Nanocables made of a transition metal wire and boron nitride sheath: Density functional calculations

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(Received 6 June 2006; revised manuscript received 30 August 2006; published 29 December 2006)

The boron nitride (BN) nanotube has a very wide band gap and can shield the nanowire encapsulated inside its cavity from outside interference. Our calculations indicate that transition metal wires can be inserted inside a variety of zigzag BN nanotubes exothermically. In particular a cobalt wire and the BN tube interact just like two giant molecules. The weak interaction between the BN tube and the wire ensures a low binding energy and a high magnetic moment that comes solely from the transition metals. High spin polarization at the Fermi level also indicates that the hybrid structure can be used as a nanocable for spintronic applications

DOI: 10.1103/PhysRevB.74.235445 PACS number(s): 73.63.Fg, 73.90.+f, 71.15.Nc, 71.20.−b

Nanowires and nanotubes are an indispensable part for the development of nanoscale electronics. The linear structures provide a desired one-dimensional (1D) transport in a much-miniaturized scale that serves as building blocks for the next generation of electronic devices. However, the transport is often subject to the influence of the environment of the circuit setting, in which an adsorption of a foreign molecule on the wire may cause a drastic change of its conduction property. It is with this in mind that the concept of nanocable, a metallic nanowire sheathed inside an insulating nanotube, is interesting.

The boron nitride nanotube is especially suitable for the task of shielding the metallic nanowire inside its cavity. With its band gap as high as 5.5 eV, it is expected to protect the encapsulated content from outside interference effectively. In fact, this has been achieved experimentally for numerous structures having the encapsulation of Mo clusters, Ni, Co, Fe, or Fe-Ni alloy nanorods/nanowires, and potassium halide single crystal.[1–5] Theoretically, density functional calculations have provided models for the encapsulation of Ni and Cu wires[6,7] in which the interaction between the wire and the BN tube is weak and the electronic structure is hardly disturbed by the BN coating, thus further proving the efficacy of such an arrangement.

It has been calculated that a Ni wire can be encapsulated by BN (8,0), (9,0), and (10,0) nanotubes, with the (9,0) case being exothermic.[6] But even this most energetically favorable configuration for the Ni wire has an extremely high formation energy of −0.04 eV per Ni atom. In this article, we report a more extensive theoretical investigation of the transition metal (TM) wire/BN nanotube structures. These include Co, Fe, and Mn wires and a variety of zigzag BN tubes. One of our main interests is in exploring the magnetism and carrier spin polarization associated with the transition metals and their dependence on the interaction between the wire and the tube.

We employ the projector augmented wave (PAW) potentials[8,9] as implemented in the VASP code[10–13] for the density functional calculations with the generalized gradient approximation (GGA). The exchange-correlation functional is provided by the version of Perdew-Wang 91 (PW91).[14,15] Normally, the PAW potentials are more accurate than the ultrasoft pseudopotentials and require higher cutoff energies. We thus use a uniform 400 eV for all the calculations, which is much higher than the 250 eV cutoff typically used for PAW potentials. All the calculations assume 1D periodicity along the tube axis. Geometric structures of both the tube and the wire inside are fully relaxed to minimize the total energy of the system until a precision of 0.01% is reached. In the calculation of energy bands, a 31 point sampling of the first Brillouin zone is taken. For the calculation of density of states, a smearing of 0.025 eV is used.

It is a fact that a 1D system may be unstable, suffering Peierls instability, for example, and undergo a configuration distortion to attain the lowest total energy. To accommodate that possibility, we allow the positions of all atoms in the BN tube/TM wire system to move in all three independent directions during the relaxation process until the optimal configuration and thus lowest total energy is reached. Such a relaxation may lead to an opening of a gap in some 1D systems. However, as we shall show, no such gap opening is found in the systems. The TM wire, along with the enclosing BN tube, has little configuration change as a result of the relaxation.

