# The electronic and mechanical properties of the XYB<sub>14</sub> complex borides studied by first-principles methods

by

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# DEDICATION

To my parents ...

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## CHAPTER 1. OVERVIEW

## 1.1 Introduction

For the good of human society, it is imperative to reduce the pollution and increase the energy efficiency of the manufacturing of goods. To achieve this, it is necessary to push the limits of material science to develop new materials that can be used in extreme chemical and mechanical environments. Over the past decade, intensive efforts have been invested to develop new superhard materials that can serve as abrasives for polishing and cutting tools and as wear-resistant and protective coatings.

The best-known superhard material to date is diamond. However, its industrial application is limited by its cost and susceptibility to chemical corrosion. Alternatively, boron compounds are promising candidates because of their excellent chemical and thermal stability. It is well accepted that superhard materials are usually comprised of a strong, covalently bonded network of atoms. This bonding usually results in a dense, highly symmetric crystal structure that is stoichiometric, for example TiB<sub>2</sub> or cubic-BN. These types of materials are difficult to chemically modify and as a result the mechanical properties are, "as made", rather than, "by design".

Recently, a class of complex borides, based upon the  $AlMgB_{14}$  crystal structure, has been proposed as a potentially superhard material. This class of crystal is unlike conventional superhard materials: the lattice of  $AlMgB_{14}$  falls into the low-symmetry orthorhombic group [1] and has a loose packed crystal structure. It is known that a variety of metal species and vacancies can occupy the metal atom sites [2, 3, 4, 5, 6, 7, 8].

1

The measured Vickers hardness of the base compound exceeds 32 GPa, and it is observed that the addition of impurity species and second phases has a significant beneficial impact on the mechanical properties [2]. At this time, there has been no systematic study aimed to explain the origin of the intrinsic hardness of the archetypal XYB<sub>14</sub>-type compound or to understand how to control its physical properties.

The goal of this project is to provide a thorough understanding of the electronic structure of the XYB<sub>14</sub> orthorhombic borides, and in particular how the electronic structure is related to its chemical composition, which can be used to control the physical properties of materials. Using first-principles methods, a series of calculations are performed to examine the relationship between the chemical bonding and the mechanical properties of XYB<sub>14</sub>. The impact of substituting different atomic species into both the metal and boron sites are investigated. The atomic-scale calculations performed here not only provide insight to the origin of the unexpected hardness of the XYB<sub>14</sub>-type crystals, but also serve as input for meso-scale models that can be used to examine the mechanical behavior of two-phase  $XYB_{14}$ -TiB<sub>2</sub> microstructure.

### **1.2** Literature review

The first XYB<sub>14</sub> crystal structure was reported by Matkovich and Economy in 1970, with X = Al and Y = Mg [1]. The structure was later re-examined by Higashi and Ito in 1983 [9]. According to Higashi and Ito, the crystal was prepared by heating the elemental boron, magnesium, and aluminum (with atomic ratio of 6:1:31) to 1500 °C, holding at the temperature for an hour, followed by cooling to room temperature. The excess aluminum was then dissolved in hot hydrochloric acid. The crystal obtained in this manner shows an orthorhombic symmetry (*Imma*) and has measured lattice parameters of 5.848, 10.312 and 8.112 Å. The crystallographic 64-atom unit cell contains four subunits of AlMgB<sub>14</sub>, and can be formulated more precisely as Al<sub>4</sub>Mg<sub>4</sub>(B<sub>12</sub>)<sub>4</sub>B<sub>8</sub>. The basic building unit is the  $B_{12}$  icosahedron. The eight B atoms that are not part of the  $B_{12}$  icosahedra are often referred as the inter-icosahedron B atoms, and are trigonal bonded to three neighboring  $B_{12}$  units. The widely opened B-network provides space to accommodate a large variety of metal species. The crystal structure of AlMgB<sub>14</sub> are heavily investigated in the literature and has been presented several times through this work [1, 9, 10]. In addition, Higashi and Ito reported a relatively high concentration of vacancies on the metal sites, upwards of 25% [9]. At the present time, it is not clear why intrinsic vacancies are formed at the metal sites and how this will influence the mechanical properties of the crystal.

Following the initial discovery of the AlMgB<sub>14</sub> crystal, the experimental focus was primarily the creation and characterization of the crystal structure for a variety of chemical compositions [2, 3, 4, 5, 6, 7, 8]. It is observed that the XYB<sub>14</sub> structure is willing to accommodate a wide variety of metal species. For example, the metal sites have been successfully doped by Li, Be, Na, Mg. For these compositions, the resulting lattice distortions are less than 5%. There has also been a great interest in working with the rare-earth elements. It is proposed that substituting a rare-earth element, such as Tb, Dy, Ho, Er, Yb, or Lu, to the Y site, might result in a magnetic semiconductor [7, 8].

Aside from the basic structural analysis, little attention was paid to the physical properties of the XYB<sub>14</sub> crystal family until 2000 when Ames Lab researchers, Alan Russell and Bruce Cook, discovered that an AlMgB<sub>14</sub> specimen produced by mechanical alloying technique exhibited superhardness [2]. The measured hardness of the Ames Lab sample had a baseline of 32 GPa. In addition, by forming a two-phase mixture with TiB<sub>2</sub>, both the hardness and wear-resistant properties can be significantly improved. The mechanical alloying approach introduces a substantial amount of impurity atoms into the sample during the fabrication process, *e.g.*, Si, C, O, and Fe. It is not clear how these impurity atoms behave in the specimen and impact its mechanical behavior. The early work of Cook *et al.* suggest that these impurities may in fact have a large impact on the overall mechanical strength.

Theoretical investigations have only played a minor role in understanding the properties of the XYB<sub>14</sub> structure. This is due to the high computational cost for studying such a large crystal. For the conventional DFT approach the computational time scales as the cube of the system size, which until recently has limited the computations to small cells containing 100s of atoms. The first *ab initio* calculation, conducted by Lee and Harmon in 2002 [10], was a monumental task and was limited to a rudimentary analysis of the electronic density of states and the elastic response of AlMgB<sub>14</sub>. Lee and Harmon also computed the electronic and elastic properties of  $Al_{0.75}Mg_{0.75}B_{14}$ , in which two vacancies were included in the unit cell. It is found that the addition of vacancies into the lattice reduces the overall elastic strength of the crystal.

Other theoretical efforts have concentrated on examining the chemical substitution on the  $XYB_{14}$  lattice. In 2008, Kölpin *et al.* investigated the phase stability and elastic behavior of XMgB<sub>14</sub> upon metal substitution, where X refers to Al, Ge, Si, C, Mg, Sc, Ti, V, Zr, Nb, Ta, and Hf |11|. It is observed that the boron atoms determine the electronic valence states. The metal atoms do not form strong covalent bonds with the neighboring boron atoms; instead they transfer their valence electrons to the entire lattice. It is concluded by Kölpin *et al.* that the more valence electrons transferred from the metal sites to the  $B_{12}$  units, the more stable the  $XMgB_{14}$  lattice will be. Additionally, they suggest that there exists a relationship between the bulk modulus of  $XMgB_{14}$  with its cohesive energy: decreasing the cohesive energy will increase the bulk modulus. In this paper, they claimed that the mechanical properties of  $XYB_{14}$  can be tuned by changing the chemical composition. However, the bulk modulus can only serves as a rough indicator of the averaged bonding strength of the crystal. For crystals that are highly anisotropic such as the  $XYB_{14}$  crystal, understanding the hardness requires a detailed analysis of the individual bonds within the crystal, in particular the critical bonds that would most likely lead to a mechanical failure.

In addition to the metal substitution, other work has also been done regarding the effects of doping the B-network. The early work of Cook *et al.* suggests that the presence of Si will enhance the macroscopic hardness of the AlMgB<sub>14</sub> specimen [2]. Theoretical studies return counter results. In 2009, Sahara *et al.* carried out a series of first principles calculations on the Si-doped AlMB<sub>14</sub> samples (M = Li, Mg, Na) [12]. In their simulations, Si atoms were substituted into all the possible atomic sites, and it was found that Si appears to favor the Mg site. The predicted bulk modulus for the Si substituted sample shows a 7% decrease.

Despite all the experimental and theoretical progress made so far, there are still many open questions that need to be answered, for example, what determines the occupancy of metal sites? How do the metal atoms influence the mechanical properties of  $XYB_{14}$ ? What is the role of impurities substituted to the B-network?

### **1.3** Dissertation organization

This dissertation begins with the general introduction to the XYB<sub>14</sub>-type crystals. Followed by this, the theoretical approach to simulate the material system will be presented. The body of this dissertation is comprised of a series of journal papers, where the first author is the primary investigator and author, and the last author is the major advisor and the author for correspondence. In Chapter 3, the role of metal species in the electronic structure of XYB<sub>14</sub> will be discussed, and it is illustrated in Chapter 4 that the off-stoichiometric metal composition is tied closely to the lattice instability of the crystal. In Chapter 5, detailed chemical analysis is performed to examine the bonding characteristics within the crystal. The relation between bonding and the mechanical strength of the crystal will be identified. In Chapter 6, the mechanical behavior of the XYB<sub>14</sub> is directly simulated based on *ab initio* methods. It is proposed here that ideal brittle cleavage model can be used as a proper indicator of the fracture strength of the  $XYB_{14}$ -type crystal. In Chapter 7, first attempt to dope the B lattice is performed, and its impact on the properties of the host materials is investigated. The dissertation is finally closed with a general conclusion chapter.

# CHAPTER 2. THEORETICAL APPROACH

## 2.1 Density functional theory

#### 2.1.1 The Kohn-Sham equation

In this project, density functional theory (DFT) [13] is used to examine the structural, electronic, and mechanical properties of the XYB<sub>14</sub>-type compounds. The critical assumption in DFT is that the potential energy terms in the Hamiltonian can be expressed as functionals of the charge density, n(r), as proposed by Kohn and Sham in 1965 [13]. Following the Hartree-Fock anstaz, DFT simplifies the many-body problem by assuming that the electrons can be treated as non-interacting particles traveling in an effective field [13, 14]. Because the nuclei are moving with negligible velocities compared to electrons, their positions are assumed to be fixed when solving the many-body electronic structure, which is the so-called Born-Oppenheimer approximation. As given in equation 2.1, the explicit form of the Kohn-Sham energy is written as a sum of the kinetic energy of the non-interacting electrons  $(T_s)$ , the external potential energy carried by ions  $(V_{ext})$ , the Hartree energy  $(E_{Hartree})$  and the exchange-correlation energy  $(E_{XC})$ which encapsulates all the quantum effects for the many body interaction.

$$E[n(r)] = T_s[n(r)] + \int n(r)V_{ext}(r)dr + E_{Hartree}[n(r)] + E_{XC}[n(r)]$$
(2.1)

From the above energy expression, an effective potential can be defined as,

$$V_{eff} = \frac{\delta\{\int n(r)V_{ext}(r)dr + E_{Hartree}[n(r)] + E_{XC}[nr]\}}{\delta n(r)}$$
$$= V_{ext}(r) + \int \frac{n(r')}{|r-r'|}dr' + \frac{\delta E_{XC}[n(r)]}{\delta n(r)}$$
(2.2)

Within these assumptions the principle task is to solve the eigenfunction problem of the Kohn-Sham equation as written in equation 2.3, in a self-consistent fashion. The self-consistent iterative solution method will be discussed later in this section.

$$\begin{bmatrix} -\frac{1}{2}\nabla^2 + V_{eff}(\vec{r}) \end{bmatrix} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$
$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$
(2.3)

#### 2.1.2 Exchange-correlation functional

In principle, all the terms in equation 2.1 can be explicitly solved, expect for the exchange-correlation functional. Up to date, many types of exchange-correlation functionals have been proposed with different levels of complexity and accuracy. The simplest treatment of the exchange-correlation is the local density approximation (LDA). Within this approximation, the real, inhomogeneous system is divided into infinitesimal volumes each treated as having a constant charge density. The exchange-correlation energy in each volume is then approximated as the energy obtained from a uniform electron gas with the same density.

As defined in equation 2.4, LDA should only be valid in describing the system with slowly varying densities. However, practically it works surprisingly well in most of the solid systems, especially for metals. It is believed that this is because the errors caused by the separated exchange and correlation effects are systematically cancelled. In general, the LDA approximation tends to underestimate the lattice constant by  $2 \sim 3\%$  and overestimates the binding energy by  $15 \sim 20\%$ .

$$E_{XC}^{\text{LDA}}[n(r)] = \int n(r)\varepsilon_{XC}^{\text{unif}}[n(r)]dr \qquad (2.4)$$

An upgraded treatment for the exchange-correlation energy is the generalized gradient approximation (GGA) in which the  $E_{XC}$  is expressed in terms of both the local charge density and the local density gradient.

$$E_{XC}^{\text{GGA}}[n(r)] = \int n(r)\varepsilon_{XC}^{\text{GGA}}[n(r), \nabla n(r)]dr \qquad (2.5)$$

Because of the dependence of the users choice for  $\nabla n(r)$ , the GGA approximations are often referred to as "semi-local" functionals. For many covalent and weakly bonded systems, GGA tends to provide a better approximation than LDA, but this is not universally true. In this work, the GGA functionals are used to examine the electronic structure of XYB<sub>14</sub>, in particular, the ones proposed by Perdew-Wang (PW91) [15], and Perdew-Burke-Ernzerhof (PBE) [16].

