Atomic bonding in the AlLiB_{14}

L. F. Wan^{a,b}, S. P. Beckman^{b,*}

^a*The Molecular Foundry, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

^b*Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA*

Abstract

The underlying nature of atomic bonds in the orthorhombic AlLiB_{14} crystal is studied using first-principles methods. Significant charge transfer is observed upon bonding, which is responsible to maintain good mechanical strength of the crystal. Individual bonding or anti-bonding states are identified which explains the correlation between the optimal mechanical strength and the electronic occupation of individual atomic orbitals. When the Fermi level is 0.35 eV inside the valence band the crystal has its maximum strength, which is the nominal position of the Fermi level in the experimentally-observed, off-stoichiometric orthorhombic borides. These results indicate that the soft-phonon modes previously identified in the literature allow the crystal to reach the optimal stability. Due to the unique crystallographic symmetry, the impact of uniaxial compressive strain on the individual bonds is also examined in the end.

1. Introduction

The complex boride crystal family, based on the AlLiB_{14} compound, has been studied extensively in recent years because of its unique electronic and mechanical properties. [1, 2, 3, 4, 5, 6] The crystal structure, shown in figure 1, has layers of triangularly arranged B_{12} icosahedra with metal ions between these layers. Although the compound can accommodate a variety of metal species, the AlLiB_{14} is the archetypical structure because experimentally it is found to be nearly stoichiometric, whereas many of the other compounds, such as AlMgB_{14} are typically off stoichiometric. [7, 8, 9] The B atoms are strongly covalently bonded to each other forming a rigid structure and the metal atoms contribute their valence electrons to this B-network. [10, 11] Although this compound is known to possess a number of promising properties, such as good mechanical strength, high melting temperature, and excellent resistance to chemical corrosion, there is yet to be a detailed report explaining the relationship between the electronic structure and local atomic bonding that is responsible for these properties.

In this article, the electronic structure, which directly determines the atomic bonding and physical properties of AlLiB_{14} , is carefully studied by *ab initio* methods. The charge density, which directly demonstrates local bonding, is examined and explained. The local bonding, anti-bonding, and non-bonding nature of the electronic states are determined and these are related to the mechanical strength of the crystal. [12] The impact of uniaxial compressive strain on the atomic and electronic states is determined and explained.

2. Methods

The density functional theory based approach implemented in the **QuantumEspresso** source code [13] is used to determine the electronic structure of AlLiB_{14} . Vanderbilt-type ultrasoft pseudopotentials [14] are used in place of the all electron ion potentials, and the generalized gradient approximation (GGA) is used for the exchange-correlation energy. [15] The wave function is approximated as a plane-wave expansion truncated at a cut-off energy of 950 eV and the Brillouin zone is sampled using a $4 \times 4 \times 4$ Monkhorst-Pack mesh. [16] This allows the forces on the ions to be converged to an accuracy of 5 meV/Å. The calculated lattice parameters for AlLiB_{14} are $a = 5.86$, $b = 10.38$, and $c = 8.16$ Å,

*Corresponding author

Email address: sbeckman@iastate.edu (S. P. Beckman)

which are in good agreement with those reported in the literature. [1, 7]

To analyze the bonding characteristics, the crystal orbital Hamilton population (COHP) analysis is performed, where the electronic wave function is represented by a set of localized atomic-like orbitals as implemented in the SIESTA code. The detailed parameter set used in the simulation can be found in Ref. [12] and [6]

3. Results and Discussions

3.1. Charge density

Within the AlLiB_{14} crystal structure there are five unique B sites, as identified in figure 1. The B_{12} icosahedra layers are stacked in the y -direction. The B_1 (green) apex sites in the icosahedra allow for direct bonding between the B_{12} via B_1 - B_1 bonds that extend between the layers. Within the B_{12} layers, in the xz -plane, each icosahedra unit is bonded to four neighbors at their B_4 (yellow) sites. The B atoms that do not belong to an icosahedra are referred to as inter-icosahedra B and are identified as B_2 (black) sites. Each inter-icosahedra B atom appears to be bonded to three nearby B_{12} at either B_5 (red) or B_3 (blue) sites located inside the icosahedra. The Al (cyan) and Li (pink) are located between the layers of B_{12} .

