Switching On Magnetism in Ni-doped Graphene

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Magnetic properties of graphenic carbon nanostructures, relevant for future spintronic applications, depend crucially on doping and on the presence of defects. In this paper we study the magnetism of the recently detected substitutional Ni (Ni\textsubscript{sub}) impurities. Ni\textsubscript{sub} defects are non-magnetic in flat graphene and develop a non-zero magnetic moment only in metallic nanotubes. This surprising behavior stems from the peculiar curvature dependence of the electronic structure of Ni\textsubscript{sub}. A similar magnetic/non-magnetic transition of Ni\textsubscript{sub} can be expected by applying anisotropic strain to a flat graphene layer.

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I. INTRODUCTION

Graphenic carbon nanostructures have opened new research routes in nanoelectronics. In particular, their magnetic properties are receiving much attention, both experimental and theoretically, mainly in relation to spintronics. Spin- qubits and other spintronic devices seem feasible due to the very long spin relaxation and decoherence times in graphene and to the fact that the magnetism of the edge states of graphenic nanoribbons can be controlled by applying external electric fields. Magneto-optical properties are also being actively studied. All these properties are drastically influenced by the presence of defects and dopants. For example, strong magnetic signals in nanocarbons have been reported after irradiation that seem to be associated with the creation of defects. Thus, the magnetic and transport properties of carbon systems can in principle be engineered using these additional degrees of freedom.

In a recent x-ray adsorption study, Ushiro et al. have demonstrated the presence of important amounts of substitutional Ni (Ni\textsubscript{sub}) impurities in purified carbon nanostructures synthesized using Ni containing catalyst. Such Ni\textsubscript{sub} impurities were also observed by Banhart et al. in electron microscopy images of onion-like graphenic particles. In general, due to the stability of the substitutional configuration, the incorporation of transition metals to the carbon layer during growth or saturating existing vacancies seems a likely process. In spite of this, the magnetic properties of substitutional transition-metal impurities in graphenic systems have not been studied in detail. Instead, most theoretical studies have focused on adsorbed transition-metal atoms on fullerenes and single-walled carbon nanotubes (SWCNTs). Few calculations to date have considered Ni\textsubscript{sub} impurities and little attention was paid to the magnetic properties.

In this paper we present a first-principles density functional theory (DFT) study of Ni\textsubscript{sub} defects in graphene and armchair and zigzag SWCNTs of different diameters. We have discovered that the magnetic moment of substitutionally Ni-doped graphene can be controlled by applying mechanical deformations that break the hexagonal symmetry of the layer, like curvature does. Surprisingly, Ni\textsubscript{sub} impurities are non-magnetic in flat graphene. However, their magnetic moment can be switched on by applying curvature to the structure. Furthermore, the magnetic moment of Ni\textsubscript{sub} also becomes a signature of the metallicity of the structure: only metallic tubes develop a moment that depends on the tube diameter and Ni concentration. This behavior stems from the peculiar curvature dependence of the electronic structure of the Ni\textsubscript{sub} impurity.

II. METHODOLOGY

Our calculations have been performed with the SIESTA code using the generalized gradient approximation (GGA) to DFT and Troullier-Martins pseudopotentials. Our Ni pseudopotential includes a pseudo-core with a core matching radius of 0.53 a.u. in order to perform non-linear core corrections for the description of exchange and correlation. We have tested that this pseudopotential yields the correct magnetic moment and band structure for bulk Ni. We have used an energy shift of 50 meV to define the radii of the different orbitals. A double-\(\zeta\) polarized (DZP) basis set has been used for the calculation of the magnetic moments and electronic band structures of all our systems. However, we have checked that a double-\(\zeta\) (DZ) basis set yields to almost identical relaxed structures as the DZP basis and, therefore, we have used the smaller DZ basis for the relaxations of systems containing more than \(\sim 100\) atoms (our supercells contain up to 512 atoms, see Fig. 5 below). Atomic coordinates...
III. RESULTS AND DISCUSSION

Figure 1 (a) illustrates the typical equilibrium structure of Ni$_{\text{sub}}$ in the case of a (5,5) SWCNT. The Ni atom appears displaced \( \sim 0.9 \) Å from the carbon plane. Although both outward and inward displacements can be stabilized, the outward configuration is always more stable. The calculated Ni-C distances \( d_{\text{Ni-C}} \) are in the range 1.77-1.85 Å in agreement with experiment.\(^{14,15}\) Armchair tubes exhibit two slightly shorter and one larger values of \( d_{\text{Ni-C}} \), the opposite happens for (n,0) tubes, whereas for graphene we obtain a threefold symmetric structure with \( d_{\text{Ni-C}} = 1.78 \) Å. Ni adsorption inhibits the reconstruction\(^{22}\) of the carbon vacancy. Furthermore, we have checked that a symmetric structure is obtained even when starting from a relaxed vacancy. The Ni binding energy is quite large: 7.9 eV for graphene and about 8.5 eV for (5,5) and (8,0) tubes. The calculated adsorption energy of Ni on the surface of the same tubes is \( \sim 2.5 \) eV.\(^{20}\) Thus, we can conclude that the formation of Ni$_{\text{sub}}$ defects by passivation of existing carbon vacancies is a very likely process both for graphene and for SWCNTs.

