

# An *ab initio* investigation of boron nanotube in ringlike cluster form

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Four types of boron nanotubes (BNTs) in the form of double-ring basic units are theoretically predicted. The structure, stability, and electronic properties of these stable BNTs are investigated by the first-principles calculations. The BNT formed by the basic unit with one hole every six atoms on each ring is found to be more stable than those with other three types of basic units. By increasing diameter for boron ring, the stability is enhanced. The density of state demonstrates that BNTs formed by these basic units are metallic. © 2010 American Institute of Physics.

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Boron has a rather fascinating chemical property of forming diverse structures. Stable boron clusters can be constructed from the following two basic units only: a pentagonal pyramidal B<sub>6</sub> unit and a hexagonal pyramidal B<sub>7</sub> unit.<sup>1</sup> Furthermore, since Boustani investigated the small boron clusters and postulated the “Aufbau principle,” the boron nanostructures (quasiplane, ring, nanotube, and fullerene) have generated tremendous interest.<sup>2–26</sup> Among these studies, boron nanotube (BNT) has specially attracted more attention because of its special properties superior to other one-dimensional nanomaterials. The formation of BNT derived by the quasiplanar clusters was both theoretically predicted and experimentally synthesized.<sup>2,3</sup> Indeed, the existence of pure boron single-wall nanotubes has been confirmed in experimental studies.<sup>5,6</sup>

The structure and stability of basic unit play a key role for synthesizing nanotubes. It is well known that carbon nanotube is formed by rolling a single graphite layer into a cylinder. As far as the existence of BNT is concerned, one naturally postulates that the planar boron structure may be rolled into a BNT. The sheet models have been proposed in literature.<sup>11</sup> However, the boron sheet is not very stable for its large deformation and buckling, which is very different from the stable graphite sheet. Sheet model with holes, obtained by removing atoms from a flat triangular sheet has been suggested.<sup>12,13</sup> Another possible kind of basic unit for synthesizing BNT is the double-ring tubular (DRT) clusters. Such idea is mainly based on the fact that the DRT configuration is the most stable structure among various isomers of B<sub>20</sub>, B<sub>24</sub>, B<sub>30</sub>, B<sub>36</sub>, and B<sub>96</sub> clusters.<sup>20–23</sup> Moreover, the DRT clusters have been detected in experiments.<sup>25</sup> Our previous study also showed that for large sized boron clusters the three-ring tubular and DRT configuration are more stable than other ones.<sup>26</sup> Therefore, it is desirable to explore the stability, structure, and electronic properties of BNTs derived from the DRT clusters. In this letter, we report four types stable BNTs formed by the DRT clusters based on the results of binding energy and electronic properties.

We employed CASTEP<sup>27</sup> code within the generalized gra-

dient approximation treated by Perdew–Burke–Ernzerhof exchange–correlation potential<sup>28</sup> to perform first-principles calculations for exploring the structural and electronic properties of BNTs. Norm-conserving pseudopotentials were used. The calculations were performed using the plane-wave cutoff energy of 320 eV. The Brillouin zone sampling was performed using special *k* points generated by the Monkhorst–Pack scheme with parameters 1 × 1 × 7, which was used for the one dimensional infinite structures. The supercell geometry was taken to be a cubic cell with lattice constant sufficiently large to avoid interaction between the nanotubes (allowing at least 12 Å between nanotubes).

The basic units and corresponding BNT are displayed in Fig. 1, configuration *a* is double-ring basic unit. The number of boron atoms in each ring is *n*, one ring is rotated at an angle of  $\pi/n$  with respect to the other ring in order to form the staggered configuration. The geometries *b*, *c*, and *d* represent basic units with one boron atom being removed per interval of four, six, and eight atoms on each ring, respec-

