PHYSICAL REVIEW B **76**, 085401 (2007)

Noncollinear coupling between magnetic adatoms in carbon nanotubes

A. T. Costa*
Instituto de Física, Universidade Federal Fluminense, 24210-346 Niterói, RJ, Brazil

C. G. Rocha and M. S. Ferreira†
School of Physics, Trinity College Dublin, Dublin 2, Ireland

(Received 28 February 2007; revised manuscript received 24 May 2007; published 1 August 2007)

The long-range character of the exchange coupling between localized magnetic moments indirectly mediated by the conduction electrons of metallic hosts often plays a significant role in determining the magnetic order of low-dimensional structures. In addition to this indirect coupling, here we show that the direct exchange interaction that arises when the moments are not too far apart may induce a noncollinear magnetic order that cannot be characterized by a Heisenberg-like interaction between the magnetic moments. We argue that this effect can be manipulated to control the magnetization alignment of magnetic dimers adsorbed on the walls of carbon nanotubes. Our results show that the magnetic coupling cannot be inferred only by total-energy differences between the ferromagnetic and antiferromagnetic configurations, the possibility of noncollinear alignments suggesting this to be a misleading practice.

DOI: 10.1103/PhysRevB.76.085401 PACS number(s): 73.22.−f, 75.30.Et, 75.30.Hx

More than a decade after the discovery of carbon nanotubes, these nanoscale cylindrical structures are still the subject of intensive scientific research due to their intriguing physical properties. Significant progress has been made to explain the intrinsic properties of nanotubes, but to expand their applicability we must understand and control how they interact with other objects. Nanotubes interacting with magnetic foreign objects offer a wide range of technologically promising possibilities within the so-called area of spintronics in molecular structures. In fact, the ability to produce sizable changes in the conductance of a nanotube due to an applied magnetic field is one of the driving forces in the research of magnetic properties of carbon-based structures.[1,2] Substrates,[3,4] substitutional impurities,[5] adsorbed atoms,[6,7] and nanoparticles[8] are some of the different magnetic foreign objects that can interact with carbon nanotubes. Among those, transition-metal magnetic adatoms have been reported to produce noticeable changes in the spin-dependent electronic structure of carbon nanotubes.[6,8] Furthermore, the formation of defect-induced magnetic moments in carbon-based materials appears as an additional possibility to manipulate the magnetic response of these systems.[9]

The transport properties of magnetically doped structures depend on the way their magnetic moments are oriented. Therefore, besides establishing how magnetic impurities affect the electronic structure of a nanotube, it is crucial to understand the nature of the coupling between these moments. Regarding magnetic adatoms, dipolar and exchange interactions are the basic mechanisms defining the alignment of their moments.[10] The former decays rather quickly as the moments are moved apart, whereas the latter depends on both the dimensionality and the nature of the interaction. Direct exchange coupling results from the overlap between wave functions centered at the magnetic impurities but also decays abruptly as the distance between them increases. Of indirect nature, the so-called indirect exchange coupling (IEC) between magnetic impurities mediated by the conduction electrons of the nonmagnetic host is known to decay more slowly and plays an important role in determining the overall magnetic alignment of the system. In fact, we have recently shown that the IEC between magnetic adatoms in carbon nanotubes is long ranged and is of Heisenberg form.[11] We have also shown that the coupling may be either ferromagnetic or antiferromagnetic, depending on the type of atoms, their separation, as well as the size and type of nanotube host.

