Electronic structure and bonding of β -rhombohedral boron using cluster fragment approach

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Theoretical studies using density functional theory are carried out to understand the electronic structure and bonding and electronic properties of elemental β -rhombohedral boron. The calculated band structure of ideal β -rhombohedral boron (B₁₀₅) shows valence electron deficiency and depicts metallic behavior. This is in contrast to the experimental result that it is a semiconductor. To understand this ambiguity we discuss the electronic structure and bonding of this allotrope with cluster fragment approach using our recently proposed *mno* rule. This helps us to comprehend in greater detail the structure of B₁₀₅ and materials which are closely related to β -rhombohedral boron. The molecular structures B₁₂H₁₂⁻², B₂₈H₂₁⁺¹, BeB₂₇H₂₁, LiB₂₇H₂₁⁻¹, CB₂₇H₂₁⁺², B₅₇H₃₆, Be₃B₅₄H₃₆, and Li₂CB₅₄H₃₆, and corresponding solids Li₈Be₃B₁₀₂ and Li₁₀CB₁₀₂ are arrived at using these ideas and studied using first principles density functional theory calculations.

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I. INTRODUCTION

Boron continues to stimulate many areas of chemistry and physics. Its contrast to carbon is often the beginning point of many discussions. Among the allotropes of carbon, graphite is thermodynamically the most stable at normal temperature and pressure. The electronic structure and bonding of diamond and graphite are well known.¹ But the allotropes of boron are too complex that these are only currently being understood in detail.²⁻⁵ The electronic structure and the relative stability that stems from it still remain to be fully understood. The observation that MgB_2 is superconducting^{6,7} at 39 K and the similarity of MgB₂ to graphite, which is a good conductor, and the structural similarities between fullerenes and β -rhombohedral boron have brought the comparison of the neighboring elements into focus once again.8 Here we use cluster fragment approach to study the electronic structure and bonding and the electronic properties of β -rhombohedral boron and compare with available experimental results.

Though there are reports of numerous allotropes of boron, only 16 are well characterized.⁹ The most important among these are the α - and β -rhombohedral boron. The latter is known to be thermodynamically most stable. There have been several theoretical and experimental studies on β -rhombohedral boron.¹⁰⁻¹⁵ However the complexity of β -rhombohedral boron has prevented detailed theoretical studies so far. A certain reduction of this complexity is achieved by relating condensed polyhedral boranes to β -rhombohedral boron just as condensed benzenoid aromatics are related to graphite. This has set the stage for detailed study of the electronic structure and bonding using modern computational methods which are presented here. Our results on graphite reproduces its long known greater thermodynamic stability than diamond.¹⁶ On the other hand, experimental relative stabilities are not reproduced by calculations for boron allotropes. While β -rhombohedral boron is known to be thermodynamically more stable than α -rhombohedral boron, computational results do not support this. The information from the band structure of β -rhombohedral boron

indicates metallic character.¹⁴ Experiments do not support this either.¹¹ The inconsistency of the results is mainly because the ideal unit cell of β -rhombohedral boron (B₁₀₅) does not represent the real structure which is B_{106.66}. There are vacancies and partial occupancies in B₁₀₅. Recently Imai and coworkers¹⁷ attempted to model the electronic structure of β -rhombohedral boron with its vacancies and extra occupancies by assuming that certain fixed sites are fully occupied and other sites are completely vacant. Here we propose model solids based on cluster fragment approach using our recently proposed mno rule^{18,19} to closely represent the electronic structure of β -rhombohedral boron. Application of the mno rule for macropolyhedral boron units that are present in B_{105} helps to explain the occupancies. We also compare theoretical electronic structure of B_{105} to the experimental results of Frang and Werheit,^{10,12} Schmechel and Werheit,^{11,20} Werheit *et al.*,¹³ and to theoretical studies of Bullet¹⁴ and devise practical models for further theoretical study. Werheit had observed a split-off upper valence band of 0.19 eV originated from atoms of the B[13] site⁵ and suggested that the intrinsic structural defects provide these electrons and compensate the electron deficiency calculated for the idealized B₁₀₅. Theoretical studies of B₁₀₅, modified by addition or substitution of foreign atoms to mimic the intrinsic defects would help to understand these observations in detail.

