Characterization and Application of Nanomaterials (2020) Volume 3 Issue 2
doi:10.24294/can.v3i2.761

ORIGINAL RESEARCH ARTICLE

Relative stability of planar clusters B_{11}, B_{12}, and B_{13} in neutral- and charged-states

Levan Chkhartishvili

Department of Engineering Physics, Georgian Technical University, Tbilisi, Georgia;
E-mail: chkharti2003@yahoo.com

ABSTRACT

Theoretically, within the diatomic model, the relative stability of most abundant boron clusters B_{11}, B_{12}, and B_{13} with planar structures in neutral, positive and negative charged-states is studied. According to the specific (per atom) binding energy criterion, B_{12}^{+} (6.49 eV) is found to be the most stable boron cluster, while B_{11}^{-} + B_{13}^{+} (5.83 eV) neutral pair is expected to present the preferable ablation channel for boron-rich solids. Obtained results would be applicable in production of boron-clusters-based nanostructured coating materials with super-properties such as lightness, hardness, conductivity, chemical inertness, neutron-absorption, etc., making them especially effective for protection against cracking, wear, corrosion, neutron- and electromagnetic-radiations, etc.

Keywords: Cluster; Charge State; Specific Binding Energy; Diatomic Model; Relative Stability; Clusters-based Coating Material; Boron

ARTICLE INFO

Article history:
Received 12 June 2020
Received in revised form 4 July 2020
Accepted 7 July 2020
Available online 20 July 2020

1. Introduction

Boron-clusters-based nanostructured coating materials due to their super-properties such as lightness, hardness, conductivity, chemical inertness, neutron-absorption, etc. can serve for effective protection against cracking, wear, corrosion, neutron- and electromagnetic-radiations, etc.[1,2]. This makes boron clusters B_n, n=1,2,3,…, interesting to be investigated in details.

Summarizing experimental and theoretical data available in the literature on all-boron nanomaterials (e.g. see our overviews on subject[3-5]), one can conclude that, according to the specific (per constituting atom) binding energy ε criterion, ultra-small, with $n \leq 20$, boron clusters prefer (quasi)planar structures, while at higher n, they should be wrapped first into cylinders and then into spheres forming boron nanotubes or boron fullerenes, respectively. In (quasi)planar clusters, ε increases with n because of increasing in mean coordination number of constituent atoms. Within the initial approximation, specific binding energy of boron clusters is expected to be almost saturated around $n \geq 10$. But, when the polarity deal into the bonding — commonly characteristic of structures of identical atoms with differently coordinated atomic sites — is taken into account, there is expected a weak maximum instead. In general features, the experimental mass-spectra fits these theoretical findings. However, formation probability peak is well-pronounced for species B_{11}, B_{12}, and B_{13}. Naturally, such a behavior is related not only to the energy-factor, but mainly to the process kinetics. Usually, boron clusters are formed by the ablation of elemental boron or boron-rich solid materials, main structural motifs of which are slightly deformed regular icosahedra of boron atoms B_{12}[6].

Present paper aims to theoretically study the relative stability of most abundant boron clusters B_{11}, B_{12}, and B_{13} with (quasi)planar structures in different charged-states.

2. Method of calculations

In clusters of identical atoms, binding energy per atom, i.e., specific binding energy, serves for the key factor determining their relative stabilities and, consequently, concentrations of clusters with different numbers of atoms in the products of ablation of corresponding solid materials.

Based on various ab initio methods specific binding energy and some other important physical characteristics of boron clusters were numerically calculated by Boustani *et al*. (summarizing of these studies see in the study of Boustani[7]) and some other teams (see above cited reviews and references therein). But, more vividly these species can be descried based on the diatomic model. It should be noted that such model-based approach provides quite good quantitative results as well.

