

## Boron fullerenes: From $B_{80}$ to hole doped boron sheets

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We demonstrate the existence of a family of stable *boron fullerenes* containing  $80n^2$  atoms that is related to the family of  $60n^2$  carbon icosahedral fullerene series and is compatible with the recently proposed stable boron sheets composed of triangular and hexagonal motifs. All electron density-functional calculations on the  $B_{320}$ ,  $B_{720}$ ,  $B_{1280}$ , and  $B_{2000}$  confirm their stability and show that the quantum size effects open up electronic band gaps in the boron fullerenes at  $B_{1280}$ . Boron fullerenes below  $B_{2000}$  have valence electronic structure identical to their corresponding carbon cousins from  $60n^2$  family.

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Since the discovery of carbon fullerenes and nanotubes, several studies have examined the possible existence of hollow cage structures for the neighboring element, boron.<sup>1-5</sup> Boron, with three valence electrons in  $2s$  and  $2p$  orbitals, can form  $sp^2$  hybridized orbitals. The crystalline forms of boron contain  $B_{12}$  icosahedral units, but the most stable structure of bulk boron is controversial.<sup>6-8</sup> In cluster form, for very small sizes containing up to 20 atoms, it prefers planar or quasi-planar structures. The planar to three-dimensional transition in boron clusters seems to occur around  $B_{20}$ .<sup>9,10</sup> Around this size the double ring tubular structures are more favorable. The extended planar honeycomb sheet, i.e., graphene equivalent of boron, is electron deficient and unstable.<sup>11,12</sup> The addition of a boron atom at the center of each hexagon results in a triangular sheet which is electron rich. This sheet is compatible with Aufbau principle of Boustani,<sup>4</sup> which suggests that the most stable boron nanostructures would be based on buckled triangular motifs.<sup>13</sup> The flat triangular sheet buckles when optimized and is more stable than the planar honeycomb sheet. The nanotubes formed by curling up the buckled triangular sheets are metallic.<sup>11</sup>

During the last year, a number of interesting works on boron nanostructures have been reported (cf. Fig. 1).<sup>14-20</sup> In the first of these, a stable hollow cage structure of 80 boron atoms was reported by Szwacki *et al.*<sup>14</sup> The most interesting aspect of the  $B_{80}$  is its structural resemblance with  $C_{60}$  fullerene. The basic framework of the  $B_{80}$  fullerene is similar to that of  $C_{60}$  with 12 pentagonal and 20 hexagonal rings (see Fig. 1). The  $B_{60}$ , an exact analog of  $C_{60}$ , is electron deficient and unstable. However, an addition of 20 boron atoms at the center of each hexagonal ring stabilizes the electron deficient  $B_{60}$  to give the stable  $B_{80}$  fullerene. The  $B_{80}$  fullerene is isovalent (equal number of valence electrons) with  $C_{60}$ . Szwacki *et al.*<sup>14</sup> explained the stability of  $B_{80}$  fullerene in terms of its structure of six interwoven double rings.

About the same time, Tang and Ismail-Beigi,<sup>15</sup> and Yang *et al.*<sup>16</sup> proposed novel boron sheets that consist of combinations of triangular and hexagonal rings (cf. Fig. 1). These boron sheets are obtained by removing atoms from flat triangular sheets and can be viewed as hole doped triangular sheets. This arrangement provides optimal balance of the

electron count. Density-functional calculations show that these sheets are metallic and that they are the most stable boron sheets known so far. Their stability is explained as a consequence of competition between three-center and two-center bondings,<sup>15</sup> which incidentally also explains the stability of the closed shell  $B_{80}$  fullerene. The nanotubes obtained from these boron sheets are metallic or semiconductors depending on the diameter and are the most stable boron nanotubes predicted so far.<sup>16,17</sup>

In this Rapid Communication, we use this new understanding of the bonding picture in the boron sheet to show the existence of an infinite series of boron fullerenes that are analogous to the  $60n^2$  icosahedral carbon fullerenes. The two limits of this infinite boron fullerene series are the  $B_{80}$  fullerene<sup>14</sup> and the most stable boron sheet composed of triangular and hexagonal rings.<sup>15,16</sup> We illustrate a procedure to construct proposed  $80n^2$  fullerenes starting from the boron sheet. For a given  $n$ , the boron fullerene from the  $80n^2$  fullerene series has exactly the same number of valence electrons as the corresponding  $60n^2$  carbon fullerene series. We

