CHAPTER 5

BONDING IN EXTENDED SYSTEMS
5.0. INTRODUCTION

Computational material science has advanced itself in characterizing new materials with the desired properties providing rational approach to their synthesis\(^1\) thereby rapidly replacing explorative synthesis involving ad-hoc procedures. Polyhedral boranes, despite their very complicated three dimensional networks, is ideal for such design as their skeleton can be systematically perceived as a network of some comprehensible molecular fragments whose bonding requirements are known.\(^2\) An extended fusion of pentagonal pyramids through an edge has been selected for an elaborate study to verify the applicability of the generalized \(mno\) rule to extended systems.

Though, many borides have \(B_{12}\) and \(B_6\) units as primary building blocks,\(^i\) condensed structures where individual units share one or more vertices in common are also ubiquitous.\(^3\) The superconducting \(\text{MgB}_2\), in which adjacent \(B_6\) rings share a common edge, serves as an ideal example.\(^4\) Here, a novel and promising extended boride structure is proposed which is constructed from edge sharing molecular skeletons observed in macropolyhedral boranes and its bonding is explored through first-principle calculations. The model structure is isomorphic to the \(\text{MgB}_4\) structure observed earlier\(^5\) but has sigma-pi characteristics of the \(\text{MgB}_2\) structure and shows remarkable rigidity with various cations. Though both \(\text{MgB}_2\) and \(\text{MgB}_4\) shows adherence to the electron counting rules only the former exhibits superconductivity. However the minimal requirement for the existence of a boride phase seems to be its adherence to electron counting rules though there are notable exceptions.
5.1. EDGE-SHARING PENTAGONAL PYRAMIDS IN EXTENDED STRUCTURE: A THEORETICAL BORIDE NETWORK

The recent discovery of superconductivity\textsuperscript{6} in MgB\textsubscript{2} at a relatively high transition temperature of 39K renewed interest in the electronic properties of intermetallic borides. There had been several attempts to synthesize borides of light metals in the hopes of achieving a higher superconducting transition temperature. Standard BCS theory of superconductivity\textsuperscript{7} predicts enhanced transition temperatures for materials containing lighter elements due to their higher phonon frequencies.

Among various modes of condensation in polyhedral fragments, edge sharing is found to be dominant for polyhedral networks.\textsuperscript{2e} This is evident from the observation that the majority of macropolyhedral boranes characterized experimentally have edge-sharing skeleton. Hence the choice of edge sharing network is ideal for extended networks. Besides, edge sharing offers structural similarity to the MgB\textsubscript{2} structure that holds great promise for superconducting electronics due to its characteristic double gap.\textsuperscript{9} Though such edge shared polyhedral networks are known in MgB\textsubscript{4}, the 2c-2e bond between a ring and a cap atom of two adjacent chains disturbs the distinct o and n framework which is observed in MgB\textsubscript{2}. In order to maintain that framework of MgB\textsubscript{2}, we choose the edge sharing pentagonal network forming linear chains. However, unlike hexagonal rings in MgB\textsubscript{2}, pentagonal rings prefer capping by a boron atom due to ring-cap matching.\textsuperscript{9} With these considerations, we chose pentagonal pyramids as building blocks for the extended structure.
5.1.1. Description of the Structure

Condensation of pentagonal pyramids by sharing an edge between adjacent B\textsubscript{6} units can be made to form a linear chain. Capping of the adjacent rings can be done either on the same side or at the opposite sides. However, the \textit{trans} form in which adjacent caps are at the opposite side are favorable over the \textit{cis} form (Figure 1) since proximate cap-cap interactions in \textit{cis} form are only weakly bonding.\textsuperscript{10} These linear chains can be extended in two dimensions by placing them parallel so that their unshared ring boron atoms are connected to each other by a two-centered two electron (2c-2e) bond. This can lead to two isomeric forms depending on whether the caps on the adjacent chains are \textit{trans} or \textit{cis} as illustrated in Figure 2.

