Iron oxide doped boron nitride nanotubes: structural and magnetic properties

Ronaldo J C Batista, Alan B de Oliveira and Daniel L Rocco

Departamento de Física, Universidade Federal de Ouro Preto, Ouro Preto, MG, 35400-000, Brazil

E-mail: batista.rjc@iceb.ufop.br

Received 26 May 2010, in final form 13 July 2010
Published 10 August 2010
Online at stacks.iop.org/JPhysCM/22/355302

Abstract
A first-principles formalism is employed to investigate the interaction of iron oxide (FeO) with a boron nitride (BN) nanotube. The stable structure of the FeO-nanotube has Fe atoms binding N atoms, with bond length of roughly \( \sim 2.1 \) Å, and binding between O and B atoms, with bond length of 1.55 Å. In case of small FeO concentrations, the total magnetic moment is \((4 \mu_{\text{Bohr}})\) times the number of Fe atoms in the unit cell, and it is energetically favorable to FeO units to aggregate rather than randomly bind to the tube. As a larger FeO concentration case, we study a BN nanotube fully covered by a single layer of FeO. We found that such a structure has a square FeO lattice with Fe–O bond length of 2.11 Å, similar to that of FeO bulk, and total magnetic moment of 3.94 \( \mu_{\text{Bohr}}/\text{Fe atom} \). Consistent with experimental results, the FeO covered nanotube is a semi-half-metal which can become a half-metal if a small change in the Fermi level is induced. Such a structure may be important in the spintronics context.

1. Introduction
In the last decades near one-dimensional systems, such as nanowires [1], nanotubes [2] and organic molecules [3], have attracted the attention of the scientific community. A great part of this interest is due to their potential for applications in micro- and nano-technological devices. In particular, ferromagnetic nanotubes may be of scientific and industrial interest because they potentially serve as tunable fluidic channels for tiny magnetic particles, data storage devices in nanocircuits, and scanning tips for magnetic force microscopes [2, 4]. Moreover, it has been recently shown that ferromagnetic iron oxide nanotubes can be used as building blocks for spin-based devices [5].

The possibility of delivering information based on the electron spin, as well as on its charge, was a technology breakthrough. The addition of an extra degree of freedom—which comes with the electron spin—to a conventional charge-based device increases the original quantity of information which can be manipulated in some orders of magnitude. Important applications of spintronics include magnetic field sensors, read heads for hard drives, galvanic isolators, and magnetoresistive random access memory to cite a few [6, 7]. The control of the electron spins is a crucial issue for spin-based electronics. In this sense, the so-called half-metals, i.e., materials which have a metal-like behavior for one spin channel and are semiconductor for the other one, become essentially important for developing spin-based electronics since they may work as spin filters [5]. The first evidence of half-metallic behavior is due to the theoretical work of de Groot et al, in which a Mn-based Heusler alloy was studied [8]. Recently, Shan et al [9] have observed that the half-metallic Co-based full-Heusler alloy Co\(_2\)FeAl\(_{0.5}\)Si\(_{0.5}\) exhibits the highest effective spin polarization at 300 K and has the weakest temperature dependence of spin polarization among all known half-metals. This latter characteristic becomes very important since spintronics devices are commonly used at room temperature.

Some ferromagnetic oxides also present half-metallic behavior. We can cite, for instance, CrO\(_2\) [10] and some members of the mixed valence perovskites (manganite), such as La\(_{2}\)Sr\(_{1/2}\)MnO\(_3\) [11]. In the spintronics context, one important ferromagnetic oxide is Fe\(_3\)O\(_4\) (ferrite) [5]. Such an oxide presents high Curie temperature (\(\sim 858\) K) and half-metallicity, which was predicted by Zhang and Satpathy [12] and later confirmed by Liao et al [13]. Recently, it has been reported that Co ferrite fabricated by thermal oxidation presents spin-filter efficiencies of 44% and 4.3% at 10 K and room temperature [14], respectively, showing that such
Fe₂O₃ nanotubes are efficient half-metals which can form the basis for spin-filter devices [5, 13]. It has been shown that such a system is an interesting candidate to be experimentally synthesized. Thus, it is reasonable to consider BN nanotube-based systems as convenient candidates for application as building blocks in spin-filter devices [5, 15, 16]. In this direction, Xiang and co-workers have studied Ni encapsulated BN nanotubes by means of $ab$ initio calculations. They have found that such a material presents semi-half-metallic behavior, which can become half-metallic after doping electrons more than 1.4 $e/\text{unit cell}$ [5]. Another BN nanotube-based half-metal was reported by Min et al [16], who performed first-principles calculations on AuV(Cr) quantum wires adsorbed on a (5, 5) BN nanotube.

