycloaddition bond. The same picture is found if instead with N, one vacancy is healed with an O atom. That is, the spin density and positive charge density is, once again, localized on the C atoms surrounding the vacancy with the tendency for charge delocalization as in the N case. The charge distribution also shows a negative charge developing on the O atom and a positive charge on its neighboring three C atoms.

The spin distribution is found to be the same if the O or the N dopant is replaced by a B atom. However, a positive charge accumulates on the B atom and around the vacancy site, although in the latter case the accumulated charge is reduced as compared to the case of the two vacancies. Negative charge is found in the next nearest neighbor sites to both defects. The same qualitative picture as with the B dopant is found with P and S dopants. However, we observed quantitative differences with respect to the positive charge accumulation around the vacancy. This is particularly very small in the presence of the P dopant and becomes zero in the presence of the S dopant.

These results indicate that the electronegativity of the dopant plays a crucial role in the overall charge distribution, although it does not significantly affect the spin distribution. This is made more clear by the charge accumulation vs. relative electronegativity results for the adatoms shown in Fig. 3 obtained using both Mulliken population and NBO analysis. In particular, strong electronegative dopants (O, N) accumulate negative charge, resulting in a reduction of the negative

charge accumulation on the cycloaddition bond, while less electronegative (or electropositive) elements (B, P, Si, S) accumulate positive charge and, as a result, the positive charge accumulation around the vacancies is reduced or eliminated.

When both vacancies are healed by N (Fig. 2 bottom panel), spin density becomes extensively delocalized across both monomers, although the nitrogen atoms themselves possess only a small positive spin density. In contrast, the charge distribution becomes completely localized at the two substitutional sites, with both N atoms developing a large negative charge and the three C atoms neighboring the N atom at each site developing a large positive charge.

A similar picture is rediscovered if both vacancies are healed with O atoms instead of with N atoms. However, the situation changes if the vacancies are healed either with B, P, Si, or S atoms. In this case, while extensive spin delocalization is found as with N and O dopants, positive charge density is accumulated as a result of B, P, Si, S dopants. Negative charge is found on the C atoms neighboring the dopants.

Defects in SWCNs. Our results for defects in (5,5)-SWCN are summarized in Fig. 4. As illustrated in the top panel, the results for two vacancies in SWCN are qualitatively very similar to those for $[C_{59}]_2$. In all these cases the *trans* configuration was found to be the most stable. An extensive delocalization of charge over the SWCN exhibiting the same features as in $[C_{59}]_2$ is found. The spin density of the system is found to be localized on C atoms surrounding the vacancy sites. When one of the vacancies in SWCN is healed by a single N atom (Fig. 4, middle panel), the same qualitative picture is found as for the $[C_{59}]_2$N.

When both vacancies are healed by N atoms, once again, the most stable state was found to be the one with nitrogens

in the *cis* configuration. As seen in the bottom panel of Fig. 4, the spin density becomes delocalized across the nanotube, particularly over both caps at the two ends of the nanotube. This is in agreement with Ref. 9. As in the case of $[C_{59}]_2N$, neither N atom possesses any significant spin density. Also, as in the case of $[C_{59}]_2N$, the charge distribution becomes completely localized at the two substitutional sites, with both N atoms developing a large negative charge and the three C atoms neighboring the N atom at each site developing a large positive charge. There is also a considerable accumulation of negative charge at sites which are second nearest neighbors to the vacancy sites. The same features are found when the system is in one of its lower charged states (anion-doublet, di-anion triplet, and di-cation triplet states). Contrary to the vacancy cases, the highest-occupied-molecular-orbital– (HOMO-) lowest-unoccupied-molecular-orbital (LUMO) gap in the N cases was found to be much smaller in the singlet states ($\approx 0.32-0.44$ eV) compared to that of the triplet states ($\approx 0.61-0.78$ eV). Another noticeable difference between vacancies and nitrogen defects is the large energy difference between the HOMO-spin-up and the HOMO-spin-down orbitals (≈ 0.4 eV) as compared with the corresponding result (≈ 0.1 eV) for the vacancy cases.

Additionally, we have also considered the simultaneous presence of two vacancies and two N adatoms at C cites near the vacancies. In this test case we examined the relative strength of a vacancy defect relative to that of a N impurity. The spin density in this case is not affected by the presence of the N adatoms but rather accumulates around the vacancy sites. At the same time, the N atoms attract electrons and become negatively charged (i.e., even in the presence of the vacancies). Positive charge is still found to accumulate around the vacancy sites while only a small spin delocalization marks the presence of N adatoms.