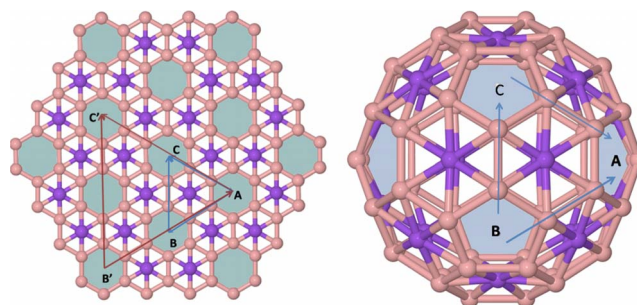


FIG. 1. (Color online) A piece of the most stable hole doped boron sheet (left). If purple/dark gray atoms are omitted one gets graphene sheet. The  $B_{80}$  fullerene (right) can be constructed by pasting triangle  $ABC$  (cut from boron sheet) on the 20 triangular faces of icosahedron. If triangle  $ABC$  is cut from graphene and pasted on icosahedron faces one gets  $C_{60}$  fullerene. Each triangle obtained from boron sheet has exactly  $n^2$  extra atoms than the one cut from graphene sheet. The  $80n^2$  boron and  $60n^2$  carbon fullerenes are related similar to alpha-boron and graphene sheets.

then perform all electron density-functional calculations on  $B_{80}$ ,  $B_{320}$ ,  $B_{720}$ ,  $B_{1280}$ , and  $B_{2000}$ , smallest five members of the family. Our calculations not only show that each boron fullerene in this series is more stable than the preceding member but also pinpoint the size regime ( $B_{1280}$ ) at which the quantum size effects set in and open up the *band* gap. Below this size, the calculations show striking similarities between the valence electronic structure of the boron fullerenes and their carbon cousins. These calculations connect the  $B_{80}$  fullerene to the most stable boron sheet.

Figure 1 shows a piece of *hole* doped boron sheet along with  $B_{80}$  fullerene. If the atoms at the center of hexagonal rings (colored dark gray and purple online) are omitted then one gets a piece of graphene sheet. The members of the proposed boron fullerenes can be generated from the boron sheet by cutting equilateral triangles and pasting them on to the triangular patches of icosahedron. The triangles  $ABC$  in Fig. 1 when pasted on 20 triangular faces of icosahedron will result in  $B_{80}$  fullerene. The equilateral triangle  $ABC$  is obtained by starting from the center of a hole (point A) and taking a step to the center of an adjacent hexagon (with central atom). The second similar step is taken along a direction at  $120^\circ$  to the previous one. Thus one step in each direction will take us from point A to point B, which defines the edge of the triangle. Larger equilateral triangle  $AB'C'$  can be constructed by taking two steps in each of two directions. The  $AB'C'$  triangles when pasted on icosahedron will give the  $B_{320}$ . The equilateral triangles obtained by taking  $(n, n)$  from a hole to another hole can be used to construct  $n$ th member of the  $80n^2$  fullerene. Note that if equilateral triangle is cut from graphene sheet instead of boron sheet one obtains the corresponding member of  $60n^2$  carbon fullerene. We use such procedure to construct the  $B_{80}, B_{320}, B_{720}, B_{1280}, B_{2000}, \dots$  from boron sheet and the  $C_{60}, C_{240}, C_{540}, C_{960}, C_{1500}, \dots$  from graphene sheet. Each boron fullerene in this series has exactly the same number of valence electrons as its *parent* carbon fullerene. The structural models of the  $B_{320}$ ,  $B_{720}$ ,  $B_{1280}$ , and  $B_{2000}$  fullerenes are illustrated in Fig. 2. These boron fullerenes are basically cages made from interlocking of larger double rings of boron atoms. The increased number of double rings of larger radii enhances the stability of these larger fullerenes. The  $80n^2$  boron fullerenes are the finite analogs of the most stable boron sheet. This can also be understood by computing the *hole density* for the fullerene series. This hole density in the asymptotic limit should approach  $1/9$ , the value obtained by Tang and Ismail-Beigi<sup>15</sup> for the most stable boron sheets. Following these authors, we define the *hole density* as  $\eta = \frac{n_{\text{hole}}}{n_t}$ , where  $n_{\text{hole}}$  is the number of rings without an atom at the center (holes) and  $n_t$  is the total number of atoms there would be if the fullerene were built from a triangular lattice (i.e., the fullerene built using Aufbau principle). As the boron fullerenes are built from the corresponding icosahedral carbon fullerenes, the total number of hexagonal rings ( $n_h$ ) for a given  $n$  is  $\frac{60n^2-20}{2}$ . Each fullerene has exactly 12 pentagonal rings; hence,  $n_t = 60n^2 + n_h + 12 = 90n^2 + 2$ . Similarly, the number of holes in the boron fullerene is given by  $n_{\text{hole}} = n_h - (80n^2 - 60n^2) + 12 = 10n^2 + 2$ . Hence, the hole density