In this paper, we report the total electronic energies, band structures, and projected density of states (PDOS) of B_{105} and model structures that retain the electron count required for the experimental β -rhombohedral boron. The results obtained are compared with experimental data.^{10–14} The instability of the crystal structures is also discussed. In Sec. II, we describe the details of the computational methods. The results and discussion of the electronic structure and bonding are presented in Sec. III. Finally in Sec. IV the conclusions of this work are presented.

II. COMPUTAIONAL DETAILS

We have carried out first principles quantum mechanical calculations in the frame work of density functional theory

System	Smood	Lattice parameters (Å)					Energy
	group	a	b	с	Vol (Å)	Density	(eV)
Lithium	IM-3M	3.424	3.424	3.424	40.17	0.573	-190.027
Beryllium	P93/MMC	2.277	2.277	3.563	16.00	1.869	-30.8920
Diamond	FD-3M	3.534	3.534	3.534	44.16	3.612	-155.824
Graphite	P63/MMC	2.440		7.026	36.23	2.202	-155.962
α -boron-B ₁₂	R-3M	4.973	4.973	4.973	83.35	2.584	-77.754
β -boron-B ₁₀₅	R-3M	10.14	10.14	10.14	823.4	2.288	-77.471
β -boron-B _{106.83} ^a	R-3M	10.13	10.13	10.13	820.3	2.715	
$Li_8Be_3B_{102}$	R-3M	10.13	10.13	10.13	815.3	2.413	-9548.05 ^b
$Li_{10}CB_{102}$	R-3M	10.08	10.08	10.08	807.9	2.433	-9987.81 ^b

TABLE I. Lattice parameters and the energy per atom calculated using GGA/PBE for lithium, beryllium, model solids and for the allotropes of carbon and boron.

^aThese are the experimental values.

^bThese are the total electronic energies.

(DFT). The ground state structures were obtained using the Cambridge Sequential Total Energy Package (CASTEP) code²¹ implemented in Materials Studio (San Diego, CA).²² The unit cell optimizations are carried out using nonlocal corrected generalized gradient approximation (GGA) (Ref. 23) based on the Perdew-Burke-Ernzerhof (PBE) formulation.²⁴ The ultrasoft pseudopotentials (USP) description was used for all atoms.^{25,26} For the crystal lattice, integration over the symmetrised Brillouin zone was performed using k points generated via the Monkhurst-Pack scheme.²⁷ The band curve was obtained by broadening discrete energy levels on a grid of k points using Gaussian smearing functions. The geometry optimization was done by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method²⁸ and density mixing was done by the Pulay scheme. The solid state structures studied are graphite, diamond, B₁₀₅, Li₈Be₃B₁₀₂, and Li₂CB₅₄H₃₆ are studied at GGA Becke-Perdew, slater-type orbitals (STO) basis set with double zeta (DZ) without polarization functions using the Amsterdam Density Functional (ADF) package.²⁹ The optimized parameters are given in Table I.

III. RESULTS AND DISCUSSION

The detailed geometry and the crystal structure of boron allotropes^{2,30,35} are described elsewhere and are summarized here for the ease of discussion. Electron deficiency of boron leads to multicenter bonding in its allotropes. There are several of them with partial occupancy (intrinsic defect) and impurities (extrinsic defect).¹ The thermodynamically most stable boron allotrope is β -rhombohedral boron. But our calculations suggest that the α -rhombohedral boron is about 0.28 eV/atom more stable than B₁₀₅, β -rhombohedral boron with the idealized unit cell (Table I). This is in contrast to the experimental results. The α -rhombohedral boron contains one B₁₂ unit in its unit cell and hence 36 valence electrons.