The aim of this work is to investigate the structural, electronic, and magnetic properties of structures composed of BN nanotubes and iron oxide. Such hybrid structures may present the previously described advantages of both components. Among the ferromagnetic oxides, the iron oxides are particularly interesting since: (i) Fe, O, FeO and Fe₂O₃ are often present in the synthesis process of boron nitride nanotubes [17–20], moreover, hybrid structures composed of BN doped with Fe or FeO have been theoretically predicted [21, 22] and synthesized [23, 24]; (ii) iron oxides are important in the spintronics context. It has been shown that Fe₂O₃ nanotubes are efficient half-metals which can form the basis for spin-filter devices [5, 13].

In this work, we employ first-principles calculations to investigate the interaction of iron oxide, FeO, with a (10, 0) BN nanotube. We found that FeO molecules and BN nanotubes may form stable structures. The binding energy of a FeO molecule and the tube is 1.85 eV, which is 1.25 eV larger than the binding energy of the tube with an iron atom [22]. We also found that it is energetically preferable for FeO molecules to aggregate rather than randomly bind to the tube. In the case of small FeO concentrations, the total magnetic moment is (4 $\mu_{\text{Bohr}}$) times the number of Fe atoms in the unit cell. As a larger FeO concentration case, we investigate the BN nanotube fully covered with a single layer of FeO. Such a structure presents a total magnetic moment of 3.94 $\mu_{\text{Bohr}}$/Fe atom. Consistent with the experimental results of Liao et al [13], the FeO covered nanotube is a semi-half-metal which can theoretically become half-metal if a small change in the Fermi level is induced ($\sim$0.11 eV). Due to the high value of binding energy between FeO molecules and the BN nanotube (1.85 eV), we expect that no special condition and/or artifacts (such as flattening the nanotube in order to increase its reactivity [25, 26]) should be required to obtain the FeO doped BN nanotubes. Therefore, such a system is an interesting candidate to be experimentally synthesized.

2. Methodology

Our first-principles methodology is based on the density functional theory (DFT) as implemented in the SIESTA program [27]. We used the generalized gradient approximation (GGA) as parameterized in the Perdew–Burke–Ernzerhof scheme (PBE) [28] for the exchange–correlation functional. The ionic core potentials were represented by norm-conserving scalar relativistic Troullier–Martins [29] pseudopotentials in Kleinman–Bylander nonlocal form [30]. The fineness of the real-space grid integration was defined by a minimal energy cutoff of 120 Ryd [31]. The geometries were fully optimized until all the force components became smaller than 0.04 eV $\text{Å}^{-1}$. The solutions of the Kohn–Sham equations were expanded in a basis set composed of numerical atomic orbitals of finite range [32]. To describe the Fe and O orbitals, two functions were employed per angular momentum plus polarization orbitals, the DZP basis set [32]. In the case of N and B orbitals, two functions were employed per angular momentum, the DZ basis set.

We used two types of super-cells in our calculations. The first one, tetragonal with $a = 26$ Å and $c = 13$ Å, contains 60 BN pairs and one or two FeO molecules. We used a $2 \times 2 \times 3$ Monkhorst–Pack grid to sample the respective Brillouin zone. The second super-cell, which is tetragonal with $a = 35$ Å and $c = 4.4$ Å, contains 20 BN pairs and 20 FeO units (fully covered nanotube). The respective Brillouin zone was sampled by a $1 \times 1 \times 6$ Monkhorst–Pack grid.

In order to test the reliability of our calculations, we have compared results for the $\text{B}_6\text{N}_{36}$ fullerene, the cubic BN, the FeO molecule, and the FeO bulk using the methods described above with other theoretical and experimental results. Regarding the properties of the $\text{B}_6\text{N}_{36}$ fullerene, we have found the mean distance of each atom to the center of the cage equal to 3.956 Å, which is in excellent agreement with the value obtained by Zope et al [33], 3.94 Å. The HOMO–LUMO gap obtained by us, 4.7 eV, also agrees very well with the Zope et al findings, 5.0 eV.

