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Bonding and doping of simple icosahedral-boride semiconductors

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Abstract

A simple model of the bonding and doping of a series of icosahedral-boride insulators is presented. Icosahedral borides contain clusters of boron atoms that occupy the 12 vertices of icosahedra. This particular series of icosahedral borides share both the stoichiometry $B_{12}X_2$, where X denotes a group V element (P or As), and a common lattice structure. The inter-icosahedral bonding of these icosahedral borides is contrasted with that of $B_{12}O_2$ and with that of α-rhombohedral boron. Knowledge of the various types of inter-icosahedral bonding is used as a basis to address effects of inter-icosahedral atomic substitutions. The inter-icosahedral bonding is maintained when an atom of a group V element is replaced with an atom of a group IV element, thereby producing a p-type dopant. However, changes of inter-icosahedral bonding occur upon replacing an atom of a group V element with an atom of a group VI element or with a vacancy. As a result, these substitutions do not produce effective n-type dopants. Moreover, partial substitution of boron atoms for atoms of group V elements generally renders these materials p-type semiconductors.

Keywords: Icosahedral-boride; Boron subphosphide; Boron subarsenide; $B_{12}P_2$; $B_{12}As_2$

1. Introduction

Boron-rich solids are defined as materials that have boron as their primary constituent. Boron-rich solids often contain very stable clusters of boron atoms.

Icosahedral borides are materials based on 12-atom boron clusters in which boron atoms occupy the 12 vertices of icosahedra. Fig. 1 illustrates the rhombohedral unit cell of two simple icosahedral-boride insulators: $B_{12}P_2$ and $B_{12}As_2$ [1]. These crystals are composed of 12-boron-atom icosahedra and two-atom chains (P_2 or As_2) that reside between icosahedra. Covalent bonds between boron atoms link the boron icosahedra to one another. In addition, the atoms of the two-atom chains bond covalently to one another. Each atom of a two-atom unit also bonds to boron atoms of each of the three neighboring icosahedra.

The icosahedral clusters are bound together by electron-deficient (metallic) bonding. In particular, the electrons responsible for the internal bonding of an icosahedron are distributed over its surface. Since icosahedra are spheroids, these internal-bonding electrons occupy molecular orbitals that may be characterized as possessing *s*, *p*, *d*, and *f* molecular symmetry. [2,3] However, for an icosahedron the most energetic orbitals, the seven *f*-orbitals, are split into a four-fold-degenerate manifold and a three-fold-degenerate manifold. Boron icosahedra are found to each have 13 internal-bonding orbitals: one *s*-orbital, three *p*-orbitals, five *d*-orbitals, and four of the *f*-orbitals [3]. Thus, filling of an icosahedron's internal-bonding orbitals requires 26 (2×13) electrons [4].

Each boron atom has three second-shell electrons. If one of these electrons is used to form a bond external to an icosahedron, only 24 electrons (2×12) are available for an icosahedron's internal bonding. Since two additional electrons are required to fill an icosahedron's internal bonding orbitals, the boron icosahedra have a bi-electron affinity.

The affinity of each icosahedron for two-electrons is fulfilled in the icosahedral-boride insulators considered here. In particular, each icosahedron accepts two electrons donated from each two-atom chain.

Distinctive properties of these unusual electrical insulators make them potentially useful. In particular,

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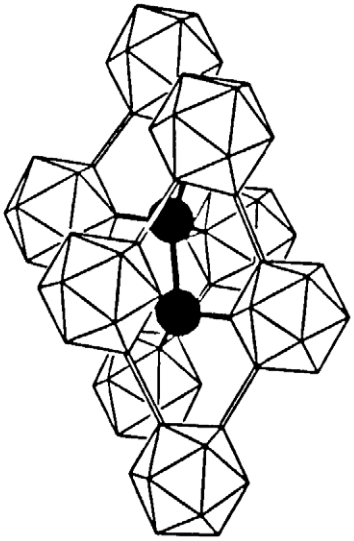

Fig. 1. The ideal structure of $B_{12}X_2$-type icosahedral-boride insulators is illustrated, where X refers to a pnictide atom, an atom of a group V element. Boron atoms occupy the 12 vertices of icosahedra. Two pnictide atoms, shown as large solid dots, are bonded to one another to form a two-atom chain. Each pnictide atom is also bonded to a boron atom in each of three adjacent icosahedra.

these solids are very hard, have very high melting temperatures, have wide energy gaps and manifest a remarkable resistance to radiation damage [1,5,6]. In particular, vacancies and interstitials produced by radiative bombardment spontaneously recombine, "self-heal," even at very low temperatures [5,6].

