

Icosahedral B₁₂, macropolyhedral boranes, β -rhombohedral boron and boron-rich solids

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Abstract

The preference for icosahedral B₁₂ amongst polyhedral boranes and elemental boron is explained based on an optimization of overlap model. The ingenious ways in which elemental boron and boron-rich solids achieve icosahedron-related structures are explained by a fragment approach. The Jemmis *mno* rules are used to get the electron requirements. The extra occupancies and vacancies in β -rhombohedral structures are shown to be inevitable results of electron requirements. The detailed understanding of the structure suggests ways of doping β -rhombohedral boron with metals for desired properties. Theoretical studies of model β -rhombohedral solids with metal dopings provide support for the analysis.

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1. Introduction

Icosahedral B₁₂ occurs as a repeating motif in the chemistry of the compounds of boron, elemental boron and boron-rich solids [1]. This overwhelming preference for icosahedral structure cannot be accidental. It appears as a building block in most of the allotropes of boron. In fact the many structural peculiarities of elemental boron appear to be the result of attempts at generating maximum number of boron atoms in the icosahedral environment. Thus it is important to know the reason for the preference. We review explanations for the preference of boron for icosahedron and the electron counting rules that would help to put icosahedra together in different ways with a view to construct allotropes of boron. This fragment approach also leads to an understanding of several boron-rich solids.

The preference for icosahedral boron is dramatically noticed also in the chemistry of polyhedral boranes. The

electronic structure of polyhedral boranes has been studied by many groups over the years [2–12]. It goes to the credit of Wade who organized the information available from various studies and introduced an easily applicable electron counting rule to explain the charge and the number of hydrogens found in polyhedral boranes. According to Wade's rules, a closo polyhedral borane B_{*n*}H_{*n*} requires $n+1$ skeletal electron pairs for stability so that the structure is dianionic. Structures with n varying from 5 to 13 are known experimentally [13]. All of them follow the Wades $n+1$ rule. When the structure has one missing vertex, the structure is classified as nido and requires $n+2$ electron pairs. With two vertices missing the structure is termed arachno and the electron requirement is $n+3$ skeletal electron pairs. While all of these polyhedral structures that obey the Wade's rules may be stable, their relative stabilities differ considerably. These variations cannot be gauged by the electron counting rules. Icosahedral B₁₂H₁₂²⁻ is known to be the most stable of all polyhedral boranes. B₁₀H₁₀²⁻ and B₆H₆²⁻ follow these. B₇H₇²⁻ is rather unstable [12]. We begin the discussion by reviewing our explanation for the relative stabilities of polyhedral boranes.

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Given that icosahedral boranes are the most stable ones, it is natural to expect B_{12} as building blocks in constructing allotropes of boron. This is very much in tune with the construction of graphite from benzene by polycondensation. The Hückel rule [14] helps to count electrons while condensing benzene to naphthalene and its higher homologs [15]. Graphite can be considered as a polycondensation product of benzene in two dimensions. It is necessary to find an electron counting rule to conduct a similar process of condensation for B_{12} unit in three dimensions. In addition to edge sharing, an icosahedron provides triangular face-sharing, four atom sharing and single atom sharing as possible modes of condensation. We have introduced a rule, the *mno* rule, [16–18] for this purpose which will also be reviewed. Armed with these ideas we examine the structure of allotropes of elemental boron and boron-rich solids. We study specifically the doped structures which would have no vacancies in the idealized unit cell of the β -rhombohedral boron.

