Small-radius clean and metal-doped boron carbide nanotubes: A density functional study

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We present the results of *ab initio* density functional theory calculations of the atomic and electronic structure of small radius boron carbide nanotubes, and the effects of doping these tubes with Li and Cu atoms. We have found that undoped narrow tubes are more energetically favorable than the corresponding boron carbide strips. The effects of doping on the atomic and electronic structure of these tubes have been found to be dependent on the size and symmetry of the tubes, and the type of dopant atoms.

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I. INTRODUCTION

A decade has passed since the discovery of carbon nanotubes,¹ and the list of different materials from which nanotubular structures can be formed has been rapidly expanding. Noncarbon nanotubes such as BN, (Ref. 2), BC₂N, (Ref. 3), B_xC_yN_z, (Ref. 4), BC₃, (Ref. 3), CN_x, (Ref. 5), GaN, (Ref. 6), WS₂, (Ref. 7), MoS₂, (Ref. 7), NiCl₂, (Ref. 8), SnS₂, (Ref. 9), Te, (Ref. 10), Bi, (Ref. 11), NbSe₂, (Ref. 12) and TiSe₂ (Ref. 13) have been observed experimentally and studied theoretically. It has been suggested that the ability of a material to exist in a layered three-dimensional bulk structure may be a prerequisite for the formation of corresponding nanotubular structures.¹⁴ This has prompted a number of theoretical studies focused on the physical and chemical properties of hypothetical nanotubes made from various layered materials.^{15–24} Theoretical studies have also been conducted on nanotubes based on superconducting materials such as NbSe₂, (Ref. 16), Ca(Al_xSi_{1-x})₂, (Ref. 19) and Sr(Ga_xSi_{1-x})₂ (Ref. 19). This includes MB₂ materials [$M = \text{Mg, Al, Sc, Ti, Al, Be}$ (Ref. 25) Be (Ref. 26)] that are related to the recently discovered layered superconductor MgB₂ (transition temperature $T_C \sim 40$ K).²⁷ Research on the noncarbon MB₂-type nanotubes has been stimulated mainly by the theoretical prediction that introducing curvature into superconducting layered systems might lead to an increase of T_C in cylindrical MB₂ wires.²⁸

In this paper we study, using *ab initio* density functional theory (DFT), the properties of clean boron carbide (BC) nanotubes, and BC nanotubes doped with Li and Cu atoms. As layered semiconductors, CuBC and LiBC are isovalent with, and structurally similar to, the medium-temperature superconductor MgB₂. Both consist of hexagonal BC layers with alternating boron and carbon atoms. It has been predicted that hole doping of LiBC would lead to superconductivity of this material.²⁹ Calculations by Mehl *et al.*³⁰ have shown that the full replacement of the Mg atoms by Cu in MgB₂, and the partial replacement of boron atoms by carbon, to form a Cu BC-like layered compound, might increase its transition temperature to ~ 50 K. Theoretical work has also shown that single-walled carbon nanotubes (SWCNTs), as well as BN, B_xC_yN_z, BC₃ and hypothetical pure boron-based nanotubes, have comparable strain energies.¹⁵ This suggests that other stoichiometries of boron-containing carbon nanotubular structures may also be stable. Previous calculations

that we have performed using the DFT tight binding (DFT-TB) method have shown that charged BC nanotubes are stable and energetically viable.³¹

Due to the effects of electron confinement, small-radius carbon nanotubes have been predicted to possess very unusual features. These include a large split in the *G*-like raman modes, softening of the radial breathing modes, closing of the semiconducting gap, and possible enhancement of the electron-phonon coupling causing these ultranarrow nanotubes to be superconducting at relatively high temperatures (~ 15 K).³² It has also been shown that nanotubes of small radius can be relatively easily formed for some types of noncarbon nanotubes. For example, narrow MoS₂ nanotubes with an almost uniform subnanometer diameter have been produced in a catalyzed reaction using C₆₀ as a growth promoter.³³ In this paper we show that narrow BC nanotubes are energetically more stable than the corresponding strips obtained from boron carbide hexagonal sheets. We also show that doping BC tubes with Cu atoms results in the formation of covalent bonds between the dopant atoms and the carbon atoms on the tubular shell, while the bonding of Li with the boron and carbon atoms has a predominantly ionic character. These two effects are shown to dominate the structural and energetic properties of narrow BC tubes.