![Figure 1](image)

A linear Chain of edge-sharing pentagonal pyramids in \textit{cis} and \textit{trans} forms.

To extend the structure in three dimensions, we can place the layers of these two dimensional skeletons, one over the other by connecting the capping boron atoms through a 2c-2e bond. Similar to the 2-D network, the 3-D network also exists in two isomeric forms with respect to the position of capping atoms across the one-dimensional chain. For the 3D network, the two types a and b which have \textit{trans} and \textit{cis} orientations with respect to the link across 1D chains are shown in Figure 3. The unit cell of this structure

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is orthorhombic and falls in the space group *Cmcm* for the *trans* orientation and *Immm* for the *cis* orientation (Figure 3).

![Figure 2](image1)

Figure 2
Connection of the capping boron atoms of edge-sharing *trans* pentagonal pyramids by 2e-e bonds to form a 2-dimensional network. (a) and (b) represent the resulting *trans* and *cis* forms respectively.

![Figure 3](image2)

Figure 3
The orthorhombic unit cell of edge sharing trigonal-pyramidal network. (a) gives the unit cell due to the *trans* orientation of the caps in the adjacent chains and (b) is the unit cell due to the *cis* orientation.
Both the structures have twelve vacancies in a unit cell where cations can be occupied which can be categorized into three distinct types. Four of them lie exactly opposite side of the capping boron atom in the pentagonal ring and originates from the 1-D network itself. These are termed as capping voids and are denoted as CAP. The next group of four vacancies originates from the 2-D network due to the 2c-2e linkage between the ring boron atoms on adjacent chains and connects the four capping voids. These form octagonal channels (Channel-1) when a 3-D network is formed. The third type of four voids again forms channels (Channel-2) and is characteristic of the 3-D network that is formed due to the 2c-2e bonds between the caps of the adjacent 2-D networks. They are of different sizes depending on the boride skeleton. Channel-2 in a form is connected with one adjacent capping void, whereas in the b form either it is connected with both the capping voids on its sides or it will be isolated by the cap-cap 2c-2e bonds in which case it will be octagonal. Two such channel-2 voids will be alternating in the b form. These voids and channels can accommodate cations to satisfy its electronic requirements. It is related to the boride network found in MgB$_4$ that also has edge sharing of pentagonal pyramids, but unlike the known MgB$_4$, the present skeleton forms a linear array resembling MgB$_2$.

5.1.2. Determination of Electronic Requirements for Bonding

The electronic requirements of this hypothetical skeleton can be evaluated using our recent electron counting paradigm.$^2$ According to the rule, a macropolyhedral skeleton that has n vertices and m cages will require n+m electron pairs for its skeletal bonding. Absence of one or more vertices will require additional electron pairs. Hence, an edge-shared condensation of two closo pentagonal bipyramids B$_{12}$H$_{10}$ will require
14 electron pairs for its skeletal bonding. If two of its vertices are removed from the trans position to give the edge-sharing pentagonal pyramid B_{10}H_{8}, the number of electron pairs remains the same i.e., 14 since extra electron pairs have to be added for the missing vertices. Since only ten electron pairs are available, this molecule will exist with 6- charge or will have six bridging hydrogen atoms (B_{10}H_{14}). To verify the electronic requirements, B_{10}H_{14} is optimized (Figure 4) at B3LYP/6-31G* level^{11,12} of theory and found that it is a minimum on the potential energy surface, confirming our electron count.

![Figure 4](image.png)

The geometry of B_{10}H_{14} optimised at B3LYP/6-31g* level of theory.