A well known drawback of applying LDA or GGA to study semiconducting or insulating systems is the underestimated band gap. This is mainly because the appearance of the spurious self-interaction term in LDA or GGA formalism. In the Hartree-Fock formalism, this self-interaction is completely cancelled by the non-local exchange interaction. However, in LDA or GGA, this interaction is not exactly cancelled and there is spurious self-interaction term left, which is considerable for inhomogeneous systems. The presence of self-interaction energy clearly impairs the accuracy of predicting the band gaps for most semiconductors. One way to reduce the effect of self-interaction energy is to use hybrid functionals, which combine certain fractions of the non-local Hartree-Fock exchange with other semi-local exchange energies [17]. For example, the widely used PBE0 functional has a mixture of 1/4 Hartree-Fock exchange and 3/4 PBE-GGA exchange energies [18].

$$E_{XC}^{\text{PBE0}} = \frac{1}{4}E_X^{\text{HF}} + \frac{3}{4}E_X^{\text{PBE}} + E_C^{\text{PBE}}$$
(2.6)

In recent years, a new hybrid functional form has been developed, which is known as the HSE functional [19]. Based on the PEB0 functional, it further divides the PBE exchange

term into the long-ranged and short-ranged contributions, as shown below.

$$E_{XC}^{\text{HSE}} = \frac{1}{4} E_X^{\text{HF, SR}}(\mu) + \frac{3}{4} E_X^{\text{PBE, SR}}(\mu) + E_X^{\text{PBE, LR}}(\mu) + E_C^{\text{PBE}}$$
(2.7)

Here, the semi-empirical screening factor  $\mu$  is determined as a compromise between speed and accuracy in the simulation. The utilization of HSE hybrid functional has been well tested for many semiconducting oxides. In this work, the HSE functional is the first time to be used in the borides system, and the results are compared to the experimental studies.

#### 2.1.3 Self-consistent field

Once appreciate approximations are made to calculate the exchange-correlation functional, the Schrödinger-like Kohn-Sham equation can be solved within a self-consistent field (SCF), as illustrated in Fig. 2.1. First, an initial charge density is assigned for the system and then the Kohn-Sham Hamiltonian operator is constructed based on this charge density. Next the Kohn-Sham equation is solved as an eigenvalue problem using the basis selected to represent the eigenfunction. The calculated eigenvectors give the electronic wavefunctions associated with each Kohn-Sham energy state and are used to determine the new charge density. Comparing the new to the old charge density, if the difference is smaller than a predefined tolerance factor, then the electronic relaxation is complete; otherwise, the algorithm is repeated using a new guess for the charge density based on mixing the old and new charge densities.

### 2.2 Basis sets

The key problem in DFT is to solve for eigenvalues and eigenfunctions in equation 2.3. The obtained eigenvalues refer to the Kohn-Sham energy states of the system and the eigenfunctions are often called the basis set on which the electronic wavefunctions are



Figure 2.1 A schematic illustration of the self-consistent loop in DFT.

projected. In practice, before entering the SCF loop, the eigenfunction,  $\phi_i$  must first be represented as an expansion of known functions.

One popular approach is to use planewaves (PWs), which naturally impose the periodic boundary condition while providing a complete, unbiased basis set [20]. To solve the electronic structure in a periodic lattice, the Blöch's theorem is often used. According to the Blöch's theorem, the complex wavefunction for a periodic solid system is expressed as the product of two terms, a planewave that varies across the crystal based on the wave vector, k, and a function with the periodicity of the lattice, u(r), as written below.

$$\phi_k(r) = e^{ik \cdot r} u_k(r) \tag{2.8}$$

Here, the wave vector k represents a set of planewaves within the first Brillouin zone. Incorporating Blöch's theorem into equation 2.3, results in the electronic wave-function not only depending on the eigenstate, i, but also the wave vector, k. In principle, the k values should be continuous within the first BZ; however, in practice, the electronic structure is solved on a discrete k-point mesh. In some special cases, for example, when the density of states or band structure is calculated, a highly dense k-point sampling is needed.

Despite the success of utilizing the PW methods, the large number of PWs that is required to capture the shape of wavefunction significantly limits its computational efficiency. Even with the use of pseudopotentials, PW-based calculation is usually limited to the system that is less than 100 atoms.

Another set of functions that can be used to represent the eigenfunctions is, numerical atomic orbitals (NAOs). NAOs can accurately represent the eigenfunctions using considerably fewer terms, and therefore provide a more rapid solution of larger systems. As written in equation 2.9, this basis is characterized by a spherical harmonic term and a radial function term.

$$\phi_{Ilmn}(\vec{r}) = R_{Iln}(|\vec{r}_I|)Y_{lm}\left(\frac{\vec{r}_I}{|\vec{r}_I|}\right)$$
(2.9)

Here, I is the index of atom, l and m are the angular momentum and n is the number of multiple orbitals with the same quantum momentum. The spherical harmonic term is fixed for different orbitals, whereas the radial function term allows a great deal of flexibility to be modified. For example, one can change the size of the function to include more number of orbitals per atom, which is often known as multiple- $\zeta$  function. One can also modify the shape and the range of the radial function. Once the basis set is well defined, the Schrödinger-like Kohn-Sham equation is solved on a three-dimensional real space grid.

The challenge of using NAOs lies in the fact that there is no systematic way to choose the shape of the orbitals to provide a complete basis set that spans the Hilbert space. The choice of the atomic basis set strongly depends on the local chemical environment. To ensure that NAOs based calculations accurately reproduce the fundamental physical properties of the system, the results from NAOs calculation must be carefully compared to a representative set of PWs calculations.

Compared to the PW method, useful information regarding the bonding characteristics can be directly extracted from the NAO representations. The most widely used bonding indicators are the Mulliken-based approaches, such as Crystal Orbital Overlap Population (COOP), where overlap population is calculated between two atomic centered orbitals. Apparently, this approach is highly sensitive to the choice of atomic orbitals; thus the results are biased. An upgraded version of the COOP algorithm is called Crystal Orbital Hamilton Population (COHP) analysis [21]. In this approach, all the band structure energies are rewritten as sums of pair contribution from atomic orbitals. Instead of partitioning electrons to the orbitals as the COOP formalism does, the COHP method partitions the eigenvalues to the attributed overlapping orbitals. As a consequence, the results are less sensitive to the basis set and also easier to visualize. For example, the bonding characteristic between two neighboring atoms can be directly plotted along with the total density of states at the same energy range. In principle, a negative COHP value indicates the bonding states because of the lowered energy due to bonding, whereas a positive value corresponds to the anti-bonding states. The knowledge of bonding or anti-bonding states can provide direct insight to the change of bonding strength when these states are filled or emptied.

### 2.3 Pseudopotentials

The electronic calculations can be significantly simplified by introducing the concept of pseudopotentials, especially for the PW method [20]. As shown in equation 2.2, the first term of the effective potential is the external potential attributed by the electron-ion interactions. In practice, one may replace the all-electron ionic potential with a pseudopotential. As shown in Fig. 2.2, the deeply bound core electrons are highly localized and therefore they are chemically inert. Only the valence electrons are actively involved in forming bonds in solids. By considering the valence electrons only in the system, the deep potential in the core region, written as  $-\frac{Ze^2}{r}$ , can be replaced by a much smoother potential. In Fig. 2.3, an example is given for generating the Al pseudopotential. A cutoff radius,  $r_c$ , is always needed during the construction of the pseudopotentials. In the case of Al, a  $r_c$  of 2.0 and 1.5 *a.u.* is picked for the 3*s* and 3*p* orbital, respectively. In principle, the cutoff radius has to be soft enough to only require a relatively small basis set to represent the wavefunctions; in the mean time, maintain the transferability to allow it to be used in different chemical environments.



Figure 2.2 An example of spherical charge density of Al atom. The core includes the  $1s^22s^2sp^6$ -states and the valence refers to the  $3s^23p^1$ -states.



Figure 2.3 A pseudopotential generated for Al atom with only considering the  $3s^23p^1$  valence states.

The main advantage of employing pseudopotential is the capability of reducing the

size of basis set that is required to represent the electronic eigenfunctions of the system. As illustrated in Fig. 2.4, by ignoring the core electrons, the pseudo-wavefunction has no radial node inside the core region. However, beyond the core region, both the pseudopotential and the corresponding pseudo-wavefunction must exactly match the all-electron potential and all-electron wavefunction. In this work, a set of pseudopotentials are generated and used. Before making any productive runs, the constructed psedupotentials must be carefully tested to ensure all the required physics are well captured.



Figure 2.4 A comparison of wavefuction produced by the all-electron (AE) potential and pseudopotential (PS).

# 2.4 Summary

In summary, first-principles, DFT methods have been extensively used in calculating the electronic structure of molecular and crystalline systems. The direct output from solving the Kohn-Sham equation is the eigenfunctions, which give the charge density, and the eigenstates, which give the electronic energy. In addition to directly using the DFT output, the results can be analyzed. The total density of states (DOS) is the number of Kohn-Sham electron states present within an infinitesimal range of energy. Projecting the Kohn-Sham wavefunctions onto a set of orthogonalized atomic-like wavefunctions that are localized on the atomic sites and then analyzing the DOS for the states localized on each atomic site creates a projected density of states (PDOS), which gives insight regarding the bonding within the crystal. The first derivative of the total energy with respect to the atomic spatial coordinates gives the forces on the atoms, which allows for the optimized crystal structure to be determined. The second derivatives of the total energy with respect to certain types of perturbation gives the physical properties of the crystal, such as elastic tensor, dielectric tensor, piezoelectric tensor, dynamical properties. These response function (second derivatives of total energy) can be solved by applying perturbations to the Hamiltonian in the traditional DFT technique, which is often known as density functional perturbation theory. At present, three types of perturbations, i. e. atomic displacement, lattice strain, electric field are implemented in most of the DFT softwares. Combining at least two of them gives the properties as listed above.

# CHAPTER 3. CHEMICAL DOPING THE XYB<sub>14</sub> COMPLEX BORIDES

A paper published in Materials Letters

L. F. Wan and S. P. Beckman

# Abstract

In this paper we demonstrate the possibility of chemically doping the orthorhombic  $XYB_{14}$  crystal by controlling the metal atoms that occupy the X and Y sites. It is found that the B atoms create a network of covalent bonds in the crystal and create states near the band gap and Fermi level. The metal atoms are ionically bonded to the crystal and donate their valence electrons to the B-network. By carefully controlling the composition of the metal atom sites it may be possible to create a semiconducting medium with AlLiB<sub>14</sub> given as an example.

# 3.1 Introduction

Boron based compounds exhibit a broad and interesting array of physical properties such as high melting point, high Seebeck coefficient, high hardness, and low specific gravity [22, 23, 24, 25, 26]. The origin of boron's unique behavior is also the origin of the challenge to understanding it: boron's electronic structure allows it to readily form a wide variety of bonds to create a multitude of crystalline structures. For example, B is able to bond with metal atoms, M, to form a wide variety of stoichiometric compounds including M<sub>4</sub>B, MB, MB<sub>2</sub>, MB<sub>6</sub>, and MB<sub>12</sub> [22, 24, 27, 28]. Surprisingly these families of complex borides are not functionally modified as are most engineering materials, *e.g.*, Si is substitutionally doped, polymers have side-chains grafted to them, and nanowires have chemical adsorbates on their surfaces. The borides are used *as is* which limits their properties to those present by coincidence rather than properties by design. In this paper a method of chemical doping is presented that will facilitate controlling the electrical, and possibly other, properties of this class of complex borides.

This paper focuses on the metal boride,  $XYB_{14}$ , where X and Y are metal atoms. This structure was originally discovered by Matkovich and Economy in 1970 [1] and investigated by Higashi in 1983 [9]; however, it garnered little scientific interest until 2000 when Cook *et al.* observed that creating the AlMgB<sub>14</sub> compound via mechanical alloying yielded a specimen with superhard mechanical strength [2]. The observed hardness is surprising because the atomic structure is relatively open and has low symmetry, whereas most superhard materials are dense, stoichiometric compounds with high symmetry. Another aspect of Cook's specimen that is intriguing is the relatively large number of impurities, including Ti, Si, C, O, and second phases, including TiB<sub>2</sub> and Al<sub>2</sub>MgO<sub>4</sub>.

Although fully dense, single phase specimens of  $AlMgB_{14}$  are still difficult to synthesize, several preparation methods have been proposed that can produce samples with densities that are greater than 90% of the theoretical [3, 26, 29, 30, 31]. From these processing studies it is found that the preparation plays an important role in establishing the properties [30]. The variability may be due in part to changes in the crystal stoichometry [2, 9] and in part due to the impact of microstructure [32].

