

Magnetism of covalently functionalized carbon nanotubes

Elton J. G. Santos,^{a)} D. Sánchez-Portal, and A. Ayuela

Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain and Centro de Física de Materiales-MPC, Centro Mixto CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain

(Received 14 April 2011; accepted 14 July 2011; published online 8 August 2011)

We investigate the electronic structure of carbon nanotubes functionalized by adsorbates anchored with single C-C covalent bonds. We find that despite the particular adsorbate, a spin moment with a universal value of $1.0 \mu_B$ per molecule is induced at low coverage. Therefore, we propose a mechanism of bonding-induced magnetism at the carbon surface. The adsorption of a single molecule creates a dispersionless defect state at the Fermi energy, which is mainly localized in the carbon wall and presents a small contribution from the adsorbate. This universal spin moment is fairly independent of the coverage as long as all the molecules occupy the same graphenic sublattice. The magnetic coupling between adsorbates is also studied and reveals a key dependence on the graphenic sublattice adsorption site. © 2011 American Institute of Physics.

[doi:10.1063/1.3623755]

Ferromagnetism in otherwise nonmagnetic materials has been experimentally reported for a number of nanoscale systems.^{1–3} A very active line of research leads to carbon-based materials, which is related to the field of spintronics. Most of these experiments on carbon are related to lattice imperfections or disorder. Some examples are given by proton-irradiated thin carbon films,^{1,2} nitrogen- and carbon-ion-implanted nanodiamond,⁴ pyrolytic graphite containing a high defect concentration,⁵ or by vacancies created by scanning tunneling microscopy in multilayered graphene.⁶ We propose that despite of these defective systems, the well known sidewall functionalization⁷ could also be used to induce a magnetic state in single wall carbon nanotubes (SWNT).

In this Letter, we show that when a single C-C covalent bond is established with a chemisorbed adsorbate at the carbon surface, a spin moment is induced in the system. This moment has a universal value of $1.0 \mu_B$, independent of the nature of the adsorbate, and we show that this effect occurs for a wide class of organic and inorganic molecules with different chemical activity (e.g., alkanes, polymers, diazonium salts, aryl and alkyl radicals, nucleobases, amido, and amino groups, acids). When several adsorbates are simultaneously adsorbed at the wall, we have found that, for metallic or semiconducting SWNTs, only the configurations with all the adsorbates in one sublattice develop a spin moment. We refer to the two sublattices that define the bipartite structure of a graphene layer. Metallic tubes exhibit a ferromagnetic (FM) behaviour, while, for semiconducting tubes, FM and antiferromagnetic (AFM) spin solutions are almost degenerate. For molecules at opposite sublattices, no magnetic solution can be stabilized in both types of nanotubes.

Our findings are obtained within the density functional theory⁸ as implemented in the SIESTA code.¹² We use the generalized gradient approximation⁹ and Troullier-Martins¹⁰ pseudopotentials. The structures in the periodic supercell method contain up to 310 atoms¹¹ with adsorbate concentrations (defined as the ratio between molecules and the number

of atoms in the SWNT) ranging from 0.6% to 25.0%. The atomic coordinates were relaxed using a conjugated gradient algorithm until all the force components were smaller than $0.04 \text{ eV}/\text{Å}$. To prevent spurious interactions the minimum distance between the walls of neighboring SWNTs was 18 Å . The real-space grid used to calculate the Hartree and exchange-correlation contribution to the total energy and Hamiltonian was equivalent to a 150 Ry plane-wave cutoff. The k -point sampling was equivalent to a $1 \times 1 \times 136$ sampling¹³ of the Brillouin zone of a single tube cell. We have done some calculations using the VASP code.^{14,15} We used projected-augmented-wave potentials with a well converged plane-wave cutoff of 400 eV. The rest of computational details was fixed as in the SIESTA method. The results obtained with VASP are almost identical to those obtained with SIESTA.

In order to understand the origin of a common spin moment when a covalent bonding is attached to the tube wall, the spin polarized band structure of a CH_3 molecule chemisorbed on top of a C atom is shown in Figure 1 for (a) (5,5) and (b) (10,0) SWNTs. In both cases, a defect state appears pinned at the Fermi level (E_F) with full spin polarization. This state is mainly composed by p_z orbitals of the C neighbors to the saturated site, with almost no contribution from the adsorbate. In fact, a detailed Mulliken analysis of this p_z -defect state assigns a small contribution of the spin moment to the adsorbate. This indicates that the adsorbate has a primary role in creating the bond with the nanotube and the associated defect level, but it does not appreciably contribute to the spin moment. More complex adsorbates, notwithstanding of the biological and chemical activity (e.g., alkanes, polymers, diazonium salts, aryl and alkyl radicals, nucleobases, amido, and amino groups, acids), show a similar behaviour. This is observed in the density of states (DOS) per spin channel for metallic (5,5) and semiconducting (10,0) SWNTs shown in Figures 1(c) and 1(d), respectively. Several common points are worth mentioning: (i) All molecules induce a spin moment of $1.0 \mu_B$ localized at the carbon surface; (ii) the origin of the spin polarization corresponds to

^{a)}Electronic mail: eltonjose_gomes@ehu.es.