2. Results and discussion

The packing of boron and boron-rich solids involve nearly all icosahedral B_{12} clusters, which is the predominant building block of the allotropes of elemental boron. Many experimental and theoretical calculations show that the icosahedral arrangement is the most favored one for boranes [12,13]. Comparison of the fragments of icosahedral borane and the regular icosahedron, leads to an explanation for the specific preference of boron for icosahedron [19]. The icosahedron can be thought of as being constructed from two pentagonal pyramids. According to the Wade's rule the pentagonal pyramidal B_6H_6 requires a charge of -4 to be stable. The stable neutral borane, B_6H_{10} [20], has four bridging hydrogens in the B_5 ring. The terminal B–H bonds are directed towards the capping BH group by about 25° so that there is better overlap between the p orbitals of the BH group and the π MOs of the B_5 ring. A similar angle can be calculated from solid geometry for the pentagonal pyramid obtained by dividing the icosahedron into two. This angle of 26.6° is nearly the same as what is needed naturally for the borane pentagonal pyramid as shown in the Fig. 1. Thus while forming the icosahedral borane from the two pentagonal pyramids, there is no need to have any major compromise in overlap. This is not true for other polyhedral structures. For example, during the formation of a closo pentagonal bipyramidal borane from a pentagonal pyramidal borane and a B–H group, the terminal B–H bond of the B_5 ring has to be brought from their optimum angle of 25° in the pentagonalpyramidal borane to 0° in $B_7H_7^{2-}$. Thus the structure is not very stable. Given that icosahedron is the most favored polyhedra for boron, it is easy to explain the structure of α -rhombohedral boron.

2.1. α -rhombohedral boron (α - B_{12})

The mechanism by which the individual B_{12} units in α - B_{12} obtain two extra electrons has been explained many

times before and is added here for completeness [21]. The α - B_{12} crystal structure was first proposed by McCarty and further determined by Decker and Kasper [22]. Among the allotropes of boron α - B_{12} has the simplest form. It contains one B_{12} unit in the rhombohedral Bravais lattice in the space group $R\bar{3}m$ with lattice parameters $a = 5.05 \text{ \AA}$ and $\alpha = 58.06^\circ$. It constitutes crystallographically two independent atomic sites. Among the 12 vertices of B_{12} , six are polar and the rest of six are equatorial sites. The polar sites are connected to the neighboring B_{12} units through $2c-2e$ bonds. Each equatorial site is connected to three neighboring B_{12} units via $3c-2e$ bonds as shown in Fig. 2. The $2c-2e$ B–B inter-icosahedral bonds are almost aligned with the rhombohedral edges. The distortion is found to be 1.94° . In principle all the 12 vertices can form $2c-2e$ bonds with the neighboring B_{12} units, but the five-fold symmetry does not allow translational periodicity. In addition this needs two extra electrons per B_{12} unit to stabilize the unit cell. Hence it chooses a resourceful way of connectivity to avoid the extra electrons. A B_{12} unit needs 38 electrons to stabilize the unit cell, 26 electrons ($n+1$ electron pairs) for the cluster bonding and 12 electrons for $exo-2c-2e$ bonds. But B_{12} contains only 36 valence electrons. The extra requirement of two electrons is met by the two electrons saved from the formation of the six $3c-2e$ bonds ($6-(6 \times 2)/3$). The recent band structure calculations also reveal this point along with many experimental and theoretical results [23–25]. The stability of the polyhedral boranes is governed by the Wade's $n+1$ skeletal electron pair rule and the stability of the B_{12} unit in the solid is anticipated by the work of Longuet-Higgins [26].

2.2. β -rhombohedral boron (B_{105})

The structure of β -rhombohedral boron involves clusters of B_{12} units condensed in novel ways. It is necessary to analyze the rules that govern the condensation of polyhedral boranes. Recently we introduced the *mno* rule for this purpose [17]. According this rule, a polyhedral structure with m polyhedra, n vertices and o single-atom bridges between polyhedra requires $m+n+o$ electron pairs for stability. The β -rhombohedral boron is thermodynamically the most stable allotrope of boron. Most of the atoms in β -rhombohedral boron form a part of an icosahedral or near icosahedral structure with many vacancies and extra occupancies. We discuss the β -rhombohedral boron crystal structure with a view to understand the organization of the various clusters of boron atoms, in relation to the structure of boranes, and to find ways to model the structure.