II. METHOD AND PROCEDURE

We have carried out *ab initio* DFT spin-polarized calculations based on the plane wave pseudopotential method (VASP)^{34,35} within the generalized gradient approximation (GGA)³⁶ for the exchange and correlation energy. For the modeling of the carbon, boron, and copper atomic interactions we have used standard ultrasoft (US) pseudopotentials,³⁷ and for the Li atom we have employed the US pseudopotential with *p*-semi-core states^{37,38} and an energy cutoff of 286.7 eV.

Calculations have been conducted for: (i) an infinite, single layered BC hexagonal sheet with alternating boron and carbon atoms placed on the nodes of the “honeycomb” lattice, (ii) infinite, narrow boron-carbide strips which are “cut” from the BC hexagonal sheet (see Fig. 1), and (iii) infinite BC tubes formed from the infinite narrow boron carbide strips. The initial tubular geometries for the selected zigzag and armchair BC nanotubes were obtained by rolling up the corresponding infinite, narrow boron carbide sheets.

FIG. 1. Schematics of BC strips: (a) (9,0), and (b) (4,4). The direction of the periodic boundary conditions (PBC) is indicated by the large arrow. The boron atoms are denoted by white circles, and the carbon atoms by gray circles.

The dimensions of the unit cells have been chosen large enough to ensure that there are negligible interactions between neighboring strips or tubes.

The geometries of the boron carbide layers, strips, and tubes were fully relaxed with respect to the atomic positions and their unit cell lengths, using the conjugate gradient technique. The geometries were assumed to have converged when all of the forces acting on each of the atoms were less than 10^{-5} eV/Å. The sets of $\mathbf{k}$ points were generated using the standard Monkhorst-Pack scheme.³⁹ For optimization of the BC strips (which are infinite in the x direction) we employed a $6 \times 2 \times 1$ $\mathbf{k}$ -point mesh, while for optimization of the infinite BC layer and tubes we have used a $3 \times 3 \times 3$ $\mathbf{k}$ -point mesh. Our tests have shown that the $3 \times 3 \times 3$ $\mathbf{k}$ -point mesh gives a very good representation of the structural properties of the tubes and the main energetic trends (i.e., the relative stabilities of the fully optimized doped and clean tubes) compared to finer $\mathbf{k}$ -point meshes. We have also conducted test calculations based on the two-ring model to check the stability of different sites for doping by Li atoms.⁴⁰

The electronic structure for a single BC layer was calculated using a mesh of 24 $\mathbf{k}$ points along the Γ -M-K- Γ high symmetry directions of the first Brillouin zone. The electronic density of states (DOS) plot for the BC layer has been obtained using a smearing factor of 0.4 eV, while for the BC tubes a smearing factor of 0.2 eV has been employed.

The energies of free C, B, Li, and Cu atoms in vacuum, which are needed to calculate the binding energies for the Li(Cu) doped nanotubes and the heat of formation of the BC layer, were obtained using a large rectangular periodic unit cell with side length ~ 30 Å and the $3 \times 3 \times 3$ $\mathbf{k}$ -point mesh generated using the standard Monkhorst-Pack scheme.³⁹

III. RESULTS AND DISCUSSION

A. Infinite BC layer

We have found that a single, infinite hexagonal BC layer is a planar structure. The converged total energy per boron

TABLE I. Heat of formation of a single infinite BC layer per B-C pair.

E_{BClayer} (eV per B-C pair)	-15.021
E_{Cvacuum} (eV per B-C pair)	-1.323
E_{Bvacuum} (eV per B-C pair)	-0.298
Heat of formation of a BC layer	
$E_{\text{Bvacuum}} + E_{\text{Cvacuum}} - E_{\text{BClayer}}$ (eV per B-C pair)	13.400

carbon pair of the infinite hexagonal BC layer is much lower than the sum of the energies of the isolated carbon and boron atoms (see Table I). The BC layer is therefore energetically stable. The average bond length of the optimized layer was found to be 1.52 Å. The electronic band structure and the total DOS for this single, infinite BC layer are presented in Figs. 2(a) and 2(b), respectively. As can be seen, this system is metallic. The main features of the calculated electronic band structure are in good correspondence with the band structure previously calculated for a “charged” BC layer using the semiempirical DFT-TB method.