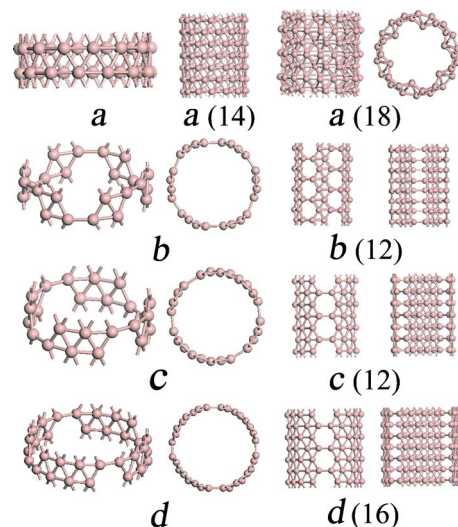


FIG. 1. (Color online) Front and top view of the basic units and corresponding nanotubes. The structure *a* is the DRT-based basic unit. The *b*, *c*, and *d* represent the structures with holes, in which nearest neighboring holes in the same ring are separated by four, six, and eight boron atoms, respectively. The data in brackets indicate the numbers of the boron atoms on each ring of the nanotubes.

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TABLE I. The bond length between borons in each ring ( $L_1$ ), the bond length between neighboring borons in two rings ( $L_2$ ), the average diameter in each ring ( $D_{ave}$ ), and the average binding energy per atom ( $E_b$ ) of the four types BNTs. The data in brackets indicate the numbers of boron atoms on each ring.

Type	Nanotube	$L_1$ (Å)	$L_2$ (Å)	$D_{ave}$ (Å)	$E_b$ (eV/atom)
<i>a</i>	0-hole-ring(14)	1.735	1.692	7.76	5.560
<i>a</i>	0-hole-ring(15)	1.721	1.683	8.06	5.611
		1.702–1.740		9.88	
buckled- <i>a</i>	0-hole-ring(18)	1.562–1.628	2.073/1.761	7.54/9.05	5.694
		1.702–1.740		11.47	
buckled- <i>a</i>	0-hole-ring(21)	1.540–1.610	1.753–2.096	9.05/10.29	5.734
<i>b</i>	3-hole-ring(12)	1.590/1.651	1.625/1.701	8.00	5.912
<i>b</i>	4-hole-ring(16)	1.590/1.652	1.630/1.700	10.42	5.942
<i>c</i>	2-hole-ring(12)	1.620–1.740	1.658–1.678	7.53	5.925
<i>c</i>	3-hole-ring(18)	1.630–1.727	1.700–1.718	11.15	5.962
<i>c</i>	4-hole-ring(24)	1.612–1.735	1.658–1.738	14.68	5.978
<i>d</i>	2-hole-ring(16)	1.611–1.730	1.658–1.734	9.50	5.938

tively. The nanotubes formed by these basic units are named as *a*-, *b*-, *c*-, and *d*-type nanotubes. The corresponding structural data for these types BNTs are listed in Table I, including the number of boron atoms in each ring of these basic units, the B–B bond lengths, and the diameter of the ring. In order to well understand the basic units, the open double rings on them are shown in Fig. 2. For the *a*-type nanotube, only the results of those nanotubes with 14 and 15 atoms on each ring are listed in this table. By increasing the ring diameter, *a*-type nanotube becomes buckled, the B–B bond length is shortened in each ring, but is lengthened between two rings. Figure 1 shows the *a*-type BNT and the buckled *a*-type one, of which the number of boron atoms are 15 and 18 on each ring, respectively. For the *a*-type nanotube, boron atoms on one ring do not form a circular configuration but a zigzagged structure. The results of the buckled *a*-type nanotubes are in excellent agreement with those reported in Ref. 11. According to the average binding energy ( $E_b$ ), buckled *a*-type nanotubes are more stable than *a*-type one. This is due to strong  $\sigma$  bonds of *sp* hybridization along the ring direction.<sup>11</sup>

It is well known that pure boron compounds have neither a purely covalent nor a purely metallic behavior. The multi-centered bonds exist in boron structures. The existence of three-centered bonding in a flat triangle sheet have been reported in previous work.<sup>11</sup> Tang *et al.*<sup>12</sup> confirmed that the triangle sheet has a surplus of electrons in antibonding states. The presence of these electrons reduces the stability of the flat sheet model and ultimately leads to the deformation of