The β -rhombohedral boron crystal structure was first proposed by Hoard et al. [27] and further studied by Geist et al. [28], Callmer [29] and Slack et al. [30,31]. The crystal structure of β -rhombohedral boron has a distorted face-centered cubic (*fcc*) lattice (rhombohedral). It has 105 boron atoms in its idealized unit cell, in the space group $R\bar{3}m$ with lattice constants $a = 10.145 \text{ \AA}$, $\alpha = 65.28^\circ$. The

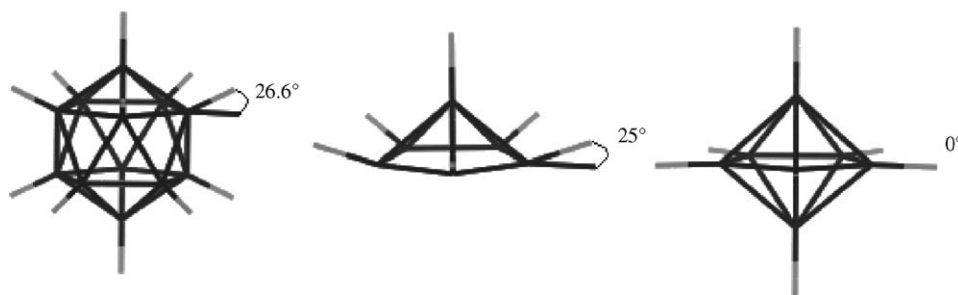


Fig. 1. Schematic illustration of the angle that B–H makes with the B_5 plane in icosahedral $B_{12}H_{12}$, pentagonal pyramidal B_6H_{10} (bridging hydrogens are removed for clarity), and pentagonal bipyramidal B_7H_7 , respectively.

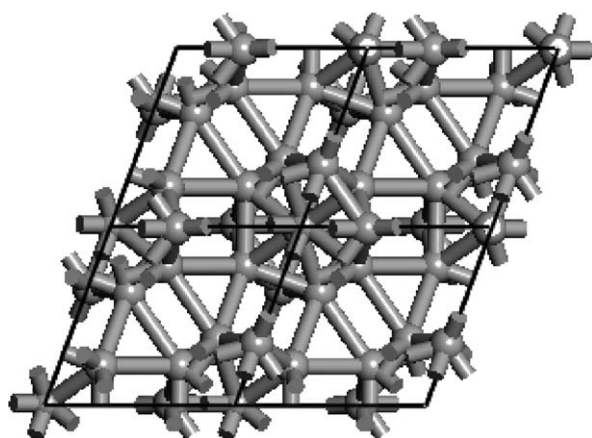


Fig. 2. The crystal structure of α -rhombohedral boron, where the six vertices of B_{12} are connected through $3c-2e$ bonds linking adjacent icosahedra in the basal plane and rest of the six are connected through $2c-2e$ bonds with the neighboring icosahedra.

main structural moiety in the B_{105} unit cell is B_{84} polyhedron, where a central icosahedron is surrounded by twelve B_6 pentagonal pyramids ($B_{12}@B_{12}@B_{60}$), and these large B_{84} soccer ball clusters are placed at the points of the rhombohedral lattice. This allows six of the half icosahedra of each B_{84} unit to link together at the mid points of the edges of the cell forming further icosahedra. By this way the chain of B_{12} icosahedral units run through the structure along each of the rhombohedral cell edges. The remaining six half icosahedra are linked to six different B_{10} units. Two such B_{10} units are linked through an additional boron atom at the center of the rhombohedral cell. This is the only atom that is not part of any icosahedral arrangement in the entire unit cell. Therefore rhombohedral unit cell can be viewed as B_{84} which is centered at each vertex, plus $B_{10}-B-B_{10}$ unit situated along the main body diagonal ($B_{105} = B_{84} + B_{10}-B-B_{10}$) as shown in Fig. 3. The structure of the unit cell can also be viewed in another way which helps to estimate the electronic requirements for the ideal β -rhombohedral boron. The unit cell can be separated at the points where the external bonds represent nearly localized $2c-2e$ bonds [21]. This gives fragments consisting of one central B_{12} unit, six half icosahedral fragments, which forms three icosahedra for electron counting purpose and a B_{57} unit as shown