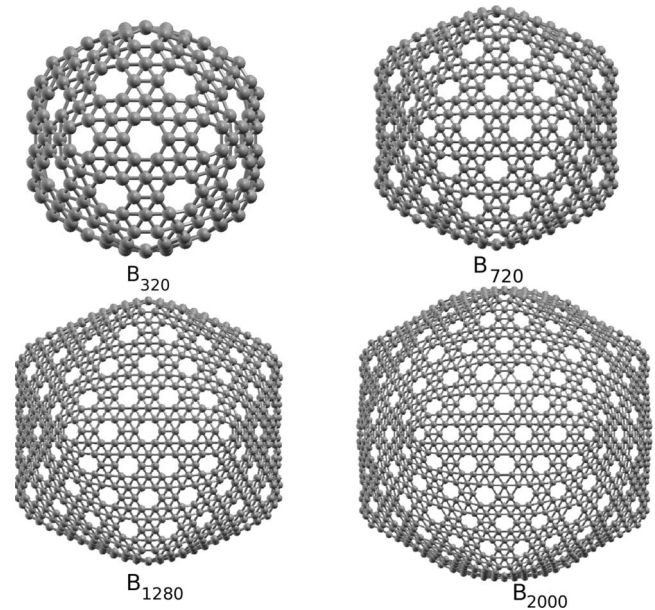


FIG. 2. The  $B_{320}$ ,  $B_{720}$ ,  $B_{1280}$ , and  $B_{2000}$  boron fullerenes from the  $80n^2$  boron fullerenes series.

$$\eta = \frac{10n^2 + 2}{90n^2 + 2}.$$

As  $n \rightarrow \infty$ ,  $\eta$  becomes  $\frac{1}{9}$ ; thus, for very large fullerene the hole density approaches the value ( $1/9$ ) of the most stable boron sheets.<sup>15</sup> The  $80n^2$  boron fullerenes hence are closed finite analogs of the most stable boron sheets.

The larger  $60n^2$  carbon fullerenes have greater binding energy (BE) than the  $C_{60}$  fullerene due to relief in the strain as a consequence of reduction in the curvature.<sup>21,22</sup> Similarly, the larger boron fullerenes are expected to be energetically more favorable than the  $B_{80}$  fullerene. To ascertain if this indeed is the case, we have performed all electron density-functional calculations on  $B_{320}$ ,  $B_{720}$ ,  $B_{1280}$ , and  $B_{2000}$ . We use fully analytic implementation of density-functional theory (DFT) with Slater's exchange parameter obtained from the exact atomic energy of boron atom.<sup>23,24</sup> The  $6-311G^{**}$  basis set with 18 basis functions per atom is used to express molecular orbitals. The structures are optimized using icosahedral symmetry until the root-mean-square gradient was less than 0.0001 Hartree/Bohr. (For  $B_{1280}$  and  $B_{2000}$ , the convergence criterion was relaxed to 0.01 Hartree/Bohr). While the  $B_{80}$  fullerene has been shown to have lower  $T_h$  symmetry,<sup>25,26</sup> the energy gain upon symmetry reduction is only about 0.0006 eV/atom, and structural distortions from icosahedral symmetry are very small. So to make the present calculations feasible, the larger boron fullerenes have been constrained to have icosahedral symmetry. The binding energies of optimized boron fullerenes presented in Table I show that their stability increases as their size increases. All fullerenes studied are more stable than the recently proposed  $B_{80}$  fullerene.<sup>14</sup> The binding energy increases systematically with size and will approach the cohesive energy of the *most* stable boron sheets in our model. Our model yields larger binding energy for  $B_{80}$  fullerene than previously reported

