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Structural, energetic and electronic properties of intercalated boron–nitride nanotubes

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Abstract. **The effects of chirality and the intercalation of transitional metal atoms inside single walled BN nanotubes on structural, energetic and electronic properties have been considered in this paper. The thermodynamic stability of BN nanotubes can be improved by the intercalation of cobalt or nickel. BN nanotubes can behave like an ideal non-interacting hosts for these one-dimensional chains of metal atoms. Their electronic properties are insignificantly modified.**

Keywords. **Intercalated boron–nitride nanotubes; quantum chemical calculations.**

1. Introduction

According to theoretical studies, carbon nanotubes are predicted to be either metallic or semiconductor, depending on helicity and diameter of the tube (Hamada *et al* 1992). Furthermore, the curvatures and geometry of the tube causes important deviations in their electronic properties and anomalous magnetic properties (Lu 1995).

Nanotubes can be doped endohedrally by atoms or radicals to get some interesting properties. Rubio *et al* (1996), have studied the properties of chains of potassium and aluminum in carbon and boron–nitride nanotubes. The smaller bond length for linear chain of K and Al atoms, as compared to value for a bulk *bcc* (K) and a bulk *fcc* (Al), has been understood in terms of a reduction of the coordination number from the bulk system to the linear chain (Zhao *et al* 2002).

However, we expected that BN tubes serve as non-interacting hosts for incorporation of other metal atoms since their bandgaps are large. Then, considering that insulators are much less polarizable than metals and semimetals, it is expected that other metal atoms are intercalated in the inner region of the BN nanotubes.

The aim of this study was to determinate the structural, energetic and electronic properties of the pure/intercalated boron–nitride nanotubes. In order to examine these properties, we explored theoretical models. The effects of chirality and transitional metal (Fe, Ni, Co) intercalation, inside of the single walled BN nanotubes are investigated. The analysis of electronic properties has been carried out by density of state plots.

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2. Methodology

In this paper, various intercalated BN nanotubes with one-dimensional chains of metal atoms, have been submitted to molecular-mechanics (Allinger 1977) and semiempirical molecular orbital calculations (Stewart 1989) at *PM*3 levels (Dewar *et al* 1985) using the Spartan'02 software.

To obtain the densities of state (DOS) of these nanotubes, Hückel tight-binding calculations by BICON–CEDIT package (Brandle *et al* 1997) have been performed.

3. Results and discussion

We consider the following types of the BN nanotubes: (10,0), (5,5) and (7,3)BN intercalated with one-dimensional chains of four metal atoms (figure 1).

3.1 *Thermodynamic and kinetic stability*

Table 1 shows comparative variation enthalpies of formation (per atom) of the doped boron nitrogen tubes with different atoms. The tubes doped with cobalt and nickel behave like ideal non-interacting hosts stabilizing the BN nanotubes whereas the iron atoms lead to instability of the tubes. It is worth noting that according to our results for all the considered tubes, the intercalation one-dimensional chains of cobalt or nickel in armchair BN nanotubes are more energetically favourable.

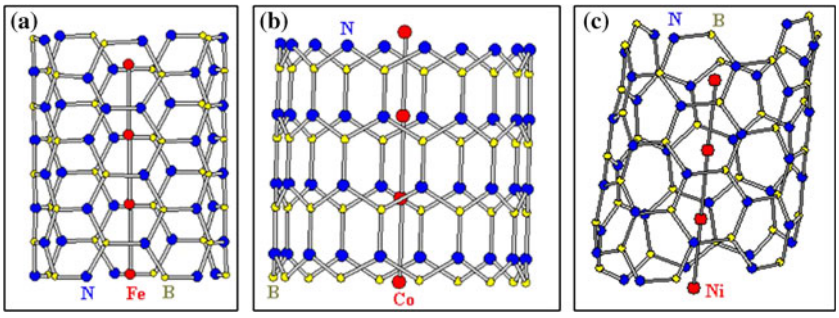

Figure 1. The structure intercalated boron–nitride nanotube with one-dimensional chains of metal atoms (Fe, Ni, Co): (**a**) armchair; (**b**) zigzag and (**c**) chiral tube.

Table 1. Calculations of the ΔH/atom for intercalated BN nanotubes.

	ΔH (kcal/mol)/atom			
Tube geometry	Tube&Co	Tube&Ni	Tube	Tube&Fe
(10,0)	−74·87	−27·71	−15·26	−13·04
(7,3)	−75·44	−30·39	−17·41	−15·05
(5,5)	−79·7	−32·09	−22·05	−17·89

Table 2. Calculations of the $E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}$ for intercalated nanotubes.

	$E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}$ (eV)			
Tube geometry	Tube&Fe	Tube&Ni	Tube&Co	Tube
(10,0)	3·54	4·81	4·94	5·57
(7,3)	2·05	3·96	3·61	4·28
(5,5)	3·38	6·74	7·27	8·67

The intercalated BN nanotubes attendance small values of their energy gaps ($E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}$), (table 2), so they are kinetically unstable relative to their pure analogues.

3.2 *Density of states*

One of the current research topics in this area is the influence of the different chiralities and a type of intercalated transition metal atom on electronic properties of the tubes. This includes the ability to use density of states. The results obtained for (10,0)BN nanotubes are revealed in figure 2. From the DOS(E) plots, it is obvious that the lowest bands (valence band) are composed of N($2s$) derived states and the conduction bands corresponding to N($2p$) and B($2s$, $2p$) derived states, respectively.