Figure 1 (b) shows the magnetization density for a Ni$_{\text{sub}}$ impurity in graphene. Panel (b) shows the calculated band structure for a Ni$_{\text{sub}}$ impurity in a 4\( \times \)4 graphene supercell. The size of the circles and squares corresponds to the amount of Ni 3d and 4s character respectively. Energies are referred to the Fermi energy.
The crucial role of the host states also explains the delocalization of the in-plane $sp$ lobes of the carbon neighbors with the Ni $3d_{xz}$ and $3d_{yz}$ orbitals appearing ~0.5 eV above $E_F$.

As a consequence of this electronic structure, with the Ni $3d$ states well below $E_F$ and no flat bands crossing $E_F$, the magnetic moment of the Ni$_{sub}$ impurity in graphene is zero. Interestingly, the three levels appearing close to $E_F$ in Fig. 2 are reminiscent of those found for the unreconstructed carbon vacancy in graphene. The presence of a Ni atom stabilizes such symmetric structure of the vacancy and slightly shifts the two levels coming from the $sp$ lobes (now C $2sp$-Ni $3d$ antibonding levels) to higher energies. This contributes to stabilize the paramagnetic solution and renders a Ni$_{sub}$ impurity with zero spin polarization in the flat layer of graphene.

The basic picture described above is still valid for the electronic structure of the Ni$_{sub}$ impurity in SWCNTs. However, the modifications that appear due to the curvature of the carbon layer are responsible for the appearance of a magnetic moment. Figure 3(a) shows the band structure of a paramagnetic calculation of a (5,5) SWCNT with a Ni$_{sub}$ impurity every four unit cells. Here the distance between neighboring Ni$_{sub}$ impurities is similar to that of the graphene layer in Fig. 2(b), although the Ni concentration is 2.5 times lower (1.3%). Comparing these two Figures we can appreciate the effects of curvature. The degeneracy between $d_{xz}$ and $d_{yz}$ states is removed (x-axis taken along the tube axis and y-axis along the tangential direction at the Ni site). The $d_{yz}$ contribution is stabilized by several tenths of eV and a quite flat band with strong $d_{yz}$ character is found pinned at $E_F$ close to the Brillouin-zone boundary. Under these conditions the spin-compensated solution becomes unstable and a magnetic moment of 0.48 $\mu_B$ is developed. Figures 3(b) and (c) show, respectively, the band structure for majority and minority spins. The exchange splitting of the $d_{yz}$ level is ~0.4 eV and the energy gain with respect to the paramagnetic solution is 32 meV. Similar results are obtained using the VASP code.

In general, whenever a flat impurity with appreciable Ni $3d$ character becomes partially filled we can expect the appearance of a magnetic moment. The population of such an impurity level occurs at the expense of the simultaneous depopulation of some of the delocalized carbon $p_z$ levels of the host structure. For this reason the development of a magnetic moment is more likely for Ni$_{sub}$ impurities in metallic structures like the armchair tubes. The crucial role of the host states also explains the delocalized character of the magnetization density depicted in Fig. 1(b). However, it is important to stress that the driving force for the formation of a magnetic moment associated with the Ni$_{sub}$ impurity in a SWCNT is the local curvature of the carbon layer that shifts the energy position of one of the impurity levels downwards until it crosses $E_F$. A schematic representation of this phenomenon can be found in Fig. 4 where we also emphasize the similarities between the levels of the Ni$_{sub}$ defect and those of the unreconstructed carbon vacancy. At large tube diameters we must recover the limit of flat graphene with zero magnetic moment.

For semiconducting tubes the situation is somewhat different. The $d_{xz}$ and $d_{yz}$ derived levels will remain unoccupied unless their energies are shifted by a larger amount that pushes one of them below the top of the valence band. Therefore, if the tube has a large enough gap the magnetic moment will be zero irrespective of the tube diameter. We have explicitly checked that a zero magnetic moment is obtained for (8,0) and (10,0) semiconducting tubes for Ni concentrations ranging from 1.5% to 0.5%. The different magnetic behavior of Ni$_{sub}$ impurities depending on the metallic and semiconducting character of the host structure provides a route to exper-
mentally identify metallic armchair tubes.