Development of specialized semiconductor devices based on these icosahedral-boride insulators requires that they be doped. This article broaches purposeful and unintentional doping of these materials. In particular, general consideration of the effects of atomic substitutions within these icosahedral-borides' two-atom chains is begun. To initiate the discussion, the bondings of three different types of icosahedral-boride two-atom chains are described. Then, the principles by which these stoichiometric materials are bonded are exploited to predict effects of different atomic substitutions. The ideas presented here can only provide guidance to doping of these icosahedral borides. Indeed, doping of even a conventional semiconductor is often very subtle.

2. Bonding in $B_{12}X_2$-type icosahedral-boride insulators

Three types of chain bonding occur among $B_{12}X_2$-type icosahedral-boride insulators. These three types of bonding are exemplified by (1) $B_{12}P_2$ and $B_{12}As_2$, by (2) $B_{12}O_2$, and by (3) α-rhombohedral boron.

As represented schematically in Fig. 2, in $B_{12}P_2$ and $B_{12}As_2$ each pnictide (group V) atom forms four bonds. Each pnictide atom bonds to a boron atom in each of the three adjacent icosahedra. In addition, the two pnictide atoms bond with one another. In particular, X-ray diffraction studies indicate the build-up of electronic charge between bonded atoms with the inter-atomic separation being very close to the sum of the atoms' covalent radii [7]. The angles between a pnictide atom's four bonds indicate near-tetrahedral bonding. In particular, in $B_{12}P_2$ the angle between the bond linking phosphorus atoms and a phosphorus atom's bond to a boron atom is 105.7° rather than 109°, the angle for ideal tetrahedral bonding [8]. Similarly, in $B_{12}As_2$ the angle between the bond linking arsenic atoms and that of an arsenic atom's bond to a boron atom is 103° [8].

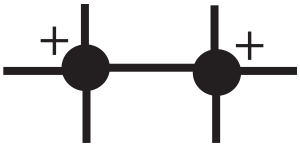

Fig. 2. The bonding of the two-atom chain of pnictide atoms in $B_{12}X_2$-type icosahedral-boride insulators is depicted schematically. Each pnictide atom is bonded to three boron atoms and to another pnictide atom. Each pnictide atom assumes a positive charge as it donates an electron to fulfill the internal-bonding of boron icosahedra.

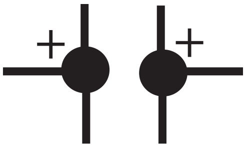

Fig. 3. The bonding of the two oxygen atoms of electrically insulating $B_{12}O_2$ is depicted schematically. Each oxygen atom only bonds to three boron atoms. The complex comprising an oxygen atom and the surrounding boron atoms assumes a positive charge as it donates an electron to fulfill the internal-bonding of boron icosahedra.

To accomplish near-tetrahedral bonding the ground-state configuration of a pnictide atom's electrons undergoes two alterations. First, one electron is removed from the pnictide atom: $s^2p^3 \rightarrow s^2p^2 + \mathrm{e}$. This electron is accepted in an icosahedron's internal-bonding orbital. Second, one of the pnictide atom's valence electrons is promoted from an s-level to a p-level in order to produce the sp^3-hybridization required to form four tetrahedral bonds: $s^2p^2 \rightarrow sp^3$.

Very different bonding prevails in $B_{12}O_2$. As schematically illustrated in Fig. 3, $B_{12}O_2$ has no bond between oxygen atoms. That is, X-ray diffraction studies indicate that (1) the inter-oxygen separation is much larger than the oxygen–oxygen covalent bond length and that (2) there is no build-up of electronic charge between the two oxygen atoms [9,10]. The boron and oxygen isotope dependencies of the Raman spectra also indicate the absence of a bond between the chain's two oxygen atoms [11]. Thus, each oxygen ion is just linked to boron atoms of neighboring icosahedra. Concomitantly, the oxygen atoms of $B_{12}O_2$ are not in near-tetrahedral coordination. Rather, each oxygen atom nearly lies in the plane of the neighboring boron atoms that reside in each of three adjacent icosahedra. Specifically, the angle between the line connecting oxygen sites and a line connecting an oxygen site to one of its three neighboring boron atoms is 96.5° rather than 90° [8].