The slow decaying rate of the IEC makes the indirect interaction dominant when magnetic objects are sufficiently far apart. However, it becomes comparable to the direct exchange coupling when the objects are brought closer together. In this situation, the proximity of two magnetic moments may give rise to unusual ordering. Recent calculations indicate that the magnetization alignment of magnetic dimers adsorbed on the surface of a three-dimensional metal is often neither ferromagnetic nor antiferromagnetic but follows a noncollinear order.[12] The origin of such a non-Heisenberg behavior lies in the competition between the direct and indirect contributions to the exchange coupling and should arise when localized magnetic moments embedded in a metallic host are in close proximity. It is the purpose of this paper to show that such an effect also occurs when magnetic dimers are adsorbed on the walls of a metallic nanotube. Since the IEC decays more slowly in low-dimensional hosts, we argue that nanotubes are likely to expand the range of separations for which this competition can induce noncollinear alignments. In other words, the effect of noncollinear magnetization alignment of dimers should be more robust in nanotubes than in flat substrates of higher dimensionality.

We consider a dimer made of two magnetic atoms, labeled A and B, adsorbed on the walls of an infinitely long carbon nanotube and schematically represented in Fig. 1. Magnetism in these atoms is driven by an intra-atomic Coulomb interaction that, when treated in mean-field approximation through a self-consistent procedure, can be described by an effective spin-dependent potential located at the atomic positions. In this way, the electronic structure of the entire system is well described by a Hamiltonian in a basis of localized atomic orbitals. In such a basis, this tight-binding-

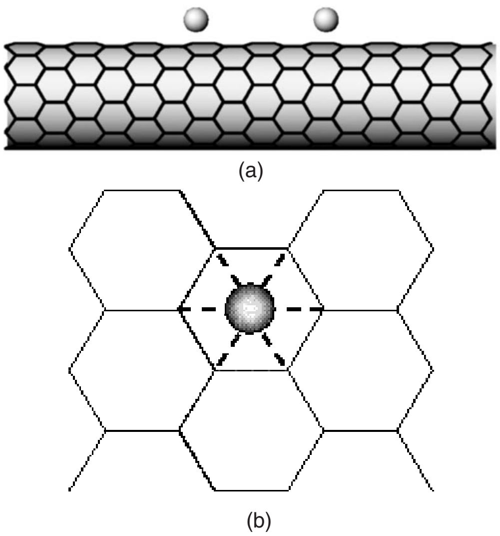

FIG. 1. (a) Schematic diagram representing a magnetic dimer formed by two magnetic atoms adsorbed on the surface of a carbon nanotube. (b) A more detailed diagram shows a two-dimensional depiction of the magnetic adatom above the hexagonal lattice of the nanotube. The dashed lines highlight to which nearest-neighbor sites the adatom is connected by a hopping parameter t.

like Hamiltonian is fully determined by the on-site potentials and hopping integrals.

We assume that the magnetic moments of the individual adatoms are initially parallel, hereafter referred to as the ferromagnetic configuration. In this configuration, the Hamiltonian of the entire system written in the basis $|j\rangle$ of atomic orbitals centered at a site j is given by $\hat{H}=\hat{H}_{NT}+\hat{H}_D+\hat{V}_C$, where $\hat{H}_{NT}=\Sigma_{j,j'}|j\rangle\gamma\langle j'|$ is the Hamiltonian of the individual nanotube, $\hat{H}_D=|a\rangle\epsilon_a\langle a|+|b\rangle\epsilon_b\langle b|+|a\rangle\tau\langle b|+|b\rangle\tau^\dagger\langle a|$ is the Hamiltonian associated with the dimer, and $\hat{V}_C=\Sigma_\ell t\{|a\rangle\langle\ell|+|\ell\rangle\langle a|\}+\Sigma_{\ell'}t^\dagger\{|b\rangle\langle\ell'|+|\ell'\rangle\langle b|\}$ refers to the coupling between the adatoms and the nanotube. The parameters γ, ϵ_a, ϵ_b, and t are all matrices in spin and orbital spaces and correspond to the hopping between nearest-neighbor sites in the nanotube, the on-site potentials of atom A and of atom B, and the hopping between the nanotube atoms and the adatoms, respectively. Likewise, the basis $|j\rangle$ represents vectors in the same linear space. It is evident from the expressions above that sites $j=a$ and $j=b$ label the two adatoms and the indices ℓ and ℓ' label the nanotube sites that are coupled to those respective atoms. These latter sites are schematically illustrated in Fig. 1(b) where a magnetic adatom lying just above the center of the nearest hexagon is connected to its nearest carbon atoms. It is worth mentioning that there are two fundamental differences between $\hat{H}$ and the Hamiltonian considered in Ref. 11. The inclusion of a hopping τ between atoms A and B that accounts for the direct interaction due to their proximity is the first difference, followed by the fact that the magnetic adatoms are now located above the centers of the nanotube hexagons, as opposed to being immediately above the carbon atoms.