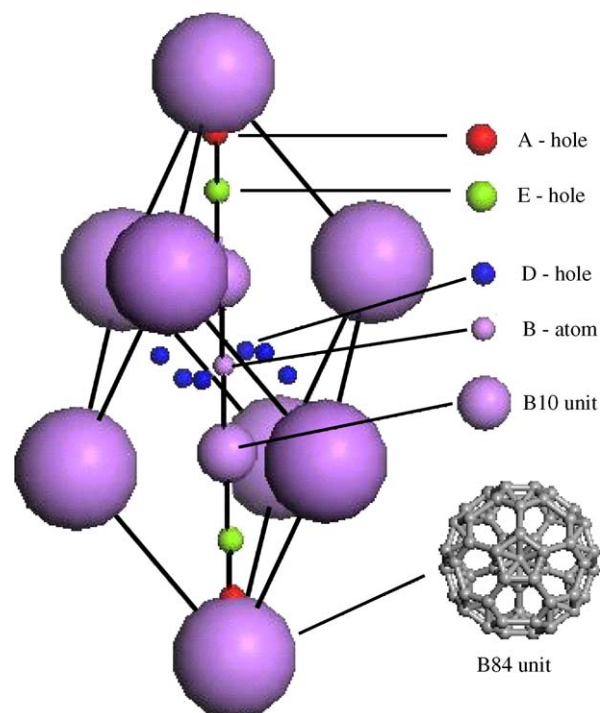


Fig. 3. The crystal structure of β -rhombohedral boron, where the B_{84} soccer ball units occupy the vertices of the unit cell. The $B_{10}-B-B_{10}$ chain occupies the main body diagonal. The types of holes that are present in the unit cell are shown here.

in Fig. 4. The B_{57} unit can be divided into two B_{28} units connected together by a central boron atom $B[15]$. The $B_{28}-B-B_{28}$ chain is situated along the main body diagonal of the rhombohedral unit cell. Each B_{28} unit has three icosahedral structures, in which each B_{12} units shared a triangular boron face with the other two. Even though the central capping atom in the B_{28} unit distorts the icosahedral geometry considerably, as a first approximation, one can assume that the B_{12} clusters of B_{28} have nearly icosahedral geometry.

The model proposed by Hoard et al. constitutes 15 crystallographically independent atomic sites and these are fully occupied. But it is thought that one of these sites contains statistical vacancies. Slack, observed that the $B[13]$ site situated in B_{57} unit is partially vacant and five different symmetry equivalent interstitial sites, $B[16]-B[20]$

are partially occupied. The observed occupancies of different β -rhombohedral boron samples are tabulated in Table 1. We make use of this information of Slack's β -rhombohedral boron to evaluate the electronic requirements and use the same numbering in the discussion. The *mno* rule indicates that the B_{57} unit has three electrons more than necessary i.e. B_{57}^{+3} is the stable unit (Table 2). One of the ways of removing the +3 charge is by forming the nido structure with one atom less, B_{56} . It translates to occupancy of $100 \times 5/6 = 83.33\%$. But the percentage of occupancy of B[13] is lower than 83.33%. This is compensated by the partially occupied B[17] interstitial site which is clear from the experimental data shown in Table 1. The B[17] site is near the *D* hole and is within bonding distance to B[13] and B[15] sites, which are