To fill their internal-bonding orbitals, each icosahedron must receive an electron from each oxygen atom of $B_{12}O_2$. An oxygen cation will be left with one electron in each of its three *p*-orbitals. This change of an oxygen atom's atomic configuration is depicted as: $s^2p^4 \rightarrow s^2p^3 + e$. Thus, the oxygen ion has three unpaired electrons that are available to bond with the unpaired electrons of the three neighboring boron atoms.

The representation of the bonding between an oxygen cation and its three boron neighbors is uncertain. The charge density of the s^2p^3 atomic configuration is spherically symmetric. Promotion of an *s* electron, while not increasing the number of bonding electrons from three, would foster sp^2-directed trigonal bonds between an oxygen cation and each of its three boron neighbors: $s^2p^3 \rightarrow (sp^2)(p_z^2)$. However, an oxygen cation also attracts electrons from its surroundings. Thus, the formal positive charge attributed to an oxygen cation is dispersed over the complex comprising the oxygen atom and the three boron atoms adjacent to it [12].

In α-rhombohedral boron no atoms occupy the sites of the chain atoms. In this case, each two-site chain can be viewed as comprising two vacancies. The internal bonding states of icosahedra are filled as they accept an electron from one of the three boron atoms adjacent to each vacancy. The remaining two electrons from these three boron atoms form a three-center bond [13]. As illustrated in Fig. 4, this three-center bond comprises a singlet pair of electrons that occupies the center of the equilateral triangle whose vertices are the three boron atoms adjacent to the vacancy [1,13].

The examples described in Figs. 2–4 detail the major alterations in bonding that accompany changes of the occupants of chain-atom sites in $B_{12}X_2$ icosahedral borides. Based on this understanding, the effects of dopants and defects at these locations are now addressed.

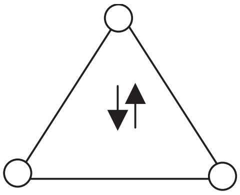

Fig. 4. α-rhombohedral boron is an electronic insulator composed of icosahedra that occupy the positions depicted in Fig. 1. However, no atoms occupy the chain-atom positions. In this instance, the three boron atoms that would bond to each pnictide atom of Fig. 1 bond together through the formation of a three-center bond. As depicted above, a three-center bond comprises a singlet pair of electrons surrounded by the three boron atoms.

3. Bonding of atomic substitutions in $B_{12}X_2$-type icosahedral-boride insulators

Bonding changes associated with substituting atoms of group IV elements (e.g., Ge) and atoms of group VI elements (e.g., Se) for atoms of group V elements in $B_{12}X_2$-type icosahedral-boride insulators are now considered. In addition, the bonding accompanying creating a vacancy by removing an atom of a group V element is addressed. Finally, the bonding associated with replacing an atom of a group V element with a boron atom is also addressed.

Atoms of both group IV and group V elements can engage in tetrahedral bonding. However, each atom of a group IV element contains one less valence electron than does an atom of a group V element. Thus, replacing an atom of a group V element with an atom of a group IV element in a $B_{12}X_2$-type icosahedral-boride insulator will remove an electron from a bonding state. The removed electron will come from the filled valence state with the highest energy. Thus, as illustrated in Fig. 5, substituting an atom of a group IV element for an atom of a group V element introduces a hole in the band of states associated with the internal bonding of icosahedra. The resulting chain is left with a net formal charge of +1. As a result of its formal charge being reduced from +2, this chain will tend to attract holes.

Now consider substituting an atom of a group VI element for an atom of a group V element. The bonding of the atom of the group VI element is presumed to be like that of oxygen in $B_{12}O_2$. Thus, an electron is transferred from the atom of the group VI element to icosahedral internal-bonding states. The resulting cation of the group VI element bonds to the three neighboring boron atoms. The other component of the chain, a cation of a group V element, is also affected by the atomic substitution. In particular, the cation of the group V element has no unfilled orbital on the atom of the group VI element with which to form a bond. Thus, as illustrated in Fig. 6, one of this cation's electrons is left unpaired in a non-bonding orbital. The chain comprising both group V and group VI cations retains a formal charge of +2.