Likewise, the electron counting can be extended to the infinite chains. Edge-sharing closo network will require a -2 charge irrespective of the number of units in the chain and can be ignored for an infinite chain. However removal of a vertex from the closo skeleton to form the edge sharing pentagonal pyramids (Figure 1) will require one electron pair per individual units. In the orthorhombic unit cell discussed above, there are eight such pentagonal pyramids effectively. Hence the unit cell requires 16 electrons. These electrons can be made available to the network by sufficient cations of appropriate size in the available voids. Though all the twelve voids in the network can accommodate cations, only eight of the voids are chosen for Mg, to arrive at different isomeric MgB_{4}.
structures. This enables a verification of the rigidity of different *isostructural* boride networks, and also provides a means to compare their energetics with the known $\text{MgB}_4$ structure. However, to get a compact network, all the twelve voids have to be filled. Hence these networks allow room for substituting $\text{Mg}^{2+}$ with monovalent cations. We chose the a form for the ternary phase, replacing some $\text{Mg}^{2+}$ ions by $\text{Li}^+$ and adding one more $\text{Li}^+$ in the extra void which results in the stoichiometry of $\text{Li}_2\text{MgB}_8$.

Extended structure calculations on the three-dimensional network of edge-sharing pentagonal pyramids are done using extended H"uckel based band structure program Yaehmop.\(^{13}\) The advantage of this simplistic method is that it gives valuable chemical insight of the structure and can be done for highly charged unit cells with ease. The structure was computed with 64 kpoints set in the orthorhombic space group keeping the B-B distances of the optimized $\text{B}_{7}\text{H}_{7}^{2-}$ molecule. Thus while the ring B-B distance is 1.657 Å, the cap to ring B-B distance is 1.830 Å. Geometrical optimization of the metal borides; $\text{Li}_2\text{MgB}_8$ and $\text{MgB}_4$ structures were done by a set of plane wave calculations using the CASTEP 5.2 simulation code.\(^{14,15}\) A generalized gradient approximation (GGA)\(^{16}\) was used for the exchange and correlation potential. An energy cutoff of 310 eV generated a basis set that allowed the total energy of the system to converge to $2.0\times10^{-5}$ eV atom\(^{-1}\). For the Crystal lattice, integration over the symmetrized Brillouin zone were performed using k-points generated via the Monkhurst-Pack scheme.\(^{17}\) Simultaneous optimization of crystal lattice parameters and atomic relaxation were performed under the space group symmetry constraints. For comparison, the experimentally reported $\text{MgB}_4$ structure is also computed at the same level. Ultra-soft pseudo potentials were used throughout for boron (s, p) and cations (s, p, d).
5.1.3. Results and Discussion

i. Li₂MgB₈

The stability of the trans boride (Figure 3, a) based extended systems is tested by optimizing the unit cell with appropriate cations in the vacancies. A possible way of achieving the electronic requirement by filling all the available vacancies in a unit cell is by considering bimetallic systems involving alkali metals and alkaline earth metals.

The trans form of the boride corresponding to the structure in Figure 3 a with a space group of \textit{Cmcm} is optimized using Li and Mg ions; resulting in a stoichiometry of Li₂MgB₈. Here Mg is placed at the four capping voids and the Li ions occupy both the channels. With such an arrangement, the boride skeleton is found to be very stable with reasonable B-B bond lengths. The different types of B-B bonds present are Bs-Bu (between a shared and a non-shared atom in a pentagonal ring), Bs-Bs (between two shared atoms within a ring), Bs-Bc (between the shared atom and a cap atom within a pentagonal pyramid), Bu-Bc (between the non-shared atom and a cap atom within the pyramid), Bu-Bu (2c-2e bond between two ring atoms of two adjacent chains), Bc-Bc (2c-2e bond between two cap atoms of adjacent chains). The various bond distances in the optimized boride skeleton of Li₂MgB₈ are 1.713 Å (Bs-Bu), 1.767 Å (Bs-Bs), 1.843 Å (Bu-Bc), 1.853 Å (Bs-Bc), 1.800 Å (Bu-Bu) and 1.842 Å (Bc-Bc) respectively. Each chain of a fragmented 2-D network is inclined to the adjacent one by an angle of 171.5°; inverse stacking of these make the complete 3-D network. The geometry of the optimized system with a view along the ac plane is given in Figure 5. The direction of the tilt at both the sides of the chain of pentagonal rings is opposite to each other, giving a ladder like appearance along the c-axis.
The extended view of the optimized geometry of $\text{Li}_2\text{MgB}_8$ along the ac plane.