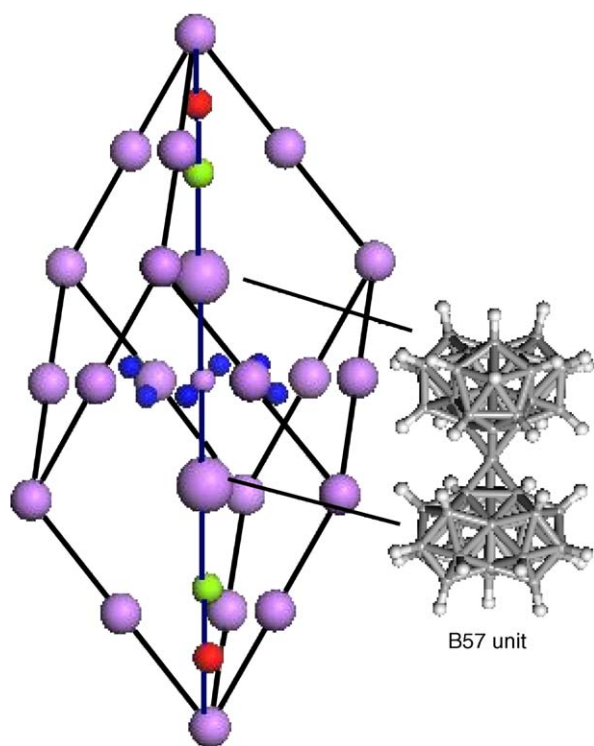


Fig. 4. The crystal structure of β -rhombohedral boron, where the B_{12} icosahedral units occupy the vertices and edge centers of the unit cell. The B_{57} – B – B_{57} unit occupy the main body diagonal.

involved in the capping. This site has an occupancy range 3.2–9.7% in the same three samples. It is as if the structure has overcorrected than what is required. The atoms removed by over correction is compensated by the B[17] sites not far from it. Hence the total percentage of occupancy of B[13] can be assumed as (80.9, 82.7, 83.0), respectively, which strongly indicates that one boron atom is missing in the β -rhombohedral boron. The rest of the five partially occupied interstitial sites B[16], B[18] to B[20] provide the extra electrons required for the individual icosahedral B_{12} units.

Within the bonding distance of B[1], B[5], and B[7], the atoms belonging to the four electron deficient icosahedra. B[18], B[19] and B[20] are almost at the periphery of the B_{84} soccer ball. The partial occupancies of these atoms add up to 38.8%, 45.3%, and 44.3% in the three different samples. This translates to 7.0, 8.6, and 8.64 electrons not far from the eight electrons that are necessary for the four B_{12} units (Table 1). Thus the ideal unit cell does not represent 105 atoms of β -rhombohedral boron unit cell. At the B_{57} unit, one boron atom is missing, so that three extra electrons are removed. At the same time, the interstitial boron atoms, $2.66 (= 8/3)$ of them provide eight electrons so that the unit cell has $(105 - 1 + 2.66)$ 106.66 boron atoms, which is near to 106.83 as proposed by Slack et al. The 106.66 boron atoms or 320 electrons per unit cell are also strongly supported by the metal-doped β -rhombohedral boride experimental structures (Table 3). However the above picture of electron sufficient β -rhombohedral boron demands a relook at the commonly accepted reason for the distortion of the B_{12} units in the β -rhombohedral boron. It is assumed that electron deficiency of B_{12} units by two electrons lead to a Jahn–Teller distortion so as to lift the degeneracy of partially filled degenerate levels [32–34]. If this were true, one does not anticipate partially occupied sites. However, there are several extra occupancies and vacancies in β -rhombohedral boron as described above. The distortions observed in the icosahedral units in the β -rhombohedral boron structure are perhaps due to the low symmetry of the idealized unit cell itself. The central B_{12} unit of B_{84} will be distorted even if it is possible to have a -2 charge per B_{12} . Recently we have done band structure calculations on ideal B_{105} unit cell which precisely indicates

Table 1

Percentage of partially substituted and interstitially occupied sites of different crystal structures of β -rhombohedral boron

No.	Crystal structure	Site no. [symmetry multiplicity] % of occupancy						# of B/unit cell
		13[6]	16[6]	17[6]	18[6]	19[6]	20[12]	
1	Hoard	100.0	0.000	0.000	0.000	0.000	0.000	105.00
2	Geist	66.67	33.33	0.000	0.000	0.000	0.000	105.00
3	Callmer	73.40	24.80	0.000	0.000	0.000	0.000	104.89
4	Slack(i)	77.70	25.80	3.200 ^a	5.800	7.200	0.000	106.37
5	Slack(ii)	73.00	28.40	9.700	7.400	7.000	2.50	106.83
6	Slack(iii)	74.50	27.20	8.500	6.600	6.800	3.70	106.86

^aHas [12] symmetry multiplicity than general [6].