Computational efforts have been pursued to investigate the intrinsic atomic properties of the XYB<sub>14</sub> crystal family. These studies have primarily focused on the elastic response and the influence of adding impurity species to the elastic behavior. Lee and Harmon were the first to calculate the elastic constants and  $AlMgB_{14}$  [10]. The behavior of a crystal both with and without vacancies was compared and it was found that removing 25% of the Al and Mg atoms substantially diminished the elastic response. The influence of metal species on the elastic properties and binding energy of the XMgB<sub>14</sub> crystal family and AlYB<sub>14</sub> sputtered films was investigated by Kölpin *et al.*, and it was found that the phase stability is related to the transfer of the metal atoms' valence electrons to the B-network [11, 33]. Charge density analysis was performed by Letsoalo and Lowther and it was concluded that there exists a greater charge build-up between the B–B bonds in the AlMgB<sub>14</sub> than in other materials, due to the metal species that, "induce relaxation," in the B-network [34]. Other theoretical studies have focused not on the metal atom species, but direct substitution onto the B-sites [12, 34].

In spite of the progress made so far, there is still little understanding of what controls the properties of the XYB<sub>14</sub> crystal family or how to use our understanding to engineer the behavior. Here we extend the existing theoretical work to demonstrate the relationship between the chemical composition at the metal sites and the electronic structure by comparing the prototypical crystals,  $AlMgB_{14}$ ,  $AlLiB_{14}$ , and  $MgMgB_{14}$ . The unique bonding characteristics of boron provide this crystal family both a set of strong covalent bonds, due to the extended network of B atoms, and ionic bonds that bind the metal atoms to this network. We explore the possibility of exploiting this situation to create an XYB<sub>14</sub> based semiconductor in which the covalently bonded network of B atoms provide the framework to conduct charge and the metal atoms are used to dope the B-network, essentially controlling the charge carrier concentration.

#### 3.2 Methods

The crystal structure and electronic properties of  $XYB_{14}$  are calculated by firstprinciples, density functional theory (DFT) methods [13, 35]. The exchange-correlation energy is expressed as a local functional of the charge density including the local gradient [15], and ultra-soft pseudopotentials are used to replace the all-electron ion potentials [36]. The wave function is represented by a plane wave basis that is truncated at 900 eV, and the Brillouin zone is sampled using the Monkhorst-Pack [37] algorithm with a  $4 \times 4 \times 4$  grid. These parameters are selected to ensure that the calculated forces on the ions are converged to an accuracy of better than 5 meV/Å.

### **3.3** Results and Discussions

The lattice parameters for AlMgB<sub>14</sub>, AlLiB<sub>14</sub>, and MgMgB<sub>14</sub> are calculated and agree well with the experimentally determined structures that are published in the literature [1, 3, 4]. Using DFT it is relatively straight forward to qualitatively determine the change in the electron distribution when isolated atoms are bonded to form a crystal. By this approach it is observed qualitatively that the B atoms form covalent bonds between themselves and the metal atoms forfeit electrons to the B network. By calculating the projected density of states and performing population analysis it is possible to further verify that the states at the band edges are strongly influenced by the covalent bonds between the B atoms and that the metal atoms are ionically bonded to the crystal. These observations have been well established and reported elsewhere [10, 11, 12, 34].

The implications of this have yet to be explored. In particular, if the states at the band edges, near the Fermi level, are from the covalently bonded B and the metal atoms' primary role is to contribute electrons to the B, then presumably changing the valency of the metal atoms will impact the position of the Fermi level in the density of states. The total density of states (TDOS) are determined and plotted in figure 3.1. Assuming that each metal atom donates its valence electrons to the B, then each Al atom will contribute three electrons, each Mg two electrons, and each Li one. For a 64-atom unit cell the AlMgB<sub>14</sub> crystal will have four more electrons from the AlMgB<sub>14</sub> unit cell



Figure 3.1 The total density of states of the  $AlMgB_{14}$ ,  $AlLiB_{14}$ , and  $MgMgB_{14}$  compounds. The vertical dashed lines indicate the Fermi energy. In this paper, the energy zero is chosen arbitrarily as the maximum of valence band.

and recalculating the atomic and electronic structure. <sup>1</sup> It is shown in figure 3.1 that  $AlMgB_{14}$  with a 4 electron deficit has a distribution of states that is nearly identical to the fully compensated  $AlMgB_{14}$ ; however, the Fermi level has shifted to approximately the same position as that observed in the  $AlLiB_{14}$  and  $MgMgB_{14}$  density of states.

It is intriguing that the XYB<sub>14</sub> crystal family has a moderate sized band gap and that the Fermi level can be controlled by atomic substitution to the metal sites. By carefully controlling the composition, it may be possible to create a crystal that behaves as a doped semiconductor. Consider for example the AlLiB<sub>14</sub> crystal, which has a Fermi level that is only slightly inside the conduction band. The charge density associated with the conduction band is determined to be  $1.0 \times 10^{18}$  cm<sup>-3</sup>, which is equivalent to heavily doped n-type Si.

This consideration can be taken a step further by examining what would happen if a metal is placed in intimate contact with  $AlLiB_{14}$ . A rectifying Schottky junction is formed if the metal's work function is greater than the semiconducting boride. Using

<sup>&</sup>lt;sup>1</sup>A uniform background charge is added to ensure the neutrality of the computational cell.

DFT, the work function is determined by calculating the potential of a 2D semi-infinite crystal slab in vacuum with the work function defined as the difference between the electrostatic potential in vacuum and the Fermi energy of the slab [38]. For AlLiB<sub>14</sub> the (001), (100), and (010) surfaces have calculated work functions of 4.46, 5.21, and 6.04 eV respectively. These numbers are of course idealized and in any engineering situation the surfaces of the crystal will be highly tailored to optimize the work function and mitigate problems such as Fermi level pinning due to dangling bonds [39, 40]. From the calculations here it is predicted that a metal with a work function between 5 and 6 eV placed in contact with the (001) AlLiB<sub>14</sub> surface will create a Schottky barrier with a depletion width of approximately 10 nm [41].

One potential application for this type of junction is in a solid-state neutron detector. Boron is known to have a huge neutron capture cross-section, 3800 barns [42], and this particular crystal has a B atomic density of  $11.4 \times 10^{23}$  cm<sup>-3</sup>, which is 3 times larger than boron carbide [43], A crystal from the XYB<sub>14</sub> family that is chemically doped could act both as the neutron capture medium and as the electronics used to measure the deposited energy. Such a medium could find direct use in existing detector designs, and may allow for improvement of these devices by increasing their overall efficiencies [44, 45, 46, 47, 48].

#### 3.4 Summary

In conclusion we reiterate that boron based compounds are remarkably versatile due to boron's ability to form a diverse set of bonds. Unlike most engineering materials, the borides do not typically have functionalized properties by design and instead are used as is, without modification. Here the electronic structure of the  $XYB_{14}$  crystal family is studied using first-principles methods. The bonding in this crystal family is unique in that it has both a network of strong covalent bonds, similar to those found in tetrahedral semiconductors, and metal atoms that are ionically bonded to the covalent network. This family is shown to have a band gap with the Fermi level near the gap. The states at the edges of the gap are from the covalent network of B atoms and the metal atoms donate their valence electrons to the B network. This insight allows the position of the Fermi level to be controlled by selectively occupying the X and Y sites with metals having different valency. In this manner the crystal is functionally modified to become a doped semiconductor. It is further demonstrated that it may be possible to use AlLiB<sub>14</sub> to create a rectifying Schottky junction.

One can speculate that the observations presented here may have implications beyond the creation of a semiconducting boride. Takeda *et al.* reports that  $AlMgB_{14}$  possesses a large Seebeck coefficient; however, it has an inadequate electrical conductivity for practical application as a thermoelectric [26]. By appropriate chemical doping it may be possible to overcome this limitation, which may make the XYB<sub>14</sub> compound a favorable candidate in the search for new thermoelectric materials. The observations in this paper may also have bearing for the mechanical and vibrational properties of XYB<sub>14</sub>. As the Fermi level is moved through the density of states, electrons will be preferentially removed from states localized near specific B sites. This suggests that the chemical doping reported here could be used to tune the electron-phonon coupling in this crystal.

# 3.5 Acknowledgement

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# CHAPTER 4. VACANCY STABILIZED XYB<sub>14</sub> STRUCTURES

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# Abstract

In this work, the lattice instability of the  $XYB_{14}$  structure is examined by calculating the phonon vibrational modes. Three soft phonon modes are observed for the stoichiometric  $AlMgB_{14}$  composition, whereas no soft modes are found for its counterpart off-stoichiometric composition. The intrinsic vacancies formed at the metal sites stabilize the entire boron lattice by removing undesired charges carried by the metal atoms. As a result, the Fermi levels of the  $XYB_{14}$  compounds stay closely at the band gap.

# 4.1 Introduction

Although boron compounds have been used by humans for centuries, their crystal structure and bonding properties are complex due to boron's capability to engage in diverse bonding configurations, and as a result many of these materials are not well understood. An excellent example is the class of boron-rich compounds that has the chemical formula  $XYB_{14}$ , where X and Y are metal atoms. This crystal family has

recently attracted the attention of the technical community due to its unique electronic and structural properties [2, 7, 8, 26, 29, 30, 32, 31]. Within the atomic unit cell, there are five unique boron sites. Four are located within the  $B_{12}$  icosahedra subunits that make up much of the covalently bonded B-network and one B site resides between the  $B_{12}$ .

According to the Jemmis mno electron counting rules [49], each  $B_{12}$  icosahedron is two-electron deficient and it has been shown that the metal species ionically bond to the rigid, covalently-bonded B-network, donating electrons to stabilize the  $B_{12}$ . This approach successfully explains the relative stability of different crystal families by characterizing the impact of the metal atoms electronegativity on the stability of the system [11]. It is concluded that the greater the electron contribution to the B from the metal the greater the stability. However, studying the valence electron concentration (VEC) alone cannot explain the stability of the compound. For example, the AlMg $B_{14}$ compound has been found to have an off-stoichiometric composition of  $Al_{0.75}Mg_{0.78}B_{14}$ where 25% of the metal sites are vacant [9]. The effective charge per icosahedron is -2.30 for the AlMg $B_{14}$  compound and is -1.73 for the off-stoichiometric  $Al_{0.75}Mg_{0.75}B_{14}$  [11]. Why is a structure with metal site vacancies, having a lower VEC preferred?

Here first-principles, density functional theory (DFT) methods are used to examine the phonon vibrational modes to search for lattice instabilities that can be explained from the electronic structure. The AlLiB<sub>14</sub> compound is studied because it is known the diffraction data to be nearly stoichiometric [50] and therefore serves as an exemplar XYB<sub>14</sub> structure. The AlMgB<sub>14</sub> compound and its off-stoichiometric counter-part,  $Al_{0.75}Mg_{0.75}B_{14}$ , are also investigated. For common boron-rich borides, four types of optical phonon vibrational modes are expected [51, 52]: low frequency "librational" modes, which are the collective rotations of the B<sub>12</sub> icosahedra; medium frequency intraicosahedra modes, which are the vibrations between the atoms in the icosahedra; high frequency inter-icosahedra modes, which are the collective vibrations between the icosa-
hedra; and finally the vibrational modes involved with foreign atoms, in this case, the metal atoms. These characteristic vibrational modes will be identified as well as the soft-modes, which signify structural instability.

# 4.2 Methods

The ground state properties of the XYB<sub>14</sub> crystal family are calculated using the DFT plane wave method encoded in the Quantum Espresso software [13, 20, 35]. The exchange-correlation energy is approximated using the generalized gradient approximation (GGA) [15]. Ultrasoft pseudopotentials with non-linear core corrections are used in place of the all-electron ion potentials [36]. The plane wave expansion is truncated at 950 eV and the Brillouin zone is sampled using the Monkhorst-Pack algorithm with a  $4 \times 4 \times 4$  mesh to assure that the calculated forces on each atom are accurate to better than 5 meV/Å [20, 37]. Using this approach the calculated lattice parameters, shown in Table 4.1, agree with experimentally and theoretically determined values in the literature.

Compositions	a (Å)	b (Å)	c (Å)
AlMgB <sub>14</sub> (This work)	5.902	10.346	8.112
AlMgB <sub>14</sub> (Cal. from Ref. $[11]$ )	5.895	10.378	8.154
$Al_{0.75}Mg_{0.75}B_{14}$ (This work)	5.852	10.261	8.082
$Al_{0.75}Mg_{0.75}B_{14}$ (Cal. from Ref. [11])	5.838	10.308	8.113
$Al_{0.75}Mg_{0.78}B_{14}$ (Exp. from Ref. [9])	5.848	10.312	8.112
AlLiB <sub>14</sub> (This work)	5.861	10.382	8.150
AlLiB <sub>14</sub> (Cal. from Ref. $[53]$ )	5.897	10.345	8.107
$Al_{0.956}LiB_{14}$ (Exp. Ref. [50])	5.8469	10.3542	8.1429

Table 4.1 Comparison of the lattice parameters for selected  $XYB_{14}$  type crystals.