B. Narrow BC strips

To model narrow, infinite BC strips with open edges, we employed planar BC strips within a periodic orthorhombic

FIG. 2. Electronic structure for a single infinite BC layer: (a) band structure; (b) total DOS. The Fermi energy is indicated by the dashed line.

TABLE II. Properties of clean BC nanotubes.

BC nanotube (<i>n</i> , <i>m</i>)	Mean diameter (Å)	Mean bond length (Å)	Total energy (eV/atom)
(6, 0)	4.99	1.54	7.38
(4, 4)	5.92	1.54	7.40
(5, 5)	7.45	1.53	7.43
(9, 0)	7.69	1.55	7.40
(10, 0)	8.46	1.55	7.41
(12, 0)	10.06	1.54	7.41

unit cell. This unit cell had a repeat length equivalent to two complete hexagonal rings along the direction corresponding to the longitudinal axis of the infinite tube that could be formed from one of these strips (see Fig. 1). In the other two orthogonal directions the cell repeat length was chosen large enough to prevent any interactions between the open edges of neighboring strips.

The structural stability of the infinite narrow strips was found to depend strongly on their width and edge topology. Moreover, the armchair edges of the zigzag strips underwent significantly more reconstruction during the course of optimization than the almost nondeformed open zigzag edges of the armchair strips [compare Figs. 1(a) and 1(b)].

C. Clean BC nanotubes

We have conducted geometry optimization calculations for clean (6,0), (9,0), (10,0), and (12,0) zigzag BC tubes, and (4,4) and (5,5) armchair BC tubes. Values for some of the properties of these tubes obtained from these calculations are presented in Table II. The mean BC bond length for all calculated tubes was found to be 1.54 Å, which is slightly longer than the value of 1.52 Å determined for the hexagonal layer. The (6,0) tube, which is the narrowest we have studied [see Fig. 3(a)], was found to have a mean diameter of 4.99 Å, while our largest calculated BC tube [(12,0)] has a mean diameter of 10.06 Å. All the BC tubes were found to preserve both their hollow shape and the hexagonal boron carbon network on the tubular shells. The tubular cross section of the narrow armchair (4,4) BC tube was found to acquire a symmetric rectangular shape, as can be seen from Fig. 3(b). Figure 4 shows the total energy of clean BC tubes, and the corresponding BC strips, plotted as a function of the initial diameter of the tubes that are formed from the strips. These results show that the formation of narrow BC nanotubes is energetically more favorable than the formation of the corresponding BC strips. This is due to the elimination of the chemical energy of the dangling bonds at the open edges of the strips when the tubular structures are formed. We have also found that the total energy of clean BC nanotubes increases with decreasing radius, and hence with increasing curvature of the tubes (see Fig. 4). This energy dependence is similar to that found for SWCNTs (Ref. 41).

In the remainder of this paper we shall only consider the most narrow of the above-mentioned tubes; namely, the (6,0) zigzag, and (4,4) armchair BC tubes. The calculated total

FIG. 3. End and side views of two optimized small diameter BC nanotubes: (a) (6,0), and (b) (4,4). The dotted lines indicate the repeat length of the periodic unit cell.

DOS for these two BC nanotubes are shown in Fig. 5(a). Both of these tubes were found to be metallic. A charge density plot for the clean (4,4) BC tube is presented in Fig. 5(b) and shows pronounced charge asymmetry in the boron carbon bonding with greater charge localization in the vicinity of the carbon atoms. Similar charge distributions within the boron carbon hexagonal network have been shown to occur for both single-walled BC₃ tubes⁴² and LiBC clusters.⁴³

D. Doped BC tubes

It has been predicted that doping of small-diameter carbon nanotubes may enhance their superconducting properties.³² One of the aims of the present paper, inspired by these ideas, was therefore to determine the extent to which doping by Li or Cu atoms could modify the structural, energetic, and electronic properties of small-diameter BC nanotubes. Test calculations suggested that positioning the chemisorbed metal

FIG. 4. Total energies (in eV per BC pair) of BC tubes and strips as a function of their corresponding tubular diameter (taken to be that of the unrelaxed tube). The value for the infinite BC layer is indicated by the dashed line.