The application of the Fermi's old diatomic model[8] to the multi-atomic structures is based on the property of interatomic bonding to be saturated. In the initial, i.e., pair interactions, approximation the binding energy of a structure simply equals to the sum of energies of interactions between neighboring atoms. Based on the pair interactions approximation, microscopic theory of expansion and its generalization to the periodical structures allow correct estimation of the thermal expansion coefficient for number of crystalline substances[9]. Despite its simplicity, the diatomic model is still successfully used to calculate anharmonic effects in solids[10]. An analogous approach was used by us to explain isotopic effects of thermal expansion and melting in all-boron lattices[11-15].

Suppose that the index $i = 1,\dots, n$ numbers the atoms constituting cluster of n atoms, and C_i are their coordination numbers, respectively. In the initial approximation, binding energies between each pair of adjacent atoms E_0 are equal, and it turns out that:

$$\varepsilon \approx \frac{E_0}{2n}\sum_{i=1}^{i=n} C_i \qquad (1)$$

Here, the factor ½ is introduced to correct the double sum which includes every pair of neighboring atoms twice. We used approximated formula (1) to estimate ground-state binding energy of all-boron nanostructures, mainly, boron nanotubes[16-18].

However, clusters are finite structures of atoms and, consequently, coordination numbers of sites at center are higher than that at periphery. This leads to the redistribution of the outer valence shell electrons and, as a result, differences between binding energies of neighboring atomic pairs. Note the report[19] on high-pressure experiments and ab initio evolutionary crystal structure predictions that explore the structural stability of boron under pressure and reveal a partially ionic high-pressure boron phase.

Our formulation of the first approximation to the diatomic model theory takes into account corresponding polarity of the bonds. In case of identical constituent atoms, it is obvious to assume that these electrons between the atoms are divided proportionally to their coordination numbers. This implies that the atoms develop non-zero effective static atomic charges with charge numbers Z_i determined from the relation:

$$\frac{nZ_i}{V} = 1 - \frac{nC_i}{\sum_{j=1}^{j=n} C_j} \qquad (2)$$

respectively, Here V is the total number of the outer valence shell electrons in the atoms constituent cluster.

Thus, the binding energy per atom in the first approximation, i.e., including correction related to the interatomic bonds polarity, is:

$$\varepsilon \approx \frac{1}{2n}\sum_{i=1}^{i=n}(E_0 C_i - E_1 Z_i \sum_{k_i=1}^{k_i=C_i} Z_{k_i}) \qquad (3)$$

Where the index $K_i = 1,\ldots,C_i$ numbers the nearest neighboring atoms of i -atoms, respectively;

$$E_1 = \frac{e^2}{4\pi\varepsilon_0 d} \qquad (4)$$

is the energy-dimension parameter (e and ε_0 are elemental charge and electric constant, respectively); and d is the initial bonds length in the equilibrium.

In our previous studies[20-23], relations (2), (3), (4) are used to estimate effective static atomic charges, dipole moment, and specific binding energy in the boron planar clusters.

Further improvement of this approximation means determination of the equilibrium bond length in the first approximation as well. It can be done by the minimization of the system potentials energy including bond length-dependent vibrational and electrostatic interaction energies[24].

Within the frame of the diatomic approach, further refinement of the clusters' binding energy and other ground-state parameters can be achieved by abandoning the requirement for equality of all the bond lengths. In another study of mine [25], a general theoretical frame for further studying is provided. Finally, we have got a set of linear equations determining not precisely planar, but quasi-planar equilibrium cluster configurations.

Finally, all the above described theory-levels of the diatomic approach are summarized in the mini-review[26].

