Boron nitride nanotubes as templates for half-metal nanowires

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Abstract
We investigate by means of a GGA + U implementation of density functional theory the electronic and structural properties of magnetic nanotubes composed of an iron oxide monolayer and (n, 0) boron nitride (BN) nanotubes, with n ranging from 6 to 14. The formation energy per FeO molecule of FeO covered tubes is smaller than the formation energy of small FeO nanoparticles, which suggests that the FeO molecules may cover the BN nanotubes rather than aggregating locally. Both GGA (PBE) and Van der Waals functionals predict an optimal FeO–BN interlayer distance of 2.94 Å.

Depending on the diameter of the tube, novel electronic properties for the FeO covered BN nanotubes were found. They can be semiconductors, intrinsic half-metals or semi-half-metals that can become half-metals if charged with either electrons or holes. Such results are important in the spintronics context.

1. Introduction
Metal oxides are ubiquitous in nature. Their combination with nanotubes may lead to materials which present several novel properties. Besides the pure scientific interest that lies on those systems, there are many potential technological applications based on them. Since 1995 it has been possible to use nanotubes as templates for metal oxides nanocomposites and nanostructures, as was shown by Ajayan et al [1]. The combination of nanotubes with magnetic oxides can produce magnetic nanowires which could be used as tips for magnetic scanning microscopes or to control the spin polarization of electrons, which is very important in the spintronics context. Indeed, it has been shown that iron oxide nanotubes are half-metals [2] that can be used as core material for spin-filter devices [3].

Boron nitride (BN) structures are insulators and non-magnetic. In this sense it is reasonable to consider BN nanotubes (instead of carbon nanotubes) as the ideal template for half-metal nanowires [4–6]. For example, Xiang et al have studied Ni encapsulated BN nanotubes using ab initio calculations. They report that such a material presents semi-half-metallic behavior, which can become half-metallic after doping electrons more than 1.4 e per unit cell [4]. Min and collaborators [6] have found a BN nanotube-based half-metal performing first-principles calculations on AuV(Cr) quantum wires adsorbed on a (5, 5) BN nanotube.

In previous works [7, 8] it has been shown that FeO molecules strongly interact with BN structures, where the Fe and O atoms bind to the N and B atoms through covalent bonds, respectively. In particular, such an interaction is stronger in sites where the local curvature of BN structures is larger. In fact, the tube curvature is essential to match the hexagonal lattice of the boron nitride nanotube with the square lattice of an FeO layer. Besides the curvature, it is also necessary that the unit cell of the two lattices is commensurate along the tube axes in order to have the two lattices matched. It is important to stress that due to the values of the Fe–O and B–N bond lengths (2.15 and 1.45 Å for the FeO bulk and the hexagonal BN, respectively [8]) the unit cell of zigzag BN nanotubes is commensurate with the unit cell of a square FeO layer within an error of 1% (see figure 1). Thus it is possible to construct FeO covered BN tubes with the same number of Fe, O, N and B atoms.
Figure 1. Structure of FeO covered boron nitride (BN) nanotube. The FeO molecules form a square lattice (bottom panel) which is commensurate with the BN hexagonal lattice along the tube’s axis. The Fe–O and B–N bond lengths in the optimized structures (approximately 2.13 and 1.42 Å, respectively) are very close to the values of bond lengths of FeO bulk (2.15 Å [8]) and hexagonal boron nitride (1.45 Å [8]), respectively.

In this work we apply first-principles formalism to investigate the effect of the tube diameter on the stability and on the electron transport properties of FeO covered BN nanotubes. We have observed that due to the effect of the curvature, the interaction between the FeO layer and BN tubes and the quantization of wavevectors, the electronic structure is diameter dependent. As a result, a rich variety of electron transport properties was found: (i) the (6, 0) tube is a semiconductor; (ii) the (10, 0) is a half-metal; (iii) the (11, 0) is a semi-half-metal which could become a half-metal if doped with holes; (iv) the (14, 0) is a semi-half-metal which could become a half-metal if doped with electrons. Regarding the structural properties, we have found that the tube diameter determines the distance between the FeO layer and the BN tube. This happens because the interaction between the BN nanotube and the FeO layer is weaker than the Fe–O and B–N bonds. The formation energy per FeO molecule of FeO covered tubes is smaller than the formation energy of small FeO nanoparticles which suggests that the FeO molecules may cover the BN nanotubes rather than aggregating to form the FeO bulk. We also propose a continuous model for the FeO covered BN nanotube’s formation energy which predicts that BN tubes with diameter of roughly 13 Å are the most stable ones.