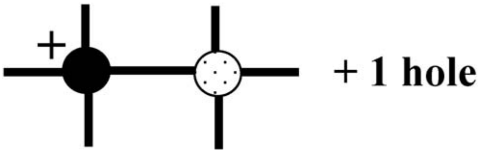

Fig. 5. The chain bonding associated with substituting an atom of a group IV element for an atom of a group V element in the $B_{12}X_2$-type icosahedral-boride insulators is schematically illustrated. The dotted and solid circles denote group IV and group V atoms, respectively. The solid lines depict bonds occupied by a pair of electrons. A hole is introduced within the band of icosahedral internal-bonding states.

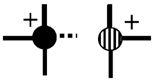

Fig. 6. The chain bonding associated with substituting an atom of a group VI element for an atom of a group V element in the $B_{12}X_2$-type icosahedral-boride insulators is schematically illustrated. The vertically striped and solid circles denote the group VI and group V atoms, respectively. The solid lines depict two-electron bonds. The dashed line indicates a singly occupied orbital.

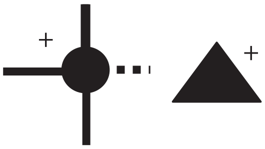

Fig. 7. The chain bonding associated with removing an atom of a group V element in the $B_{12}X_2$-type icosahedral-boride insulators is schematically depicted. The triangle and the solid circle denote the three-center bond at the site of the vacancy and the group V atom, respectively. The solid lines depict two-electron bonds. The dashed line indicates a singly occupied orbital.

Now consider introducing a vacancy by removing an atom of a group V element. Each of the three boron atoms adjacent to the vacancy provides a valence electron that can engage in bonding. The vacancy can fulfill one role of the atom of the group V element by donating one of these electrons toward filling (strongly electronegative) icosahedral internal-bonding orbitals. As evidenced in the inter-icosahedral bonding of α-rhombohedral boron, the remaining two valence electrons can form a three-center bond (albeit weak) that links the three boron atoms with one another. The vacancy also affects the cation of a group V element that remains in the chain. As illustrated in Fig. 7, one of this cation's electrons is left unpaired in a non-bonding orbital. Again, the chain comprising the vacancy and a cation of the group V element has a formal charge of +2.

Significant densities (several atomic percent) of boron atoms typically replace atoms of group V elements in $B_{12}X_2$ type icosahedral borides. A refinement of X-ray diffraction data from a sample of $B_{12}P_2$ produced by CVD finds that about 30% of the locations of group V elements are occupied by boron atoms [14]. A boron atom in the chain can bond to the three boron atoms of neighboring icosahedra. In particular, three coplanar orbitals can be formed upon promoting one of the three valence electrons of a boron atom: $s^2p \rightarrow sp^2$. Thereby, a boron atom can utilize all three of its valence electrons to bond to boron atoms on each of three adjacent icosahedra. The boron atom then remains formally neutral as no electron is donated to the internal bonding of icosahedra. The chain's boron atom also does not provide a partially filled orbital with which the other atom of the chain can form a bond. Thus, as depicted in Fig. 8, an electron of the cation of the group V element that cohabits the chain remains localized in a half-filled non-bonding orbital. The chain comprising a boron atom and a cation of the group V element has a formal charge of +1.

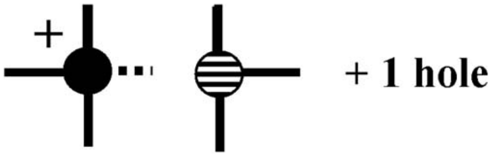

Fig. 8. The bonding associated with substituting a boron atom for an atom of a group V element in the $B_{12}X_2$-type icosahedral-boride insulators is schematically depicted. The horizontally striped and solid circles denote the boron and the group V atoms, respectively. The solid lines depict two-electron bonds. The dashed line indicates a singly occupied orbital. Each boron atom substituted for an atom of a group V element introduces a hole among icosahedral internal-bonding orbitals.