The \textit{exo} bonds of each pentagonal ring which consists of the 2e-2e bond with the ring atom on the adjacent chain is found to be bend by $10.5^\circ$ with respect to the plane of the ring. This bending helps in an effective ring-cap overlap for both boron and magnesium with the $B_5$ ring.\textsuperscript{9} This indicates that there is considerable covalent interaction between Mg and the pentagonal open face as in the case of MgB$_2$. The bending is towards the boron cap and away from the Mg because this bending of the \textit{exo} B-B bond towards the boron cap helps in a better overlap between them. This indirectly benefits the overlap between the pentagonal ring and the Mg atom as well which occupies the opposite cap position. Due to the difference in the size of the two caps, both of them have overlap advantage on bending. The channels in between are large enough to
accommodate the Li\textsuperscript{+} ions. The band structure and DOS (Figure 6) of the optimized Li\textsubscript{2}MgB\textsubscript{8} shows the material to be a finite gap semiconductor with an indirect band gap of around 0.5 eV in the Y-G region.

![Figure 6](image)

**Figure 6**
The band structure and DOS of Li\textsubscript{2}MgB\textsubscript{8} of an orthorhombic unit cell belonging to Cmcm space group

The major difference between MgB\textsubscript{2} network and the present boride network is the existence of capping boron atoms. This capping stabilizes the perpendicular p\textsubscript{z} orbitals of the pentagonal rings and may remove the bands arising from them away from the frontier region. Hence an extended structure calculation is performed on the optimized structure to analyze the nature of bands around the Fermi level. The projected DOS of the perpendicular p\textsubscript{z} orbitals of the ring atoms calculated using yaehmop is given in Figure 7.
The projected DOS of the p\textsubscript{z} orbitals of the ring boron atoms in Li\textsubscript{2}MgB\textsubscript{8}.

The DOS is almost zero exactly at the Fermi level as observed in Figure 6. However, the density of states is found to be relatively high around the Fermi region, with major contribution from the p\textsubscript{z} orbitals of ring boron atoms, making a striking similarity to the superconducting MgB\textsubscript{2} band structure.

A similar stoichiometry of Li\textsubscript{2}MgB\textsubscript{8} in the cis form corresponding to Figure 3b, fails to converge. This is presumably because of the absence of bending of the exo 2c-2e bonds in the cis orientation as both the rings joined by a 2c-2e bond has its caps in the same side. To substantiate this conjecture, the energetic stability of various isomorphic forms of this boride network discussed earlier, are analyzed using pure Mg\textsuperscript{2+} doping.

\textbf{ii. MgB\textsubscript{4}}

The electronic requirement of the boride network can also be achieved by replacing the two Li ions in Li\textsubscript{2}MgB\textsubscript{8} by Mg\textsuperscript{2+} ion, resulting in MgB\textsubscript{4}. Here only eight vacancies per unit cell are filled. MgB\textsubscript{4} phase is already known where a similar network of edge shared pentagonal pyramids connects to another by forming 2c-2e bonds between
a ring atom and a cap atom. In addition changing the positions of the Mg ions will generate three isomeric forms in the trans form itself. But one of them converged to another form and the trans-boride MgB$_4$ isomers are reduced to two. Hence we have four isomers of MgB$_4$ to compare which includes one cis boride network and the experimental MgB$_4$ as well. The relative energies (R.E. in kcalmol$^{-1}$) of the various isomers of MgB$_4$ with respect to the experimental one, with their space groups (G), cell parameters and volume of the primitive cell (V in Å$^3$) are given in Table 1 for comparison. In general, the hypothetical isomers are more spacious presumably due to the availability of additional unfilled voids.

Table 1. The relative energies (R.E.), space group (G), cell parameters and volume of the unit cell of various isomers of MgB$_4$.