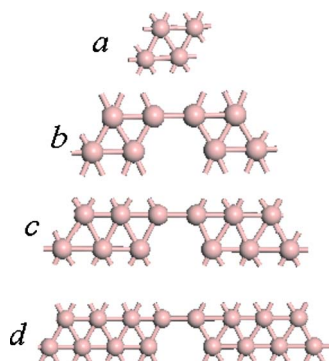


FIG. 2. (Color online) Open double rings of the basic units. The structure *a* is basic form of open double rings with 0 holes; *b*, *c*, *d* present basic forms of open double rings, in which neighboring holes of the same ring are separated by four, six, and eight boron numbers, respectively.

the flat triangle sheet into the buckled triangle sheet. Therefore, we attempt to discard boron atom on each ring of basic unit to check its stability. Interestingly, the  $E_b$  of the *b*-, *c*-, and *d*-types nanotubes are higher than that of the *a*-type nanotube. Moreover, the electronic population of B–B bond between two rings is improved from 1.01 e of *a*-type to 1.25 e in *b*-type ones. In addition, the graphiticlike basic unit was optimized, but the zigzag nanotube is easily deformed.

For completeness on the description of the studied BNTs, it is important to analyze their structural and electronic properties. The B–B bonds of *b*-, *c*-, and *d*-types nanotubes are about 1.60 Å and is shorter than that of *a*-type one. Moreover, at the proximity of the discarded boron position, the B–B bond lengths are about 1.70 Å. The minimum bond lengths are 1.71 Å and 1.62 Å for  $\alpha$ - and  $\beta$ -boron, respectively.<sup>29–31</sup> In well-known fullerene B<sub>80</sub>,<sup>7</sup> the neighboring B–B distances are about 1.727 Å for longer bond and 1.677 Å for shorter bond, respectively. The neighboring B–B distance becomes shorter on each ring, so the diameter of *c*-type nanotube is smaller than that of *a*-type one. For example, the average diameter is about 7.76 Å for *a*-type nanotube with 14 boron atoms on each ring, but the average diameter is 7.53 Å for *c*-type nanotube with 12 boron atoms on each ring, as shown in Table I.

We would like to discuss the difference in structures and energy between the present nanotubes and ones reported in Refs. 14 and 13. Tang and Ismail-Beigi<sup>12</sup> suggested two models of planar boron sheet ( $\alpha$ -sheet and  $\beta$ -sheet). Then, BNT formed by the  $\alpha$ -sheet was studied by two groups.<sup>13,14</sup> The main structural character of these nanotubes is that there are two boron atoms between the centers of two nearest neighboring holes (as shown in Fig. 1 of Ref. 13). For the present nanotube with holes (*b*-, *c*-, and *d*-types), there is no atom between the centers of two nearest neighboring holes (as shown in Fig. 1). The *b*-type nanotubes is similar to that formed by the  $\beta$ -sheet suggested in Ref. 12. The main structural difference of the *b*-, *c*- and *d*-types BNTs is the number of the boron atoms between the nearest neighboring holes in their basic units (the DRT clusters). In order to clearly show such difference, we plot the open DRT basic units in Fig. 2. As seen in this figure, for the *b*-, *c*-, and *d*-types DRT, there are four, six, and eight atoms between the nearest neighboring holes.

For the binding energy, the present four-types of nanotubes are energetically competitive to those based on the

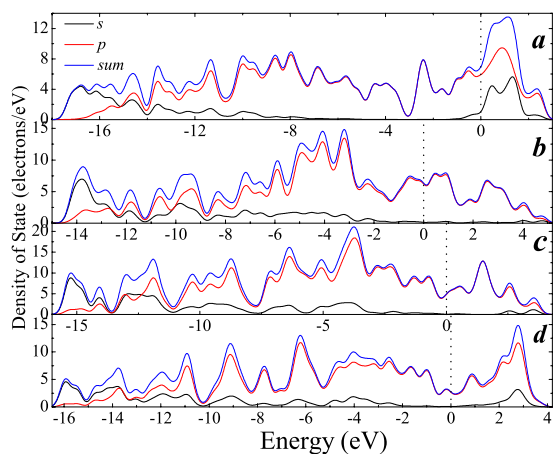


FIG. 3. (Color online) Total and orbital-decomposed density of states for nanotube formed by basic units *a* (15), *b* (16), *c* (24), and *d* (16). The values of brackets is the atomic numbers of each ring in different basic units.