Out of these, ten electrons contribute to the exohedral bonding and the rest to cluster bonding. According to Wades n+1 skeletal electron pair rules³¹ for polyhedral boranes icosahedral B₁₂ needs two additional electrons for stability. Nature found a way to stabilize the B₁₂ units in α -rhombohedral boron. The 12 vertices of the B₁₂ unit make connections to the nearest B_{12} units. Six of the 12 vertices form 2c-2e (1.761 Å) bonds and the remaining six make 3c-2e (2.024 Å) bonds, saving two electrons (6–(6×2/3)) per B_{12} unit. Hence the structure is electron sufficient. The band structure of α -rhombohedral boron points to a semiconductor behavior with an indirect band gap from the top of the valence bands at Z to the bottom of conduction bands at G of 1.63 eV. The direct band gap at G is found to be 2.0 eV (Fig. 1). The band gap details are in good agreement with the available experimental and theoretical results.^{32,33} On the other hand the valence band of the β -rhombohedral boron (B_{105}) is not completely filled (Fig. 1). It shows β rhombohedral boron to be metallic which is contradictory to the experimental observation that it is a semiconductor.²⁰ The top three bands of the valence region cross over to the Fermi region and are dispersed within the 0.67 eV near the Fermi region. A significant forbidden gap of about 1.47 eV from the Fermi region to the bottom of the conduction band at F is observed. The indirect gap between the top most band just above the Fermi region at G and the bottom of the conduction band at F is found to be 1.03 eV. This unit cell has 105 atoms. So there are 315 electrons available to fill the valence band. But the full valence band can accommodate 320 electrons. The three bands just above the Fermi region could accommodate the rest of the five electrons, if sufficient electrons were available. The deficiency of five electrons is in good agreement with the previous theoretical results proposed by Bullet.¹⁴ This indicates that B₁₀₅ is electron deficient and unstable.

If the B₁₀₅ is electron deficient, structural deformations with partial occupancies would be anticipated. To understand this, we examined the crystal structure of the β -rhombohedral boron proposed by Slack *et al.*^{2,3} in detail. ELECTRONIC STRUCTURE AND BONDING ...

G



F

G

FIG. 1. (Color online) Calculated band structure of α -rhombohedral boron and β rhombohedral boron along their high symmetry points of Brillouin zone. Fermi energy level is indicated by a dotted line.

The crystal structure proposed contains six partially occupied sites along with the standard B_{105} (B_{57} +4 B_{12}) structure proposed by Hoard et al.⁴ The partially occupied sites must have significance in filling the valence band sufficiently. In order to rationalize this problem transparently we use the recently proposed mno rule. According to 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. Application of this rule³⁴ to the fragments indicates the following. The B_{57} unit must have +3 charge. Each of the four B_{12} units should have -2 charge. This is in tune with requirement of five valence electrons calculated by Bullet¹⁴ to fill the valence bands completely. Amazingly the partial vacant site in B_{57} ($B_{57}^{+3} \sim B_{56}$) takes care of the +3 charge of B_{57}^{+3} , by having only B_{56} atoms. This reduces the unit cell to 104. In addition there are extra occupancies adding up to 2.66 B atoms. These bring in eight electrons, so that the required 320 electrons are realized.³⁵ Partial occupancy and vacancies, therefore, are not to be treated as defects of the crystal structure, but a requirement that nature dictates to stabilize the β -rhombohedral boron.