The energy required to rotate the magnetic moment of one adatom relative to the other is given by[11]

$$\Delta\mathcal{E}(\theta)=\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega\left[\frac{1}{1+e^{\beta(\omega-\mu)}}\right]\mathrm{Im}\,\mathrm{Tr}\ln[1+2V_x^2(1-\cos\theta)\times G^{\uparrow}_{a,b}(\omega)G^{\downarrow}_{b,a}(\omega)], \tag{1}$$

where θ is the angle of rotation and V_x is a matrix in orbital space representing the strength of the local exchange potentials. $G^{\sigma}_{m,\ell}(\omega)$ represents the propagator between sites $j=\ell$ and $j=m$ for electrons of spin σ and energy ω in the ferromagnetic configuration, and the trace is over orbital indices. Regarding the fraction within brackets, $\beta=1/k_BT$, where k_B is the Boltzmann constant and T is the temperature.

For the sake of simplicity, the electronic structure of the system will be treated here within the single-band tight-binding model. The expressions above are very general and by no means restricted to such a simple case. The results obtained here can be easily extended to a multiorbital description but bring no qualitative difference. This is justified by the fact that the main features of the IEC are predominantly determined by the extended electrons of the host, in this case the nanotube, whose electronic structure is known to be well reproduced by a single-band tight-binding model. Having transition-metal atoms in mind, the adatoms are then described by a fivefold degenerate d band with the appropriate occupation to represent typical magnetic materials. In this way, rather than matrices in orbital indices, all quantities in the integrand of Eq. (1) become scalar. As mentioned above, in what concerns the indirect (tube-mediated) exchange coupling, the most important features are determined by the tube's electronic structure; the magnetic adatoms serve merely as a source of local spin polarization. The direct coupling should be more sensitive to details of the adatoms' electronic structure, but our direct hopping parameter serves as an effective hopping, encompassing the effects of hoppings between different d orbitals.

The energy variation $\Delta\mathcal{E}(\theta)$ can be calculated by inserting the appropriate Green's function matrix elements $G^{\uparrow}_{a,b}(\omega)$ and $G^{\downarrow}_{b,a}(\omega)$ into Eq. (1) and evaluating the corresponding energy integral. The Green's functions are evaluated firstly in the absence of any magnetic impurities through a standard renormalization procedure[13] and subsequently renormalized through Dyson's equation to account for the presence of the magnetic adatoms in a self-consistent fashion. As far as the tight-binding parameters are concerned, the on-site potentials ϵ_a and ϵ_b are easily determined by the aforementioned self-consistent procedure and follow from the appropriate selection of the d-band occupation. The hopping parameter $\gamma=2.7$ eV is known to describe well the π band of carbon nanotubes.[14,15] The only remaining parameters to be specified are the coupling t describing the electronic hopping linking the adatoms with the nanotube and the proximity parameter τ that accounts for the direct interaction between nearby adatoms.