# 4.3 **Results and Discussions**

The frozen-phonon method is used to determine the vibrational modes. Displacements of 0.01 Å are used to ensure the validity of harmonic approximation. These compounds have an exceedingly large unit cell, containing 64 atoms, and solving the dynamical matrix results in 192 unique eigenvalues and eigenvectors. The phonon eigenvalues are plotted in Fig. 4.1. To assist in visualization each phonon energy is plotted as a Gaussian with a width of  $5.5 \text{ cm}^{-1}$ .



Figure 4.1 The phonon frequency population for selected  $XYB_{14}$  type crystals. The frequency associated with each phonon normal mode is represented as a Gaussian function with a width of 5.5 cm<sup>-1</sup>.

At zero frequency, three acoustic phonon modes appears as all the atoms moving coherently. The boron librational modes occur between 180 and 320 cm<sup>-1</sup>, which are approximately in the same range as boron carbide [51]. The intra-icosahedra vibrations have frequencies ranging from 350 to 800 cm<sup>-1</sup>. The stronger inter-icosahedra bonds show higher vibrational frequencies, which are typically higher than 700 cm<sup>-1</sup>. This frequency ordering confirms that the XYB<sub>14</sub> crystal are inverted-molecular structures, and the B–B bonds inside the icosahedra are weaker than those between the icosahedra. The highest optical frequencies, greater than 1000 cm<sup>-1</sup>, are due to the vibrations of the B atoms that occupy the apex positions of each icosahedra and bond to one another across the layer of metal atoms. This is consistent with previous observations that the B–B bonds that connect the icosahedra in the y-direction are the strongest in the crystal [54].

The phonon modes involved with metal atoms are shown at relatively low frequency regime. The vibrations involving only the metal atoms in the B lattice have frequencies lower than  $300 \text{ cm}^{-1}$ . In addition there are vibrational modes involving the metal atoms, Al, and the B<sub>12</sub> icosahedra at between 300 and 450 cm<sup>-1</sup>.

The vibrational spectral population of  $AlLiB_{14}$  and  $Al_{0.75}Mg_{0.75}B_{14}$  are very similar with the principal differences being in the 0 to 500 cm<sup>-1</sup> range, where the masses of the metal atoms have the greatest impact. The higher frequency portion of the spectra are qualitatively the same. Surprisingly these two are more similar than the stoichiometric  $AlMgB_{14}$  spectra is to either. Most notably the stoichiometric  $AlMgB_{14}$  spectra has a set of three soft-modes. Examining the eigenvectors of the soft modes, which give the atomic displacements, it is clear that these are associated with certain atoms moving out of the lattice.

It is demonstrated previously that the electronic structure of  $XYB_{14}$  obeys rigid band model fairly well [55]. The removal of metal atoms is not expected to influence the bonding structure of  $XYB_{14}$ . However, the total number of valence electrons contributed from the metal atoms are changed. As a result, the Fermi level moves through the electronic states. For the composition as  $Al_{0.75}Mg_{0.75}B_{14}$ , the valence bands are fully filled and the conduction bands are completely open, leaving the Fermi level at the valence band maximum. When more electrons are attributed by the metal atoms, the higher energy conduction bands begin to be filled. For example, in the AlMgB<sub>14</sub> structure, the Fermi level resides about 2 eV inside the conduction bands. The observed lattice instability of AlMgB<sub>14</sub> might due to the electron occupation to the conduction bands. This cause of lattice instability has also been reported in many other boron compounds, such as metal tetraborides and metal diborides [56, 57]. In these boron compounds, the lattice instabilities are eliminated by rearranging the lattice to settle in a lower symmetry state; whereas in the XYB<sub>14</sub> structure, because the metal atoms do not contribute to the bonding, the lattice is stabilized by introducing metal site vacancies.

Applying a simple counting scheme, we begin by restating that each  $B_{12}$  is twoelectron deficient. Although the  $B_{12}$  are essential parts of the crystal, it is insufficient to only consider these when determining the compensating charge needed. It is tempting consider the inter-icosahedra B as trigonally bonded to its neighboring icosahedra, and therefore satisfied by the three valence electrons intrinsic to B; however, careful inspection of the charge distribution shows that the three-fold rotation symmetry is in fact broken and only the mirror plane associated with the *Imma* space group passes through this site. In addition, the inter-icosahedra B also forms a covalent bond with the inter-icosahedra B across the layer of metal atoms as is shown in Ref. [58]. Therefore each inter-icosahedra requires the addition of one electron to satisfy its bonding geometry.

In each of the 64-atom XYB<sub>14</sub> unit cell, there are 4 units of the  $B_{12}$  icosahedra, 8 inter-icosahedra B atoms and 4 X and Y metal atoms. Within the simple electron counting approach, one can conclude that totally 16 number of valence electrons are needed for each XYB<sub>14</sub> unit cell to to stabilize the covalently bonded B-network. In the case of the stoichiometric compound, AlLiB<sub>14</sub>, the valency of the metal atoms is exactly 16. In comparison, AlMgB<sub>14</sub> has a total of 20 valence electrons. However, by placing a vacancy at 25% of each metal this count is reduced to 15, which is the case for the off-stoichiometric Al<sub>0.75</sub>Mg<sub>0.75</sub>B<sub>14</sub> composition. More experimental verified examples are given in Table 4.2. In all of these experimentally determined compositions, the valence electron count have a value around 16. To look back in the electronic structures, this electron configuration will put their Fermi level either at the band edges or in the band gap. As a result, these  $XYB_{14}$  compounds behave as semiconductors rather than metals.

Compositions	Number of valence electrons
$Al_{0.956}LiB_{14}$ (Ref. [50])	15.8
$Al_{0.75}Mg_{0.78}B_{14}$ (Ref. [9])	15.2
$Mg_{0.97}Mg_{0.97}B_{14}$ (Ref. [4])	15.5
$Al_{0.74}Ho_{0.633}B_{14}$ (Ref. [7])	16.4
$Al_{0.73}Er_{0.62}B_{14}$ (Ref. [7])	16.2

Table 4.2 Number of valence electrons carried by the metal atoms in several  $XYB_{14}$  type crystals.

This vacancy induced semiconducting behavior is not new in many of the B-rich compounds. In 1999, Schmechel and Werheit studied the vacancy formation mechanism in a variety of boron compounds, and it is concluded that the formation of vacancy is related to the number of valence electrons that are required to compensate the electron deficient B lattice [59]. For instance,  $\beta$ -rhombohedral boron has a vacancy concentration of 4.9 vacancy per unit cell [60]. Both  $\alpha$ - and  $\beta$ -tetragonal boron have missing metal atoms [61]. In the complex boron carbide structures, the vacancy concentration is directly related to the carbon content [59]. It is shown that by forming vacancies at specific atomic sites, the Fermi level moves from the conduction bands into the band gap. This explains why the experimental observed off-stoichiometric boron compounds show semiconducting properties, whereas the theoretical studied stoichiometric compositions always predict metallic behavior.

#### 4.4 Summary

In the B-rich borides, including the  $XYB_{14}$  compounds discussed here, there is a transfer of electrons to and within the B-network that allows for the covalent bonds to be fully satisfied. It is demonstrated here that the presence of excess charge results in lattice instabilities characterized by soft phonon modes. The addition of metal site vacancies stabilizes the lattice. Counting the number of bonds indicates that a total of 16 electrons are needed to stabilize the lattice and indeed this is found to be the case. Using a rigid band model, as demonstrated in Ref. [55], it is found that necessary electron occupation will place the Fermi level immediately at the band gap. An observation that leave many potential engineering applications for this compound if it can be grown and its interfaces suitably controlled.

# 4.5 Acknowledgement

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# CHAPTER 5. THE ELECTRONIC STRUCTURE OF Alli $B_{14}$

A paper submitted to Science and Technology of Advanced Materials

L. F. Wan and S. P. Beckman

# Abstract

The XYB<sub>14</sub> compound, where X and Y are metal atoms, is a unique crystal system that has demonstrated potential for application both as a high-temperature thermoelectric material and as part of a low-cost, superhard material system. Engineering this material for these applications requires understanding the relationship between the electronic structure, the localized bonds within the crystal, and the physical properties. We present here the results of a detailed first-principles investigation that relates the electronic structure of the archetypal AlLiB<sub>14</sub> compound to the localized bonds within the crystal. We conclude from these results that in principle it is possible to use the composition to control the electronic structure and, by selectively populating bonding or anti-bonding states, control the physical properties. In addition deformation potentials are calculated for hydrostatic and uniaxial compression. Finally using a hybrid functional method the band gap is determined to be 2.12 eV, which clarifies previously reported absorption data.

# 5.1 Introduction

The modernization of industrial manufacturing to allow for clean, high-efficiency operation requires the development of new materials that can perform in extreme environments. The metal borides possess not only excellent mechanical strength, high melting temperatures, and resistance to chemical corrosion, but are also found to have interesting electronic properties including a large Seebeck coefficient [26, 62, 63]. The XYB<sub>14</sub> crystal family, where X and Y are metal atoms, sparked public interest in 2000 when Cook *et al.* reported that a specimen containing AlMgB<sub>14</sub> had superhard strength [2]. Engineering this material to optimize the thermoelectric and mechanical properties for high-temperature application requires a detailed understanding of the bonding in the crystal that is currently lacking.

This relatively open, low-symmetry crystal family was first discovered in 1970 by Matkovich and Economy and was further studied by Higashi and Ito in the early 1980s [1, 9]. The metal atoms, which occupy the X and Y sites, do not covalently bond to the B, but instead are ionically bonded to the covalent network of B. It is presumed that the electrons from the metal atoms stabilize the  $B_{12}$  icosahedra found within the Bnetwork [49]. Previous theoretical studies focused on correlating the elastic properties of the crystal to its chemical composition [10, 11, 12, 34, 55, 64]. It is suggested that the X and Y sites can be selected to tune the electronic structure of the crystal and thereby control the physical properties; however, there is yet to be an explanation of how the

The relationship between the composition and the elastic properties is extensively investigated by Kölpin *et al.* in Ref. [11] and it is determined that changing the metal atoms, which donate their electrons to the B-network, has a direct impact on the bulk modulus. This is related to the transfer of electrons from the metal species to the  $B_{12}$ icosahedra. However, the bulk modulus is only an indicator of average bond strength, and understanding the hardness of a compound requires a detailed understanding of the individual bonds in the crystal and in particular the pathways that will likely fail first.

The first theoretical effort to extend beyond the homogeneous elastic response focused on the ideal fracture strength of this crystal [58]. By examining the mechanical strength for a series of fracture pathways, and it is concluded that it is the bonds that span between the icosahedral layers, the so-called  $B_2-B_2$  and  $B_1-B_1$  bonds, are critical for determining the strength of the system. To use the composition to engineer the properties it is necessary to understand how these critical bonds are related to the electronic structure.

Here the localized bonding in the crystal is examined in detail and is related to the electronic structure. From these results it is possible to correlate the relationship between the composition, electronic structure, and the desired physical properties. Although this article focuses on the mechanical properties of the archetypal AlLiB<sub>14</sub> compound, these results are generally valid for the physical properties of the entire XYB<sub>14</sub> crystal family. Following this introduction the methods are presented in section 5.2. The results are discussed in section 5.3 and a summary of the conclusions is presented in section 5.4.

#### 5.2 Methods

The first-principles, density functional theory [13] (DFT) method used here [35] approximates the exchange-correlation energy as a local functional of the charge density including the local gradient (GGA) [15]. Ultrasoft pseudopotentials are used to replace the all electron ion potentials [36]. The plane wave expression of the wave function is truncated at 950 eV and the Brillouin zone is sampled using a  $6 \times 6 \times 6$  Monkhorst-Pack mesh [37], which allows the calculated forces on the ions to have an accuracy of better than 5 meV/Å.

The SIESTA density functional theory method [65] is used in addition to the Quantum Espresso [35] algorithm. Unlike Quantum Espresso, which uses plane wave to represent the wave function, this method expresses the electronic wavefunctions as a set of localized atomic-like orbitals. From this approach the crystal orbital Hamilton populations (COHPs) can be easily determined [21]. In the calculations presented here, the atomiclike orbitals for each species is represented as a set of double  $\zeta$ -functions plus a shell polarization. A detailed description of the parameterized basis set is given in Table 5.1. Norm-conserving pseudopotentials are used for the ion potentials [66]. The exchangecorrelation energy is estimated using the generalized gradient approximation [16]. The real space integration is performed with an energy cutoff of 2380 eV and the Brillouin zone is sampled on a  $12 \times 12 \times 12$  Monkhorst-Pack grid [37].

	Orbital	$\mathrm{First}-\zeta$	$\operatorname{Second}-\zeta$
Al	$3s^2$	5.9597	5.1295
	$3p^1$	7.6524	6.0347
Li	$2s^1$	8.8136	7.0376
В	$2s^2$	5.2881	4.4391
D	$2p^1$	6.2996	4.6667

Table 5.1 The cutoff radii,  $r_c$  and  $r_m$ , for the double  $-\zeta$  functions used for each atomic species in this calculation.