TABLE I. The first two columns list boron fullerenes and their parent carbon fullerenes. The BE per atom and the valence electronic structure of boron fullerenes are presented in the remaining columns. The B<sub>2000</sub> is metallic. The electronic structure shown in the last row is that of C<sub>1500</sub>. See text for more details.

B fullerene	C fullerene	BE (eV)	Valence electronic structure
B <sub>80</sub>	C <sub>60</sub>	6.82	4h <sub>u</sub> 7h <sub>g</sub> 4g <sub>u</sub> 4g <sub>g</sub> 4t <sub>1u</sub> 1t <sub>1g</sub> 3a <sub>g</sub> 4t <sub>u</sub> 1t <sub>2g</sub>
B <sub>320</sub>	C <sub>240</sub>	6.94	17h <sub>u</sub> 23h <sub>g</sub> 16g <sub>u</sub> 16g <sub>g</sub> 15t <sub>1u</sub> 9t <sub>1g</sub> 7a <sub>g</sub> 1a <sub>u</sub> 15t <sub>2u</sub> 9t <sub>2g</sub> 41h <sub>u</sub> 50h <sub>g</sub> 36g <sub>u</sub> 36g <sub>g</sub> 31t <sub>1u</sub> 22t <sub>1g</sub> 14a <sub>g</sub> 5a <sub>u</sub> 31t <sub>2u</sub> 22t <sub>2g</sub>
B <sub>720</sub>	C <sub>540</sub>	6.96	74h <sub>u</sub> 86h <sub>g</sub> 64g <sub>u</sub> 64g <sub>g</sub> 54t <sub>1u</sub> 42t <sub>1g</sub> 22a <sub>g</sub> 10a <sub>u</sub> 54t <sub>2u</sub> 42t <sub>2g</sub>
B <sub>1280</sub>	C <sub>960</sub>	7.01	118h <sub>u</sub> 133h <sub>g</sub> 100g <sub>u</sub> 100g <sub>g</sub> 82t <sub>1u</sub> 67t <sub>1g</sub> 33a <sub>g</sub> 18a <sub>u</sub> 82t <sub>2u</sub> 67t <sub>2g</sub>
B <sub>2000</sub>	C <sub>1500</sub>	7.02	

values<sup>14</sup> but it will provide correct trends. Recently, stuffed boron cages were shown to be energetically more stable than B<sub>80</sub> fullerene, with B<sub>101</sub> cage as the most stable among those studied.<sup>18</sup> We optimized B<sub>101</sub> and B<sub>320</sub> cages by the NRLMOL code<sup>27</sup> using generalized gradient approximation and Gaussian basis set with 41 basis functions per atom. The B<sub>320</sub> fullerene is more stable than B<sub>101</sub> by about 0.05 eV.

As discussed earlier, the 80n<sup>2</sup> boron fullerenes are structurally related to the 60n<sup>2</sup> carbon fullerenes. This structural resemblance leads to interesting similarities in their electronic structure. For a given n, the 80n<sup>2</sup> boron fullerene is *isovalent* with 60n<sup>2</sup> carbon fullerene. Our DFT calculations show that they are not only isovalent but they have *identical* valence electron structure. The valence electrons in the boron fullerene occupy exactly the same irreducible representations as the electrons in the parent carbon fullerene. The valence electronic structure of the icosahedral boron fullerenes studied is given in Table I. The inspection of eigenvalues (cf. Table II) shows that the highest occupied molecular orbital (HOMO) is destabilized in boron fullerene(s) in comparison with that in the parent carbon fullerene(s). This can be understood qualitatively by treating the fullerene cage as a simple spherical well in which valence electrons freely move. Then the electronic energy is inversely proportional to the square of the radius of the well. The larger size of boron fullerenes compared to carbon fullerene means that the valence electrons in the boron fullerene experience a less attractive potential; as a result of which the eigenvalues in boron fullerene are shifted above. The higher values of the lowest occupied valence molecular orbital energies (cf. Table II) observed in case of boron fullerenes are consistent with this picture. The destabilization may also be responsible for the smaller values of the energy gap between the HOMO and the lowest unoccupied molecular orbital (LUMO) in the boron fullerenes. The electronic structure of the boron fullerenes indicates systematic decrease in HOMO-LUMO gaps. The HOMO-LUMO gaps for B<sub>80</sub>, B<sub>320</sub>, and B<sub>720</sub> are 1.0, 0.34, and 0.14 eV. The boron fullerenes are finite analogs of the hole doped alpha-boron sheet which is metallic. Likewise, carbon fullerenes are finite analogs of graphene. The carbon fullerenes evolve precisely and uniquely to the semimetal graphene sheet with two states of which only one is singly occupied at the K point in the two-dimensional (2D)