We start by assuming $\tau=0$, which corresponds to the standard IEC between magnetic objects without any direct interaction.[11] In Fig. 2, we see that the IEC has a nice sinusoidal behavior as a function of the angle between magnetizations if the adatoms are sufficiently far apart. As demonstrated many years ago by Herring,[16] the angular dependence

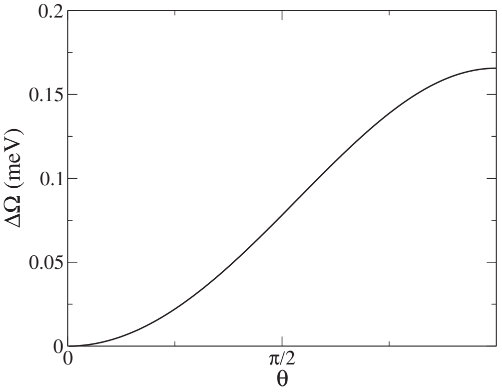

FIG. 2. Energy change $\Delta\Omega$ as a function of relative angle θ between magnetizations for two Mn atoms ($n=1.1$ electrons per atom). The hopping between magnetic atoms has been artificially turned off ($\tau=0$), and the hopping Mn-C is $t=0.4\gamma$. Each Mn atom is atop the center of a hexagon that are four unit cells apart.

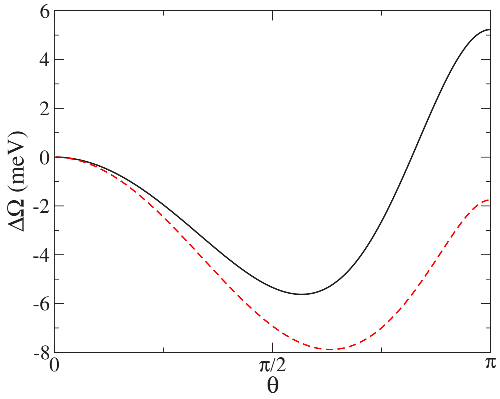

FIG. 3. (Color online) Energy change as a function of angle between magnetizations of two Mn atoms adsorbed on a (5,5) nanotube. The adatoms are located atop the centers of nearest-neighbor hexagons, connected to six C atoms each. The Mn-Mn hopping $\tau=0.47\gamma$. The dashed curve corresponds to a doped nanotube, simulated by a change in Fermi energy $\Delta E_F=0.2\gamma$.

of the energy variation follows a standard Heisenberg form $\Delta\mathcal{E}(\theta)=J_0+J_I\cos(\theta)$ only for large separations of the magnetic objects. The deviation from the traditionally assumed Heisenberg-like behavior may arise as a consequence of charge rearrangements due to the relative rotation of magnetic moments. Such rearrangements are of little importance in a three-dimensional metal because screening is extremely efficient there; such is not the case in carbon nanotubes, even metallic ones. In fact, for small separations one finds small deviations from the Heisenberg form which are nevertheless not strong enough to introduce any noncollinearity in the equilibrium states. For the Heisenberg-like case, it is simple to show that the sinusoidal behavior remains the same for arbitrary values of t and that the only effect that this parameter has on $\Delta\mathcal{E}(\theta)$ is in determining the amplitude of the cosine function, that is, on the quantity J_I.

Whereas *ab initio* calculations[17] would struggle to provide a detailed angular dependence of the total energy, they can be used to obtain the actual total energy of the system in both ferromagnetic and antiferromagnetic configurations, two quantities whose difference provides direct information on $\Delta\mathcal{E}(\theta)$ and, in turn, on the reasonable range of values for the parameter t. With that purpose in mind, *ab initio* calculations were evaluated for adatoms lying a minimum distance apart to reflect the absence of any direct interaction. The difference between the total energy values for the antiferromagnetic and ferromagnetic configurations was then used to guide us to the appropriate range of values of the hopping t. Our calculations are performed using the SIESTA code[18] within the local density approximation and generalized gradient approximation approaches for the exchange and correlation potential.[19,20] Norm-conserving pseudopotentials[21] with relativistic corrections and a split-valence double-ζ basis of pseudoatomic orbitals with an orbital confining energy of 0.05 eV and an energy cutoff of 150 Ry were used. The k-point sampling is composed of 11 k points in the axial direction of the tube and we built a unit cell with 96 atoms for the (4,4) carbon nanotube (CN) plus the two magnetic atoms. One may notice that we induced a magnetization up or down only in the magnetic atoms. The two configurations (ferro- and antiferromagnetic) for the adatoms were studied. The in-plane lattice parameter was chosen to be large enough to guarantee a negligible interaction between periodic CN images (~98 Å). All the structure was optimized by conjugate gradient with force tolerance of 0.05 eV/Å.