A typical example for the encapsulation of a Co wire is first presented. The wire has six Co atoms in the unit cell in an *ABAB* staggered triangle packing in each of the six zigzag BN nanotubes, from the (9,0) to (14,0). Figure 1 shows the six fully relaxed geometrical configurations. It is interesting to note that the wire remains in the center of the tube for different tube sizes, so the distance between any of the Co atoms in the wire and the BN tube increases with the enlargement of the tube radius. In Fig. 2 the binding energy per unit cell of the Co-encapsulating BN cable versus the distance is displayed, with the latter represented by the nearest distance between the Co wire and the BN tube. The nearest distance is defined as the shortest distance between all Co atoms of the wire and all B or N atoms of the tube. All values of the energy and distance are listed in Table I. The binding energy is defined as the difference between the total energy of the cable and the sum of the total energies of the corresponding pure BN tube and the independent Co wire, with the latter assuming the same configuration as the one in the

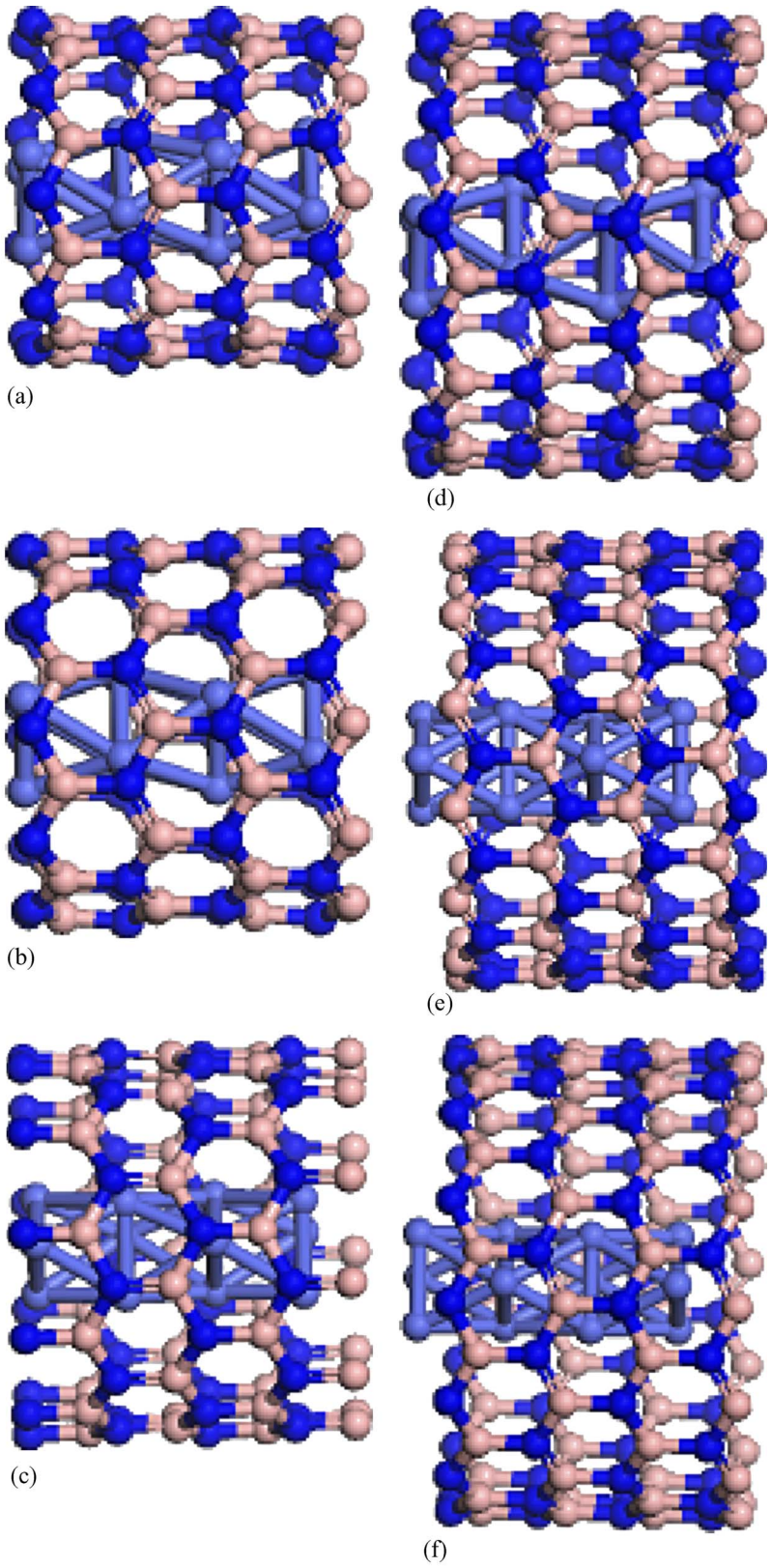

FIG. 1. (Color online) (a)–(f) represent a Co wire contained in (a) BN (9,0), (b) BN (10,0), (c) BN (11,0), (d) BN (12,0), (e) BN (13,0), and (f) BN (14,0) nanotube. Notice the different relative positions between the Co wires and the tubes.

cable. It is clear that the points shown in the figure pretty much portray an interaction between two giant molecules, with positive values of the energy indicating repulsive nature of the interaction at close ranges and negative values accounting for attractive part of the interaction. There is a minimum value that corresponds to the equilibrium distance between the two. Thus there is optimal size of the BN nanotube that is able to accommodate a specific wire in the most energetically favorable manner.

Of the six Co-encapsulated BN cables studied, only the

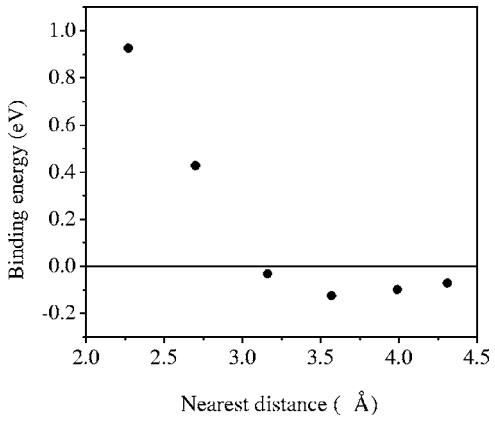