Density functional theory returns the ground state electronic energies and wave functions for a given set of external potentials so long as the basis set that represents the wave function spans Hilbert space sufficiently to represent the solution. Therefore different basis should return identical results. The energies and density of states produced by these two methods are compared to assure that the basis are fully converged. Using these approaches the predicted lattice parameters of  $AlLiB_{14}$  are accurate to within 1% of their experimentally reported values [3, 5].

# 5.3 Results and Discussions

Within the AlLiB<sub>14</sub> crystal structure, shown in Fig. 5.1 there exist five unique B sites. The B<sub>12</sub> icosahedra layers are stacked in the y-direction. The B<sub>1</sub> (green) apex sites in the icosahedra allow for direct bonding between the B<sub>12</sub> via B<sub>1</sub>-B<sub>1</sub> bonds that extend between the layers. Within the B<sub>12</sub> layers, in the xz-plane, each icosahedra unit is bonded to four neighbors at their B<sub>4</sub> (yellow) sites. The B atoms that do not belong to an icosahedra are referred to as inter-icosahedra B and are identified as B<sub>2</sub> (black) sites. Each inter-icosahedra B atom appears to be bonded to three nearby B<sub>12</sub> at either B<sub>5</sub> (red) or B<sub>3</sub> (blue) sites located inside the icosahedra. The Al (cyan) and Li (pink) are located between the layers of B<sub>12</sub>.



Figure 5.1 The atomic structure and bonding charge density,  $\Delta \rho_{\text{bonding}}$ , of the AlLiB<sub>14</sub> crystal. The atomic sites are identified in the legend, on the right. (a) shows the charge density isosurface with a value of +0.022  $e/a.u.^3$  and (b) shows an isosurface with a value of  $-0.012 e/a.u.^3$ 

The fundamental assumption of DFT is that the 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 is not always the most useful quantity, instead the bonding charge density,  $\Delta \rho_{\text{bonding}}$ , which is rendered by subtracting the charge density of the bonded structure from the sum of the charge contribution from each of the atoms treated as though they are isolated. Regions with positive  $\Delta \rho_{\text{bonding}}$ , shown in Fig. 5.1 (a), have accumulated charge during bonding, and regions with negative  $\Delta \rho_{\text{bonding}}$ , shown in Fig. 5.1 (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 Ref. [58]. 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.

The charge accumulation shown in Fig. 5.1 (a) induces the charge depletion shown in frame (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 Bnetwork to facilitate the covalent bonding between the B. Charge depletion is observed near the  $B_1$ ,  $B_3$ ,  $B_4$ , and  $B_5$  sites, away from the covalent bond charges that were noted in Fig. 5.1 (a). 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 [67] 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  $B_1$ ,  $B_2$ ,  $B_3$ ,  $B_4$ , and  $B_5$  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  $B_2$  sites have gained considerable charge, compared to the other B sites, and this charge comes from the metal species.

The density of states (DOS) and partial density of states of AlLiB<sub>14</sub>, presented in Fig. 5.2, are consistent with previous theoretical investigations [11, 55, 64]. AlLiB<sub>14</sub> is found to have a band gap of 1.26 eV and the Fermi level is located at the edge of the gap. The metal atoms have negligible contribution to the states near the band gap, and the band edge is dominated by the B 2p-states with the B<sub>2</sub> and B<sub>3</sub> 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.

From the DOS alone it is tempting to assume that the valence band edge represents the hybridization of the  $B_2$  and  $B_3$  2*p*-states and that passing the Fermi level through these states directly affects these hybridized bonds, but the actual physics is not so simple. The crystal orbital Hamilton population (COHP) [21] is calculated to determine the nature of the orbital interactions between sites: bonding, non-bonding or anti-bonding. The AlLiB<sub>14</sub> COHP, presented in Fig. 5.3, demonstrates that the valence band edge represents electrons in  $B_2$ - $B_3$  and  $B_2$ - $B_5$  bonding states and  $B_2$ - $B_2$  anti-bonding states. The  $B_1$ - $B_1$  bonds that span between the layers of  $B_{12}$  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  $B_2$ ,  $B_3$ , and  $B_5$  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  $B_2$ - $B_2$  bonds, by depopulating the anti-bonding states, and weakening the  $B_2$ - $B_3$  and  $B_2$ - $B_5$  bonds, by depopulating the bonding states. The  $B_2$ - $B_2$  bonding states have lower energy, at least 0.55 eV below the band edge; however,  $B_1$ - $B_1$  bonding states are located 0.35 eV below the band edge and moving the Fermi level below this energy will weaken the  $B_1$ - $B_1$  bonds. This analysis of the DOS and COHP demonstrates how manipulating the composition can possibly be used to selectively occupy these bonding or anti-bonding states and control the mechanical properties of the XYB<sub>14</sub> crystal family.

When a strain is applied to a crystal, the elastic energy is stored in the local bonds by changing the electronic energy, and for the icosahedral B compounds the inter-icosahedra bonds are strongly effected due to their sparse distribution. In the case of  $\alpha$ - and  $\beta$ rhombohedral B, applied strain causes rotation of the rigid B<sub>12</sub> substructures [68]. The high number density of inter-icosahedra bonds in the XYB<sub>14</sub> compound suggests that this crystal family will respond differently under loading than other B compounds. This will be apparent in both the structural and electronic response of the crystal to loading.

To assess the effect of pressure on the atomic structure, pair distribution functions (PDFs) are presented in Fig. 5.4. The top frame of Fig. 5.4 shows the atomic distances for the ground state AlLiB<sub>14</sub> crystal. Below this are the PDFs for crystals that have been strained uniaxially by 1% in the *x*-, *y*-, and *z*-directions. The averaged intraicosahedra bond length is approximately 1.81 Å, which matches well with the experimental value [50].

It is predicted by Wan and Beckman in Ref. [58] that for the  $\{010\}$  planes fracture is more likely to occur through the inter-icosahedra bonds than through the intraicosahedra bonds. The results in Fig. 5.4 confirm that uniaxial loading along the y-direction has a greater impact on the B<sub>1</sub>-B<sub>1</sub> and B<sub>2</sub>-B<sub>2</sub> 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 B<sub>2</sub>-B<sub>5</sub> and B<sub>4</sub>-B<sub>4</sub> bonds are effected, because they are aligned in the loading direction. Similarly the B<sub>2</sub>-B<sub>3</sub> and B<sub>4</sub>-B<sub>4</sub> bond distances are effected by uniaxial loading in the z-direction. Unlike the B<sub>1</sub>-B<sub>1</sub> and B<sub>2</sub>-B<sub>2</sub> bonds, which are directly aligned in the y-direction, none of the intericosahedra 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 in Ref. [58] that the fracture strength of the {100} and {001} planes is nearly independent of the location of the fracture interface.

Although AlLiB<sub>14</sub> has no pronounced icosahedra rotations, it is still observed to deform in a very anisotropic manner, which also impacts the 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 pressure along *y*- and *z*-directions. Although the effect of uniaxial strain is non-negligible, hydrostatic pressure has little impact on the band gap of AlLiB<sub>14</sub>, less than a 1 meV change for a 1.5% volume change. This differs significantly from  $\alpha$ - and  $\beta$ -rhombohedral B, which are reported to experience 17 and 70 meV/GPa changes to their band gap [68].

The relative changes to the band gap reported here are likely correct; however, it is known that the GGA used in this letter predicts band gaps that are wrong, and the 1.26 eV band gap, presented above, is probably inaccurate. Hybrid functional methods may offer a better approximation of the actual band gap, and in particular the Heyd-Scuseria-Ernzerhof hybrid functional [19, 69] is tested. The details of this calculation is given in the Supplementary Data to this paper. The hybrid functional predicts a band gap of 2.12 eV, which is significantly larger than the GGA band gap. Werheit *et al.* have measured the absorption spectrum and report that the strongest absorption occurs at 1.95 eV, which agrees well with the results here [70]. Our calculation suggests that the absorption events reported at lower energies are not due to inter-band transitions and are possibly due to the Urbach tails and deep states in the gap that are discussed in detail in Ref. [70].

#### 5.4 Conclusions

To summarize, the electronic structure of AlLiB<sub>14</sub> is investigated using first-principles DFT methods. It is apparent from the charge density and Löwdin population analysis that the charge transfer to the the B<sub>2</sub> inter-icosahedra site is significant. The B<sub>2</sub>-B<sub>2</sub> bonds contribute to the strength of the crystal across critical planes [58]. Because the atom at the B<sub>2</sub> site forms four bonds with its neighbors additional charge needs to be transferred from the metal species to this atom to stabilize the bonds. This observation suggests that the analysis in Ref. [11], where the crystal's stability is directly linked to the charge transfer from the metal species to the B<sub>12</sub> icosahedra, may not fully explain the stability of the crystal family or describe the bonding characteristics.

Based on the charge density, DOS, and COHP analysis, we are now able to answer the question, "Is it possible to tune the electronic structure to control the mechanical properties of XYB<sub>14</sub>?" In principle it is possible to use chemical doping to move the Fermi level from the band gap into the valence band, removing electrons from the B<sub>2</sub>-B<sub>2</sub> anti-bonding states, which will strengthen the crystal. However, only a modest window is available where chemical doping can be effectively used to strengthen the crystal. If the Fermi level moves too deep into the band, lower than 0.35 eV below the gap, the electrons will begin to depopulate the states localized in the B<sub>1</sub>-B<sub>1</sub> bonding states, and possibly the B<sub>2</sub>-B<sub>2</sub> bonding states as well, weakening the bonds that have been identified as critical for the overall strength of the XYB<sub>14</sub> compound. It is noteworthy that the offstoichiometric Al<sub>0.75</sub>Mg<sub>0.78</sub>B<sub>14</sub> [9], which is present in the superhard specimen prepared by Cook and Russell [2], is predicted to have its Fermi level directly in this window, meaning that the strength should be maximized [71].

The impact of strain on the structural and electronic properties is investigated. Unlike  $\alpha$ - and  $\beta$ -rhombohedral B, loading does not result in rotations of the B<sub>12</sub> subunits; instead the deformation compresses the bonds between the icosahedra. Whereas previous studies

have focused on applying hydrostatic pressure and have noted that this yields no change in the gap, here uniaxial pressure is applied and it is found that the band edges will shift their energies. It is possible that the application of hydrostatic pressure results in a complex 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.

A hybrid functional method is used to determine that the band-gap of AlLiB<sub>14</sub> is 2.12 eV. This result is compared to the absorption measurements reported in Ref. [70]. This comparison allows for a definitive identification of the fundamental inter-band absorption edge apart from the many absorption events that are also measured. It is noteworthy that a photon with a wavelength of 585 nm is required to excite an electron across a 2.12 eV band gap and this wavelength is very near the maximum in the solar spectrum. This leads one to speculate that with careful processing the XYB<sub>14</sub> crystal family may find use in photoactive applications. Of course, for engineering applications, it will be necessary to determine the band alignment relative to a known standard.

# 5.5 Acknowledgements

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Figure 5.2 The total and partial density of states for the  $AlLiB_{14}$  crystal. The nomenclature used in this figure follows the nomenclature used in Fig. 5.1. The valence band maximum is arbitrarily set as the energy zero. The dashed vertical line indicates the Fermi level.



Figure 5.3 The calculated COHP for selected atomic pairs. The nomenclature follows from Fig. 5.1 and the valence band maximum is arbitrarily set as the energy zero. A negative COHP indicates bonding interaction between the sites and a positive COHP indicates anti-bonding.



Figure 5.4 The pair distribution functions for  $AlLiB_{14}$  decomposed to show select B-B bonding pairs. A Gaussian broadening factor of 0.001 Å 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 uniaxial strain of 1% is applied in the x-, y-, and z-directions.

# CHAPTER 6. FRACTURE STRENGTH OF AlLiB<sub>14</sub>

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# Abstract

The orthorhombic boride crystal family  $XYB_{14}$ , where X and Y are metal atoms, plays a critical role in a unique class of superhard compounds, yet there have been no studies aimed at understanding the origin of the mechanical strength of this compound. We present here the results from a comprehensive investigation into the fracture strength of the archetypal AlLiB<sub>14</sub> crystal. First-principles, *ab initio*, methods are used to determine the ideal brittle cleavage strength for several high-symmetry orientations. The elastic tensor and the orientation-dependent Young's modulus are calculated. From these results the lower bound fracture strength of AlLiB<sub>14</sub> is predicted to be between 29 and 31 GPa, which is near the measured hardness reported in the literature. These results indicate that the intrinsic strength of AlLiB<sub>14</sub> is limited by the interatomic B-B bonds that span between the B layers.

# 6.1 Introduction

The development of new superhard materials that can operate under extreme conditions is critical for high-performance industrial manufacturing and is a subject that has recently received great attention [72, 73, 74]. The orthorhombic borides, formulated as  $XYB_{14}$  where X and Y are metal atoms, have been of interest to scientists and engineers for the past decade due to a report [2, 75] that AlMgB<sub>14</sub> prepared by mechanical milling can achieve a hardness between 32 and 46 GPa. The reason for the observed superhardness is not understood. It is suggested that in part the strength is due to the so-called "nanocomposite" microstructure comprised of AlMgB<sub>14</sub> and TiB<sub>2</sub>, although the hardness of each individual phase is believed to be less than the hardness of the composite [76]. There have been many studies examining TiB<sub>2</sub> [77, 78, 79, 80], but the orthorhombic boride family has received much less attention and is therefore the focus of this letter.