Having determined the range of values of the parameter t that accounts for the correct magnitude (and sign) of the indirect coupling J_I, we can now proceed to introduce a direct hopping term τ that corresponds to bringing the two adatoms closer together. As depicted in Fig. 3, a suitable choice of values for the parameter τ may induce an interesting situation in which the angular dependence of the energy variation is no longer described by a single sinusoidal function. Such a non-Heisenberg-like behavior arises as the result of a competition between the direct and indirect contributions to the magnetic coupling. Having the energy minimum at an intermediate angle $0<\theta<\pi$ means that the preferential magnetization alignment for such a magnetic dimer is of noncollinear type. Incidentally, one may notice that the effect is robust under doping or the application of a gate voltage: the dashed curve in Fig. 3 shows that the stable configuration is still noncollinear after a change of 0.2γ in the Fermi energy. It is interesting to notice that, upon doping, the energy of the antiferromagnetic state becomes smaller than that of the ferromagnetic alignment. First principles calculations that only evaluate total energies or energy differences between the two collinear states would predict a change in alignment upon doping. What our results show is that for magnetic objects close to each other, those energy differences are not enough: one must analyze the local stability around the collinear states.

Rather than the result of a fortunate choice of parameters, this noncollinearity effect is robust enough to be seen in a wide range of values for the proximity parameter τ as well as for adatoms of different nature. To assess the robustness of this effect, we introduce a parameter ζ defined as

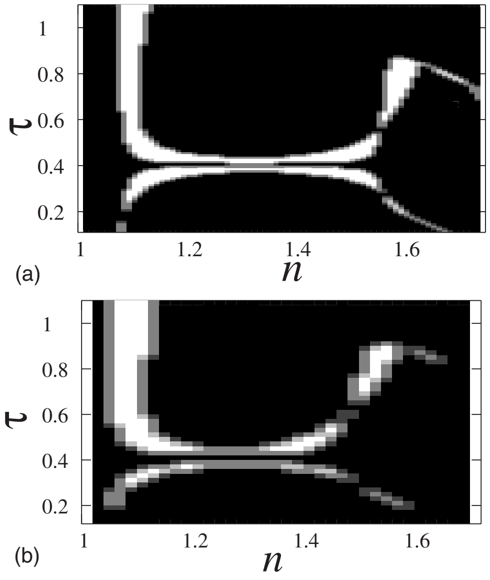

FIG. 4. Top panel: State diagram for the ground state of a magnetic dimer on an armchair (5,5) nanotube and $t=0.7$. The white region corresponds to noncollinear ground states. Bottom panel: Same as above but the Fermi energy has been shifted by 0.2γ.

$$\zeta = \mathrm{sgn}\left[\frac{\left(\frac{d^2\Delta\mathcal{E}}{d\theta^2}\right)_{\theta=0}\left(\frac{d^2\Delta\mathcal{E}}{d\theta^2}\right)_{\theta=\pi}}{\left|\left(\frac{d^2\Delta\mathcal{E}}{d\theta^2}\right)_{\theta=0}\left(\frac{d^2\Delta\mathcal{E}}{d\theta^2}\right)_{\theta=\pi}\right|}\right], \tag{2}$$