Table 2
The electron counts for the clusters based on the *mno* rule

No	Cluster	ASEP	<i>m</i>	<i>n</i>	<i>o</i>	<i>m+n+o</i>	RC
1	B ₁₂ H ₁₂	12	1	12	0	13	−2
2	B ₂₈ H ₃₁	31.5	3	28	0	31	+1
3	B ₅₇ H ₃₆	67.5	8	57	1	66	+3

ASEP for B₅₇H₃₆: 36(BH)₃₆ + (21 × 3)/2(B)₂₁ = 67.5EP.

The third column gives count on total available skeletal electron pairs (ASEP) for the cluster bonding. The last but one column gives the required skeletal electron pairs for the cluster bonding according to the *mno* rule. The last column gives the required charge (RC) on the cluster.

Table 3
Percentage of partially substituted and interstitially occupied sites of experimental and modeled metal doped β -rhombohedral borides and their corresponding volumes

No.	Crystal structure	Site no. [symmetry multiplicity] % of occupancy					# of e [−]	Vol (Å ³)
		13[6]	16[6]	A[2]	E[2]	D[6]		
1	Li ₈ B _{103.44} (a)	64.00	10.00	0.000	100.0	100.0	318.32	834.765
2	Cu _{3.72} B _{103.92} (b)	61.10	20.90	6.100	50.50	22.1,10 ^a	319.12	829.963
3	Cu _{4.14} B _{103.92} (c)	69.00	13.00	8.000	61.00	22.0,12 ^a	320.04	833.415
4	Fe _{2.12} B _{103.36} (d)	72.60	0.000	50.70	0.000	18.50	316.44	826.105
5	Hf _{2.07} B _{103.42} (e)	65.50	8.100	0.500	9.800	31.10	314.40	835.689
6	Zr _{2.04} B _{103.04} (f)	52.80	14.50	0.000	18.10	27.90	313.20	832.377
7	Cr _{2.52} B _{103.30} (g)	71.17	0.000	71.90	0.000	18.00	314.94	831.321
8	Li ₈ Be ₃ B ₁₀₂ (h)	100.0	0.000	100.0	100.0	0.000	320.00	815.339
9	Li ₁₀ CB ₁₀₂ (h)	100.0	0.000	100.0	100.0	0.000	320.00	807.985

(a) Ref. [36], (b) Ref. [39], (c) Ref. [40], (d) Ref. [41], (e) Ref. [31], (f) Ref. [42], (g) Ref. [31], (h) Ref. [23].

^aHere percentage of occupancy has [12]-fold symmetry.

the five electron deficiency of the valence band [23], which supports the previous band structure calculations done by Bullet [24]. But the calculation of the band structure of the electron sufficient unit cell, B_{106.66}, is difficult due to the presence of the partially occupied sites. Multi unit cells that give integral atom counts in this case are too large to calculate. So we modeled electron precise systems which resemble the experimental β -rhombohedral boron crystal structure based on the availability of doping sites and sufficient number of electrons.

2.3. Model β -rhombohedral boron-rich solids

We designed the electron sufficient solids that modeled the β -rhombohedral boron without any partial occupied sites using the cluster fragment approach [21,23]. We choose proper locations in the β -rhombohedral boron unit cell where the foreign atoms can be substituted in place of boron atoms or can be added at particular interstitial sites i.e. the holes present in the unit cell (Fig. 4).