The fundamental assumption of DFT is that the ground state electronic properties of a system can be described by the spatial charge distribution, and therefore it is natural to begin a study of the electronic properties by examining the charge. However, the charge density itself is not always the most useful quantity. Instead the bonding charge density $\Delta\rho_{\text{bonding}}$, which is the charge difference between the bonded system and a combination of isolated atoms, provide valuable information about charge renormalization due to bonding. In figure 1(a), regions with positive $\Delta\rho_{\text{bonding}}$ indicate accumulated charge during bonding and regions with negative $\Delta\rho_{\text{bonding}}$, shown in figure 1(b), experience charge depletion upon bonding.

Charge accumulation is observed between the layers of B creating the critical B_1 - B_1 and B_2 - B_2 bonds that are identified and discussed in the literature. [12] In the xz -plane charge accumulation is observed between the inter-icosahedra B_2 sites and the B_3 and B_5 icosahedra sites, resulting in B_2 - B_3 and B_2 - B_5 bonds. The icosahedra are directly bonded

to each other via B_4 - B_4 bonds. Charge accumulation, is also present within the icosahedra. No covalent bond charge is observed between the metal species and the B.

Figure 1: The atomic structure and bonding charge density, $\Delta\rho_{\text{bonding}}$, of the AlLiB_{14} crystal. The atomic sites are identified in the legend, on the right. Column (a) shows a charge density isosurface with a value of $+0.022 \text{ e/a.u.}^3$, which indicates charge accumulation and column (b) shows an isosurface with a value of -0.012 e/a.u.^3 , which indicates charge depletion. A more clear visualization of the crystal structure, without the charge densities, can be found in Ref. [6].

The charge accumulation shown in figure 1(a) induces the charge depletion shown in figure 1(b). In agreement with previous efforts the metal species are shown to donate charge to the B atoms. In addition there is a rearrangement of charge within the B-network to facilitate the covalent bonding between the B atoms. Charge depletion is observed near the B_1 , B_3 , B_4 , and B_5 sites, away from the covalent bond charges. It is noteworthy that there is little local charge depletion near the B_2 site compared to the other B sites. This suggests that the B_2 atoms do not contribute significant charge to the B_2 - B_2 bonds and instead the observed bond charge must come from the metal species.

Löwdin population analysis [17] confirms the qualitative features observed in the charge density. The metal species, which have a valency of 3 and 1 for Al and Li respectively, have an integrated charge of 1.70 and 0.71 electrons indicating substantial loss

especially from the Al site. The B sites, which have a valency of 3 electrons, have all gained charge with the B₁, B₂, B₃, B₄, and B₅ sites having Löwdin populations of 3.07, 3.43, 3.11, 3.03, and 3.01 electrons. From this analysis it is concluded that the B₂ sites have gained considerable charge, compared to the other B sites, and this charge comes from the metal species. The charge-deficient feature of B₂ atom also implies that when doping the B lattice with a more electron-rich element, such as C, it will prefer to occupy the B₂ site as shown in Ref. [6]

3.2. Electronic density of states

The electronic density of states (DOS) and partial density of states of AlLiB₁₄, presented in figure 2, are consistent with previous theoretical investigations. [2, 10, 11] AlLiB₁₄, within the PBE approximation, is found to have a band gap of 1.3 eV and the Fermi level is located at the edge of the gap.¹ The metal atoms have negligible contribution to the states near the band gap, and the band edge is dominated by the B 2*p*-states with the B₂ and B₃ sites making the greatest contribution. Chemically doping the metal atom sites to move the Fermi level across the gap will selectively remove electrons from these atomic orbitals.