<table>
<thead>
<tr>
<th>MgB$_4$</th>
<th>R.E.</th>
<th>G</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>V Å$^3$</th>
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<td>Expt.</td>
<td>0.0</td>
<td>$Pnma$</td>
<td>5.464000</td>
<td>4.428000</td>
<td>7.472000</td>
<td>90.0</td>
<td>90.0</td>
<td>90.0</td>
<td>180.78</td>
</tr>
<tr>
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<td>$Cmcm$</td>
<td>6.064608</td>
<td>6.064608</td>
<td>8.037695</td>
<td>90.0</td>
<td>90.0</td>
<td>42.1</td>
<td>198.02</td>
</tr>
<tr>
<td>II</td>
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<td>$Cmcm$</td>
<td>5.965752</td>
<td>5.965752</td>
<td>7.972395</td>
<td>90.0</td>
<td>90.0</td>
<td>43.4</td>
<td>194.96</td>
</tr>
<tr>
<td>III</td>
<td>33.5</td>
<td>$Immm$</td>
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<td>7.264452</td>
<td>7.264452</td>
<td>79.0</td>
<td>112.1</td>
<td>144.6</td>
<td>200.90</td>
</tr>
</tbody>
</table>

Figure 8
The optimized geometries for the isomers of MgB$_4$ in the trans form.
An isomer of the \textit{trans} boride (Figure 3a) where only the channels are filled leaving the capping voids empty is not found to be stable. The optimized structure converged to the geometry where the Mg ions are migrated from channel-2 to CAP. Such an isomer (I, Figure 8a) where channel-1 and the capping voids are occupied by Mg ions is found to be the most stable among the hypothetical structures and is less stable than the known one by 13.9 kcal/mol per formula unit. The next isomer that is energetically closer is the one where the channel-2 and the capping voids are occupied by Mg ions (II, Figure 8b) and is less stable than the known form by 19.1 kcal/mol. Thus the capping void is found to be the most preferable position for Mg in the \textit{trans} boride network. But the reverse is found to be true in the \textit{cis} boride skeleton corresponding to that in Figure 3b.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{The band and DOS of isomer I of MgB$_4$}
\end{figure}
The angle of bending of the *exo* bonds of the pentagonal ring boron atom in isomer I is 6.5° which is less when compared to Li₂MgB₈. The ring has a uniform B-B distance of 1.723 Å for both Bs-Bs and Bs-Bu, and the cap to ring distance within the pyramidal unit has expanded slightly to 1.893 Å. Between the chains, Bu-Bu distance is expanded to 1.845 Å and the Be-Be is bond shortened to 1.807 Å. The net result is an expansion of channel-1 compared to that in Li₂MgB₈ that suggests that Mg ions are slightly larger for this void than the Li ions. In isomer II, The angle of bending of the *exo* bonds of the pentagonal ring boron atom is 10.8° almost identical to that observed in Li₂MgB₈. This shows that the presence of the Mg ions in channel-2 has an additive effect for the bending. Channel-1 gets compressed while channel-2 gets expanded with the B-B distances as 1.696 Å (Bu-Bs) and 1.824 Å (Bs-Bs), 1.816 Å (Bu-Be), 1.795 Å (Bs-Be), 1.842 Å (Bu-Bu), and 1.939 Å (Be-Be). In short, the channels where the Mg ions are present are expanded. Thus while I has Mg in channel-1, the ring Bu-Bs distances are longer compared to II and in II where the Mg occupies channel-2, the B-B distances pertaining to the caps are longer. The Bu-Bu distances between the chains that are shared by both the channels are almost the same. The optimized geometries of I and II, with a view along the bc planes is shown in Figure 8. Figure 9 and 10 gives the band and DOS of I and II respectively.

The band gap of the material in both the isomeric forms is around 0.5 eV lying in T-G region. The nature of the DOS is similar to that observed in Li₂MgB₈. The band structure and DOS for the known MgB₄ is given in Figure 11 for comparison. While the DOS looks similar, the band gap in the known MgB₄ is an indirect one. Thus the
theoretical system presented here is likely to possess better conductivity than the isolated one.