Whereas most hard materials are dense, highly symmetric crystals, the XYB<sub>14</sub> structure, shown in Fig. 6.1, is relatively open and has low symmetry (*Imma*). This crystal structure, which was first reported by Matkovich and Economy in 1970, has a unit cell containing four formula units of XYB<sub>14</sub> [1]. The 64-atom unit cell can be expressed as  $X_4Y_4(B_{12})_4B_8$  to distinguish the two B allotropes. The B layers are constructed from  $B_{12}$  icosahedron that are connected to each other through the so-called inter-icosahedra B atoms that are trigonally bonded to three  $B_{12}$  units within the B layer. Recent spectroscopy evidence indicates that the B-B bonds that span between the B layers, directly connecting icosahedron, are very strong [81]. Unlike many metal-boride compounds the metal atoms are not covalently bonded to the B, but instead the metal atoms ionize and donate their valence electrons to the covalently bonded B network [10, 11, 55, 64]. As a near-superhard material, this crystal family is unique, which has led us to investigate the bonding in the crystal as it affects the crystal's mechanical strength.

Following Matkovich and Economy's work [1], Higashi and Ito synthesized several  $XYB_{14}$  compounds and used diffraction methods to refine the crystallographic data. For some of the compounds, such as AlMgB<sub>14</sub>, a relatively high concentration of vacancies, around 25%, are found at the metal atom sites [9]. Diffraction results for other XYB<sub>14</sub> compounds, such as AlLiB<sub>14</sub>, do not find such a large number of vacancies [3, 4]. Werheit



Figure 6.1 A simple schematic of the  $XYB_{14}$  crystal structure. The red spheres are the X site, the blue spheres are the Y site, and the light grey spheres are the B atoms. The short-dashed arrows denoted by  $E_{min}$  and  $E_{max}$  show the loading directions that yield the minimum and maximum Young's modulus for AlLiB<sub>14</sub>. The six planes selected for examination within the brittle cleavage model are shown as long-dashed lines and are labeled according to the nomenclature used in Table 6.1.

et al. have used Raman spectroscopy to compared the vibrational spectrum of various  $XYB_{14}$  compounds and have found that the AlLiB<sub>14</sub> crystal has less internal distortions than many other  $XYB_{14}$  structures, including AlMgB<sub>14</sub> [81]. From these results we conclude that experimental specimens of AlLiB<sub>14</sub> are likely to have fewer point defects than many other  $XYB_{14}$  compounds and consequently AlLiB<sub>14</sub> is selected as the archetypical structure for study in this letter.

Previous theoretical studies have focused on the effects of chemical substitution on the properties of the XYB<sub>14</sub> crystal family [10, 11, 12, 55]. This is in part because the system is known to accept a large number of metal species including Li, Be, Na, Mg, Al, as well as a variety of rare-earth elements, such as Tb, Dy, Ho, Er, Yb, and Lu [5, 6, 3, 4, 2, 7, 8]. In addition the superhard Ames Laboratory specimen was synthesized by a mechanical alloying method, which introduces a wide variety of impurity species to the crystal including Ti, Si, Fe, O, and C [75]. In these theoretical studies the reported figure of merit for hardness is the bulk modulus because its computation is relatively simple. However, the bulk modulus alone only gives information about the average bond strength under an applied volume dilation and does not give any information about the strength of individual bonds in the crystal. Understanding hardness requires knowledge about the local mechanisms for bond breaking as it relates to fracture in the crystal. In this letter the fracture strength of AlLiB<sub>14</sub> will be examined using an ideal brittle cleavage model. This approach allows for insight regarding the local bonding within the crystal and may lead to a strategy for improving the hardness.

# 6.2 Methods

The first-principles, density functional theory method used in this study is implemented in the SIESTA software package [13, 65]. The Perdew-Burke-Ernzerhof generalized gradient approximation is used for the exchange-correlation energy and normconserving pseudopotentials are used in place of the all-electron atomic potentials [16, 66]. The wavefunction is represented by a set of finite-range numerical atomic orbitals. Each atomic basis is extended to include double- $\zeta$  functions plus a shell polarization that is constructed using the split-valence scheme [82]. The cutoff radii used for each  $\zeta$  function are presented in Ref. [54]. Real space meshing is performed to an energy cutoff of 175 Rydberg. The Kohn-Sham energies are sampled across the Brillouin zone using a 12 × 12 × 12 Monkhorst-Pack grid [37]. The atomic structural optimization follows the conjugate gradient minimization method and the thresholds for the residual forces on atoms and the supercell are 0.005 eV/Å and 0.0005 eV/Å<sup>3</sup> respectively. The calculated lattice parameters for AlLiB<sub>14</sub> are 5.88, 10.39, and 8.15 Å, which agree well with the reported experimental values 5.847, 10.354, and 8.143 Å [3].

The ideal brittle cleavage model used here separates the  $AlLiB_{14}$  crystal into two semi-infinite, rigid atomic blocks that are pulled apart to introduce a pair of cleavage surfaces at a predefined atomic plane. This idealized approach simultaneously stretches and breaks all the bonds at the interface. Although the effect of crack tip initiation and propagation cannot be included using this method, it allows for the bond strengths localized in the crystal to be investigated. Internal atomic relaxations and lattice contractions perpendicular to the direction of elongation are forbidden. These constraints allow the strength of the bonds across the cleavage interface to be determined independent of possible near-surface atomic reconstructions, which would be present in an experimental specimen. The calculated energy of the cleaved crystal, relative to the energy of the perfect crystal, is called the decohesive energy,  $E_b$ , and is determined as a function of the interplaner spacing, x, across the specified cleavage planes. The decohesive energy is fit to the universal binding energy relation (UBER) developed by Rose *et al.* in Ref. [83], which is expressed more precisely in Ref. [84] as,

$$E_b(x) = G_b \left[ 1 - \left( 1 + \frac{x}{l_b} \right) exp \left( -\frac{x}{l_b} \right) \right].$$

When all the atomic bonds that span the cleavage interface are broken, the decohesive energy saturates to the cleavage energy,  $G_b$ . The cleavage stress is the first derivative of the decohesive energy with respect to x. The critical cleavage stress,  $\sigma_b$ , is defined as the maximum stress, and the corresponding interplanar spacing is referred to as the critical length,  $l_b$ .

#### 6.3 Results and Discussions

For AlLiB<sub>14</sub> cleavage is considered within the high-symmetry  $\{100\}$ ,  $\{010\}$ , and  $\{001\}$ families of planes. For each crystallographic direction two cleavage planes are examined: one that passes through the icosahedron, labeled B, and one that passes between the icosahedron, labeled M. These were selected to best represent the variation in the bonding for each of the sampled directions; one of the cleavage planes has many bonds that span the interface and the other few bonds. It is intended to test interfaces with the

Orientation	Cleavage energy $G_b/\text{Area} (\text{J/m}^2)$	Critical length $l_b$ (Å)	Critical stress $\sigma_b$ (GPa)		
{100}-B	7.94	0.51	57.7		
$\{100\}-M$	7.74	0.45	63.5		
{010}-B	9.16	0.49	68.4		
{010}-M	5.42	0.56	35.7		
{001}-B	8.27	0.49	62.0		
$\{001\}-M$	7.51	0.57	48.1		

Table 6.1 The numerical results for applying the ideal brittle cleavage model to the six AlLiB<sub>14</sub> cleavage planes that are shown in Fig. 6.1.

highest and lowest fracture energies. These planes are identified in Fig. 6.1. A 128-atom supercell is used to guarantee that the calculated decohesive energies are converged to better than  $0.005 \text{ J/m}^2$ . The decohesive energies, UBER fit, and derived stresses are plotted in Fig. 6.2. The computed data matches the functional form of the UBER relation very well and the resulting critical parameters are listed in Table 6.1.

The decohesive energy curves and stresses for the  $\{100\}$ -B and -M planes are very similar, the critical stresses differ by less than 10%. This is not surprising considering that the density and geometric arrangements of the B-B bonds in these planes are nearly equivalent. Whereas the  $\{100\}$  planes are very similar, the  $\{010\}$  planes are considerably different. The  $\{010\}$ -B plane passes through the B layer bisecting the icosahedron, breaking many B-B bonds, but the  $\{010\}$ -M plane passes between the B layers and therefore cuts significantly fewer bonds. Within the ideal brittle cleavage model the calculated critical stress for the M plane is 48% smaller than that of the B plane.

According to the Raman spectroscopy results reported in Ref. [81], the B-B bonds that span between the B layers and connect the icosahedron are expected to have a



Figure 6.2 The ideal brittle cleavage results for  $AlLiB_{14}$ . The left ordinate axis labels the energies and the right the stresses. The top frame gives the results for the {100} planes, the middle the {010} planes, and the bottom the {001} planes. In each frame the *B* results are red and the *M* results are blue. The decohesive energy DFT data are solid symbols, the UBER relations are solid lines, and the stresses are dashed lines.



Figure 6.3 An isosurface showing regions in an  $XYB_{14}$  crystal with positive bonding charge density. The atomic sites are color coded following the description in Fig. 6.1.

greater binding strength than the bonds inside the icosahedron. This can be examined qualitatively by plotting the bonding charge density, as shown in Fig. 6.3. <sup>1</sup> The bonding process results in a buildup of charge in the B-B bonds that bridge the B layers. In Fig. 6.3 charge accumulation between the B layers is observed both between the icosahedron and the inter-icosahedra B. The results from the ideal cleavage model, presented in Table 6.1, indicate that regardless of the anticipated high strength of the bonds at this plane, the relatively low number density of bonds causes the  $\{010\}$ -M plane to have the lowest critical stress of all the planes examined here. It can be concluded that the B-B bonds that span between the B layers are key for controlling the overall strength of the crystal.

It is the weakest planes that are of primary interest because fracture naturally transverses the weakest path through a crystal. It is these same planes that also dominate the elastic response. For a given family of planes, the elastic response to a uniaxial load applied normal to the planes should be an indicator of the relative cleavage strength;

<sup>&</sup>lt;sup>1</sup>The bonding charge density is rendered by subtracting the charge density of the bonded structure from the sum of the charge contribution from each of the atoms, treated as though they are isolated. A positive bonding charge density indicates charge accumulation and a negative value indicates charge depletion.

Stiffness coefficients	$c_{11} 526$	c <sub>22</sub>	c <sub>33</sub>	c <sub>44</sub>	c <sub>55</sub>	c <sub>66</sub>	c <sub>12</sub>	c <sub>13</sub>	c <sub>23</sub>
(GPa)		411	419	91.0	201	130	45.7	83.4	32.0
Compliance coefficients (× $10^{-12}$ m <sup>2</sup> /N)	$\frac{s_{11}}{1.98}$	$s_{22}$ 2.47	$\frac{s_{33}}{2.47}$	$^{S_{44}}_{10.99}$	$\frac{s_{55}}{4.98}$	s <sub>66</sub> 7.69	s <sub>12</sub> -0.19	s <sub>13</sub> -0.38	s <sub>23</sub> -0.15

Table 6.2 The elastic tensor components for  $AlLiB_{14}$ .

i.e., the Young's modulus should scale with the cleavage strength. For the orthorhombic  $XYB_{14}$ -type crystal there are nine unique tensor elements that can be derived from the linear stress-strain relation and the crystal symmetries. The components of the stiffness and compliance tensors for  $AlLiB_{14}$  are calculated and presented in Table 6.2. In Fig. 6.4(a), the Young's modulus, E, is represented as a function of crystallographic orientation, according to the formula,

$$\frac{1}{E} = l_1^4 s_{11} + l_2^4 s_{22} + l_3^4 s_{33} + 2l_1^2 l_2^2 s_{12} + 2l_1^2 l_3^2 s_{13} + 2l_2^2 l_3^2 s_{23} + l_2^2 l_3^2 s_{44} + l_1^2 l_3^2 s_{55} + l_1^2 l_2^2 s_{66},$$

where  $s_{ij}$  are the elastic compliance tensor components and  $l_1$ ,  $l_2$ , and  $l_3$  are the direction cosines. The representation surface in Fig. 6.4(a) is projected on the (100), (010) and (001) planes, and the results are shown in Fig. 6.4(b).

For the [010], [001], and [100] directions the Young's modulus is 293, 404 and 505 GPa. From the ideal brittle cleavage model the minimum critical stresses for these same directions are 35.7, 48.1, and 57.7 GPa, as listed in Table 6.1. Comparing these numbers demonstrates that indeed the directional representation of the Young's modulus is an accurate predictor of the relative ideal fracture strength of a particular orientation. From the results in Fig. 6.4 the minimum value of the Young's modulus is 256.0 GPa, which corresponds to a uniaxial load orientated ( $\phi = 90^{\circ}$ ,  $\theta = 44.96^{\circ}$ ), where  $\phi$  is the angle of rotation from the positive x-axis to the positive y-axis in the xy-plane and



Figure 6.4 The representation surface for the Young's modulus of  $AlLiB_{14}$  (given in GPa) as a function of crystallographic orientation. Frame (a) shows a 3D plot of the representation surface. Frame (b) shows 2D projections of the representation surface onto the (100), (010) and (001) planes and are printed in green, blue and red, respectively.