FIG. 2. Distribution of the binding energies per unit cell versus the nearest distances between the Co wires and the BN tubes looks like an interaction between two molecules.

(9,0) and the (10,0) nanocables are formed endothermically. Larger BN tubes offer exothermic interaction for the encapsulation, with the (12,0) tube being the most energetically favorable, having the binding energy of −0.13 eV per unit cell. Overall the interaction between the Co wire and the BN tubes is weak, as is expected all along, and the Co wire is effectively shielded by the chemically inert BN tube. We also notice, by inspecting the relative positions of the Co wires inside the six BN tubes, that by relaxing the configuration for each tube of a specific radius, the Co wire is shifted along the axis of the tube in search for the optimal configuration. This is also a natural result from the molecular interaction between the core and the sheath.

It is possible to study the stability of the Co wire/BN tube system from another point of view. We can, for example, define the formation energy of the composite system as the difference between the total energy of the nanocable and the sum of total energies of the pure BN tube and six independent Co atoms (for the unit cell). Under such a definition, the formation energy is much smaller than the binding energy as mentioned above. As an example, the formation energy for the Co-encapsulating (12,0) BN cable is calculated to be −23.1 eV per unit cell, showing that the nanocable is very stable against disintegrating into its constituents of the pure BN tube and individual Co atoms. The reason for this much smaller (or more negative) value as compared with the binding energy is due to the relatively robust nature of the Co wire and much of the reduced formation energy comes from its construction. However, if one goes further and takes into account the cohesive energy of bulk Co, which is 4.39 eV per atom,[16] the entire process from breaking bulk Co into individual Co atoms to the synthesis of Co wire inside the BN tube is apparently endothermic.