Brillouin zone. This means that there is a size regime, a transition point, where the similarities observed in the valence electronic structure of the boron and carbon fullerenes will disappear. Our calculations explicitly show that this transition point occurs at B<sub>1280</sub>. The HOMO-LUMO gap nearly vanishes for B<sub>1280</sub> while B<sub>2000</sub> is metallic. The bulk boron sheet is metallic.<sup>15</sup> Thus, the gap opens up at B<sub>1280</sub> due to the quantum size effects in the finite boron clusters (fullerenes). The disappearance of gap is most likely due to larger interatomic distances in boron fullerenes. Considering that the HOMO-LUMO gap is underestimated by the local approximation such as the one used in this work, the precise size at which transition occurs will be larger than the B<sub>1280</sub>. However, the trend that the quantum confinement occurs at much smaller sizes in boron fullerenes than their carbon cousins is expected to remain valid in more accurate theories.

We have shown the existence of an infinite series of 80n<sup>2</sup> boron fullerenes that connects the B<sub>80</sub> fullerene and the most stable hole doped boron sheets—two recent major discoveries on boron nanostructures. We have illustrated a procedure to generate the structures of proposed fullerenes starting from most stable boron sheet. Our calculations show (i) that

TABLE II. The eigenvalues and symmetries of the highest occupied molecular orbital and the lowest occupied valence molecular orbital. B<sub>2000</sub> is metallic.

Fullerene	HOMO		LOVMO	
	-ε (eV)	Symmetry	-ε (eV)	Symmetry
C <sub>240</sub>	5.7	h <sub>u</sub>	24.5	a <sub>g</sub>
B <sub>320</sub>	4.7	h <sub>u</sub>	20.8	a <sub>g</sub>
C <sub>540</sub>	5.3	h <sub>u</sub>	25.0	a <sub>g</sub>
B <sub>720</sub>	4.5	h <sub>u</sub>	20.8	a <sub>g</sub>
C <sub>960</sub>	5.3	h <sub>u</sub>	24.3	a <sub>g</sub>
B <sub>1280</sub>	4.4	h <sub>u</sub>	20.7	a <sub>g</sub>
C <sub>1500</sub>	5.3	h <sub>u</sub>	24.9	a <sub>g</sub>
B <sub>2000</sub>			20.7	a <sub>g</sub>



the proposed boron cages are energetically stable with increasing binding energy, ii) the smooth interpolation of the electronic properties (binding energy and the HOMO-LUMO gap) between the two limits, iii) the striking similarities in the structural and the electronic aspects of  $80n^2$  boron fullerenes, (vi) that the members of  $80n^2$  boron fullerenes except the first one have larger binding energy than the  $B_{101}$  stuffed boron fullerene,<sup>18</sup> and (v) while the members of  $80n^2$  boron fullerenes become metallic around  $n=4-5$  ( $B_{1280}$ - $B_{2000}$ ) their  $60n^2$  carbon cousins are semiconductors, The quantum size effects open gaps in  $80n^2$  boron fullerenes around  $B_{1280}$ , which highlight interesting *similarities* and *dif-*

*ferences* in the electronic structure of carbon and boron fullerenes. At this point, we would like to note that we have recently become aware of another work which describes generation of boron fullerenes using modified leapfrog algorithm.<sup>28</sup>

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