By definition, cluster binding energy is the difference between sum of energies of isolated atomic particles and energy of their bounded structure. Energy of a neutral atom exceeds that of positive ion by the ionization potential (IP), while is less by the electron affinity (EA) that of negative ion. Let Q=0, $\pm 1,\ldots,\pm n$ be the ionic charge number of the cluster, then,

$$\varepsilon_Q = \frac{QE_Q}{n} \qquad (5)$$

should be the specific binding energy correction related to its charge state if E_Q is IP or EA depending on the sign of Q. Taking into account this correction, in present work, specific binding energy of planar boron clusters are estimated from the relation:

$$\varepsilon \approx \frac{1}{n}\left(\frac{1}{2}\sum_{i=1}^{i=n}(E_0 C_i - E_1 Z_i \sum_{k_i=1}^{k_i=C_i} Z_{k_i}) + E_Q Q\right) \qquad (6)$$

3. Species studied and results

Because B_{12} icosahedral clusters are the main structural units of structural modifications of boron and boron-rich compounds, here we studied stability of planar boron clusters B_{11}, B_{12} and B_{13} with almost the same number of constituent atoms both in neutral- and charged-states.

For obtaining numerical results, one needs input parameters such as E_0 and E_1 (or d) characteristic of pair interaction between two boron atoms. They can be found e.g. from the quasi-classical B–B potential[27]: $E_0 \approx 2.80$ eV, $E_1 \approx 8.09$eV; and $d \approx 1.78$ Å. Note that this potential was successfully applied to explaining of the above mentioned isotopic effects of boron atoms also in geometric models for boron nanostructures[28].

As for IP and EA of boron atom, they equal to $E_{+1} \approx 8.30$ eV and $E_{-1} \approx 0.28$ eV, respectively[29]. Outer valence shell of the isolated B-atom contains a single 2p-electron. Consequently, their total number V=10 in B_{11}^{+}, V=11 in B_{11}^{0} and B_{12}^{+}, V=12 in B_{11}^{-}, B_{12}^{0} and B_{13}^{+}, V=13 in B_{12}^{-} and B_{13}^{0}, and V=14 in B_{13}^{-}, respectively. Obtained results of calculations confirmed the expectation that cluster-isomers with symmetrical shapes and without holes (vacant sites) in their structure, i.e., with the maximal number of interatomic bonds, should be most stable. Correspondingly, in the tables below, we present structures and characteristics only for ground-state isomers.

Table 3-1 shows that among the neutral clusters studied, the atomic charges are maximal in B_{11}, apparently because of its asymmetric structure. On contrary, symmetric clusters B_{12} and B_{13} reveal higher polarity of bonding in their charged-states.

Table 3-1. Static charge number of atomic sites in most abundant boron clusters

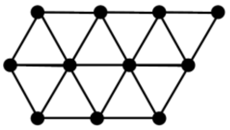
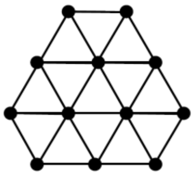
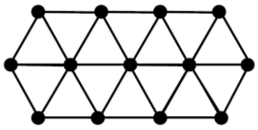
Ground-state isomer	Cluster	Coordination number	Number of sites	Static charge number
	B_{11}^{+}	2	1	+ 11/21
		3	4	+ 2/7
		4	4	+ 1/21
		6	2	– 3/7
	B_{11}^{0}	2	1	+ 10/21
		3	4	+ 3/14
		4	4	– 1/21
		6	2	– 4/7
	B_{11}^{-}	2	1	+ 3/7
		3	4	+ 1/7
		4	4	– 1/7
		6	2	– 5/7
	B_{12}^{+}	3	6	+ 5/16
		4	3	+ 1/12
		6	3	– 3/8
	B_{12}^{0}	3	6	+ 1/4
		4	3	0
		6	3	– 1/2
	B_{12}^{-}	3	6	+ 3/16
		4	3	– 1/12
		6	3	– 5/8
	B_{13}^{+}	3	6	+ 4/13
		4	4	+ 1/13
		6	3	– 5/13
	B_{13}^{0}	3	6	+ 1/4
		4	4	0
		6	3	– 1/2
	B_{13}^{-}	3	6	+ 5/26
		4	4	– 1/13
		6	3	– 8/13

Table 3-2. Specific binding energy of most abundant boron clusters

Clusters	Binding energy per atom, eV
B_{12}^{+}	6.49
B_{13}^{+}	6.34
B_{11}^{+}	6.21
B_{13}^{0}	5.60
B_{12}^{0}	5.47
B_{11}^{0}	5.34
B_{13}^{-}	5.25
B_{11}^{-}	5.24
B_{12}^{-}	5.10

From the **Table 3-2**, one can see that positively charged clusters are certainly more stable than neutral clusters, while lasts are more stable than negatively charged ones.