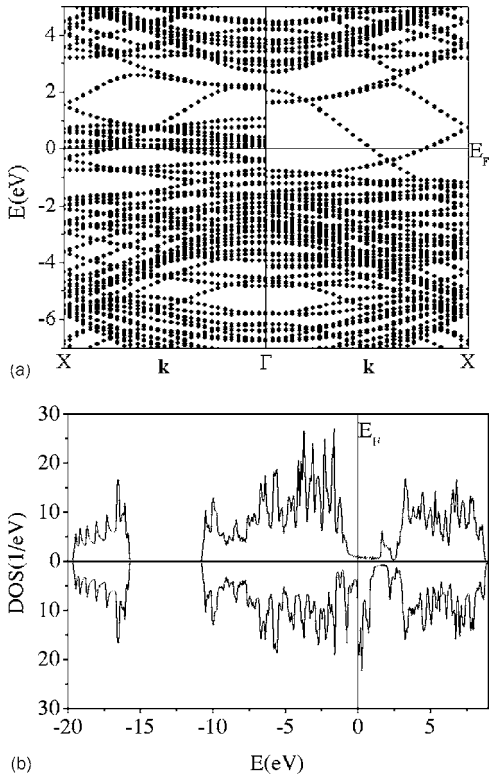

FIG. 3. (a) Band structure for the Co-encapsulating BN (12,0) cable. The right (left) panel is for the majority (minority) spin. (b) DOS (per unit cell) for the same cable with the top (bottom) panel representing the majority (minority) spin.

Calculated band structure of the Co-encapsulating (12,0) BN cable is shown in Fig. 3(a). One readily identifies the asymmetry between the energy bands of the majority spin and those of the minority spin in the proximity of the Fermi level. There are more bands crossing the Fermi level for the minority spin (left panel) than those of the majority spin (right panel). Density of states (DOS) [Fig. 3(b)] also shows a large peak near the Fermi level for the minority spin (bottom panel) in comparison with the small presence for the majority spin (top panel). Spin polarization, based on the definition of $[N_{\downarrow}(E_F)-N_{\uparrow}(E_F)]/[N_{\uparrow}(E_F)+N_{\downarrow}(E_F)]$, where $N_{\uparrow}(E_F)$ $[N_{\downarrow}(E_F)]$ represents the DOS of the majority (minority) spin at the Fermi level, is found to be 88.8%. As most

TABLE I. Some physical properties of the six Co-encapsulating BN nanotubes as shown in Fig. 1. Binding energy is calculated for each unit cell and the nearest distance is between the Co wire and the enclosing BN tube. Magnetic moment is found to increase with respect to the nearest distance.

BN tube+Co wire	(9,0)	(10,0)	(11,0)	(12,0)	(13,0)	(14,0)
Binding energy (eV)	0.93	0.43	−0.032	−0.13	−0.099	−0.072
Nearest distance (Å)	2.27	2.70	3.16	3.57	3.99	4.31
Spin polarization (%)	78.5	83.3	77.6	88.8	87.8	88.8
Moment per Co atom (μ_B)	1.52	1.87	1.87	1.92	1.98	2.00

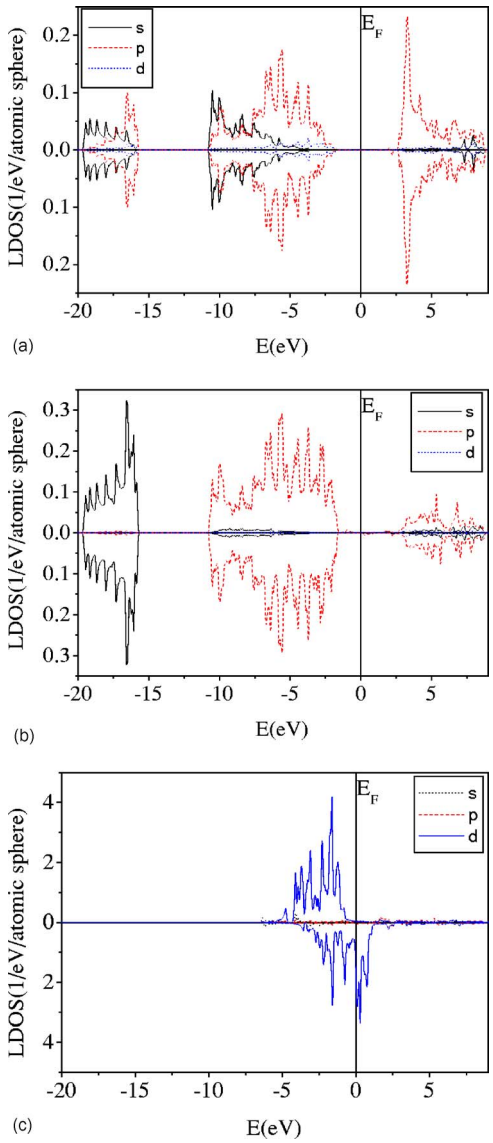

FIG. 4. (Color online) LDOS for (a) B, (b) N, and (c) Co in the BN (12,0) cable.

transport occurs around the Fermi level, this high spin polarization ensures a very high degree of passage of the preferred spin.