There are several justifications for this approach. Metal-doped endohedral boron clusters (B₁₂) are calculated to be stable [35,36]. As we have already seen, B₅₇ unit in the β -rhombohedral boron is electron rich by three electrons, the only possibility to make B₅₇ unit electron sufficient and yet retain symmetry of the solid is by substitution of boron by atoms with sufficient number of electrons (Be, C, Li, Ca,

Mg, etc.). It is found that there are three locations on B₅₇ unit where one can substitute foreign atoms providing with reduction of three electrons. These sites are the two centers of the B₂₈ units B[14] and the center of the B₅₇ unit B[15] site. Therefore the following electron precise fragments are generated (Table 2) B₂₈H₂₁⁺¹, LiB₂₇H₂₁^{−1}, BeB₂₇H₂₁, CB₂₇H₂₁⁺², MgB₂₇H₂₁, SiB₂₇H₂₁⁺², B₅₇H₃₆⁺³, Be₃B₅₄H₃₆, Li₂CB₅₄H₃₆, Be₂MgB₅₄H₃₆ and Mg₃B₅₄H₃₆. Among the many combinations examined, the structures with Be, Li, and C as replacement atoms are found to be suitable (Table 4). All structures except the clusters with Mg and Si atoms are found to be minima. But in the case of B₅₇H₃₆⁺³, Be₃B₅₄H₃₆ and Li₂CB₅₄H₃₆ imaginary vibrational frequencies of −14.33, −31.16 and −48.38 cm^{−1}, respectively, are calculated. While the imaginary vibrational frequency in a molecule indicates a higher-order stationary point and instability, these could be stable building blocks in a rigid rhombohedral framework. These small imaginary vibrational frequencies may then manifest as soft modes, indicating a structural instability. As the temperature decreases, the soft mode freezes and approaches to zero amplitude. The imaginary modes of vibrations in B₅₇H₃₆⁺³, Be₃B₅₄H₃₆, and Li₂CB₅₄H₃₆ are A_{1U} and E_U type within D_{3d} symmetry. The A_{1U} is partial rotation of two B₂₈ units in opposite direction about the B[15] center and the E_U is a bending mode of B₂₈–B–B₂₈. The stable clusters are found to have large HOMO-LUMO gaps. The bond lengths are

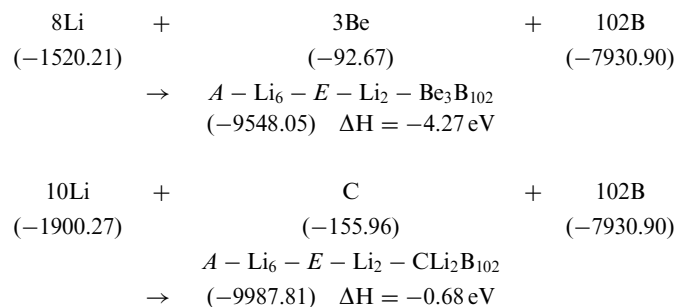
Table 4

The bond lengths, lowest vibrational frequencies and HOMO–LUMO (H–L) gaps at GGA Becke Perdew/DZ level for $B_{28}H_{21}^+$, $B_{57}H_{36}^{+3}$ and the substituted clusters

Sl. no.	Substituted cluster	Average bond distances (Å)			Min freq (cm ⁻¹)	H–L gap (eV)
		B–B	[14]-B ([13]–[15])	[14]–[15]		
1	$B_{28}H_{21}^+$	1.854	1.849	—	146.1	3.375
2	$LiB_{27}H_{21}^-$	1.887	1.864	—	156.6	2.404
3	$BeB_{27}H_{21}$	1.864	1.847	—	149.4	3.015
4	$CB_{27}H_{21}^{+2}$	1.882	1.912	—	6.4	3.331
5	$MgB_{27}H_{21}$	1.868	2.246	—	–201.6	1.133
6	$SiB_{27}H_{21}^{+2}$	1.834	2.122	—	–138.9	2.384
7	$B_{57}H_{36}^{+3}$	1.911	1.802 (1.785)	2.816	–14.3	3.427
8	$Be_3B_{54}H_{36}$	1.863	1.809 (1.843)	2.932	–31.1	2.494
9	$Li_2CB_{54}H_{36}$	1.862	1.815 (1.742)	2.744	–48.3	2.694
10	$Be_2MgB_{54}H_{36}$	1.869	1.806 (2.349)	3.545	–418.5	0.743
11	$Mg_3B_{54}H_{36}$	1.890	2.283 (—)	3.539	–137.2	0.388
12	$B_{106.66}$	1.799	1.768 (1.687)	2.726	—	—
13	$Li_8Be_3B_{102}$	1.805	1.765 (1.746)	2.790	—	—
14	$Li_{10}CB_{102}$	1.789	1.796 (1.703)	2.751	—	—