It is necessary to study the β -rhombohedral boron crystal structure with partially occupied sites in order to understand these experimental observations. Unfortunately we could not compute electronic structure of β -rhombohedral boron with partially occupied sites. The size of the unit cell that would have no fractional occupancy will be too large to compute. Instead, the requirement of additional five electrons can be met by adding or substituting appropriate atoms at proper sites of the β -rhombohedral boron unit cell without disturbing its symmetry. This generates electron sufficient β -rhombohedral boron or boron rich icosahedral cluster solids (BRICS). Here we propose some model solids based on the cluster fragment approach to emphasize the above picture in detail. In this approach the B_{105} is divided into B_{57} and four B₁₂ cluster fragments. The dangling valence in B₅₇ and B12 clusters are saturated by hydrogen atoms and hence $B_{57}H_{36}$ and $B_{12}H_{12}$ boranes are generated. The $B_{57}H_{36}$ fragment is the combination of two B₂₈H₂₁ fragments connected via a boron atom (B₂₈-B-B₂₈) as shown in the Fig. 2. According to the mno rule the stable formulas for these clusters are $B_{57}H_{36}^{+3}$, $B_{28}H_{21}^{+1}$, and $B_{12}H_{12}^{-2}$. Substitution of the central boron atom B[14] of the two B_{28} units and B[15] in the B_{57} fragment by Li, Be, and C makes the B₅₇ equivalent neutral and electron sufficient without any vacant sites. This will facilitate the study of the solid. The following fragments are thus generated $\text{LiB}_{27}\text{H}_{21}^{-1}$, $\text{BeB}_{27}\text{H}_{21}$, $\text{CB}_{27}\text{H}_{21}^{+2}$, $\text{Be}_{3}\text{B}_{54}\text{H}_{36}$,

and Li₂CB₅₄H₃₆. The optimized geometries and the vibrational frequencies of these fragments are obtained. All B₂₈ fragments were found to be minima whereas the B₅₇ fragments $B_{57}H_{36}^{+3},\ Be_3B_{54}H_{36},\ and\ Li_2CB_{54}H_{36}$ had one (-14.33 cm^-1), two (-31.16 cm^{-1},\ -27.16 cm^{-1}), and one (-48.38 cm⁻¹) imaginary vibrational frequencies respectively. It is possible that the origin of these low frequencies is in the limitation of the algorithm. Even if these are not ground states as clusters, these could be stable building blocks in a rigid rhombohedral framework. The bond lengths in these clusters are found to be similar to those of the close and stuffed polyhedral boranes.^{36,37} There is an acceptable agreement between the bond lengths of the B57 skeleton of B_{105} and the calculated $B_{57}H_{36}^{+3}$ cluster. The B-B bond distance (1.988 Å) of the two triangles (B_3) that connect the central boron atom is very close to 1.989 Å obtained from the x-ray structure. The B-B distance between the central boron atom to the boron atom of the adjacent B_3 ring in B_{105} of 1.735 Å is close to the distance of 1.785 Å calculated for $B_{57}H_{36}^{+3}$. We select positions in A and E holes in the β boron to provide the required eight electrons to the four icosahedra. The surroundings of these holes resemble the B_{12} topology. The atoms kept at hole A have sixfold symmetry and the atoms at hole E have twofold symmetry as shown in Fig. 3. Therefore A and E holes can accommodate six and two Li atoms which provide eight electrons that are required for four icosahedra. This generates the unit cells $Li_8Be_3B_{102}$ and Li₁₀CB₁₀₂. The viability of these model crystals is supported by the known boranes and the corresponding borides doped by Be, Li, and C atoms.^{38–42}

The band structure justifies our anticipation. The valence and conduction bands of $Li_8Be_3B_{102}$ are well separated in the



FIG. 2. B_{28} unit is connected to another B_{28} unit through a single boron atom bridge (B28-B-B28). The bonds that are directed out correspond to the B–H bonds of the associated $B_{57}H_{36}$ molecule obtained from this fragment.



FIG. 3. A and E holes of the optimized rhombohedral $Li_8Be_3B_{102}$ boron showing the Li positions.

given Brillouin zone. An indirect band gap of about 1.7 eV is observed from the top of valence band at G and the bottom of conduction band at F zones as shown in Fig. 4. The PDOS of Be shows that the Be bands are present just below the Fermi region as shown in Fig. 5. The PDOS of center Be atom of B₅₇ unit falls at the Fermi level. The rest of the two Be PDOS are 14 eV away from the Fermi region. The Li bands are located at the very bottom of the Fermi region, which indicated that these are localized. The valence and conduction bands of Li10CB102 are well separated. But a band can be seen very near to the Fermi surface in the G-Z direction (Fig. 4). An indirect band gap of 1.88 eV from the top of the valence band at G and the bottom of the conduction band at F is observed. The PDOS shows the presence of the carbon bands away from the Fermi region. These are dispersed in the range of 2–17 eV. Interestingly the bands generated by Li in any part of the unit cell are observed around the same energy (Fig. 5). In view of the low percentage of doping, the PDOS contribution from the hetero atom is small everywhere. The contribution of the two B₃ triangles to the band structure is substantial in the Fermi region and do not change in the doped structures. In the case of idealized