FIG. 5. (a) Total DOS for the (6,0) zigzag and (4,4) armchair BC nanotubes, and (b) charge density isosurface plotted for a section of the clean (4,4) BC tube. The arrow indicates the longitudinal axis of the tube. The boron atoms are denoted by the white circles and the carbon atoms by the dark circles.

atoms inside an isolated BC tube is more energetically favorable than placing them at sites on the outer surface of the tube. We have found that doping by metal atoms at sites outside isolated tubes leads to corrugation of the tubes, and produces less stable structures than inside doping of the tubes, with the energy difference per cell between the most stable inside and outside sites for the (4,4) BC tube being 1.55 eV for a Cu atom, and 0.88 eV for a Li atom per cell. Our test calculations on the doping of flat BC layers with Li(Cu) atoms indicated that the dopant atom prefers to stay at a distance of ~ 1.69 (1.92) Å from the BC hexagonal layer, rather than being embedded in the surface of the layer. Hence, we have focused our attention in this paper on studying the inside doping of BC tubes. Doping of these tubes was achieved by placing Li or Cu atoms at different adsorption sites inside BC nanotubes. For the (6,0) zigzag BC tubes the doping concentration was 1 Cu atom, or 1-3 Li atoms, per 12 boron carbon pairs in the periodic unit cell, while for the (4,4) armchair BC tube we used 1 Li atom, or 1-2 Cu atoms, per 16 boron carbon pairs.

E. BC tubes doped with Li

Doping the interior of narrow BC tubes with Li was found to significantly affect the structural properties of the tubes. The mean BC bond length for both the Li doped (6,0) and (4,4) BC tubes was found to be 1.55 Å, which is slightly longer than the value of 1.54 Å determined for the corresponding clean BC tubes (see Table II). As shown in Fig. 6 and Table III, the effects of doping were found to depend on both the helicity and diameter of the tubes. The (6,0) BC

FIG. 6. Optimized structures of Li-doped BC nanotubes: (a) (4,4) doped with one Li, (b) (6,0) doped with one Li, (c) (6,0) doped with two Li atoms, and (d) (6,0) doped with three Li atoms. The atoms are denoted by white (B), gray (C), and black (Li) circles. The dashed vertical lines indicate the repeat length of the periodic unit cell.

nanotube with one Li atom per cell was found to retain a cylindrical shape with the Li atom positioned on the central axis of the tube, as shown in Fig. 6(b). By contrast, in the most stable structure for the (4,4) Li-doped BC nanotube with one Li atom per cell, the Li atom is positioned away from the central axis of the tube, as shown in Fig. 6(a), and prefers to occupy a position which is closer to one of the carbon atoms on the tubular shell (C-Li distance ~ 2.28 Å) than to the boron atoms. While the hexagonal BC network of the (4,4) tube is retained, its shape is no longer symmetrical. The observed dependence of the Li atom position on the size of the BC tube is similar to results obtained from modeling the insertion of Li into carbon nanotubes^{40,44} where it was shown that the most stable position for a Li atom inside a SWCNT is strongly dependent on its radius.

In order to model the most energetically favorable positions for a Li atom inside a BC nanotube we have employed a simple “two-ring model” (shown in Fig. 7). This model

TABLE III. Properties of isolated small-diameter BC tubes doped inside with Li atoms. All the distances are in Å.

Structure, n Li atoms Inside (n,m) BC tube	1 Li (4,4)	1 Li (6,0)	2 Li (6,0)	3 Li (6,0)
Mean B-C bond length	1.55	1.55	1.55	1.56
Shortest B-C bond length	1.50	1.54	1.55	1.54
Longest B-C bond length	1.61	1.55	1.56	1.58
Tubular cross section (max)	6.05	5.02	4.96	5.00
Tubular cross section (min)	4.48	4.97	4.94	4.86
C-Li nearest neighbor distance	2.28	2.63	2.53	2.56
B-Li nearest neighbor distance	2.67	2.61	2.69	2.57
Li1-Li2 distance	-	-	2.43	1.64
Li2-Li3 distance	-	-	-	1.62
Average binding energy (eV)	2.85	3.79	3.21	1.60
Heat of formation (eV)	2.85	3.79	2.63	-1.62