Table 3-3. Specific binding energy of neutral pairs of most abundant boron clusters

Pairs of clusters	Binding energy per atom, eV
$B_{11}^{-} + B_{13}^{+}$	5.83
$B_{12}^{+} + B_{12}^{-}$	5.79
$B_{11}^{+} + B_{13}^{-}$	5.69
$B_{11}^{0} + B_{13}^{0}$	5.48
$B_{12}^{0} + B_{12}^{0}$	5.47

According to the date presented in the **Table 3-3**, preferably channels of ablation of icosahedral boron-rich materials are related to the formation of neutral pairs of differently charged clusters.

4. Discussion and conclusions

Before making conclusions based on results obtained by us, we need to discuss shortly the theoretical data available in the literature on B_{12} cluster isomers stability.

As is known, boron atoms are unique in their strong preference for forming icosahedral structural units. In the icosahedral cage $B_{12,}$ each atom has 5 other atoms as nearest neighbors. Such B_{12} units are unstable by themselves, but distorted B_{12} icosahedra do form a stable framework for boron and many boron compounds. In particular, the α-rhombohedral crystalline boron may be considered an almost perfect cubic close packing of B_{12} icosahedra. In general, the persistence of the icosahedral structure is explained by the fact that the chemical valence of boron is not completely saturated under 5-fold coordination and that there exist outwardly directed bonds which serve to link icosahedra.

The X_α-method of the scattered-wave self-consistent-field (SCF–X_α–SW) with muffin-tin-potential and local exchange was applied[30] to determine quantitatively electronic structure and binding energy of icosahedral B_{12}. Then the binding energy was used to estimate the cohesive energy of the B_{12} units in the α-rhombohedral structure. From this, an effective B_{12}–B_{12} interaction potential in the solid was constructed. The binding energy of 35.6 eV was obtained at an equilibrium bond distance of 1.96 Å, which is within 10 % of the bond distance of 1.77 Å found in B_{12} icosahedra in bulk boron. The electronic structure of B_{12} corresponded to an open-shell configuration so that such an isolated cluster would be chemically unstable.

Geometries and electronic structures of the B_{12} cluster have been investigated using a Car–Parrinello ab initio molecular dynamics simulation[31]. The icosahedral structure was found to be locally stable, but with a few dangling bonds. On annealing or melting, this structure rearranges to a more open geometry. The new structure has a significantly lower energy despite a lower coordination. But, bonds are stronger and there are no dangling bonds.

The structure and stability of small boron clusters were investigated employing density functional theory (DFT)[32]. The search for minima was performed using gradient methods at the local spin density (LSD) level. Most of the final structures prefer planar or quasi-planar forms and can be considered to be fragments of planar or spherical surfaces. A group of spherical boron clusters may exist. However, their energies are generally higher than those of the convex or quasi-planar clusters. This also means that clusters of real bulk, sections of the boron lattice, have less stable configurations. They try to close the open spheres with a small number of atoms. In particular, the distorted icosahedral B_{12} cluster with closed structure has energy by 2.01–3.28 eV higher than that of the convex B_{12} structure.