Figure 5 displays the magnetic moment per Ni$_{\text{sub}}$ atom for Ni-doped armchair tubes of different diameters. All of them present a magnetic moment that oscillates as a function of the tube diameter and the size of the supercell used in the calculation, i.e., the Ni$_{\text{sub}}$-Ni$_{\text{sub}}$ distance. For (4,4), (5,5) and (6,6) tubes the first supercell showing a non-zero magnetic moment contains four unit cells. For (7,7) and (8,8) tubes this minimum length increases up to eight and six unit cells, respectively. The appearance of a complex oscillatory pattern as a function of the Ni$_{\text{sub}}$-Ni$_{\text{sub}}$ distance is easily understood if we recall that the magnetic moment critically depends on the energy position of a particular impurity level nearby $E_F$ and the strong hybridization of this level with the delocalized states of the nanotube. Another consequence of this hybridization is the long range of the interaction between impurities: for example, the magnetic moment in (5,5) tube still presents strong oscillations in a range of Ni$_{\text{sub}}$-Ni$_{\text{sub}}$ distances between 20 and 40 Å. Unfortunately, a meaningful exploration of larger distances between impurities requires a methodology different from the ab initio supercell approach used here.

Finally, we have examined the magnetic coupling between Ni$_{\text{sub}}$ impurities in the (5,5) tube. We have doubled some of the simulation cells considered above, so they contain two Ni atoms, and calculated ferromagnetic (FM) and antiferromagnetic (AFM) arrangements. Only when the two Ni$_{\text{sub}}$ impurities shared a common C neighbor the AFM arrangement was favored by a few meV. FM configurations were the most stable in all other cases. Although more work is necessary to accurately determine the size and distance dependence of the effective exchange interaction (probably using model calculations similar to those in Ref. [34], our results indicate that Ni$_{\text{sub}}$ impurities in small diameter metallic nanotubes, where they develop a magnetic moment, can exhibit relatively large FM couplings that slowly decay with distance. For example, for Ni$_{\text{sub}}$ impurities at distances of 10 Å in a (5,5) tube we estimate a $J_{\text{eff}}$ of ~9 meV. This FM interactions can have important implications for the experimental detection of the curvature dependent magnetism of the Ni$_{\text{sub}}$ impurities described in this work and its influence in the observation of magnetism in carbon nanotube samples.

IV. CONCLUSIONS

The calculations presented here show that substitutional Ni impurities in graphenic carbon structures present a strong covalent interaction with their carbon neighbors. This interaction stabilizes the 3d levels of Ni that appear as a completely filled shell. As a consequence, Ni$_{\text{sub}}$ is non-magnetic in graphene. Two unoccupied levels of the Ni$_{\text{sub}}$ impurity appear close to $E_F$ corresponding to antibonding combinations of Ni 3d orbitals and C 2sp lobes. Curvature breaks the degeneracy of these two levels and, under appropriate conditions, shifts one of them to lower energies such that becomes partially occupied in metallic armchair tubes. In this situation the system develops a magnetic moment that exhibits a complex behavior as a function of the tube diameter and Ni concentration. However, for semiconducting zigzag tubes the Ni$_{\text{sub}}$ impurities remain non-magnetic. These results should be taken into account when studying the magnetic properties of carbon nanostructures.

In summary, curvature can be used to drive substitutional Ni impurities between a magnetic and a non-magnetic state in metallic graphenic carbon nanostructures. In particular, the magnetic properties of substitutionally Ni-doped graphene can be tuned by controlling the curvature of the layer around the Ni$_{\text{sub}}$ defects. A possible way to do this is to deposit the graphene layer on a substrate with a small lattice parameter mismatch. This can cause the undulation and local bending of the graphene layer [35,36]. Alternatively, a similar non-magnetic/magnetic transition of Ni$_{\text{sub}}$ might be obtained applying anisotropic strain to a flat graphene layer. In this regard, we are currently exploring if the formation of a magnetic moment can also be controlled by applying uniaxial strain to a flat Ni$_{\text{sub}}$-doped graphene layer.

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Because of the quite symmetric position of the Ni atom over the C vacancy the 3d_{xx} and 3d_{yz} derived bands are almost degenerate at Γ. In spite of the relatively large distance to 3d_{xz} and 3d_{yz} derived bands are highly hybridized with the carbon 2p levels, resulting in a significant broadening and shift of the impurity bands and the gap decrease, respectively. The positions of the impurity bands and the gap decrease, respectively, to ~0.5 eV that opens in the 4×4 graphene supercell. The hybridization is a signature of the strong hybridization of the impurity levels with the states of the carbon layer. Another signature of this hybridization is the gap of ~0.5 eV that opens in the graphene layer around K. Using a larger 8×8 supercell, the Ni_{sub}-Ni_{sub} distance to ~19.7 Å, the width of the impurity bands and the gap decrease, respectively, to ~20 meV and ~100 meV. The positions of the impurity bands are, however, very similar to the case of the smaller cell.