was used by Kar *et al.*⁴⁰ to study the interaction of inserted Li atoms with the walls of SWCNTs. In this model, the opposite walls of the nanotube are represented by two hexagonal benzenelike rings with boron and carbon atoms placed alternately. One-point energy calculations were carried out for different distances between the rings (which corresponded to different diameters of the BC tubes), and for the Li atom occupying different positions between the rings. The minimal energy distance of the Li atom from one of the hexagonal rings was found to be in the range 1.5 Å–2.4 Å,

depending on the separation between the hexagonal rings [see Fig. 7(b)]. When the distance between the two hexagonal rings is in the range 3 Å–4.5 Å, which would correspond to very narrow tubes, our calculations show that the most stable equilibrium position for the Li atom is located at the central position between the rings. This corresponds to the geometrical center of the modeled tubes. For larger ring separations, the central position between the two rings will not be a minimum energy position for a Li atom inserted into the tube. These simple calculations can partly explain the difference in the effects of doping by Li on the geometric structure of the more narrow (6,0) BC tube compared to the wider (4,4) tube.

We have also analyzed the energetics of doping narrow BC tubes with metal atoms. The average binding energy for doping a BC tube with N metal atoms has been calculated using the formula (Refs. 45 and 46)

$$E_{\text{BIND}} = [E_{\text{TOT}}(\text{BCtube}) + N \times E_{\text{TOT}}(\text{Mfree}) - E_{\text{TOT}}(\text{BCtube} \sim M_N)]/N, \quad (1)$$

where $E_{\text{TOT}}(\text{BCtube} \sim M_N)$ is the total energy of the fully optimized BC nanotube doped with N metal atoms, $E_{\text{TOT}}(\text{BCtube})$ is the total energy of the optimized clean BC nanotube, and $E_{\text{TOT}}(\text{Mfree})$ is the energy of the dopant metal atom in vacuum. The calculated total energy for an isolated lithium atom was -0.2825 eV. We found that the binding energy corresponding to a BC tube with one interior Li atom per cell was greater in the case of the smaller diameter (6,0) BC tube (3.79 eV) than for the (4,4) BC tube (2.85 eV). This difference in the calculated binding energies may be related to the different number of atoms on the boron carbon tubular shells of the (cylindrical) zigzag (6,0) and (deformed) arm-chair (4,4) tubes which interact strongly with the Li atom.

Previous studies of doping SWCNTs with Li have shown an almost complete charge transfer from the Li atoms to the carbon shell.⁴⁷ We might thus expect that charge transfer from Li to the shell of a BC nanotube would also be significant due to the larger electronegativity of the boron and carbon atoms compared with Li. In fact, similar conclusions

FIG. 7. (a) Two-ring model where L is the distance between the metal atom and the first BC ring. (b) Variation of the total energy as the Li atom moves between the two BC rings for different distances between the rings.

FIG. 8. (Color online) (a) Total DOS for (4,4) BC tubes both clean and doped with one lithium atom, and (b) total DOS for (6,0) BC tubes both clean and doped with 1-3 Li atoms.

have been made by Zhou *et al.* who theoretically studied lithium adsorption in boron-doped SWCNTs. (Ref. 48). To confirm that the interaction of Li with a BC nanotube has a predominantly ionic character, we have calculated the charge density difference between a (6,0) BC tube doped with 1 lithium atom and a clean (6,0) BC tube. We then integrated this charge difference within a sphere of radius 1.0 Å (which is 50% larger than the ionic radius of Li) centered on the Li atom. The total charge within this sphere was found to be only 0.076 units of electron charge. We can thus confidently conclude that the Li atom gives up most of its charge to the BC shell.

The DOS structures for the (4,4) and (6,0) BC nanotubes doped with one Li are shown in Figs. 8(a) and 8(b). As can be seen, these Li-doped BC tubes are metallic. We also observe that, apart from a shift in the Fermi energy, doping with one Li atom per cell only produces small changes in the valence band DOS of the (6,0) BC tubes. This is evidenced by the very similar structure of the DOS for the clean and Li-doped (6,0) BC tubes [see Fig. 8(b)]. In the case of the (4,4) BC tubes, however, where doping produces significant structural changes, the DOS of the clean and Li-doped tubes are seen to be fairly different.