The energy difference between the bottom of the conduction band and the top of the valence band in a semiconductor or an insulator is called the bandgap energy, E_g. The bandwidth of the bandgap provides a distinction between a semiconductor and an insulator. When the bandgap is not very large, usually ranging from 0·5 to 3·0 eV, the material is a semiconductor, while an insulator has an $E_g >$ 3 eV (Greenham and Friend 1995; Dekker 1999; Rada and Silaghi-Dumitrescu 2006). So that energy gap is larger than 3 eV and the (10,0)BN tube have insulator property. This result is in agreement with the ones predicted by Blasé *et al* (1999).

When chains of metal atoms are intercalated into the (10,0)BN nanotube, the electronic states in vicinity of the Fermi level can be significantly modified because of the new peaks associated with transitional metal atoms are found in conduction bands, figure 2(b–d). The valence bands are not affected. Instead of it, a stronger overlap in minimum conduction bands is predominantly composed of the orbital of N($2p$), B($2s$, $2p$) and Co($3d$) or Fe($3d$). The density of states near the Fermi level consists of Co($3d$) states. This will play an important role in their magnetic properties (Hacohen *et al* 1998).

Intuitively, charge transfer from nanotube to metal can be understood by shift of Fermi level towards vacuum (Wilder *et al* 1998; Esfarjani *et al* 2003). Our calculations indicate that a weak charge transfer from the BN tube to metal is taking place because of the Fermi level shifts from −13·37 eV towards vacuum (−13·21 eV for tube&Co). Then Fermi energy values confirm that (10,0)BN tube–Co interactions are stronger than the tube–Fe and the tube–Ni, respectively. Our studies on electronic population analysis show that metal atoms act as acceptor electrons (negative charge on chains of metal atoms) and tube is donor of electrons subunit (positive charge), too.

On the basis of these studies it was concluded that metal–metal and metal–BN interactions are ionic and Fe, Ni or Co act as electron acceptors. The BN nanotubes may be good hosts for the incorporation of these atoms because they behave like an ideal non-interacting hosts for the metal atoms inside and their electronic properties are insignificantly modified.

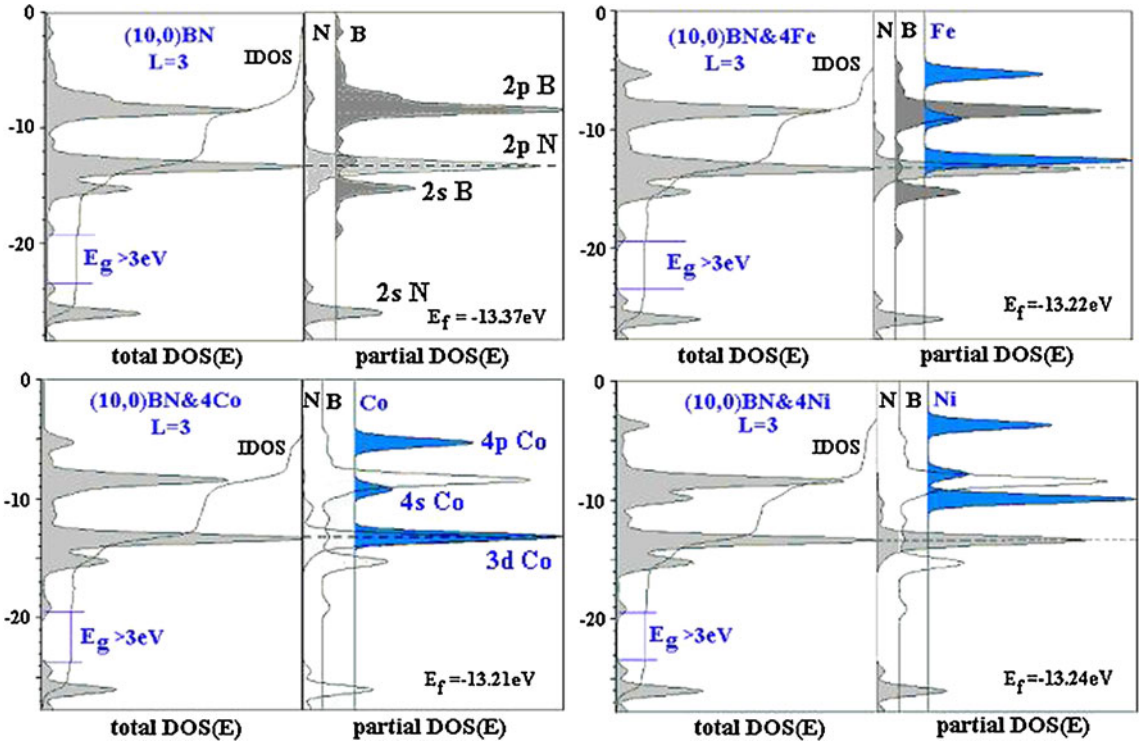

Figure 2. Total, partial DOS and IDOS diagrams for intercalated (10,0)BN tube.

4. Conclusions

According to our estimations, the intercalation one-dimensional chains of cobalt or nickel in armchair BN nanotubes are more energetically favourable. Note also that the intercalated BN nanotubes behave like insulators independent on the chiralities of the tube and intercalated atom types.

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