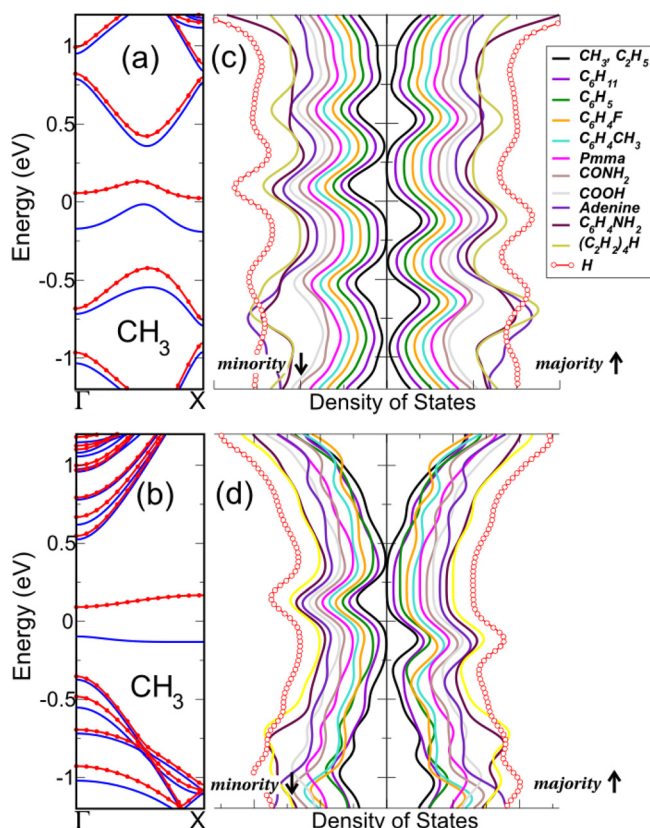


FIG. 1. (Color online) Spin polarized band structure and density of states for (a), (b) (5,5) and (c), (d) (10,0) SWNTs with a single adsorbate (per supercell) of different types chemisorbed to a carbon atom through a single C-C covalent bond. In panels (a) and (b), the blue (dark) and red (bright) lines denote the majority and minority spin bands, respectively. For clarity, the curves in panels (c) and (d) have been shifted and smoothed with a Lorentzian broadening of 0.12 eV. The Fermi energy is set to zero in all panels.

the p_z -defect state as explained above for the CH_3 molecule; (iii) the DOS around E_F follows the same pattern in all cases. This match demonstrates that the spin moment induced by the covalent functionalization is independent of the particular type of adsorbate. These results also point out the complete analogy between a single C-H bonding with more complex C-C arrangements, which is not an obvious behaviour.

Next we study the spin polarization texture induced by the adsorbates on the carbon nanotube wall. The analysis of local magnetic moments for all the adsorbates assigns general trends to both SWNTs. The C atoms that participate directly in the bond formation, at either the molecule or the surface, show a local spin moment smaller than $\sim 0.10 \mu_B$. However, the wall carbon atoms contribute with $0.40 \mu_B$ in the three first C nearest-neighbors, $-0.10 \mu_B$ in the next nearest-neighbors, $0.20 \mu_B$ in the third-neighbors. The adsorbate removes a p_z electron from the adsorption site and leave the p_z states of the nearest carbon neighbours uncoordinated and localized. This gives rise to a defect state localized in the carbon layer and reminiscent of that of a vacancy in a π -tight-binding model of graphenic nanostructures. The carbon spins polarize parallel (antiparallel) respect to the C atom that binds to the surface when sitting in the opposite (same) sublattice. Figure 2 shows the magnetization density in semiconducting (10,0) and metallic (5,5) SWNTs for several mol-