sheet model with holes reported in Refs. 13 and 14. The  $E_b$  of zigzag nanotubes (9,0) and (12,0) with the diameters of 8.6 Å and 10.8 Å are about 5.95 eV/atom and 5.98 eV/atom, respectively. The  $E_b$  is 5.97 eV/atom for armchair nanotube (7,7) with the diameter of 11.18 Å. It is shown in Table I that the  $E_b$  is about 5.96 eV/atom for the nanotube with diameter of 11.15 Å and with eighteen atoms on each ring. Therefore, the stability is enhanced as the ring diameter increases.

Figure 3 shows the density of state (DOS) for BNTs based on *a*, *b*, *c*, and *d* basic units. The number of boron atoms for these rings are 15, 16, 24, and 16, respectively. Clearly, the metallic behavior is illustrated by the existence of electron states at the Fermi level. To get a more understanding of the states on the Fermi level, the projected orbital density of states onto the *s* and *p* orbitals are displayed in Fig. 3. As seen in this figure, the states at the Fermi level are dominated by the *p* orbital electrons. However, for the *a*-type nanotubes, electrons from *s* orbital also contribute to the states at the Fermi level. Moreover, the occurrence of pseudogap near the Fermi level indicates the enhanced stability of the *c*- and *d*-type nanotubes. Meanwhile, we calculated the total electron density (shown in Fig. 4), which is evenly distributed inner and outer sides for *a*-type nanotube. As seen in Fig. 4, *a*-type BNT is in a single layer structure. With the increment of diameter for each ring, the total electronic density has an anisotropic distribution for buckled *a*-type nanotube. The electronic density distribution of *b*-, *c*-, and *d*-types nanotubes are similar to that of *a*-type nanotube, except for the positions of the discarded boron atoms.

In conclusion, four types of stable BNTs formed by the DRT configuration are predicted according to the results of

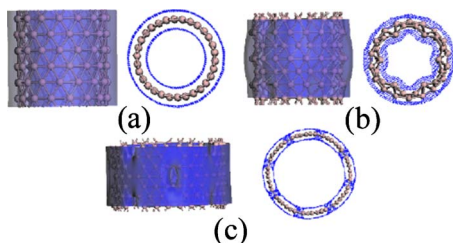


FIG. 4. (Color online) Total electron density at a contour value of 0.2 electron/Å<sup>3</sup> for nanotubes formed by: (a) *a* (15) basic unit; (b) buckled-*a* (18) basic unit; (c) *c* (24) basic unit. The values of brackets represent the atomic numbers of each ring in different basic units.

first-principles calculations. The calculated binding energy shows that they have a competing stability with the nanotubes formed by the boron sheets with holes. The highest binding energy of the BNT formed by *c* basic unit indicates its higher stability than the other three types. The calculated DOS shows that the four types of nanotubes are all metallic. Moreover, the results of binding energy imply that the nanotubes formed by the *b*, *c*, and *d* units are more stable than those formed by the basic unit *a*, which are mainly due to the strengthening of B–B bond between two rings by discarded atoms.