 $\theta$  is the out-of-plane angle of rotation from the positive z-axis to the xy-plane. This direction is drawn in Fig. 6.1 as a short-dashed arrow that is labeled E<sub>min</sub>. Assuming linear proportional scaling, the computed results for the high-symmetry orientations can be used to predict that the cleavage strength for a uniaxial load applied in the E<sub>min</sub> direction is between 29 and 31 GPa. This is the predicted lower limit of the ideal brittle cleavage strength for AlLiB<sub>14</sub>. We submit that for a brittle material, such as AlLiB<sub>14</sub>, which does not undergo extensive plastic deformation near the crack tip prior to fracture, the calculated ideal brittle cleavage strength is a reasonable estimation of the fracture strength. The physical features of fracture neglected in this ideal brittle cleavage model, including crack tip plasticity, lattice contractions, and atomic reconstructions, results in an overestimation of the cleavage energy and subsequently the actual critical energy and stress will be lower than our calculated results. The experimentally measured hardness for AlLiB<sub>14</sub> ranges between 20 and 29 GPa [3, 5], which suggests that for this material the atomic scale behavior that we have reported here plays an important role in determining the actual hardness of the material.

## 6.4 Summary

In summary, we have coupled the results from a series of ideal brittle cleavage strength calculations to the calculated orientation dependent Young's modulus to predict the fracture strength of AlLiB<sub>14</sub>. While admittedly this simplistic model neglects some of the macroscopic features of fracture associated with crack tips, lattice plasticity, and interface reconstructions, we believe that here we have demonstrated that this still may be an effective approach to gauge the strength of brittle materials, such as the XYB<sub>14</sub> crystal family. In contrast to all of the previous theoretical studies of the XYB<sub>14</sub> crystal family, which have used the bulk modulus as an indicator of the bond strength, the approach used here allows for the local bond strength to be investigated on a plane-by-plane basis. Unlike the more sophisticated, multi-scale modeling approaches, which have been deployed to study fracture in polycrystalline diamond, Si, and other metallic systems [85, 86, 87, 88], the method used here is relatively simple. We believe that our approach can be used to screen prospective structures prior to their being investigated using a more elaborate theoretical technique.

The existing picture of bonding in the XYB<sub>14</sub> crystal family is that B forms a covalent network of atoms constructed of  $B_{12}$  icosahedron. The  $B_{12}$  are stabilized by the electrons donated by the ionized metal atoms, according to the Jemmis mno rules [49]. Excess charge accumulates in the inter-icosahedra bonds, both those within the B layer and those that span between the layers. Experimental results indicate that the inter-icosahedra B-B bonds spanning between the layers are stronger than the intra-icosahedra bonds [81]. Here we find that regardless the strength of the inter-icosahedra bonds the fracture is significantly more likely to proceed between the icosahedron rather than through, due to the density of bonds at the cleavage plane. In fact the  $\{010\}$ -M planes are the weakest of those examined in this study, which suggests that the hardness of the material may be closely tied to the B-B bonding that connects the icosahedra layers. In practice, this means the intrinsic strength of this crystal family possibly can be changed, either strengthened or weakened, by the introduction of a dopant species that directly affects these bonds.

# 6.5 Acknowledgement

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# CHAPTER 7. SUBSTITUTIONAL C ON B SITES IN AlLi $B_{14}$

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# Abstract

The effect of C substitution in the AlLiB<sub>14</sub> lattice is examined using first-principles methods. The inter-icosahedra B site is found to be the most favorable B site for C substitution and the formation energy is predicted to be 1.7 eV in B-rich conditions. Substituting C does not affect the band gap, nor does it introduce defect states to the gap. An ideal brittle cleavage model is used to study the impact of C doping on the mechanical properties of AlLiB<sub>14</sub> and it is concluded that introducing C to the crystal decreases the ideal fracture strength by 3.3 GPa, which is about a 12% reduction in overall strength.

# 7.1 Introduction

The orthorhombic borides, formulated as  $XYB_{14}$ , where X and Y are metal species, have generated great scientific interest since the discovery of the ultra-hard  $AlMgB_{14}$ -TiB<sub>2</sub> nanocomposite [2]. Similar to most of the B-rich borides, the crystal structure of orthorhombic  $XYB_{14}$  is largely dominated by the B<sub>12</sub> icosahedra [1, 23]. The primitive cell contains four units of XYB<sub>14</sub>, and can be written as  $X_4Y_4(B_{12})_4B_8$  to distinguish the icosahedron in the formula. In addition to the B<sub>12</sub> subunits, there are eight individual B atoms, each of which is bonded to three neighboring icosahedra. The low crystal symmetry and open structure provides space to accommodate metal species. A schematic representation of the B network can be found in Figure 7.1. Unlike the strong covalent bonds between B atoms that hold the lattice rigid, the bonding between the metal atoms and the boron structure is relatively weak. It is believed that the role of the metal species is to ionically bond to the crystal and contribute their valence electrons to stabilize the charge deficient B<sub>12</sub> icosahedra [10, 11, 49, 64].

It is known that various metal species can be substituted in the lattice without introducing significant lattice strains from the mismatch of atomic radii [2, 4, 5, 7, 8, 9, 31]. The overall volume change of the XYB<sub>14</sub> crystal is usually less than 5% although the atomic radius of the metal elements may differ by as much as 20%. Because of the unique role of the metal atoms, many scientific investigations have been undertaken to examine the impact of metal site occupation on the electronic properties of XYB<sub>14</sub>, for example, electric conductivity, thermoelectric response, and optical excitations [26, 55, 70, 81]. Recent results also predict the possibility of controlling individual bond strengths by chemical doping the metal atomic sites [54, 55, 58].

The strength of the crystal is due to the B–B bonds; hence, a subtle change to the B lattice may strongly impact the overall bonding strength. A naturally occurring substitutional dopant in the B lattice is carbon. The superhard  $AlMgB_{14}$ – $TiB_2$  specimen prepared by mechanical milling in 2000 [75] has a high concentration of C, although due to the omnipresent nature of C in the laboratory, it is likely that C will be found even in the high-purity XYB<sub>14</sub> crystals fabricated using sophisticated techniques [89]. Due to the chemical similarity of B and C, it is difficult to experimentally distinguish the individual C atoms on the B lattice and thus the exact influence of C on the mechanical response of the crystal is unknown. In this article the role of C substitution on the  $XYB_{14}$  lattice is studied using *ab initio* methods. The AlLiB<sub>14</sub> compound is chosen as the host because experimental evidence suggests that it is stoichiometric, whereas many of the  $XYB_{14}$  structures, including AlMgB<sub>14</sub>, have a high fraction of metal site vacancies [4, 9, 81]. Following this introduction, the theoretical approach will be presented. In section 7.3 the atomic structure, energies, and electronic states of the C substitutional impurity will be discussed. The impact of this substitution on the mechanical properties will also be examined using an ideal brittle fracture model. The article will conclude with a summary of the results in section 7.4.

#### 7.2 Methods

This theoretical study is carried out using the first-principles, density functional theory [13] approach that is implemented in the SIESTA source code [65]. Norm-conserving pseudopotentials are created for each ion [66] and the exchange-correlation functional is approximated using the generalized gradient approximation [16]. The electronic wavefunction is represented by a set of numerical atomic orbitals [82]. Each atomic basis is constructed to include double  $-\zeta$  functions plus shell polarization. The relevant parameters for the pseudopotentials and atomic basis sets are given as Supplementary Data to this article. Real space integration is performed using an energy cutoff of 175 Rydberg and the Brillouin zone is sampled on a  $12 \times 12 \times 12$  Monkhorst-Pack mesh [37]. The structural optimization thresholds are chosen to ensure the residual forces on atoms and cells are smaller than 0.005 eV/Å and 0.0005 eV/Å<sup>3</sup> respectively.

Following the work of Van de Walle and Neugebauer in [90], the formation energy for an impurity atom, X, in its charge neutral state is expressed as

$$E_f(X) = E_{tot}(X) - E_{tot} \text{ (defect free)} - \sum_i n_i \mu_i$$
(7.1)

where  $E_f(X)$  denotes the formation energy of the defect, and  $E_{tot}(X)$  and  $E_{tot}$  (defect free)



Figure 7.1 An illustration of the network of B atoms of an  $XYB_{14}$  crystal for a  $2 \times 1 \times 2$  supercell. The metal species are not shown here, but can be found in Ref. [54]. The B<sub>2</sub> site, where C is substituted, is highlighted in orange.

are the total energies for supercells with and without defects. The sum expresses the change in the number of atoms,  $n_i$ , between the supercell with and without defects for each species, *i*. The chemical potential for each species is  $\mu_i$ . The chemical potentials for B and C are balanced using the B<sub>13</sub>C<sub>2</sub> compound,

$$\mu_{\rm B_{13}C_2} = 13\mu_{\rm B} + 2\mu_{\rm C}.\tag{7.2}$$

The elemental chemical potentials are upper bounded by the chemical potential of the bulk elements, i.e.,  $\mu_{\rm B} < \mu_{\rm B(bulk)}$  and  $\mu_{\rm C} < \mu_{\rm C(bulk)}$ . Here  $\mu_{\rm B(bulk)}$  is defined as the energy
per atom in  $\alpha$  – rhombohedron boron and  $\mu_{C(bulk)}$  is determined for bulk graphite. In the B-rich limit  $\mu_{B} = \mu_{B(bulk)}$  and the chemical potential for C is determined by the chemical relationship in 7.2, and similarly in the C-rich limit  $\mu_{C} = \mu_{C(bulk)}$ .

It is necessary to use convergence tests to determine the effect of supercell periodicity on the results [91, 92, 93]. It has been proposed that the calculated energy of formation scales with the inverse of both the supercell's linear dimension and cell volume [92]. Here the simulation cell is independently expanded along the x-, y-, and z- directions. The shortest lattice periodicity is in the x- direction, which has the strongest impact on the calculated results. It is found that doubling the supercell in both the x- and z- directions, results in a total energy that is converged to an accuracy of 0.1 eV. The effect of C substitution on the bonding is relatively short ranged. It is observed that the C defect only influences the atomic bonding within a radius of 4 Å. The results from this convergence study are summarized in the Supplementary Data to this article.

#### 7.3 Results and discussion

Following the nomenclature defined by Wan and Beckman in [54], the five unique B sites are identified in Figure 7.1. The results, in Table 7.1, indicate that C substitution at the inter-icosahedra,  $B_2$ , site is approximately 0.7 eV lower than the others. The energy of formation can differ by as much as 0.33 eV depending on the choice of chemical reservoirs. For the remainder of this investigation only C substitution at the  $B_2$  site is considered.

From the calculated partial density of states, shown in Figure 7.2, it is determined that the presence of C does not introduce states to the band gap; there are changes to the states within the bands only. Spatially, the influence of C on the chemical bonding is limited and only the B atoms at the  $B_2$ ,  $B_3$ , and  $B_5$  sites that are directly bonded to the C experience a change in their electronic energies.

Substitutional site	B-rich condition	C-rich condition
B <sub>1</sub>	2.67	2.33
$B_2$	1.91	1.58
$B_3$	2.67	2.33
$B_4$	2.61	2.27
B_5	2.65	2.31

Table 7.1The formation energy (in eV) for C substitution at the five B sites under<br/>B-rich and C-rich conditions.

These electronic changes impact the local atomic structure. In Table 7.2, the interatomic distances,  $R_{ij}$ , between the C defect and its first nearest neighbors are presented along with the interatomic distances for the bulk, undoped structure,  $R_{ij}^0$ . The addition of C does not disrupt the local symmetry; however, the C atom is 0.10 Å closer to the  $B_{12}$  icosahedra layer than the a B atom would usually be. The in-plane bond lengths  $R_{23}$  and  $R_{25}$  are shortened by 0.11 and 0.06 Å, respectively.

Table 7.2The interatomic distances between the C substitutional atom and its neighboring B atoms in units of Å.

Atomic pair	$R_{ij}^0$	$R_{ij}$	$R_{ij}/R_{ij}^0$
$B_2 - B_2$	2.09	2.19	1.05
$B_2 - B_3$	1.83	1.72	0.94
$B_2 - B_5$	1.75	1.69	0.97

It is anticipated that the changes to the local electronic energies and atomic structure will also be reflected in the bond strengths. The elastic stiffness coefficients, presented in Table 7.3, provide a simple approach to examining the bonding strengths. The addition of C leads to a 4% decrease of  $c_{22}$  and has little impact on the other tensor components.



Figure 7.2 The density of states projected on selected B or C 2p – states. The red solid lines and blue dotted lines represent the AlLiB<sub>14</sub> defect structure and the ideal structure respectively. The left column shows the partial density of states for B atoms within the first nearest neighbor distance from C, and the right column shows the second nearest neighbors.