F. Doping the (6,0) BC tube with 2 and 3 Li atoms

As we have shown, the (6,0) BC tube preserves its shape upon doping with one Li atom per cell. We have thus conducted a series of spin-polarized calculations to study the effects of increased concentration of Li on the structural and electronic properties of (6,0) BC tubes. As shown in Figs.

6(c) and 6(d), the optimized (6,0) BC tube doped with two or three Li atoms per cell retains a cylindrical shape with the Li atoms positioned along the central axis of the tube forming a one-dimensional wire. The structural details of these tubes do not differ significantly from those of a (6,0) BC tube doped with just one Li atom, as can be seen from comparing the datasets in Table III. The periodic unit cell, whose length was allowed to vary along the longitudinal axis of the tube, was found to undergo minimal stretching to accommodate the additional Li atoms inside the tube. The diameters of the (6,0) BC tubes doped with two or three Li atoms are slightly smaller than the diameters of both the clean (6,0) BC tube and that doped with one Li atom. The Li-Li distance for a tube doped with two Li atoms is 2.43 Å, and reduces to ~1.63 Å for a tube doped with three Li atoms (see Table III).

The average binding energy values for the (6,0) BC tubes doped with two and three Lithium atoms are also presented in Table III. The average binding energy for the (6,0) BC tube doped with three Li atoms is observed to be much lower than the other values. This is most likely due to increased repulsion of the lithium atoms as the distance between them is decreased. Another important parameter to characterize doping is the heat of formation, H_N . This can be calculated using the formula (Refs. 49 and 50)

$$H_N = E_{\text{TOT}}(\text{BCtube} \sim M_{N-1}) + E_{\text{TOT}}(M_{\text{free}}) - E_{\text{TOT}}(\text{BCtube} \sim M_N), \quad (2)$$

where $E_{\text{TOT}}(\text{BCtube} \sim M_N)$ is the total energy of the fully optimized nanotube doped with N metal atoms, $E_{\text{TOT}}(\text{BCtube} \sim M_{N-1})$ is the total energy of a fully optimized nanotube doped with $(N-1)$ metal atoms, and $E_{\text{TOT}}(M_{\text{free}})$ is the energy of a single dopant atom in vacuum. The calculated values for the heat of formation are presented in Table III. The data shows that the heat of formation decreases with increasing doping. The negative value of the heat of formation for three dopant atoms per unit cell indicates that it would be difficult to achieve high concentrations of lithium by “inside” doping of an isolated (6,0) BC tube.

The DOS plots corresponding to (6,0) BC tubes doped with two and three Li atoms are also presented in Fig. 8(b). The peak structure of the total DOS for the (6,0) BC tubes doped with one, two, and three Li atoms only changes slightly from that of the clean (6,0) BC tube. Increasing the concentration of Li atoms in the (6,0) BC tube shifts the Fermi energy upwards, but does not lead to any significant change in the density of states at this level. The charge density plot for the (6,0) BC tube doped with three Li atoms presented in Fig. 9 shows that the electronic charge is mostly located on the BC hexagonal network, with only a small amount of charge spread along the line joining the Li atoms. This shows that there is an absence of covalent bonding between the Li atoms and the atoms on the tubular shell.

G. BC tubes doped by Cu

Doping with one Cu atom per cell drastically changes the shape of the tubular shell of the (6,0) zigzag BC tube to that of an ellipse [see Fig. 10(a)]. The minimum energy configu-

FIG. 9. Charge density contour plot for the (6,0) BC tube doped with three lithium atoms for a plane containing the longitudinal axis of the tube. The vertical dashed lines indicate the walls of the tube. The contour values are in units of electron charge.

ration for the (4,4) armchair BC tube is a rectangularlike structure with the Cu atom positioned on the central axis of the deformed shell [Fig. 10(b)]. The BC bond length for the Cu-doped (4,4) BC tube was found to range from 1.46 to 1.62 Å, with an average value of around 1.53 Å (see Table IV). For the Cu-doped (6,0) BC tube, the corresponding bond length values ranged from 1.50 to 1.60 Å with an average bond length of 1.55 Å. After geometry optimization, the interatomic distance between the Cu atoms of neighboring cells was 4.84 Å for the (6,0) tube, and 5.29 Å for the (4,4) tube. For such interatomic separations, interaction between neighboring Cu atoms should be negligible.