If instead with N, both vacancies are healed with X atoms ($X=$B, P, O, Si, and S), the same qualitative picture as with the C_{60} dimer is reobtained. That is, extensive spin delocalization is developed and charge is accumulated on the X atom (positive for B, P, Si, and S, negative for O). Similarly, if only one of the two vacancies in SWCN is healed with a X atom, a large spin density becomes localized almost entirely on one of the C atoms neighboring the vacancy. The charge distribution in the vicinity of the X atom is approximately the same as in the case of two substitutional X atoms.

From the above results of C_{60} dimers and SWCNs it is clear that there are strong differences between the roles of the vacancy and the X impurity. In particular, the vacancy site has been found to act as a donor site, i.e., it serves as a center for positive charge accumulation, while at the same time (in contrast to any of the X dopants) acting also as site for spin density accumulation. Interestingly, the primary effect of the presence of the impurity X atoms appears to be (i) delocalization of the excess spin density and (ii) modification of the distribution of the electron charge density. The impurity effect is determined by its relative electronegativity with respect to the C atoms. The role of the vacancy is not affected significantly in the presence of distant impurity X atoms or neighboring X adatoms if these impurities tend to accumulate negative charge. However, if the X impurity accumulates positive charge, then the vacancies' tendency to accumulate positive charge density is reduced or eliminated. These features are not altered in the lower positive or negative charged states of the SWCNs with vacancy and substitutional N defects. These results are in very good agreement with the experimental ESR ones[12] which do not reveal spin localization around the N impurities as insinuated in Ref. 8.

Summarizing our results, it has been demonstrated that carbon vacancies promote the magnetic states of C_{60}-based systems and SWCNs. The role of carbon vacancies is not replicated satisfactorily by any of the substitutional N, B, O, Si, S, or P impurities demonstrating, thus, the unique role of vacancies in promoting the carbon magnetism.

---

*Electronic address: andriot@iesl.forth.gr

†Electronic address: rmshee0@email.uky.edu

‡Electronic address: super250@pop.uky.edu

[1] T. L. Makarova, B. Sundqvist, R. Hohne, P. Esqulnazi, Y. Kopelevich, P. Scharff, V. A. Davidov, L. S. Kashevarova, and A. V. Rakhmanina, Nature (London) **413**, 716 (2001).

[2] A. N. Andriotis, M. Menon, R. M. Sheetz, and L. Chernozatonskii, Phys. Rev. Lett. **90**, 026801 (2003).

[3] P. O. Lehtinen, A. S. Foster, Y. Ma, A. V. Krasheninnikov, and R. M. Nieminen, Phys. Rev. Lett. **93**, 187202 (2004).

[4] P. Esquinazi, D. Spemann, R. Hohne, A. Setzer, K. H. Han, and T. Butz, Phys. Rev. Lett. **91**, 227201 (2003).

[5] J. A. Chan, B. Montanari, J. D. Gale, S. M. Bennington, J. W. Taylor, and N. M. Harrison, Phys. Rev. B **70**, 041403(R) (2004).

[6] S. Talapatra, P. G. Ganesan, T. Kim, R. Vajtai, M. Huang, M. Shima, G. Ramanath, D. Srivastava, S. C. Deevi, and P. M. Ajayan, Phys. Rev. Lett. **95**, 097201 (2005).

[7] W. Andreoni, F. Gygi, and M. Parrinello, Chem. Phys. Lett. **190**, 159 (1992).

[8] G. Csanyi and T. A. Arias, Chem. Phys. Lett. **360**, 552 (2002).

[9] A. H. Nevidomskyy, G. Csanyi, and M. C. Payne, Phys. Rev. Lett. **91**, 105502 (2003).

[10] L. H. Chan, K. H. Hong, D. Q. Xiao, T. C. Lin, S. H. Lai, W. J. Hsieh, and H. C. Shih, Phys. Rev. B **70**, 125408 (2004).

[11] A. N. Andriotis, R. M. Sheetz, E. Richter, and M. Menon, Europhys. Lett. **72**, 658 (2005).

[12] F. Fulop, A. Rockenbauer, F. Simon, S. Pekker, L. Korecz, S. Garaj, and A. Janossy, Chem. Phys. Lett. **334**, 233 (2001).

[13] K. Prassides, Curr. Opin. Solid State Mater. Sci. **2**, 433 (1997).

[14] M. J. Frisch *et al.*, Gaussian, Inc., Pittsburgh, PA 2003.

[15] A. Reed, L. A. Curtiss, and F. Weinhold, Chem. Rev. (Washington, D.C.) **88**, 854 (1988).

[16] A. N. Andriotis, R. M. Sheetz, and M. Menon, J. Phys.: Condens. Matter **17**, L35 (2005).

[17] The exchange coupling constant is defined as the energy difference between the triplet and the singlet state of the system.