2. Methodology

Our first-principles methodology is based on the density functional theory (DFT) as implemented in the Siesta program [9]. We used the generalized gradient approximation (GGA) as parametrized in the Perdew–Burke–Ernzerhof scheme (PBE) [10] and the Van der Waals functional of Dion et al [11] as implemented by Romain-Perez and Soler [12] for the exchange–correlation functional. The ionic core potentials were represented by norm-conserving scalar relativistic Troullier–Martins [13] pseudopotentials in Kleinman–Bylander nonlocal form [14]. The fineness of the real-space grid integration was defined by a minimal energy cutoff of 150 Ryd [15]. A 8 × 1 × 1 Monkhorst-Pack grid was used to sample the Brillouin zone. Geometries were fully optimized using the conjugate gradient algorithm [16] until all the force components were smaller than 0.05 eV Å⁻¹. The Kohn–Sham (KS) eigenfunctions were expanded as a linear combination of pseudo-atomic orbitals of finite range consisting of double-zeta radial functions per angular momentum plus polarization orbitals (DZP). The range of each atomic orbital was determined by a common confinement energy-shift of δE = 0.01 Ryd [17].

We have also applied a GGA + U methodology to investigate the electronic properties of FeO covered nanotubes. The use of such a methodology was motivated by its ability to reproduce the observed insulating behavior for FeO bulk. The GGA approach describes accurately the structural properties of FeO bulk but it tends to over-delocalize 3d electrons, which leads to unphysical metallic behavior.

The current GGA + U implementation in the Siesta code is based on the formulation of Dudarev et al [18]. Slightly excited numerical atomic orbitals of finite range were used to calculate the local populations used in a Hubbard-like term that modifies the Hamiltonian and energy. The radii of Fe 3d and 4s orbitals are respectively 2.90 and 1.22 Å. The effective Hubbard-like terms used in the calculation are 4.65 and 0.95, for the 3d and 4s shells respectively.

3. Structural properties

In order to match the hexagonal lattice of the BN nanotube with the square lattice of the FeO layer it is necessary that the unit cell of the two lattices is commensurate along the tube axis. The lattice parameter along the tube axis of a zigzag tube is 4.35 Å (corresponding to three times the B–N bond length), using previous DFT/PBE calculations [8] on hexagonal BN. The lattice parameter of a FeO square lattice is 4.30 Å (which is twice the Fe–O bond length). The ratio between the lattice parameters of those two lattices is 0.99. Thus we can assume both structures as matching ones, since errors of 1% in lattice parameters are imposed in our calculations due to the used approximations described in section 2.

Figure 2 shows the cross section of the optimized structure of the studied FeO covered BN nanotubes. In the smallest tube cases, i.e. (6, 0), (8, 0) and (9, 0) the large curvature of the tubes imposes a large Fe–O bond length in the FeO layer. Since the sp² B–N bond is among the hardest bonds in nature, the FeO layer does not compress the BN tubes. Instead, some Fe–O bonds break up in the FeO layer. Due to the strong interaction between the FeO and the BN
Figure 2. Structure of FeO covered boron nitride (BN) nanotubes. The left column shows, from top to bottom, the structure of nanotubes composed of FeO covering the (6, 0), (8, 0), (9, 0) and (10, 0) BN tubes. The right column shows, from top to bottom, nanotubes composed of FeO covering the (11, 0), (12, 0), (13, 0) and (14, 0) BN tubes.

tube, the FeO layer covers localized portions of the tube surface—which completely changes the radial shape of the BN tube—instead of agglomerating in structures with higher coordination number. Two diametrically opposed Fe–O bonds break up in the (6, 0) tube leading to an interesting flat tube. Four Fe–O bonds break up in the (8, 0) tube resulting in a square-like cross section. In the case of a (9, 0) tube, two neighboring Fe–O bonds break up and a slightly flat tube is obtained.

In the larger tube cases (shown in figure 2), i.e. from (9, 0) to (14, 0) the increment of the tube diameter leads to a roughly linear increasing in the distance between the FeO layer and the BN tube as can be seen in figure 3.

Such a linear behavior can be understood if one observes that all the studied FeO covered tubes have the same number of Fe, O, B and N atoms and that it is much harder to compress or stretch Fe–O and B–N bonds than to stretch the bonds between the BN tube and the FeO layer. Thus, the B–N and Fe–O bond lengths do not change as much as the tube diameter increases. In this case, the perimeters of FeO and BN layers are respectively $N_{\text{FeFe}}$ and $N_{\text{BB}}$. Where $a_{\text{FeFe}}$ and $a_{\text{BB}}$ are respectively the distance between two Fe atoms and two B atoms, and $N$ is an integer number. In this sense, it is possible to show that the difference between the diameter of the FeO layer ($D_{\text{FeO}}$) and the diameter of the BN tube ($D_{\text{BN}}$) is given by:

$$D_{\text{FeO}} - D_{\text{BN}} = D_{\text{FeO}} \frac{a_{\text{FeFe}} - a_{\text{BB}}}{a_{\text{FeO}}}.$$  \hspace{1cm} (1)

Thus, in the case of large tubes the interlayer distance, $D_{\text{FeO}} - D_{\text{BN}}$, is also large. Therefore, the attractive interaction between the FeO layer and the BN tube must be small, which accounts against the stability of FeO covered nanotubes. On the other hand, the tube curvature decreases with $D_{\text{FeO}}$ and so does the elastic energy associated with it [19, 20]. Therefore, there must be a FeO covered tube whose formation energy per atom, or equivalently per FeO molecule, is a minimum.