For the cubic boron nitride, we have obtained a value for the lattice parameter of 3.643 Å, which differs by less than 1% from the experimental value of 3.6157 Å [34], and from other DFT–GGA calculations, 3.625 Å [35]. Our methodology predicts a wide band gap for the cubic boron nitride, 4.45 eV, which accurately matches other DFT–GGA calculations, 4.43 eV [35], and is consistent with the experimental result, 6.4 eV [36].

For a single FeO molecule, we have obtained a bond length of 1.620 Å, in accordance with other theoretical results, 1.606 Å [37], and with the experimental value, 1.618 Å [38]. We have also performed calculations on FeO bulk obtaining the Fe–O distance of 2.15 Å, which fairly reproduces the experimental results, 2.154 and 2.165 Å [39].

3. Results

We first studied the interaction between a single FeO molecule and a (10, 0) single wall BN nanotube. In the optimized structure, the FeO molecule forms a bridge between N and B atoms. The Fe atom binds the N atoms with bond length of 2.10 and 2.04 Å for B–N bonds parallel and non-parallel to the axis of the tube, respectively. The O atom binds B atoms with bond lengths of $\sim$1.55 Å in both cases.
The presence of the FeO molecule leads to distortions in the bonds of the nanotube. Such a bond geometry in the tube is similar to that of a FeO molecule interacting with the octahedral B\textsubscript{36}N\textsubscript{36} fullerene obtained in a previous work [21]. However, the FeO molecule does not break any B–N bond of the tube as seen in the fullerene case. The B–N bond length increases from 1.46 to 1.62 Å (parallel case) and to 1.67 Å (non-parallel case) in the BN nanotube, whereas it increases from 1.46 to 3.26 Å in the B\textsubscript{36}N\textsubscript{36} fullerene. The local curvature of B–N bonds can affect the reactivity of BN structures. To show that, we compared the values of binding energies for the cases in which the FeO molecule binds to B–N bonds parallel to the tube axis (little-bent B–N bonds), the FeO molecule binds to B–N bonds non-parallel to the tube axis (medium-bent B–N bonds), and the FeO molecule binds to B–N bonds of the edge of the B\textsubscript{36}N\textsubscript{36} fullerene (greatly-bent B–N bonds) [21]. The binding energy was defined as

$$E_b = E_{\text{tube}} + E_{\text{FeO}} - E_{\text{total}},$$

where $E_{\text{total}}$ is the calculated total energy of the BN tube plus the dopant molecule, $E_{\text{tube}}$ is the total energy of the isolated BN tube, and $E_{\text{FeO}}$ is the total energy of an isolated FeO molecule. A positive binding energy value indicates that the chemical adsorption process is exothermic. The values of binding energies are 1.7, 1.85, and 3.92 eV [21] from the little- to the greatly-bent B–N bonds discussed above. Such an analysis is consistent with other theoretical works in which the curvature due to the radial compression in the tube increases the tube reactivity [25, 26]. Similarly to the case of the fullerene, the magnetic moment of the Fe molecule does not change due to its interaction with the tube, and the total magnetic moment of the optimized structure is 4.0 $\mu_\text{Bohr}$.

In order to address the question of how additional molecules would bind to the BN tube we have considered two binding sites for an additional molecule: (i) neighboring the first molecule, as shown in figures 1(a) and (b), and (ii) far way from it, as can be seen from figures 1(c) and (d). We have found that is energetically favorable for the second molecule to bind sites nearby to the first adsorbed molecule. The total energy of the system shown in figures 1(a) and (b) is 3.46 eV lower than the total energy of the system shown in figures 1(c) and (d). In fact, when FeO molecules bind to each other the coordination number of the FeO structure approaches to the six neighboring atoms found in the FeO bulk, increasing then the energetic stability of the system. The magnetic moment of the FeO molecules does not change due to mutual interaction and the total magnetic moment of the structure shown in figures 1(a) and (b) is 8.0 $\mu_\text{Bohr}$.