where the function $\mathrm{sgn}(x)=1$ for $x> =0$ and $\mathrm{sgn}(x)=-1$ for $x<0$. Equation (2) uses the curvature of the function $\Delta\mathcal{E}(\theta)$ at $\theta=0$ and $\theta=\pi$ to define an indirect way of testing whether or not the magnetic coupling of the dimer follows a Heisenberg law. According to the definition above, $\zeta=-1$ corresponds to a Heisenberg behavior and $\zeta=+1$ corresponds to the noncollinearity effect. A more informative view is in the diagram of Fig. 4 where we have adopted a color code that uses black to represent $\zeta=+1$ and white to represent $\zeta=-1$. On the vertical axis, the proximity parameter τ runs from 10% to 110% of the electronic hopping γ, whereas the d-band occupation on the horizontal axis includes characteristic values corresponding to Fe ($n\sim 1.4\pm 0.2$ electrons) and Co ($n\sim 1.7\pm 0.2$ electrons), for instance. These values are based on the total occupation of the five d orbitals in the respective bulk metals and on the assumption that the adatoms may lose or gain up to one electron upon binding to the nanotube. It is noteworthy that the noncollinear state takes a non-negligible fraction of the diagram, indicating that the situation illustrated in Fig. 3 is far from coincidental.

Since this effect results from a competition between the direct and indirect contributions to the magnetic coupling, it is natural to suspect that one may have the ability to select the preferred alignment of the magnetizations by controlling how these two contributions are related. Although changing τ is a mathematically possible way of altering the direct contribution to the coupling, it is of little applicability once this would, in practical terms, involve varying the separation of the magnetic atoms in the dimer. A possible alternative is to change the indirect contribution to the coupling. To change the indirect coupling by moving the adatoms apart would be equally impractical but one could make use of the fact that this type of coupling can also be affected by controlling the nanotube Fermi energy. In fact, the authors have already shown[11] that the indirect coupling can be modified by tuning the Fermi energy through doping or through a carefully engineered gate voltage. The bottom panel of Fig. 4 shows a similar diagram in which the Fermi level of the nanotube host has been shifted by $\Delta E_F=0.2\gamma$. A clear distinction between the diagrams in the top and bottom panels of Fig. 4 corroborates that this is, in fact, a possible and more practical way of controlling the magnetization alignment of magnetic dimers attached to the walls of a carbon nanotube. Whereas a single isolated dimer may not be able to produce a sizable effect, a finite concentration of those dimers will undoubtedly be sufficient to produce a measurable change in the magnetization of the system.

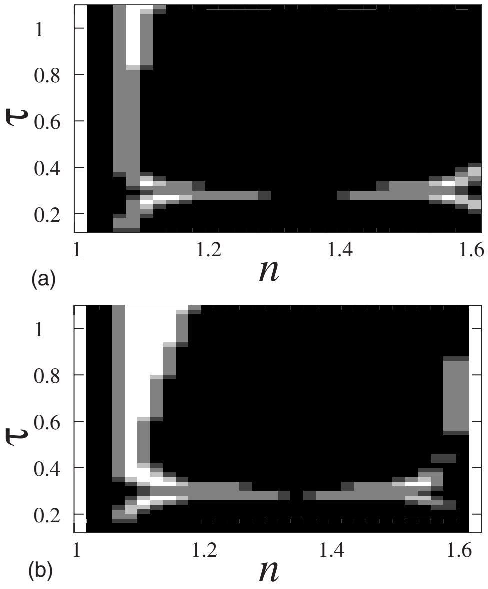

FIG. 5. State diagram for the ground state of a magnetic dimer on an armchair (5,5) nanotube and $t=0.7\gamma$ for two values of the effective Coulomb interaction: $U=20\gamma$ (top panel) and $U=12\gamma$ (bottom panel). The white region corresponds to noncollinear ground states.

In our model calculations, we must choose a value for the effective Coulomb interaction parameter U such that the Stoner criterion for the onset of magnetism is satisfied.[22] In single-orbital models, this value has to be unrealistically large due to the artificially reduced density of states at the Fermi level. It is well known that the large U limit of the Hubbard model is the Heisenberg model.[22] Since we are looking for deviations from Heisenberg-like behavior, the large U constraint may force us to underestimate the relative frequency of occurrence of noncollinearity. It is, thus, instructive to examine the behavior of the kind of state diagram presented in Fig. 4 under variations of the Coulomb parameter U. In Fig. 5, it is obvious that a smaller U results in a significantly expanded region of noncollinear ground states. It is important to notice, however, that even for the high $U=20\gamma$ we used to obtain the results in Fig. 4 noncollinear ground states occupy a significant part of the state diagram.