FIG. 5. (Color online) Calculated PDOS for B_{105} , $Li_8Be_3B_{102}$, and $Li_{10}CB_{102}$. (I) The PDOS of three boron atoms located at the centers of B_{57} (1) B[15] and of two B_{28} (2) B[14] units in the B_{105} . (II) The PDOS of three Be atoms are located at B[14] and B[15] positions and Li atoms at A and E holes in $Li_8Be_3B_{102}$. (III) The PDOS of one C and two Li at B[15] and B[14] positions in $Li_{10}CB_{102}$. (IV) The PDOS of 8 Li at A and E holes in $Li_{10}CB_{102}$.

 B_{105} , these bands are not completely filled. In experimental $B_{106.66}$ these bands are filled using the electrons available from intrinsic defects. In the model systems the doped atoms provide these extra electrons. It shows that Li is almost completely Li⁺ in the unit cell. The PDOS arising from the Be and C atoms are in the same region of energy as that obtained for the bands of the two central boron atoms of the B_{28} and the central boron atom of B_{57} (Fig. 5).

The reduction of volume of these model crystals (815.3 Å in Li₈Be₃B₁₀₂, 807.9 Å in Li₁₀CB₁₀₂) from the ideal B₁₀₅ (823.4 Å) indicates the extra stabilization obtained by doping (Table I). The mixing energies of these solids were evaluated by taking the standard binding energies of Li, Be, α -rhombohedral boron, and graphite. According to this the stabilization energies of Li₈Be₃B₁₀₂ and Li₁₀CB₁₀₂ are 4.25 and 0.67 eV, respectively. However many metal doped β -rhombohedral boron crystal structures reveal that the



FIG. 4. (Color online) Calculated band structure of $Li_8Be_3B_{102}$ and $Li_{10}CB_{102}$ along their high symmetry points of Brillouin zone. Fermi energy level is indicated by a dotted line.

doped atoms occupy the interstitial positions rather than substituting boron atoms. In order to maintain the electron count, it chooses partial occupancy as an intrinsic defect. The band gaps of the above model structures are similar to β -rhombohedral boron and some of the metal doped β -rhombohedral borides which are semiconductors.⁴³ This shows the essential similarity between β -rhombohedral boron (B_{106.66}), boron rich metal borides, and the model systems studied. These results should help to understand the conductive properties of borides. We are currently studying various properties of boron rich icosahedral cluster solids (BRICS).

IV. CONCLUSIONS

First principles calculations of graphite, diamond, α -rhombohedral boron, and β -rhombohedral boron show that graphite is more stable than diamond but β rhombohedral boron (B₁₀₅) is less stable than α rhombohedral boron. In addition the band structure indicates β -rhombohedral boron to be metallic. These theoretical re-

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sults, which are contrary to experiments, are explained using band structure calculations. Structural modifications on β -B₁₀₅ obtained by doping and substitution of strategic atoms by Li, Be, and C so as to provide an electron count of B_{106.66} are found to be appropriate. The nature and position of various doping atoms are inferred from the studies on fragments of β -rhombohedral boron designed using the *mno* rule such as B₁₂H₁₂⁻², B₂₈H₂₁⁺¹, BeB₂₇H₂₁, LiB₂₇H₂₁⁻¹, CB₂₇H₂₁⁺², B₅₇H₃₆⁺³, Be₃B₅₄H₃₆, and Li₂CB₅₄H₃₆. The idea of filling the valence band of B₁₀₅ with the requirement of five electrons by adding or substituting proper atoms unfolds a way of looking at the materials, BRICS.

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