The formation energy ($E_f$) per FeO molecule can be obtained from total energy calculations as follows:

$$\frac{E_f}{N_{\text{FeO}}} = \frac{E_c - E_f}{N_{\text{FeO}}} - \mu_{\text{FeO}},$$  \hspace{1cm} (2)

where $N_{\text{FeO}}$ is the number of FeO molecules, $E_c$ is the first-principles total energy of the FeO covered BN nanotube, $E_f$ is the total energy of the BN tube, and $\mu_{\text{FeO}}$ is the chemical potential of a FeO molecule reservoir. In this work, $\mu_{\text{FeO}}$ is defined as the total energy per FeO molecule of a square lattice of FeO.

Figure 4 shows the formation energy per FeO molecule of some tubes shown in figure 2 calculated using the PBE and Van der Waals (VdW) functionals. Both PBE and VdW predict similar values of formation energy for interlayer distances larger than 2.5 Å (the maximum calculated difference is about 20 meV, or 13% of the formation energy) which correspond to tubes whose diameter is larger than that of the (12, 0) tube. The PBE and VdW functionals also predict similar values of interlayer distances for FeO covered tubes whose diameter is larger than that of the (12, 0) tube.
PBE and VdW functionals differ by at most 0.1 eV. The functionals agree in the horizontal position of the formation energy minimum (2.94 Å assuming a quadratic behavior of near the energy minimum) but disagree in its vertical position. The VdW functional predicts a deeper energy minimum in comparison to that predicted by the PBE functional. This is expected since the PBE functional was not built to describe the attractive Van der Waals forces.

Since the square lattice of FeO is our choice of chemical potential, the infinite tube has null value of formation energy. The formation energies of all studied tubes are negative which shows that it is energetically favorable to cover a BN nanotube with a FeO layer rather than to form an isolated FeO layer. The coordination number of each atom in the FeO layer, which is four, is larger than the average coordination number of very small FeO nanoparticles (for instance, the average coordination number of a body centered cubic FeO nanoparticle with 32 atoms is 3.75). This makes the FeO surface energetically more stable than such small nanoparticles (the formation energy of the FeO nanoparticle with 32 atoms is 0.75 eV). We have also compared the stability of the FeO covered nanotubes with other possible structures which may contain uncovered areas (like islands) or FeO molecules which do not bind to the BN layer (like dots). Firstly, we have considered lines of FeO on the (10, 0) BN nanotube. The number of lines varies from 2 up to 20 (the completely covered BN tube). The formation energy per FeO molecule decreases in inverse proportion to the number of lines, which can be understood in terms of the increase of coordination number of Fe and O atoms in as much as the number of lines increases.

Subsequently, we investigated a small nanoparticle composed of four FeO molecules interacting with the (10, 0) BN tube. We found that, due to the small coordination number (3.5), the formation energy of such a small nanoparticle on the tube (1.13 eV/molecule) is significantly higher than the formation energy per molecule of the (10, 0) covered nanotube (−0.08 eV/molecule). These results indicate that coating the BN nanotube is an effective mechanism to increase the coordination number of FeO molecules and, therefore, the stability of hybrid FeO/BN nanotubes structures.

4. Electronic structure

The band structure of large FeO covered nanotubes (large enough to allow us to neglect the curvature effects) must be a superposition of the band structure of the hexagonal BN layer and the band structure of a square FeO layer since the distance between the FeO layer and the BN nanotubes increases with $D_{BN}$. BN structures (including hexagonal lattices and nanotubes) present a large energy band gap of roughly 5 eV. Therefore, electronic states near the Fermi level should be due to the FeO layer in such large tubes. Thus, as a first step to understand the band structure of the FeO covered BN nanotubes, we have investigated the band structure of the FeO square lattice.

Similarly to the case of FeO bulk, the GGA approach predicts a metallic behavior for the FeO layer while the GGA + U predicts a 1.2 eV band gap for the FeO layer (see figure 5). The GGA band structure shows several low-dispersion bands (dashed lines) near the Fermi level which are associated with the over-delocalized Fe 3d orbitals. The inclusion of the Hubbard term leads to an integer occupation of Fe 3d orbitals and more localized Fe orbitals. As a result the low-dispersion bands near the Fermi level disappear, resulting in a 1.2 eV band gap.