4. Doping of $B_{12}X_2$-type icosahedral-boride insulators

The +2 formal charge of an inter-icosahedral chain of a $B_{12}X_2$-type boride insulator makes it the natural center for a negatively charged electronic charge carrier. Furthermore, the only unfilled chain-related orbitals are anti-bonding orbitals. Thus, n-type conduction is associated with electrons that would move among chains' anti-bonding orbitals. Similarly, the formal charge of −2 of a boron icosahedron makes it a natural center for a positively charged electronic carrier, a hole. In particular, p-type conduction in $B_{12}X_2$-type icosahedral borides results from holes that move among internal-bonding orbitals of icosahedra.

Doping of $B_{12}X_2$-type icosahedral-boride insulators occurs when atomic substitutions foster n-type or p-type electronic conduction. Doping in these icosahedral borides is complex because qualitative differences in the local bonding occur when (1) an atom of a group IV element, (2) an atom of a group VI element, (3) a vacancy or (4) a boron atom replace an atom of a group V element.

As illustrated in Figs. 5–8, none of these substitutions induces occupation of a chain-related anti-bonding orbital. Thus, none of these substitutions produces n-type doping. Furthermore, as depicted in Figs. 6 and 7, the substitution of either an atom of a group VI element or a vacancy for an atom of a group V element yields an unpaired electron in a non-bonding chain-related orbital. Since these non-bonding states are unrelated to the icosahedral internal-bonding states that constitute the valence band, these states are also not associated with p-type charge carriers. Rather, the non-bonding states are expected to reside deep within the energy gap where they act as traps for electrons and holes. Electrons in singly occupied non-bonding states may be detected through their EPR signals and their contribution to the magnetic susceptibility.

By contrast, as illustrated in Figs. 5 and 8, substituting an atom of a group IV element or a boron atom for an atom of a group V element induces a hole in the band of icosahedral internal-bonding states. Concomitantly, the formal charge of an inter-icosahedral chain with one of these substitutions is reduced from +2 to +1. As a result, the hole tends to occupy internal-bonding states of icosahedra that reside near the altered inter-icosahedral chain. As such, an inter-icosahedral chain on which an atom of a group IV element or a boron atom replaces an atom of a group V element acts as an acceptor. Thus, an atom of a group IV element or a boron atom serves as a p-type dopant.

Significant densities of boron atoms are found to replace atoms of group V elements in $B_{12}X_2$-type icosahedral borides [14]. Concomitantly, these materials are generally p-type conductors [15,16]. This propensity of boron atoms to replace atoms of group V elements indicates that these substitutions carry a relatively small energetic cost. In particular, the energetic price of replacing an atom of a group V element with a boron atom is schematically written as

$$\begin{aligned} E_{\text{chain B}} - E_{\text{chain V}} &= [E_\text{P} - 3E_\text{BB}] \\ &\quad - [E_\text{I} + E_\text{P} - 3E_\text{VB} - E_\text{VV} - E_\text{IB}] \\ &= E_\text{VV} + E_\text{IB} - E_\text{I} - 3(E_\text{BB} - E_\text{VB}). \end{aligned} \tag{1}$$

here E_BB is the energy of a boron–boron bond; E_{VB} is the energy of a bond between an atom of a group V element and a boron atom; and E_VV is the energy of a bond between two atoms of a group V element. E_I represents the ionization energy of an atom of a group V element and E_IB indicates the energy of an icosahedral internal-bond. In addition, the energies to promote a valence electron from the *s*-state to a *p*-state of a cation of a group V element and of a boron atom are again approximated as equal to one another, E_P. Eq. (1) indicates that substituting three relatively strong boron–boron bonds for three boron bonds with an ion of a group V element tends to reduce the energetic cost of replacing an atom of a group V element with a boron atom within an inter-icosahedral chain.

The arguments presented above rationalize why $B_{12}X_2$-type icosahedral-boride insulators have significant densities of p-type carriers and have not been successfully doped n-type by substituting atoms of group VI for atoms of group V [15]. The p-type doping arises from significant inadvertent incorporation of boron within these material's inter-icosahedral chains. The failure of n-type doping arises because bonding of atoms of group VI and group V elements are qualitatively different from one another in $B_{12}X_2$-type icosahedral-borides.

Acknowledgments

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