3.3. Bonding characteristics

The mechanical properties of this crystal family has been studied extensively for the past decade. [8, 19, 20] and number of scientific works have attempted to relate the mechanical properties to the electronic structures. [10, 21, 22] For example, there are studies that relate the bulk modulus to the species of metal atoms in the crystal. [10] However, the bulk modulus alone only indicates the averaged bonding strength of a material. To understand the real world mechanical behavior, a detailed analysis of individual bonds is required and in particular the pathways that will likely fail first. From ideal fracture strength calculations it is determined that the B₂-B₂ and B₁-B₁ bonds are critical for determining the strength of the system and should be a primary focus. [12]

Here the localized bonding at these sites are studied by performing the COHP analysis. Unlike the

DOS, which can only identify the energy associated with selected atoms and angular momentums, the COHP results allow for the character of the states to be determined, and in particular it allows for the determination of the bonding character of the states, *i.e.*, bonding, non-bonding, or anti-bonding. [23] The AlLiB₁₄ COHP is calculated near the band gap and is given in figure 3. From these results it can be assessed that the valence band edge represents electrons in B₂-B₃ and B₂-B₅ bonding states and B₂-B₂ anti-bonding states. The B₁-B₁ bonds that span between the layers of B₁₂ are non-bonding at the valence band edge, but become bonding about 0.35 eV below the valence band edge.

This demonstrates that the electrons associated with the valence band edge are highly localized in the crystal, near the volume where the B₂, B₃, and B₅ sites juxtapose. Moving the Fermi level into the states at the valence band edge removes electrons from this localized region and has the effect of strengthening the B₂-B₂ bonds, by depopulating the anti-bonding states, and weakening the B₂-B₃ and B₂-B₅ bonds, by depopulating the bonding states. The B₂-B₂ bonding states have lower energy, at least 0.55 eV below the band edge; however, B₁-B₁ bonding states are located 0.35 eV below the band edge and therefore moving the Fermi level below this energy will weaken the B₁-B₁ bonds and weaken the crystal overall.

It is noteworthy that AlMgB₁₄ is not observed experimentally. Instead the off-stoichiometric Al_{0.75}Mg_{0.75}B₁₄ is reported both in the early crystallographic experiments [7] and for the superhard specimen prepared by Cook and Russell [8]. The calculated electronic structure for the off-stoichiometric compound has a Fermi level directly in the energy window described above, meaning that the strength should be maximized. [24]

Further Wan and Beckman recently have reported that stoichiometric AlMgB₁₄ has a soft-mode lattice instability. [9] The collective atomic displacements associated with this mode indicate the metal atoms will beat against the network of B atoms. Removing electrons, dropping the Fermi level just below the valence band as described above, stabilizes the compound. This suggests that there is indeed a mechanism that results in the ejection of excess metal atoms, that stabilizes the lattice and results in maximizing the critical B-B bond strength.

¹Using more sophisticated functional, such as the HSE functional, the band gap is opened to 2.1 eV as discussed in Ref. [18] However, the DOS lineshapes are very similar for both functionals and therefore the characteristics of the electronic states are reliable for the PBE calculation.

When a strain is applied to a crystal, the elastic energy is stored in the local bonds by changing the electronic energy, and for many of the B-rich borides that are composed of B₁₂ icosahedral, the inter-icosahedra bonds are strongly impacted due to their sparse distribution. In the case of α - and β -rhombohedral B, applied strain causes rotation of the rigid B₁₂ substructures. [25] In contrast, the high number density of inter-icosahedra bonds in the AlLiB₁₄ compound suggests that this crystal family will respond differently under loading than other B compounds. To assess the effect of pressure on the atomic structure, pair distribution functions (PDFs) are presented in figure 4. The top frame of figure 4 shows the atomic distances for the ground state AlLiB₁₄ crystal. Below this are the PDFs for crystals that have been compressively uniaxially strained by 1% in the x -, y -, and z -directions. The averaged intra-icosahedra bond length is approximately 1.81 Å, which matches well with the experimental value. [7]