A high magnetic moment of $1.92\mu_B$ is also obtained for each Co atom inside the (12,0) tube, while the BN tube per se is hardly magnetized at all. This is certainly due to the weak interaction between the Co and BN. As shown in Figs. 4(a) and 4(b), respectively, B and N of the encapsulating structure each has a symmetric distribution of local density of states (LDOS) for either spin, which is essentially the same as that of a pure BN nanotube. LDOS in Fig. 4(c), however, indicates the Co wire is solely responsible for the high magnetic moment and spin polarization. Figures 5(a)–5(c) further illustrate the nature of interaction between the wire and the sheath. Each of the three plots represents the charge distribution on a plane perpendicular to the cable for the majority spin, minority spin, and the difference of the two spins respectively. All three indicate extremely small overlap of charges from the coating and the wire. Figure 5(c)

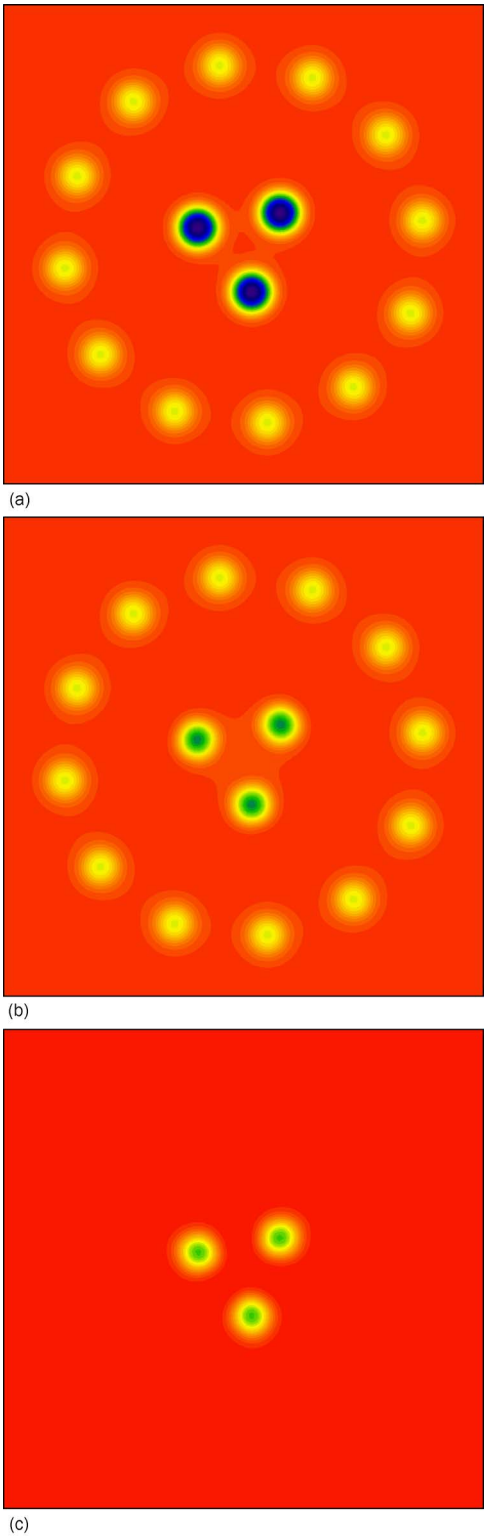

FIG. 5. (Color online) Charge density for (a) the majority spin, (b) the minority spin, and (c) difference of the two spins in a plane penetrating perpendicularly the BN (12,0) cable. Magnitude of the charge density is expressed by colors, with the red at one end of the spectrum being the smallest and the blue at the other end the largest.

in particular shows that magnetism is confined within the wire. This wire, if taken out of the BN cable with its con-

TABLE II. The same physical properties as in Table I for Mn-encapsulating and Fe-encapsulating BN cables.