Based on ab initio quantum-chemical methods, accurate calculations on small boron clusters were carried out to determine their electronic and geometric structures[33]. The geometry optimization with a linear search of local minima on the potential-energy surface (PES) was performed using analytical gradients in the framework of the restricted Hartree-Fock SCF approach. Most of the final structures of the boron clusters are composed of two fundamental units: either of hexagonal or of pentagonal pyramids. The resulting quasi-planar and convex structures can be considered as fragments of planar surfaces and as segments of nanotubes or hollow spheres, respectively. In particular, the most stable isomers of B_{12} clusters are 2 planar and 1 convex clusters. In contrast to the convex or the quasi-planar clusters, the structures of the cage-clusters are rather similar to those of the well-known α- and β-rhombohedral boron crystals, or to those of the boron hydrides. The energies of the cage-clusters on average are between 2 and 5 eV higher than those of the convex or the quasi-planar clusters.

Taking into account that interesting features of elemental boron and boron compounds are the occurrence of highly symmetric icosahedral clusters and rich chemistry of boron also dominated by cage-structures, in the study of Zhai *et al.*[34], the authors reported experimental and theoretical evidences that small boron clusters prefer planar structures and exhibit aromaticity and antiaromaticity according to the Huckel rules, akin to planar hydrocarbons.

The electronic and geometric structures, including binding energies, of small and neutral boron clusters have been investigated using DFT[35]. Linear, planar, convex, quasi-planar, open-cage and cage structures have been found. None of the lowest energy structures and their isomers has an inner atom; i.e., all the atoms are positioned at the surface. Within size range under the consideration, the planar and quasi-planar (convex) structures have the lowest energies. In particular, 11 different structures of B_{12} cluster were investigated. Their binding energies are ranging from 4.037 to 4.599 eV/atom. The first lowest energy isomer is a convex structure containing three dovetailed hexagonal pyramids. Only ninth and tenth isomers are cages, slightly distorted icosahedral structures without the central atom.

Among the several aromatic boron clusters, B_{12} and B_{13}^{+} are unique. They show three distinct sets of sextets, resulting in extraordinary kinetic stability. A novel way to analyze them was proposed in the study of Kiran *et al.*[36], in which the cluster is partitioned as inner and outer rings. The molecular orbital analysis, based on this fragmentation, reveals that the delocalized valence electrons in B_{12} and B_{13}^{+} clusters can be trifurcated leading to triple aromaticity, which is unique to these clusters.

Recently, Bhattacharyya *et al.*[37]conducted a comprehensive numerical study of the ground-state structures of isomers of B_{12} cluster. Geometry optimization was performed at a level of theory employing the extended basis sets. Once the geometry of a given isomer was optimized, its ground state energy was calculated more accurately at the level of theory employing even larger basis set. Thus, computed values of binding energies of various isomers are expected to be quite accurate. Geometry optimization revealed 10 distinct isomers. The vibrational frequency analysis performed on the 3 lowest energy isomers showed them to be stable. While, in boron-rich solids, icosahedron is the basic structural unit, in the isolated form, it was demonstrated to be unstable. The disc-like lowest-energy structure of B_{12} cluster can be seen as a consequence of the Jahn–Teller distortion of its icosahedral isomer. Computed binding energies per atom are 4.60 and 4.31 eV for quasi-planar and icosahedral isomers with C_{3v} and C_{2h} point group symmetries, respectively. This work, based upon ab initio geometry optimization, verifies early results and predicts the B_{12} icosahedron to be higher in energy as compared to the lowest energy quasi-planar B_{12} cluster. This clearly illustrates the tendency of the icosahedral structure towards distortion to a lower symmetry one, consistent with the Jahn–Teller theorem.

Thus, neutral B_{12} icosahedral clusters constituting boron-rich materials, on ablation have to be converted into (quasi) planar disc-like isomer with higher specific binding energy. The charged cluster B_{13}^{+} also should have higher stability. Consequently, the formation of B_{11}, B_{12} and B_{13} clusters in different charged-states is expected.