Although some qualitative information about the 1D energy bands of large studied FeO covered nanotubes can be obtained by slicing the energy dispersion of the FeO layer (in the directions expressed by $D_{BN}k_y = 2\pi n$, where $n$ is an integer), it is not possible to obtain from the energy dispersion of the FeO layer quantitative information about the studied tubes. For instance, by slicing the energy dispersion of the FeO layer, we found that the bottom of the conduction band of a (10, 0) should be below the lowest unoccupied majority spin states while the bottom of the conduction band of a (14, 0) should be below minority spin states, which is in agreement with the calculated energy dispersion for such tubes (see figure 6). On the other hand, by slicing the energy dispersion of the FeO layer we expect the band gap to increase in as much as the diameter of the tube decreases, however, the band gap decreases with the diameter in as much as the tube size decreases from (14, 0) up to (10, 0), as shown in figure 6. The (10, 0) FeO covered BN nanotube presents a band gap (0.5 eV) much smaller than the value expected by slicing the energy dispersion of the FeO layer (1.7 eV). Such differences are due to the curvature and the interaction of the FeO layer with the BN tube. The effect of the curvature can be investigated by performing calculations on pure FeO tube with the same geometry of FeO covered BN nanotubes but without the inner BN nanotube. For a pure (14, 0) FeO layer

Figure 4. Formation energy, $E_f$, divided by the number of FeO molecules, $N_{FeO}$, calculated according to equation (2), as a function of the interlayer distance, $D_{FeO} - D_{BN}$.
Figure 5. Band structure of a FeO square lattice. Left panel: PBE calculations. Right panel PBE + U calculations. Continuous red lines: majority spin states. Dashed black lines: minority spin states. The inclusion of the Hubbard term leads to an integer occupation of Fe 3d orbitals and more localized Fe orbitals. As a result the low-dispersion bands near the Fermi level disappear which leads to a 1.2 band gap. The Fermi level was set to zero.

Figure 6. Band structure of FeO covered BN nanotubes shown in figure 2: (a) (10, 0) FeO covered BN nanotube; (b) (11, 0) FeO covered BN nanotube; (c) (12, 0) FeO covered BN nanotube; (d) (14, 0) FeO covered BN nanotube. (e) Band structure of a (14, 0) FeO layer. (f) Band structure of a (14, 0) FeO covered BN nanotube charged with $-e/4.3 \text{ Å}$. Continuous red lines: majority spin states. Dashed black lines: minority spin states. The Fermi level was set to zero.

we have found a band gap of 0.5 eV which is much smaller than the value obtained by slicing the energy dispersion of the FeO layer (1.4 eV). Due to the interaction with the BN nanotube the band gap of the FeO layer increases to 0.9 eV, which shows that both curvature and interaction with the BN tube are determinants of the electronic properties.

The curvature and the interaction of the FeO with the BN tubes lead to interesting transport properties. The (14, 0) FeO covered BN nanotube is a semi-half-metal which becomes half-metal upon electron doping (see figure 6). As is possible to see in figure 6, the bottom of the conduction band of the neutral (14, 0) tube is 0.5 eV below the first unoccupied
minority spin states, therefore, upon electron doping it is possible to change the Fermi level to allow the conduction of electrons only through majority spin states. Since the top of the valence band of the (11, 0) tube is 0.6 eV above the lowest occupied majority spin states, the (11, 0) FeO covered BN nanotube should become a half-metal upon hole doping. The (10, 0) nanotube is an intrinsic half-metal, the Fermi level crosses the highest bands with negative curvature as is possible to see in figure 6.

5. Conclusions

In summary, we have applied first-principles formalism to investigate the effect of the tube diameter on the stability and on the electron transport properties of FeO covered BN nanotubes.

Regarding structural properties, we observed that the increment of the tube diameter leads to a roughly linear increase in the distance between the FeO layer and the BN tube (see figure 3). Both GGA (PBE) and Van der Waals functionals predict an optimal FeO–BN interlayer distance of 2.94 Å.

For the electronic structure we have found a rich variety of electron transport properties for this system: (i) the (6, 0) tube is a semiconductor; (ii) the (10, 0) is a half-metal; (iii) the (11, 0) is a semi-half-metal, which could become a half-metal if doped with holes; (iv) the (14, 0) is a semi-half-metal which becomes a half-metal if doped with electrons. Similarly to the case of FeO bulk, the GGA functional predicts a metallic behavior for a FeO layer while the GGA + U predicts a semiconductor behavior.

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