The results previously described suggest that additional FeO molecules tend to bind to the BN tube nearby to already bound molecules. If the number of FeO molecules is sufficiently large, the tube could be fully covered by a FeO layer forming a magnetic nanotube only 1.28 nm in diameter (see figure 2). This case is particularly interesting since magnetic nanotubes of iron oxide, Fe\textsubscript{2}O\textsubscript{3}, have presented the spin-filter effect and anomalous magnetoresistance [13]. Figure 2 shows the geometry of the (10, 0) BN nanotube covered by a layer of FeO proposed in this study. We have

Figure 1. Different points of view for the BN nanotube with two bound FeO molecules. (a) Two bound neighboring FeO molecules viewed along the x- and (b) z-direction and (c) two distant bound FeO molecules viewed along the y- and (d) z-axis. The configuration shown in panels (c) and (d) is 3.46 eV more energetic than the one shown in (a) and (b). Thus it is energetically preferable to the system to have additional FeO molecules binding nearby already bound FeO molecules.
considered an initial geometry for the FeO layer as a quasi-hexagonal structure in which each Fe atom binds to a N atom and to three O atoms (see figure 2(a)). Nevertheless, the optimization of the structure increases the coordination number of each Fe atom. After the geometry optimization, Fe and O atoms form a square lattice in which each Fe atom binds to four O atoms, as one can see from figure 2(b). Such a layer presents similarities to the FeO bulk. Besides the angle formed by adjacent Fe–O bonds, which is about $90^\circ$, the average bond length between Fe and O atoms, 2.11 Å, is also similar to that calculated for the FeO bulk, 2.15 Å. Such results indicate that several layers of FeO on a BN nanotube would present a local crystal structure similar to that of the FeO bulk. However, due the curvature of the FeO layers, such nanotubes may present novel properties compared with those of the FeO bulk.

We have observed that the system formed by a single FeO layer on the BN tube presents electronic properties which contrast with those of the FeO bulk. Figure 3 shows the band structure for minority spin shows that the FeO covered nanotube is a semi-half-metal with a band gap of 0.5 eV at roughly 0.11 eV above the Fermi level.

The band structure for minority spin shows a peak at the Fermi level. As mentioned by Xiang et al [5], such a change in the Fermi level could be induced by applying a gate voltage in a MOSFET-like system. The observed semi-half-metallicity in BN tubes covered by FeO makes it highly suitable to be the building blocks for spin-filter devices, just as the case of iron oxide nanotubes seen in the work of Liao et al [13]. We have found that the total magnetic moment per Fe atom, 3.94 $\mu_{\text{Bohr}}$, decreases in comparison to that of small FeO concentration 4.0 $\mu_{\text{Bohr}}$.

Figure 4 shows the density of states projected on the BN tube (dashed lines) and Fe (dotted–dashed lines) and O (continuous lines) atoms for the majority (top panel) and minority (bottom panel) spins. It is possible to see in both panels a strong hybridization between Fe and O orbitals which is consistent with the Fe–O covalent bonds. It is also possible to see in the regions between $-6.5$ and $-4.0$ eV, in the case of minority spin, and $-7.0$ and $-5.5$ eV, in the case of majority spin, a hybridization between the Fe, O and tube orbitals which suggests a covalent interaction between the FeO layer and the
BN tube. A Mulliken’s population analysis shows a transfer of electrons from the FeO layer to the tube (\(\sim 0.17 \text{ e/FeO unit}\)) which also suggests a strong interaction. A strong interaction between the BN tube and the FeO layer is consistent with the high value of binding energy we have found between the FeO molecule and the tube. Due to the interaction with the FeO layer, BN states appears in the large gap of the BN tube. Nevertheless, near the Fermi level, the density of states projected on the tube is small compared to the density of states projected on Fe and O atoms which indicates that electron transport must occur mainly in the FeO layer.

4. Conclusions

In summary, our first-principles calculations show that FeO and BN nanotubes may form stable structures. We found a high value of the binding energy for the FeO molecule adsorbed in a (10, 0) BN nanotube, i.e., 1.7 eV for a FeO molecule parallel to the tube axis and 1.85 eV for a non-parallel molecule. We also noticed that it is energetically favorable for an additional FeO molecule to aggregate nearby adsorbed molecules instead of bind sites away from it. In case of small FeO concentrations, the total magnetic moment per unit cell is the magnetic moment of the Fe atom (\(4 \mu_{\text{Bohr}}\)) times the number of Fe atoms in the unit cell. In case of a layer of FeO molecules covering the BN nanotube, the total magnetic moment in the unit cell decreases to 3.94 \(\mu_{\text{Bohr}}\). The BN nanotube covered with a single layer of FeO molecules is a semi-half-metal which may become a half-metal if a small change in the Fermi level is induced.

Acknowledgments

This work was partially supported by the Brazilian agencies CNPq and FAPEMIG. The authors thank H Chacham for critically reading this work.

References

[23] Band o Y and Sato T 2001 *Chem. Phys. Lett.* **350** 1