



Why does a metal get an insulator? Consequences of unfilled bands on boron crystals

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ABSTRACT

A longstanding issue why boron crystals such as β -rhombohedral boron are insulator, while band calculations predict metals, has been solved. The issue is intimately related to another property of the crystal, namely breaking of stoichiometry. The presence of unfilled bands requires reconstruction of chemical bonds. Usually, for simple structures, the energy barrier is so high that the bond reconstruction rarely occurs. For large unit cells, the degree of internal freedom increases, and accordingly the chance to meet other energy minima in the atomic configuration increases. Such reconstructions of bonds take place when the valence requirement is fulfilled. This often occurs for boron crystals by breaking the stoichiometry. This mechanism is described for various boron crystals in a step-by-step approach.

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1. Introduction

Band theory is the standard model in solid-state physics. Given a crystal structure, we can calculate the band structure, and judge whether the crystal is metal or insulator. The theory is so successful for a vast amounts of crystals that we are prone to fall in a pitfall that the judgement is done only on this ground. In actual situations of crystals, it is important to recognize that the crystal structure is also variable. There are many choices for the structure when the cell size is large.

For a long time, solid-state physicists in boron physics had been beset with a big problem: for almost all polymorphs of boron, the band calculations indicate that the crystal must be a metal, while it is a semiconductor in experiment [1–3]. Crystals of β -rhombohedral boron (abbreviated as β -rh B), α -tetragonal boron (α -tet B), and boron carbides are such instances, if we assume perfect symmetry for these crystals. This conclusion of the band calculation does not depend on details of individual methods of calculation. These crystals have odd numbers of valence electrons, so that the band theory definitely dictates metallic property. Only α -rhombohedral boron (α -rh B) was an exception, until γ -orthorhombic boron (γ -orth B) was discovered [4,5].

Another big problem of boron crystals, which is seemingly different from the first one, is that these crystals have appreciable

amounts of structural defects. For β -rh B, there are many vacancies and interstitials. For α -tet B, it is known that no pure α -tet B exists. The actual structure always contains impurities such as N and C with appreciable amount. For boron carbides, transposition of C and B frequently occurs. In addition, the composition itself fluctuates, so that experimentalists have difficulty to control the composition accurately. Why the crystal contains so many defects is a long-debated issue. The origin of the defects of boron crystals was once discussed in connection to Jahn–Teller effects [6]. However, Jahn–Teller effects are too general to give a sufficient account for the current problem. The Jahn–Teller theorem only states that a structure of high symmetry becomes necessarily unstable, if the valence is partially occupied. But, the theorem says nothing about what is the final structure after distortion. Alternation of bonds, which is most likely to occur, is out of the vicinity of the local minimum point.

Recently, the basic mechanisms for these two problems have been solved. The fact is indeed that these two problems are deeply related each other. Experimentalists already appreciated that there is a good correlation between these two [7]; whenever there is disagreement in the electronic structure between band calculation and experiment, defects are always associated with. For summary of the correlation, see Table 1 of paper [7] by Schmechel and Werheit. However, many studies had to be required before full understanding for the mechanisms was achieved.

The first breakthrough is the finding that for β -rh B the presence of defects is the zero-temperature property. Usually, in conventional semiconductors, defects are introduced only because of

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Table 1

Valence counting for various boron crystals with high symmetry (S.G. space group): N_{el} the number of valence electrons, N_b the number of bonds, and N_d the electron deficiency. Third block of rows lists the information of bonds: the number of nearest neighboring B_{12} units followed by the detailed classification. For each type of *intericosahedral* bonds, the label, the number of bonds n , and the bond length l in Å are listed. For *intraicosahedral* bonds, the average values is listed. Fourth block of rows lists the information of orbitals. For each crystal, the number of orbitals of the *intra* and *intericosahedral* bonds per B_{12} are listed, for each the number of occupied electrons is shown. For the labels of bond and orbitals, refer to the text.

Polymorph formula S.G.	α -Rh B_{12} $R\bar{3}m$	γ -Orth $2B_{12} +$ $2B_2 Pnmm$	α -Tet $4B_{12} +$ $2B P4_2/nmm$	β -Rh B_{105} $R\bar{3}m$				
N_{el}	36	84	150	315				
Bonds	n	l	n	l	n	l		
intra- n of $N B_{12}$	6	1.79	12	1.80	12	1.80		
inter- (per B_{12})	r 3	1.67	t 2	1.66	t 2	1.65		
	e 2	2.02	s 4	1.82	s 4	1.70		
			s' 4	1.82	s' 4	1.83		
			w 2	1.67	w 2	1.64		
Interstitial B			i 2	1.73				
Orbitals	B_{12}	el	B_{12}	el	B_{12}	el		
Intra-	13	26	26	52	52	104		
Inter-	σ 3	6	σ 10	20	σ 20	40		
	Δ 2	4	σ' 4	8	σ' 8	16		
Interst.			2	4				
N_b	18	36	42	84	80	160	160	320
N_d		0		0		-10		-5
Ref.	[23]		[4]		[24]		[11]	

randomness at finite temperatures, in other words, the entropic contribution. The first density-functional-theoretic (DFT) calculation for the defects of β -rh B appeared by Masago *et al.* [8]. In their calculation, an interchange of atom positions between B(13) and B(16) sites was examined, resulting in a good agreement in the structure with experiment. Moreover, the important thing of their calculation is that introducing defects in this way reduces the total energy. This indicates that the defect state of β -rh B is a ground-state property. This role of the defects has been confirmed by Widom and Mihalkovič [9] and Setten *et al.* [10] by including further defects which are found for β -rh B [11–14].