Our calculations performed within the diatomic model using quasi-classical B–B interatomic potential, lead to following hierarchies in the formation probabilities of single boron clusters in various charged states and their neutral pairs: $B_{12}^{+} > B_{13}^{+} > B_{11}^{+} > B_{13}^{0} > B_{12}^{0} > B_{11}^{0} > B_{13}^{-} > B_{11}^{-} > B_{12}^{-}$ and $B_{11}^{-} + B_{13}^{+} > B_{12}^{+} + B_{12}^{-} > B_{11}^{+} + B_{13}^{-} > B_{11}^{0} + B_{13}^{0} > B_{12}^{0} + B_{12}^{0}$, respectively.

The obtained results would be helpful in controlling the synthesis of nanoboron materials with specific engineering properties.

References

1. Becker R, Chkhartishvili L, Martin P. Boron, the new graphene? Vacuum Technology & Coating 2015; 16 (4): 38–44.
2. Becker R, Chkhartishvili L, Martin P. Tribological applications for boron. Vacuum Technology & Coating 2015; 16 (10): 36–41.
3. Chkhartishvili L. Micro- and nano-structured boron. In: Perkins GL (editor). Boron. Compounds, production and application. New York: Nova Science Publishers; 2011.p. 221–294.
4. Chkhartishvili L. Nanoboron (An overview). Nano Studies 2011; 3: 227–314.
5. Chkhartishvili L. All-boron nanostructures. In: Kharisov B I, Kharissova O V, Ortiz–Mendez U (editors). CRC concise encyclopedia of nanotechnology. Boca Raton: CRC Press; 2016. p. 53–69.