The  $c_{22}$  coefficient corresponds to the crystal's response to uniaxial loading parallel to the  $C-B_2$  bond. The substituted C on the  $B_2$  site has only a minor impact on the bonding within the icosahedra, thus the diminished  $c_{22}$  coefficient is primarily due to the bonding between the icosahedra layers, i.e., the  $C-B_2$  bond.

Previous studies demonstrate that the ideal brittle cleavage model [84] can be used in conjunction with the elastic stiffness tensor to predict the intrinsic hardness of the XYB<sub>14</sub> crystal [58]. The effect of C substitution on the fracture strength is investigated for the cleavage planes illustrated in Figure 7.1 and the cleavage energy and critical stress for each are given in Table 7.4. The addition of C decreases the fracture stress by about 3.3 GPa on the  $\{010\}$ -M<sub>1</sub> plane. Following the procedure outlined in Wan and

Compounds	Elastic stiffness coefficients (GPa)								
1	$c_{11}$	$c_{12}$	$c_{13}$	$c_{22}$	C <sub>23</sub>	C <sub>33</sub>	c <sub>44</sub>	$c_{55}$	c <sub>66</sub>
AlLiB <sub>14</sub> with C	529	45.5	83.3	394	31.1	422	92.9	199	132
$AlLiB_{14}$	526	45.7	83.4	411	32.0	419	91.0	201	130

Table 7.3 The elastic stiffness coefficients for  $AlLiB_{14}$  structure with and without C.

Beckman [58] it can be approximated that the fracture strength of C doped AlLiB<sub>14</sub> is 12% lower than that of pure AlLiB<sub>14</sub>.

Table 7.4A comparison of ideal brittle cleavage parameters for selected cleavage planes<br/>in ideal AlLiB $_{14}$  and the corresponding C defect structure.

Composition	Orientation	Cleavage energy $G_b/\text{Area} (\text{J/m}^2)$	Critical length $l_b$ (Å)	Critical stress $\sigma_b$ (GPa)
AlLiB <sub>14</sub> with C	$\{010\}-M_1$	4.85	0.57	31.53
MILID <sub>14</sub> with C	$\{010\}-M_2$	5.15	0.54	34.82
AlLiB <sub>14</sub>	{010}-M	5.42	0.56	35.73
AlLiB <sub>14</sub> with C	$\{001\}-M_1$	7.06	0.56	46.27
111111114	$\{001\}-M_2$	7.34	0.58	47.01
AlLiB <sub>14</sub>	{001}-M	7.51	0.57	48.12

### 7.4 Summary and Conclusions

In this paper, the influence of C impurities on the structural and mechanical properties of  $AlLiB_{14}$  is discussed. Due to its size and chemical similarity to B the addition of C does not introduce substantial lattice strain. The structural and electronic changes exist for the nearest neighbor sites only, within 4 Å of the defect. Electronic states are not introduced to the band gap by the addition of C and the changes to the projected density of states are only observed for the  $B_2$ ,  $B_3$ , and  $B_5$  atoms that are directly bonded to the C. This suggests that C impurities do not strongly affect the electrical properties of the system.

The C atom changes the bonding and mechanical properties of the system locally in the lattice. The equilibrium position of the C atom is slightly closer to the B layer than the  $B_2$  atom that it replaces and the strength of the bonds between the B-layers is weaker. A simulation of ideal brittle cleavage predicts that the addition of C will lead to a  $0.3 \text{ J/m}^2$  reduction of the decohesive energy for a cleavage surface introduced between the C-B<sub>2</sub> bonds. It is predicted that this will reduce the overall fracture strength of the crystal by approximately 3.3 GPa or 12% of 28 GPa.

However, the energy of formation for substitutional C is relatively large, 1.7 eV. Even at high temperatures, for example 1800 K, the equilibrium concentration for C is only around  $2.2 \times 10^{18}$  per cm<sup>3</sup>. This suggests that C impurities will not reside in isolation on the B lattice, but instead gather in interstitial sites or at interfaces, such as grain boundaries, or possibly form defect complexes involving multiple C atoms or vacancies.

It is concluded that the concentration of isolated C atoms on B lattice sites is relatively low, but locally their presence will strongly impact the strength of the crystal. If the C atoms cluster they may serve as a nucleation site for cracks in this crystal family. It would be beneficial for future studies to focus on the interaction of C atoms within the lattice and at interstitial sites. It would be particularly interesting to understand the barriers to diffusion of C within the lattice.

## 7.5 Acknowledgements

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#### CHAPTER 8. CONCLUSIONS

This thesis is devoted to understanding the origin of unexpected hardness of the  $XYB_{14}$  crystal family and explaining how the mechanical properties are tied to its electronic structure. The role of substitutional C atom are clearly identified, and its influence on the mechanical behavior of the host material are well examined. A simple ideal brittle cleavage model is tested and proved to be applicable to predict the hardness of  $XYB_{14}$  crystal from the atomic-scale calculations. The details of the results are summarized as follows.

The first-principles DFT method is employed to study the electronic structure of  $XYB_{14}$  crystal. It is found that the electronic structure of  $XYB_{14}$  is dominated by the covalently bonded B-network. The metal atoms are not strongly bonded with any neighboring B atoms; instead, they transfer their valence electrons to stabilize the charge deficient B lattice. It is found that the electronic structure of  $XYB_{14}$  obeys rigid band model fairly well. By changing the number of valence electrons attributed by the metal atoms, one can easily move the Fermi level through the density of states.

A simple electron counting scheme reveals that the charge deficient B lattice is stabilized by accepting 16 electrons from the metal atoms, which help to fully fill the valence bands. Once extra electrons are contributed by the metal atoms, the conduction bands begin to be occupied, which leads to structural instability of the crystal. Here, this phenomenon is well studied by observing soft vibrational modes of the lattice. By forming vacancies at the metal sites, excess charge are removed from the lattice and as a result, the XYB<sub>14</sub> behaves as semiconductors, rather than metals. To some extent, the formation of metal vacancies may give rise to a variety of interesting features of this crystal family. For example, the open space between the B-network may provide free channels to diffuse small ions. The lattice imperfection may also help to scatter phonons, which reduces the lattice contribution to the thermal conductivity. This is particularly noteworthy for the thermoelectric applications.

Having understood the role of individual atoms in the electronic structure of  $XYB_{14}$ , we can move forward to discuss how the electronic structure determines its mechanical behavior. Ultimately, the question we want to answer is: is it possible to improve the mechanical properties of  $XYB_{14}$  by tuning its electronic structure. As concluded in Chapter 5, by emptying the electronic occupation of certain anti-bonding orbitals at the valence band edge, it is possible to enhance the corresponding bonding strength. However, only a very narrow window is available to strength the crystal by repopulating the localized B–B electronic states.

To complete the analysis of the electronic structure of  $XYB_{14}$ , a hybrid functional approach is used to give a better approximation of the band gap energies. It is well known that the traditional LDA- or GGA-DFT method tends to underestimate the band gap for many semiconducting or insulating systems, although the general shape of the bands is believed to be reliable. A simple correction to the band gap is to use hybrid functionals, which incorporate certain fraction of true Hartree-Fock exchange energy. As discussed in Chapter 5, using the HSE hybrid functional, a band gap around 2 eV is predicted for the AlLiB<sub>14</sub> compound. In addition, applying external stress has a minor impact on the band gap energy, which is primarily due to the strong mechanical strength of the crystal. It is noted that the 2 eV band gap energy responds to a strong photon absorption peak in the solar spectrum. Therefore, this crystal family may also be useful for certain photoactive applications.

A big limitation of the first-principles methods is the small system size that it can effectively investigate. Because all the quantum effects are taken into account, the system size is usually restricted to within 100s atoms. To understand and predict the macroscopic properties of this crystal family, for example, hardness, one need to deploy appropriate semi-empirical model that can be used in larger scale simulations. The first-principles methods, on the other hand, can provide input parameters for these semi-empirical models and also give insight to the bond breaking mechanism as it related to crack propagation in the crystal. In this work, the ideal brittle cleavage model is used to approximate the fracture strength of the AlLiB<sub>14</sub> crystal. It allows us to examine the bonding strength of the crystal on a plane-by-plane basis. It is observed that the overall bonding strength of the crystal is tied closely to the localized B–B bonds that span between the icosahedra layers. In addition to the ideal brittle cleavage model, a simple relationship between the macroscopic hardness and the orientation-dependent Young's modulus is identified. This finding offers a very effective way to characterize the macroscopic hardness of the XYB<sub>14</sub>-type crystal from the atomic level.

Experimentally it is observed that C is a natural dopant in the boron structures due to the chemical similarity between B and C. By comparing the formation energy for placing C atom at different B sites, it is concluded that C is energetically prefer to occupy the inter-icosahedron B site. The corresponding formation energy is predicted to be approximately 1.7 eV. It should be pointed out here that 1.7 eV is a relatively large energy for substituting foreign atom in solids. Even at high temperature (for example 1800 K), the equilibrium concentration for C is only on the order of 10<sup>18</sup> per cm<sup>3</sup>. This indicates that C impurity atoms might not be willing to reside in the B lattice; instead diffuse into interstitial sites or take a position at the interface or grain boundary. In addition to the large formation energy, the substitution of C atom will weaken the fracture strength of the host by approximately 12%, because of the diminished intericosahedron B–B bonds that connect the icosahedra layers.

To summarize, this work provides detailed investigations on the relation between the electronic structure and mechanical properties of the  $XYB_{14}$  crystal. A vacancy formation mechanism is proposed that explains the origin of the off-stoichiometric nature of many of the  $XYB_{14}$  compound. By analyzing the bonding structure of the material, it is found that, in principle, the bonding strength of the crystal can be enhanced by carefully repopulating certain electronic states. However, doping the B lattice with C predicts a lowered bonding strength of the crystal. Hopefully, the knowledge gained here may assist future development of this crystal family.

## APPENDIX A. SUPPLEMENTARY MATERIALS TO CHAPTER 5

#### Using the Heyd-Scuseria-Ernzerhof functional

It is well-established in the literature that the use of standard local/semi-local approximations in calculating the exchange-correlation energy results in significant underestimation of the band gap for semiconductors. In this work, the Heyd-Scuseria-Ernzerhof hybrid functional is used, which tends to provide a better estimation of the band gap energy for semiconductors [19]. The electronic calculation is carried out using the VASP source code [94]. For the ion potentials the projector augmented wave method is used within the Perdew-Burke-Ernzerhof flavor [16, 95]. The results are fully converged for a 318.6 eV cutoff energy and  $6 \times 6 \times 4$  k-point sampling [37]. As expected, the hybrid functional calculation yields a significantly larger band gap, around 2.12 eV, compared to the 1.26 eV gap predicted using the generalize gradient approximation.

# APPENDIX B. SUPPLEMENTARY MATERIALS TO CHAPTER 7

### Atomic basis for the electronic calculations

The parameterization for each atomic species used in the basis set is presented in Table B.1.

Element	Valence configuration	First $-\zeta$ $(r_c)$	Second $-\zeta$ $(r_m)$
Al	$3s^2$	5.9597	5.1295
	$3p^1$	7.6524	6.0347
Li	$2s^1$	8.8136	7.0376
В	$2s^2$	5.2881	4.4391
	$2p^1$	6.2996	4.6667
C	$2s^2$	4.4068	3.3893
$\sim$	$2p^2$	5.2497	3.5188

Table B.1 The cutoff radii for the double  $-\zeta$  functions.

## Convergence tests on calculating formation energies

Convergence tests are performed with respect to supercell size for C substituted to the inter-icosahedra  $B_2$  site. In Fig. B.1, the simulation cell is expanded along the

x-direction. It is observed that the calculated formation energies fit well with the relation proposed in Ref. [92]. The obtained formation energies are summarized in Table. B.2 as a function of supercell configuration. From these calculations and the energy relation in Ref. [92] it is concluded that a  $2 \times 1 \times 2$  supercell configuration is adequate to predict the formation energy of C substitution to within an accuracy of 0.1 eV.

Table B.2 The formation energy of C substituted to the inter-icosahedra  $B_2$  site as a function of supercell configuration. The results are calculated under the B-rich condition. The number of k-points is halved as the supercell is doubled due to folding of the Brillouin zone.

Supercell	BZ sampling	Formation energy (eV)
$1 \times 1 \times 1$	$12 \times 12 \times 12$	1.91
$2 \times 1 \times 1$	$6 \times 12 \times 12$	1.81
$1 \times 2 \times 1$	$12 \times 6 \times 12$	1.88
$1 \times 1 \times 2$	$12 \times 12 \times 6$	1.86
$2 \times 1 \times 2$	$6 \times 12 \times 6$	1.74



Figure B.1 The formation energy for C substituted to the B<sub>2</sub> site, plotted as a function of supercell dimension in the x-direction. The DFT results are obtained for  $1 \times 1 \times 1$ ,  $2 \times 1 \times 1$ , and  $4 \times 1 \times 1$  supercells. The dashed line is Eqn. (2) in Ref. [92] fitted to the data.

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