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- <sup>1</sup>I. Boustani, *Phys. Rev. B* **55**, 16426 (1997).
- <sup>2</sup>I. Boustani, A. Rubio, and J. Alonso, *Chem. Phys. Lett.* **311**, 21 (1999).
- <sup>3</sup>H. J. Zhai, B. Kiran, J. Li, and L. S. Wang, *Nature Mater.* **2**, 827 (2003).
- <sup>4</sup>S.-J. Xu, J. M. Nilles, D. Radisic, W. J. Zheng, S. Stokes, K. H. Bowen, R. C. Becker, and I. Boustani, *Chem. Phys. Lett.* **379**, 282 (2003).
- <sup>5</sup>D. Ciuparu, R. F. Klie, Y. Zhu, and L. Pfefferle, *J. Phys. Chem. B* **108**, 3967 (2004).
- <sup>6</sup>B. Kiran, S. Bulusu, H. J. Zhai, S. Yoo, X. C. Zeng, and L. S. Wang, *Proc. Natl. Acad. Sci. U.S.A.* **102**, 961 (2005).
- <sup>7</sup>N. G. Szwacki, A. Sadrzadeh, and B. I. Yakobson, *Phys. Rev. Lett.* **98**, 166804 (2007).
- <sup>8</sup>I. Boustani and A. Quandt, *Europhys. Lett.* **39**, 527 (1997).
- <sup>9</sup>A. Quandt and I. Boustani, *ChemPhysChem* **6**, 2001 (2005).
- <sup>10</sup>I. Boustani, A. Quandt, E. Hernandez, and A. Rubio, *J. Chem. Phys.* **110**, 3176 (1999).
- <sup>11</sup>J. Kunstmann and A. Quandt, *Phys. Rev. B* **74**, 035413 (2006).
- <sup>12</sup>H. Tang and S. Ismail-Beigi, *Phys. Rev. Lett.* **99**, 115501 (2007).
- <sup>13</sup>X. Yang, Y. Ding, and J. Ni, *Phys. Rev. B* **77**, 041402(R) (2008).
- <sup>14</sup>A. K. Singh, A. Sadrzadeh, and B. I. Yakobson, *Nano Lett.* **8**, 1314 (2008).
- <sup>15</sup>Q. B. Yan, X. L. Shen, Q. R. Zheng, L. Z. Zhang, and G. Su, *Phys. Rev. B* **78**, 201401(R) (2008).
- <sup>16</sup>Q. B. Yan, Q. R. Zheng, and G. Su, *Phys. Rev. B* **77**, 224106 (2008).
- <sup>17</sup>A. Y. Liu, R. R. Zope, and M. R. Pederson, *Phys. Rev. B* **78**, 155422 (2008).
- <sup>18</sup>D. L. V. K. Prasad and E. D. Jemmis, *Phys. Rev. Lett.* **100**, 165504 (2008).
- <sup>19</sup>U. Riaz, S. Ahmad, and S. M. Ashraf, *Nanoscale Res. Lett.* **3**, 45 (2008).
- <sup>20</sup>S. Chacko, D. G. Kanhere, and I. Boustani, *Phys. Rev. B* **68**, 035414 (2003).
- <sup>21</sup>W. An, S. Bulusu, Y. Gao, and X. C. Zeng, *J. Chem. Phys.* **124**, 154310 (2006).
- <sup>22</sup>K. C. Lau, M. Deshpande, R. Pati, and R. Pandey, *Int. J. Quantum Chem.* **103**, 866 (2005).
- <sup>23</sup>I. Boustani, A. Quandt, and A. Rubio, *J. Solid State Chem.* **154**, 269 (2000).
- <sup>24</sup>J. Wang, Y. Liu, and Y. C. Li, *ChemPhysChem* **10**, 3119 (2009).
- <sup>25</sup>M. A. L. Marques and S. Botti, *J. Chem. Phys.* **123**, 014310 (2005).
- <sup>26</sup>F. Y. Tian and Y. X. Wang, *J. Chem. Phys.* **129**, 024903 (2008).
- <sup>27</sup>S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M. C. Payne, *Z. Kristallogr.* **220**, 567 (2005).
- <sup>28</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>29</sup>B. F. Decker and J. S. Kasper, *Acta Crystallogr.* **12**, 503 (1959).
- <sup>30</sup>J. L. Hoard, D. B. Sullenger, C. H. L. Kennard, and R. E. Hughes, *J. Solid State Chem.* **1**, 268 (1970).
- <sup>31</sup>B. Callmer, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **33**, 1951 (1977).