In summary, we have shown that the proximity of two magnetic adatoms attached to the walls of carbon nanotubes may induce the formation of noncollinear alignment of their magnetizations. This effect is the result of a competition between the direct and indirect contributions to the exchange coupling, which become comparable when the magnetic adatoms are not too far apart. Due to the long-range character of the IEC in low-dimensional structures, carbon nanotubes are ideal candidates to display the non-Heisenberg behavior discussed in this paper. Moreover, the ability to control the indirect coupling through a careful selection of the Fermi energy of nanotubes opens the road to the possibility of controlling the magnetization of nanotube-based systems doped with magnetic dimers. Finally, it is important to highlight that *ab initio* calculations that rely on total-energy differences between the ferromagnetic and antiferromagnetic configurations to assign the most favorable alignment for the moments may be misleading, given that this would never give intermediate angles as possible solutions.

The authors gratefully acknowledge many enlightening conversations with R. B. Muniz. M.S.F. acknowledges the financial support of Science Foundation Ireland and Enterprise Ireland. A.T.C. acknowledges financial support received from CNPq and FAPEMIG from Brazil.

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*antc@if.uff.br

†ferreirm@tcd.ie

[1] K. Tsukagoshi, B. W. Alphenaar, and H. Ago, Nature (London) **401**, 572 (1999).

[2] L. E. Hueso, J. M. Pruneda, V. Ferrari, G. Burnel, J. P. Valdes-Herrera, B. D. Simons, P. B. Littlewood, E. Artacho, A. Fert, and N. D. Mathur, Nature (London) **445**, 410 (2007).

[3] M. S. Ferreira and S. Sanvito, Phys. Rev. B **69**, 035407 (2004).

[4] O. Cespedes, M. S. Ferreira, S. Sanvito, M. Kociak, and J. M. D. Coey, J. Phys.: Condens. Matter **16**, 155 (2004).

[5] S. B. Fagan, R. Mota, R. J. Baierle, A. J. R. da Silva, and A. Fazzio, Mater. Charact. **50**, 183 (2003).

[6] S. B. Fagan, R. Mota, A. J. R. da Silva, and A. Fazzio, Phys. Rev. B **67**, 205414 (2003).

[7] S. B. Fagan, R. Mota, R. J. Baierle, A. J. R. da Silva, and A. Fazzio, Physica B **340**, 982 (2003).

[8] C. K. Yang, J. Zhao, and J. P. Lu, Phys. Rev. Lett. **90**, 257203 (2003).

[9] Yuchen Ma, A. S. Foster, A. V. Krasheninnikov, and R. M. Nieminen, Phys. Rev. B **72**, 205416 (2005).

[10] D. Altbir, P. Vargas, J. d'Albuquerque e Castro, and U. Raff, Phys. Rev. B **57**, 13604 (1998).

[11] A. T. Costa, D. F. Kirwan, and M. S. Ferreira, Phys. Rev. B **72**, 085402 (2005).

[12] A. T. Costa, R. B. Muniz, and D. L. Mills, Phys. Rev. Lett. **94**, 137203 (2005).

[13] C. G. Rocha, T. G. Dargam, and A. Latgé, Phys. Rev. B **65**, 165431 (2002).

[14] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **61**, 2981 (2000).

[15] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).

[16] C. Herring, in *Magnetism*, edited by George T. Rado and Harry Suhl (Academic, New York, 1966), Vol. IV.

[17] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992).

[18] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. **65**, 453 (1997); P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996).

[19] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[20] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[21] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[22] K. Yosida, *Theory of Magnetism*, 2nd ed. (Springer, Berlin, 2006).