Computational details are given in Ref. [22].

found to be similar to those of the closo and stuffed polyhedral boranes [35]. The specific combinations used are Be_3 and $LiCl$ at the B[14], B[15] and B[14] positions of β -rhombohedral boron to achieve the electron precise B_{57} unit. Let us now look at the remaining part of the unit cell. The four icosahedra here are electron deficient by two electrons each. It needs eight electrons extra per unit cell to satisfy the electron requirements of the four icosahedra. The holes that are present in the β -rhombohedral boron are well suited to add the extra electrons. Using the experimental information of metal-doped β -rhombohedral boron, the preferred holes to dope the foreign atoms can be located. The sites near by A , E , and D holes can accommodate the required number of electrons. Adding appropriate atoms to these locations, one can design numerous β -rhombohedral borides with full occupancy and without disturbing its crystal symmetry. Resultantly to accommodate five electrons ($8-3=5$) we choose Li, Be, and C atoms in those particular positions. Thus we study the following unit cells having right number of electrons: $A-Li_6-E-Li_2-Be_3B_{102}$, $A-Li_2-D-Li_6-Be_3B_{102}$, $E-Li_2-D-Li_6-Be_3B_{102}$ ($Li_8Be_3B_{102}$), and $A-Li_6-E-Li_2-CLi_2B_{102}$ ($Li_{10}CB_{102}$). The computational details and the electronic structure calculations of boron clusters and the β -rhombohedral arrangements of above structures are discussed elsewhere [23]:



The binding energy of these two model solids are found to be 4.27 and 0.68 eV, respectively, as shown in the above equations. We have modeled the experimental Li_8B_{104} where the Li atoms are occupied at E and D sites, leading to the electron precise $E-Li_2-D-Li_6-Be_3B_{102}$. The A and D site preference is checked with $A-Li_2-D-Li_6-Be_3B_{102}$. The mixing energies show that the former is 5.5 eV and the later is 5.6 eV stable. The extend of partial occupancy in Li_8B_{104} decreased from the experimental $B_{106.66}$. Perhaps tuning the electron count based on cluster fragments approach would reduce the partial occupancy ($Li_8Be_3B_{102}$) further. The valence band of the modeled solids was found to be filled completely. The band gaps of the models are found to be similar to the β -rhombohedral and some of the metal-doped β -rhombohedral borides which are semiconductors [25,37,38]. This provides a partial understanding of the semiconducting nature of the β -rhombohedral boron.

3. Conclusions

The preference of icosahedral B_{12} units by boron is reviewed. The *mno* rule is applied to understand the electronic structure and bonding of elemental boron, boron-rich solids and macropolyhedral boranes. The electron sufficient nature of α -rhombohedral boron is very clear due its resourceful way of sharing electrons through $3c-2e$ bonds, where vacant or partially occupied sites are not seen in the lattice. The mystery of five missing electrons of the β -rhombohedral boron was understood through cluster fragment approach. The vacancy and partial occupancies of the unit cell is shown to be necessitated by the electron requirement of the system. We have modeled the solids to understand the semiconducting nature of β -rhombohedral boron by reducing the complexity through doping with the required number of atoms at the appropriate places in the unit cell.

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