6. Albert B, Hillebrecht H. Boron: Elementary challenge for experimenters and theoreticians. Angewandte Chemie International Edition 2009; 48(46): 8640–8668.
7. Boustani I. Towards novel boron nanostructural materials. In: Springborg M (editor). Chemical Modelling: Applications and theory. Cambridge: Royal Society of Chemistry; 2011. p. 1–44.
8. Fermi E. Molecules, crystals, and quantum statistics. New York, Amsterdam: W. A. Benjamin INC; 1966.
9. Novikova SI. Thermal Expansion of Solids. Moscow: Nauka; 1974.
10. Slutsker AI, Gilyarov VL, Luk'yanenko AS. Energy features of an adiabatically loaded anharmonic oscillator. Physics of the Solid State 2006; 48(10): 1947–1953.
11. Chkhartishvili L, Gabunia D, Tsagareishvili O, *et al*. Estimation of isotopic composition effect on substance melting temperature. Bulletin of the Georgian National Academy of Sciences 2004; 170(3): 530–532.
12. Chkhartishvili LS, Gabunia DL, Tsagareishvili OA. Estimation of the isotopic effect on the melting parameters of boron. Inorganic Materials 2007; 43(6): 594–596.
13. Chkhartishvili LS, Gabunia DL, Tsagareishvili OA. Effect of the isotopic composition on the lattice parameter of boron. Powder Metallurgy and Metal Ceramics 2008; 47(9-10): 616–621.
14. Gabunia D, Tsagareishvili O, Chkhartishvili L, *et al*. Isotopic composition dependences of lattice constant and thermal expansion of β-rhombohedral boron. Journal of Physics: Conference Series 2009; 176(012022): 1–10.
15. Chkhartishvili L, Tsagareishvili O, Gabunia D. Isotopic expansion of boron. Journal of Metallurgical Engineering 2014; 3 (3): 97–103.
16. Chkhartishvili L. On quasi-classical estimations of boron nanotubes ground-state parameters. Journal of Physics: Conference Series 2009; 176(1): 1–9.
17. Chkhartishvili L. Molar binding energy of the boron nanosystems. In: Konuk A, Kurama H, Ak H, *et al*. (editors). Proceedings of the 4th international boron symposium. Ankara: Osmangazi University; 2009. p.153–160.
18. Chkhartishvili L. Nanotubular boron: Ground-state estimates. In: Chikoidze E, Tchelidze T (editors). New developments in materials science. New York: Nova Science Publishers; 2011. p. 67–80.
19. Oganov AR, Chen J, Gatti C, *et al*. Ionic high-pressure form of elemental boron. Nature 2009; 457(7251): 863–867.
20. Chkhartishvili L, Becker R. Effective atomic charges and dipole moment of small boron clusters. Proceedings of the ICANM 2015. Ottawa: IAEMM; 2015. p. 130–147.
21. Becker R, Chkhartishvili L. Dipole moment of quasi-planar boron clusters. Nano Studies 2015; 11: 29–48.
22. Chkhartishvili L, Becker R, Avci R. Relative stability of boron quasi-planar clusters. In: Darsavelidze G, Guldamashvili A, Chedia R, *et al*. (editors). Proceedings of the international conference "Advanced Materials & Technologies". Tbilisi: Universal; 2015. p. 42–46.
23. Chkhartishvili L. Small elemental clusters in pair interaction approximation. Proceedings of the ICANM 2016. Montreal: IAEMM 2016. p. 128–132.
24. Chkhartishvili L. Planar clusters of identical atoms in equilibrium: 1. Diatomic model approach. American Journal of Nano Research & Applications 2017; 5(3-1): 1–4.
25. Chkhartishvili L. Quasi-planar elemental clusters in pair interactions approximation. Open Physics 2016; 14(1): 617–620.
26. Chkhartishvili L. Boron quasi-planar clusters. In: Pogrebnjak A D (editor). A mini-review on diatomic approach. Proceedings of the IEEE 7th international conference on nanomaterials: Applications & properties (NAP—2017), Part 4, Track: Nanomaterials for electronics, spintronics and photonics; Sumy: Sumy State University; 2017. p. 1–5.
27. Chkhartishvili L, Lezhava D, Tsagareishvili O. Quasi-classical determination of electronic energies and vibration frequencies in boron compounds. Journal of Solid State Chemistry 2000; 154(1): 148–152.
28. Chkhartishvili L, Mamisashvili N, Maisuradze N. Single-parameter model for multi-walled geometry of nanotubular boron. Solid State Sciences 2015; 47: 61–67.
29. Hayes WM (editor-in-chief). Handbook of Chemistry and Physics (94th Ed.). Boca Raton: CRC Press; 2013. p. 10–147 & 10–197.
30. Bambakidis G, Wagner RP. Electronic structure and binding energy of the icosahedral boron cluster B_{12}. Journal of Physics and Chemistry of Solids 1981; 42(11): 1023–1025.
31. Kawai R, Weare JH. Instability of the B12 icosahedral cluster: Rearrangement to a lower energy structure. The Journal of Chemical Physics 1991; 95(2): 1151–1159.
32. Boustani I. Structure and stability of small boron clusters. A density functional theoretical study. Chemical Physics Letters 1995; 240(1-3): 135–140.
33. Boustani I. Systematic ab initio investigation of bare boron clusters: Determination of the geometry and electronic structures of Bn (n = 2–14). Physical Review B 1997; 55(24): 16426–16438.
34. Zhai H, Kiran B, Li J, *et al*. Hydrocarbon analogues of boron clusters — planarity, aromaticity and antiaromaticity. Nature Materials 2003; 2(12): 827–833.
35. Atis M, Ozdogan C, Guvenc ZB. Structure and energetic of Bn (n = 2–12) clusters: Electronic structure calculations. International Journal of Quantum

Chemistry 2007; 107(3): 729–744.

36. Kiran B, Kumar GG, Nguyen MT, *et al*. Origin of the unusual stability of B_{12} and B_{13}+ clusters. Inorganic Chemistry 2009; 48(21): 9965–9967.
37. Bhattacharyya P, Boustani I, Shukla A. First principles electronic structure study of B_{12} isomers: Jahn–Teller distortion flattens the icosahedron into a disc. arXiv:1802.01072v1 [physics.atm-clus] 4 Feb 2018; 1–32.