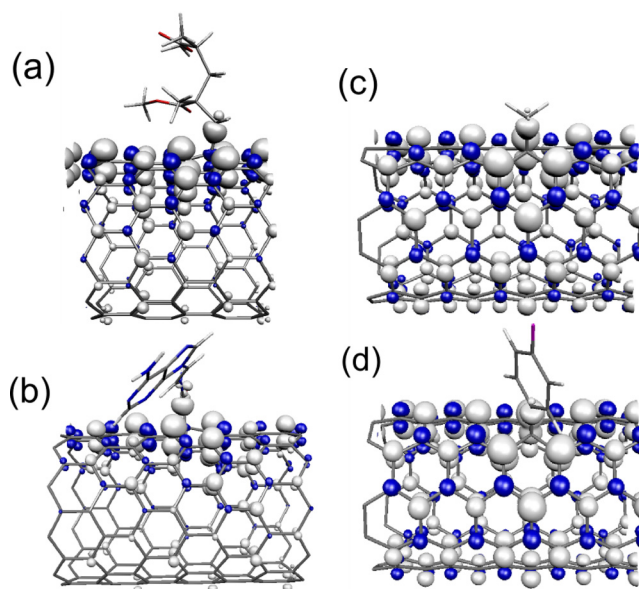


FIG. 2. (Color online) Isosurface for the magnetization density induced by some adsorbates at the SWNT surface: (a) Pmma and (b) Adenine group in a (10,0); (c) CH_3 and (d) $\text{C}_6\text{H}_4\text{F}$ in a (5,5). Majority and minority spin densities correspond, respectively, to light and dark surfaces, which alternate on the honeycomb lattice with long decaying order in all cases. The cutoff is at $\pm 0.0133 e^-/\text{bohr}^3$.

ecules: (a) Pmma polymer chain,¹⁶ (b) Adenine group nucleobase,¹⁷ (c) CH_3 molecule¹⁸ and (d) $\text{C}_6\text{H}_4\text{F}$ salt.¹⁹ The spin density in the metallic (5,5) (Figures 2(c) and 2(d)) is more spread over the whole surface than in the semiconducting (10,0) (Figures 2(a) and 2(b)). This indicates that electronic character of the nanotube wall plays a role in mediating the interaction between adsorbates.

Now we address the energy stability of the different magnetic solutions when two molecules are adsorbed. We focus on a chemisorbed molecule at the nanotube surface by looking at H as an example. For the metallic (5,5) and semiconducting (7,0) SWNTs, we calculate the variation of the total energy for several spin alignments as a function of the distance between the adsorbates at large dilution ($\sim 0.6\%$ adsorbate concentration). The used geometry along tubes is shown in the insets of Figures 3(a) and 3(b). One H is sited at the origin; another in different positions along the tube axis (see background pictures). Several observations can be first made on the stability when two adsorbates are located at the same sublattice (AA configurations). In the metallic (5,5), the FM configuration is most stable than the non-magnetic one (PAR). The energy difference between these two spin solutions along the tube axis oscillates, and no AFM solution could be stabilized at all. In the semiconducting (7,0), the FM and AFM solutions are almost degenerate, with a small energy difference (exchange coupling).

If the two molecules are now located at different sublattices (AB configurations), we were not able to stabilize any magnetic solution for both nanotubes. Instead the system is more stable without a local spin moment. This behaviour for adsorbates at opposite sublattices can be traced back to the interaction between the defect levels. While for AA configurations the interaction is negligible, for AB ones this interaction opens a bonding-antibonding gap around E_F in the p_z defect band and, thus, contributes to the stabilization of PAR

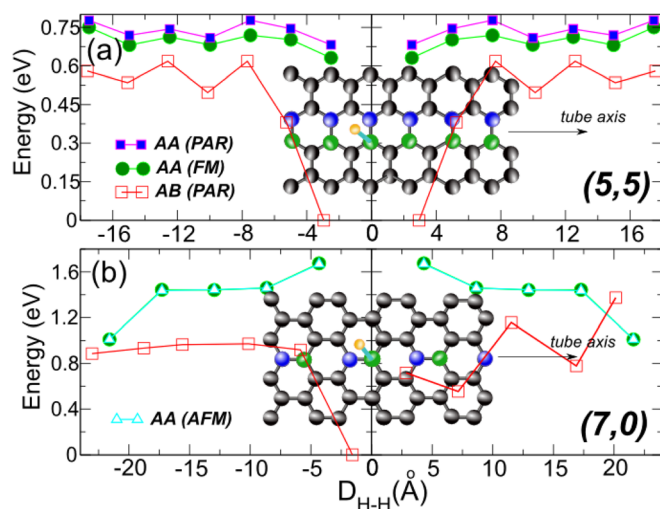


FIG. 3. (Color online) Variation of total energy with the H positions for the distinct magnetic solutions in the two graphitic sublattices (AA and AB) for (a) (5,5) and (b) (7,0) SWNTs. The empty and filled squares correspond to PAR spin solutions in AB and AA sublattices, respectively. The circles and triangles indicate the FM and AFM solutions, respectively, at the same sublattice.