Figure 10
The band and DOS of isomer II of MgB$_4$

Figure 11
The band and DOS of the known form of MgB$_4$
Since the cis boride in Li$_2$MgB$_8$ where Mg occupied the capping voids did not converge, an isomer where they are left vacant is tried for MgB$_4$. Thus MgB$_4$ in the cis geometry where the CAP are left vacant and the Mg atoms occupy channel-1 & 2 is found to be possible theoretically. The CAP in cis-boride is found to be inappropriate for metals. The optimised geometry of MgB$_4$ (isomer III) along the ab plane belonging to the space group *Immm* of the orthorhombic unit cell is shown in Figure 12. The pentagonal rings of the various chains lie on the same plane. The Bs-Bs distance of 1.674 Å is shorter than that compared to Li$_2$MgB$_8$. The ring to cap distance within the pentagonal ring (1.837 Å) is comparable with Li$_2$MgB$_8$. While the Bu-Bu distance between the chains (1.923 Å) is little longer than that observed in Li$_2$MgB$_8$, the Bc-Bc distance (1.809 Å) is shortened. The lengthening of the Bu-Bu distance is presumably to compensate for the shortening of the B-B distance within the ring so as to maintain the size of channel-1 to accommodate the Mg$^{2+}$ ions. Similarly channel-2 need to be smaller as there is only one Mg$^{2+}$ ion in contrast to Li$_2$MgB$_8$, where channel-2 is fully connected with the capping void and both are filled.

**Figure 12**
An extended view of the optimized geometry of cis-MgB$_4$ along the ab plane.
The projection of the $p_z$ orbitals of ring boron atoms in the cis boride skeleton of MgB$_4$.

The band structure on the resulting optimized MgB$_4$ (isomer III) is shown in Figure 13. Isomer III of MgB$_4$ is found to be less stable than the known one by 33.5 kcal/mol$^{-1}$. However the results show that the borane framework is rigid. This isomer of MgB$_4$ seems to possess the smallest Fermi gap of 0.1 eV.
The total DOS shows small amount of density at the Fermi energy. This may be due to the insufficient k-sampling. A projection of the $p_z$ orbitals of the ring boron atoms from extended Hückel calculations are shown in Figure 14. As in the case of Li$_2$MgB$_8$, the $p_z$ orbitals of the ring boron atoms are concentrated along the Fermi region. The DOS is higher at the Fermi region, which is considered to be one of the factors responsible for superconductivity. A proper tuning of the skeleton with different types of isoelectronic atoms may result in very interesting electrical properties.

5.2. CONCLUSIONS

The stability of borides based on an edge shared pentagonal pyramid framework has been explored. The charge requirement in their 3-D network is compensated by cations in the various types of holes present. The two isomeric forms of the 3-D network - cis and trans - are stabilized by ions like Li and Mg. The trans boride is found to be stable as Li$_2$MgB$_8$ where all the possible vacancies are filled and also with MgB$_4$. MgB$_4$ have one type of vacancies left empty resulting in different isomers. It is observed that Mg always prefers the CAP void in the trans-boride skeleton. Thus one with two channels filled is unstable. The reverse is found to be true in the cis-boride skeleton of MgB$_4$. An isomer where Mg occupies the two channels is found to be more favorable. The different isomers of MgB$_4$ are compared with the known form. The band structure shows that the designed materials have smaller band-gaps than the experimental one. The greater DOS at the Fermi region also promises superconducting properties, and can be achieved by better tuning of the nature of the cations. The presence of $p_z$ orbitals at the Fermi region shows that the conductivity will be primarily due to the \( \pi \)-type orbitals.
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11. B3LYP is Becke’s three parameter hybrid method with LYP correlation functional:
   (a) Becke, A. D. *J. Chem Phys* 1993, 98, 5648. (b) Lee, C.; Yang, W.; Parr, R. G.