The differences in structure of the small-radius Cu-doped and Li-doped BC tubes can be explained by the different properties of the dopant atoms, such as their size and bonding preferences. Li atoms, which are quite small and very light, have only one *s* electron in their outer shell and hence tend to form ionic bonds by giving up this electron to more electronegative atoms (boron and carbon atoms in our case). A Cu atom, on the other hand, is much larger and heavier, and due to its electronic structure can form either ionic (4*s* electrons) or covalent (3*d* electrons) bonds, depending on the environment. The tendency of Cu atoms to form a covalent bond, and the different shell symmetry of the (6,0) zigzag and (4,4) armchair BC tubes, can explain the observed differences in the atomic structures of the Cu-doped tubes. The unique combination of the value of the diameter and the symmetry of the armchair (4,4) BC tube makes strong inter-

FIG. 10. Optimized structures of Cu-doped BC nanotubes: (a) (6,0) BC tube doped with one Cu atom, (b) (4,4) BC tube doped with one Cu atom, and (c) (4,4) BC tube doped with two Cu atoms. The Cu atoms are denoted by the black circles and the vertical dashed lines indicate the extent of the periodic unit cell.

actions between the *d* orbitals of the dopant Cu atom(s) and four Carbon atoms on opposite sides of the tubular shell especially favorable, and results in the stabilization of the rectangularlike shape of the doped (4,4) tube shown in Fig. 10(b). This is further illustrated by the charge density plot presented in Fig. 11(b). The smaller diameter zigzag (6,0)

TABLE IV. Properties of the (6,0) and (4,4) BC nanotubes doped with Cu. All the distances are in Å.

Cu-doped BC nanotube	1 Cu-doped (6,0)	1 Cu-doped (4,4)	2 Cu-doped (4,4)
Mean B-C bond length	1.55	1.53	1.55
Shortest B-C bond length	1.50	1.46	1.50
Longest B-C bond length	1.60	1.62	1.61
Mean B-Cu distance	2.37	3.01	2.79
Mean C-Cu bond length	2.15	2.20	2.36
Tubular cross section (max)	5.74	6.18	5.98
Tubular cross section (min)	3.95	4.40	4.73
Binding energy (eV)	4.32	2.98	3.37
Heat of formation (eV)			3.76

FIG. 11. Slices of the total charge density distribution for Cu-doped BC tubes: (a) (6,0) BC tube with one Cu atom per cell, (b) (4,4) BC tube with one Cu atom per cell, and (c) (4,4) BC tube with two Cu atoms per cell. In each case, the cross section on the left is for a plane containing the copper atom(s) and normal to the longitudinal axis of the tube, while the plot on the right includes the Cu atom(s) and the longitudinal axis of the tube. The graduated scales on the extreme right define the charge distribution in units of electron charge. The arrows denote the tube axis, and the vertical dashed lines indicate the walls of the tubes. The gray dashed lines in the left-hand figures indicate the directions of the nearest neighbor interactions between the dopant Cu atom(s) and the carbon atoms on the tubular shell.

tube, on the other hand, does not provide such commensurate symmetric sites for bonding of the Cu atom with the carbon atoms on the shell. This results in an elliptical deformation of the cross section of the (6,0) BC tube upon doping, as shown in Figs. 10(a) and 11(a).

We have also studied the effect of increased concentration of Cu atoms on the properties of the (4,4) BC tube. The optimized structure of the (4,4) BC tube doped with two Cu atoms per cell is shown in Fig. 10(c). As can be seen, this tube retains the rectangularlike cross section produced by doping with just one Cu atom per cell. Also, as in the case of doping with one Cu atom, the two Cu atoms form predominantly covalent bonds with the four closest carbon atoms of the tubular shell. The distance separating the two Cu atoms in this case is only 2.77 Å, which gives rise to significant interactions between them, as illustrated in Fig 11(c).

FIG. 12. DOS for the (6,0) and (4,4) Cu-doped BC tubes: (a) *l*-projected density of states for the copper atom for doping with just one Cu atom per cell, (b) total DOS for a clean (4,4) BC tube, and (4,4) BC tubes doped with one and two Cu atoms per cell. The Fermi energy in each case is indicated by the vertical dashed line.