Tube	BN (13,0)+Mn wire	BN (14,0)+Fe wire
Binding energy (eV)	−0.11	−0.077
Nearest distance (Å)	3.72	4.17
Spin polarization (%)	51.2	74.3
Moment per metal atom (μ_B)	4.13	3.00

figuration intact, has only a slightly higher moment of $2.03\mu_B$ per Co atom. Its energy bands are also very similar to those shown in Fig. 3 in the energy range of about 2 eV above and below the Fermi level. We further relax the wire and find that the independent wire actually has negligible variation from the one inside the BN tube. The small reduction of the moment for its being contained inside the BN nanotube and the similarity of energy bands is another testimony to the weak interaction between the wire and the BN tube.

In fact, all six configurations of Co-encapsulating cables have very high spin polarization, as is shown in Table I. Magnetic moment per Co atom, however, increases with the nearest distance and, therefore, with the decrease of the interaction. As the table indicates, the moment for the (14,0) cable is only $0.03\mu_B$ smaller than that of an independent Co wire.

We also consider antiferromagnetism (AFM) for the system. Both the nanocable and pure wire systems are structurally relaxed and calculated for total energies by assigning antiparallel spins to the adjacent TM atoms along the tube axis. The result shows that the AFM system has a higher total energy than the ferromagnetic (FM) case and therefore cannot represent ground state. Take, for example, the case of BN (12,0) cable with the Co wire: the AFM nanocable is about 1.5 eV higher per unit cell in total energy and the pure wire is 1.3 eV/cell higher for AFM. This preference of FM for BN cable has also been corroborated by the cited calculation on Ni wires.[6]

The same structure relaxation and energy band calculations are also applied to other transition metal wires inserted inside BN nanotubes. Table II lists two typical cases in which Mn and Fe wires are sheathed in BN (13,0) and (14,0) nanotubes respectively. Both structures are formed exothermically with comparable binding energies. Magnetic moment per metal atom is $4.13\mu_B$ and $3.00\mu_B$ for Mn and Fe, respectively. The Fe wire, however, has a higher spin polarization of 74.3%, and the Mn wire having a smaller 51.2%. But either of the two structures is a very efficient conduit for preferential passage of the minority spin. The encapsulated wire can also have configurations with more or less than six transition metal atoms per unit cell. As an example, we study two BN tubes (9,0) and (10,0) each containing a Ni wire with eight Ni atoms per unit cell. Both cables are endothermic in their formation due to shorter distance and thus stronger interaction between the wire and the tube. Spin polarization is high for either cable, with the (10,0) cable having 65.2% and the (9,0) reaching 98.4%.

One synthesis route for these coaxial nanocables is likely to be a vapor-liquid-solid growth mechanism, as has been achieved in the filling of Ni and $NiSi_2$ wires inside BN tubes,[4] in which a metal foil is used during the catalytic growth of the BN nanotubes. Another way of making the nanocables may involve a two-stage process, using a carbon layer as an intermediary, which has also successfully produced TM wires-enclosed BN tubes.[3] Practical application of the coaxial TM wire/BN cables can be found by using the spin-valve effect, in which the nanocable is sandwiched between two ferromagnetic electrodes and the alignment (misalignment) of the spins of the electrodes will increase (decrease) the conductance of the transport process. In another possible scenario, applied magnetic field can be used to facilitate or thwart the transport by changing its direction relative to the spin polarization of the cable. In either case, electron transport could be tuned by outside control.

In summary, we have investigated systematically the interaction between a Co nanowire inserted inside BN nanotubes of different sizes. The interaction is found to be weak, thus the Co wires are shown to be safely sheathed inside the BN coating. We have also calculated the spin-polarized band structures of the BN cables encapsulating the Co as well as Mn, Fe, and Ni wires. All cases provide high spin polarizations and magnetic moments coming solely from the transition metals. The hybrid structures can therefore be applied to circuits that demand preferential transport of electrons with a specific spin.

This work has been financed by the National Science Council of the Republic of China, under Grant No. NSC 95-2112-M-182-001-MY3. We are also grateful for the computational supports provided by the National Centers for Theoretical Sciences and High-performance Computing of the ROC, and UNC-Chapel Hill Academic Technology and Network.

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