solutions. If the gap is larger than the spin splitting of the majority and minority spin defect bands the system will be non-magnetic.^{20,21} In fact, our detailed analysis of the band structure fully confirmed this explanation. However, it is worth noting that AB adsorption seems to be always more stable in our calculations. This indicates that if the adsorption takes place at random sites, the magnetic solutions will only be stable for low density functionalization. On the other hand, calculations at high adsorbate coverage (from 12.5% to 25% concentration) show that for adsorbates in the same sublattice, the system stabilizes the magnetic solutions. The interaction between molecules remains quite small and they generate a spin moment of $\sim 1.0 \mu_B$ per molecule independently of the coverage. For even higher concentrations, $\sim 50.0\%$, the chemisorbed molecules are not structurally stable, and half of them move away from the surface.

In summary, we have shown that sidewall covalent functionalization creates new routes to achieve magnetism in carbon nanotubes. Despite the adsorbate, and its chemical or biological activity, a spin moment with a value of $1.00 \mu_B$ is induced in the nanotubes when the molecule is attached through a single C-C bond. We find that adsorbates at the

same sublattice order magnetically. For adsorbates at the different sublattices, their strong interaction prevents the formation of local spin moment.

We acknowledge support from Basque Departamento de Educacion and the UPV/EHU (Grant No. IT-366-07), the Spanish Ministerio de Educaci3n y Ciencia (Grant No. FIS2010-19609-CO2-02) and the ETORTEK program funded by the Basque Departamento de Industria and the Diputacion Foral de Guipuzcoa.

- ¹P. Esquinazi, D. Spemann, R. H3hne, A. Setzer, K. H. Han and T. Butz, *Phys. Rev. Lett.* **91**, 227201 (2003).
- ²H. Ohldag, T. Tyliczszak, R. H3hne, D. Spemann, P. Esquinazi, M. Ungureanu, and T. Butz, *Phys. Rev. Lett.* **98**, 187204 (2007).
- ³P. Crespo, R. Litran, T. C. Rojas, M. Multigner, J. M. de la Fuente, J. C. S3nchez-L3pez, M. A. Garc3a, A. Hernando, S. Penad3s, and A. Fern3ndez, *Phys. Rev. Lett.* **93**, 087204 (2004).
- ⁴S. 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).
- ⁵P. Esquinazi, A. Setzer, R. H3hne, C. Semmelhack, Y. Kopelevich, D. Spemann, T. Butz, B. Kohlstrunk, and M. L3sche, *Phys. Rev. B* **66**, 024429 (2002).
- ⁶M. M. Ugeda, I. Brihuega, F. Guinea, and J. M. Gomez-Rodriguez, *Phys. Rev. Lett.* **104**, 096804 (2010).
- ⁷A. Hirsch, *Angew. Chem. Int. Ed.* **41**, 1853 (2002).
- ⁸W. Kohn and L. J. Sham, *Phys. Rev.* **140**, 1133A (1965).
- ⁹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ¹⁰N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ¹¹Typical calculations with single adsorbates have been performed using supercells containing 4 unit cells for both (n, n) and $(n, 0)$. Armchair tubes with $n=4, 5, 6, 8, 10$, and zigzag tubes with $n=7, 8, 10, 14$, have been studied. Tests with up to 7 unit cells have also been performed. The supercells used to calculate the exchange couplings contained 15 and 11 unit cells for (5, 5) and (7, 0), respectively.
- ¹²J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordej3n, and D. Sanchez-Portal, *J. Phys. Condens. Matter* **14**, 2745 (2002).
- ¹³H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ¹⁴G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- ¹⁵G. Kresse and J. Furthm3ller, *Phys. Rev. B* **54**, 11169 (1996).
- ¹⁶R. Haggemueller, H. H. Gommans, A. G. Rinzler, J. E. Fisher, and K. I. Winey, *Chem. Phys. Lett.* **330**, 219 (2000).
- ¹⁷P. Singh, J. Kumar, F. M. Toma, J. Raya, M. Prato, B. Fabre, S. Verma, and A. Bianco, *J. Am. Chem. Soc.* **131**, 13555 (2009).
- ¹⁸R. K. Saini, I. W. Chiang, H. Peng, R. E. Smalley, W. E. Billups, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.* **125**, 3617 (2003).
- ¹⁹J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley, and J. M. Tour, *J. Am. Chem. Soc.* **123**, 6536 (2001).
- ²⁰E. J. G. Santos, D. S3nchez-Portal, and A. Ayuela, *Phys. Rev. B* **81**, 125433 (2010).
- ²¹J. J. Palacios, J. Fernandez-Rossier, and L. Brey, *Phys. Rev. B* **77**, 195428 (2008).