The average binding energy and heat of formation for the Cu doped (4,4) BC tubes have been calculated using expressions (1) and (2) with $M=\text{Cu}$, and a total energy for a free copper atom of -0.234 eV. The results are presented in Table IV. The average binding energy of 4.32 eV for a (6,0) BC tube doped with one Cu atom per cell is significantly higher than that for the corresponding (4,4) BC tube (2.98 eV). Doping the (4,4) BC tube with a second Cu atom is seen to be energetically favorable with the average binding energy increasing by 0.39 eV. The corresponding heat of formation is positive and equal to 3.76 eV. This is related to the formation of Cu-Cu bonding as evidenced by the charge density distribution in Fig. 11(c).

The DOS of the (6,0) and (4,4) BC tubes doped with Cu atoms are shown in Fig. 12. In each case, the Cu-doped BC tubes are seen to be metallic. Comparison with the DOS of the corresponding clean BC tubes plotted in Fig. 5(a) reveals that doping with Cu produces significant changes. The valence band DOS of these narrow BC tubes is strongly influenced by the formation of covalent bonds between the copper atom(s) and the boron carbide tubular shell. For both the (6,0) and (4,4) BC tubes with a single Cu atom per cell, the DOS in the valence band region is dominated by a very large contribution from the Cu-*d* states [Fig. 12(a)]. Increasing the

doping of the (4,4) BC tube by adding a second Cu atom per cell also significantly changes the DOS structure. This can be seen from Fig. 12(b). As for the case of a single Cu atom per cell, it is mostly the valence band part of the DOS that is affected.

IV. DISCUSSION AND CONCLUSIONS

Using the *ab initio* DFT method we have investigated the structural and electronic properties of narrow BC nanotubes. We have shown that infinite narrow BC tubes are energetically more stable than the corresponding strips of boron carbide hexagonal sheets. We have also found that isolated clean BC tubes keep their tubular shape and that their total energy decreases with increasing diameter of the tube. Both boron carbide hexagonal layers and clean BC tubes are metallic.

Doping has been shown to strongly affect the atomic and electronic properties of narrow BC tubes, with the effect depending on the diameter and helicity of the tubes, and the type of dopant atom. (6,0) and (4,4) BC tubes doped with Cu and Li were determined to be metallic. Doping with Li has been shown to produce a tubular structure with the dopant atom positioned on the longitudinal axis for the (6,0) tube, but with the dopant atom bonded to one side of the tubular shell for the (4,4) BC tube. We have found that increased doping with Li (up to three lithium atoms per unit cell) does not significantly change the shape of the (6,0) BC tube. Doping with Li has also been found to shift the Fermi energy level, but no significant change in the DOS at this level has been observed. Calculations of the binding energy and heat of formation indicate that it would be difficult to achieve high concentrations of Li inside isolated, narrow (6,0) BC tubes. The bonding between the Li atoms and the boron carbon network has been determined to be of predominantly ionic character. It is the repulsive interactions between the Li ions that is believed to make the Li-doped BC tubes less stable at higher doping concentrations.

We have shown that doping narrow BC tubes with Cu leads to very different effects to those observed for Li dopant atoms. In contrast to Li, Cu atoms inside a (6,0) BC tube are bonded to one side of the shell, while in the (4,4) BC tube they are located along the central longitudinal axis and give rise to a regular, rectangularlike cross section for the shell. This rectangularlike shape is retained as the concentration of Cu is increased. The electronic structures of the (4,4) and (6,0) BC tubes both change significantly as a result of doping with Cu, with the valence band DOS being greatly enhanced by contributions from the Cu *d* orbitals. Analysis of the charge density distribution and projected DOS reveals a predominantly covalent character for the bonding between the *d* orbitals of the Cu atoms and the C atoms on the shell. Predominantly covalent bonds are also formed between the Cu atoms themselves. Our results show that the symmetric rectangularlike structure of the isolated (4,4) BC tube doped with higher concentrations of Cu is stabilized by the formation of these covalent bonds between the Cu dopant atoms. This is in contrast to the (6,0) tubes doped with Li. These tubes acquire their cylindrical shape due to charge transfer from the Li atoms to the shell, but are destabilized by the repulsive interaction between the dopant atoms at high concentration.

In conclusion, we have characterized both clean and doped BC nanotubes and shown them to be viable structures. The stability of these tubes under heat or mechanical treatment, however, still remains a subject for further careful investigation.

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