The fact that the defect is a ground-state property itself is not for the first time for boron physics. Kleinman's group demonstrated reduction of the crystal energy by introducing defects for boron carbides [15,16] and α -tet B [17]. But, in these crystals, the presence of foreign atoms makes the role of defects more obscure; the properties are attributed to the specific properties of foreign atoms. In fact, they speculated that the insulating property of $(B_{12})(CBC)$ was ascribed to a different origin such as Mott–Hubbard insulator [16].

Another breakthrough was needed to establish true understanding for the role of the defects. Such a ground-state associated with defects is not unique, but indeed it has been clarified that there are numerous degenerate or nearly degenerate configurations [9,18]. Ogitsu *et al.* characterized it as frustrated system [18,19]. A similar idea of defects was suggested for boron carbides by Balakrishnarajan *et al.* [20]. Even before, people already knew that the defect state is not unique for an obvious reason of the random nature of defects. But, the significance of degeneracy was not taken seriously. An interesting mechanism of fulfilling unfilled bands was hidden behind this degeneracy.

Many authors have contributed in part by part to the solution of the metal/insulator issue, although the proposal of frustrated system is the most important. An individual paper treats a specific crystal from its own point of view, and the logics, methods, and terms are different from author to author, so that it may be difficult to extract a clear stream of logics from the literature. The purpose of

this paper is demonstration of the process how the metal/insulator issue is solved in a more transparent way.

The first part of this paper shows that the presence of unfilled bands in the valence band always leads instability to the perfect boron crystals with high symmetry, resulting in the breaking symmetry and deviation from the stoichiometry. This is shown by enumerating various polymorphs of boron crystals including recent-discovered γ -orth B. The second part shows that the defects of boron crystals have their origin in the chemical bonding. We will show that the structural flexibility of large unit cells is essential for generating of those defects. In particular, the deviation from stoichiometry is a common consequence of unfilled bands.

2. Valence counting description

As described in Introduction, sophisticated methods of band calculation are unnecessary for the current purpose. A crude method of the valence counting is enough, and is even better for its clear interpretation. For materials composed of covalent bonds, the valence requirement is expressed as,

$$N_{el} = 2N_b, \quad (1)$$

where N_{el} is the number of valence electrons and N_b is the number of bond orbitals (or simply bonds). The electron deficiency N_d is the difference between these two quantities: $N_d = N_{el} - 2N_b$. For boron crystals, $N_{el} = 3N_{at}$, where N_{at} is the number of atoms in a cell. The utility of valence counting is shown for vast amounts of materials, and hence it is enough to refer to original studies for a specific subject of boron only; [21] for hexaborides and [22] for icosahedral boron crystals.

In band theory, N_b may be re-interpreted as the number of valence bands. Those molecules satisfying the valence requirement, Eq. (1), must be stable by forming strong covalent bonds. The solid-state analogue of this statement is that a crystal having an even number of electrons must be an insulator. For a variety of real crystals, this statement is not always true, as is well known for divalent metals. A specific form of band dispersion could yield unfilled bands, resulting in metallic property. In contrast, for odd-number valence electrons, breaking of Eq. (1) necessarily leads to metallic property, no matter how complicated the band dispersions are. In this paper, we are mainly concerned ourselves with the later case and hence no detailed band calculation is needed.

In this paper, we attempt this simple counting rule to icosahedron-based boron crystals, including recently discovered γ -orth B. On the outset, we summarize the result of valence counting method and the related crystal structures in Table 1. One point for interest is mentioned. The average length of *intraicosahedral* bonds is almost constant over all the icosahedron-based boron crystals, *i.e.*, 1.80 Å. Since the specific volume per atom decreases in the order of α -tet, α -rh, and γ -orth, (see Table 2 of Ref. [2]), this constancy of the average radius of icosahedron implies a shortening of the *intericosahedral* bond. Another result of compressing the unit cell is deforming of the icosahedron, which is a commonly observed feature in boron-rich solids [25]. In the following, we will work on Table 1 one by one.

2.1. α -Rhombohedral boron

Since the icosahedron is the common building block for boron crystals, we have to know how the valence electrons should be counted. This was done in old time by Longuet–Higgins and Roberts [22]. There are 13 *intraicosahedral* orbitals in the B_{12} unit, which accommodate 26 electrons. There are 12 outward orbitals for the B_{12} unit. By putting the B_{12} unit in the crystalline environment

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