It is predicted by Wan and Beckman that for the {010} planes fracture is more likely to occur through the inter-icosahedra bonds than through the intra-icosahedra bonds. [12] The results in figure 4 confirm that uniaxial loading along the y -direction has a greater impact on the B₁-B₁ and B₂-B₂ bond lengths than any of the other atomic distances. The effect of loading in the xz -plane is more complicated. In the case of compression in the x -direction, the distance between the B₂-B₅ and B₄-B₄ bonds are effected, because they are aligned in the loading direction. Similarly the B₂-B₃ and B₄-B₄ bond distances are impacted by uniaxial loading in the z -direction. Unlike the B₁-B₁ and B₂-B₂ bonds, which are directly aligned in the y -direction, none of the inter-icosahedra bonds in the xz -plane are directly parallel to the loading directions. As a result of this complex geometry and numerous bonds, the strain is distributed within the B layer. This helps to explain the observation that the fracture strength of the {100} and {001} planes is nearly independent of the location of the fracture interface. [12]

Although AlLiB₁₄ has no pronounced icosahedra rotations, it is still observed to deform in a very anisotropic manner, which will impact its electronic structure. The volume deformation potential, $\alpha_v = dE_g/d\ln(V)$, where E_g is the band gap, is around -4.5 eV for uniaxial loading in the x -direction and

3 eV, for loading along y - and z -directions. Although the effect of uniaxial strain is non-negligible, hydrostatic pressure has little impact on the band gap of AlLiB₁₄, less than a 1 meV change for a 1.5% volume change. This differs significantly from α - and β -rhombohedral B, which are reported to experience 17 and 70 meV/GPa changes to their band gap upon hydrostatic loading. [25] It is possible that for AlLiB₁₄ the application of hydrostatic pressure results in a rearrangement of the states at the band edges, which may cause a rigid, uniform shift of the gap; however, this cannot be assessed without a detailed study of the band alignment.

4. Summary

The electronic structure of AlLiB₁₄ is examined in detail using density functional theory. Significant amounts of charge is built up between the inter-icosahedra B atoms, which contribute to the bonding strength between the icosahedra layers. However, it is observed that under uniaxial loading the inter-icosahedral B₁-B₁ and B₂-B₂ are weaker than the intra-icosahedral bonds, indicating that these are the critical bonds for controlling the strength.

Using COHP it is determined that placing the Fermi level around 0.35 eV inside the valence band results in depopulating the B₂-B₂ antibonding states while leaving the B₁-B₁ bonding states occupied. This is exactly the location of the Fermi level for the superhard, off-stoichiometric Al_{0.75}Mg_{0.75}B₁₄ reported by Cook and Russell. [8] The recently reported vibrational spectra of AlMgB₁₄, AlLiB₁₄, and Al_{0.75}Mg_{0.75}B₁₄ indicates the presence of a lattice instability that possibly results in the ejection of excess metal atoms. [9] The results here demonstrate that this naturally leads to maximizing the strength of the critical B-B bonds.

It is noteworthy that although the results here are likely representative of many sp-valent metal borides, such as AlLiB₁₄ and AlMgB₁₄, recently reported results suggest that bonding in the yttrium compound AlYB₁₄ is very different. [26, 27] In particular the Y d-states play a significant role near the top of the valence band. Investigating the bonding and electronic structure of these compounds is a topic for future studies.

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Figure 2: The total and partial density of states for the AlLiB_{14} crystal. The nomenclature used here follows that given in figure 1. The dashed vertical line indicates the Fermi level, which is set at the bottom of the conduction bands.

Figure 3: The calculated COHP for selected atomic pairs. The nomenclature follows from figure 1 and the Fermi level is arbitrarily set as the energy zero. A negative COHP indicates bonding interaction between the sites and a positive COHP indicates anti-bonding.

Figure 4: The pair distribution functions for AlLiB_{14} decomposed to show select B-B bonding pairs. A Gaussian broadening factor of $0.001 \text{ \AA}$ is applied to the histogram data to assist in viewing the interatomic distances. The top frame shows the data for the perfect crystal and the bottom frames show the distributions when a compressive, uniaxial strain of 1% is applied in the x -, y -, and z -directions.

- **B₁**
- **B₂**
- **B₃**
- **B₄**
- **B₅**
- **Al**
- **Li**

(a) **(b)**