



Applying an electron counting rule to screen prospective thermoelectric alloys: The thermoelectric properties of YCrB_4 and Er_3CrB_7 -type phases

J.W. Simonson*, S.J. Poon

Department of Physics, University of Virginia, 382 McCormick Rd., Charlottesville, VA 22904-4714, USA

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ABSTRACT

An electron counting rule, which was recently expanded to study molecular organometallics, boranes, and metallocenes, is utilized herein to predict the formation of a semiconducting gap or pseudo-gap in the density of states of deltahedral crystalline solids at or near the Fermi energy. It is suggested that this rule may be exploited to screen intermetallic compounds for prospective thermoelectric materials. The rule was applied to several structure types of known deltahedral boride and borocarbide compounds, and its predictions were compared to those of first principles electronic structure calculations when such were available in the literature or to published reports of transport properties. In addition, the rule has been used to predict the properties of several materials for which the electronic structure and properties have not hitherto been reported. In accordance with these predictions, layered ternary boride intermetallic compounds with structure types YCrB_4 and Er_3CrB_7 were synthesized, and the electrical resistivity and Seebeck coefficients of these alloys were measured from room temperature to 1100 K. Alloys of composition RMB_4 ($\text{R}=\text{Y}, \text{Gd}, \text{Ho}$; $\text{M}=\text{Cr}, \text{Mo}, \text{W}$) were found to be n-type semiconductors and to exhibit thermopower up to ~ 70 – $115 \mu\text{V}/\text{K}$; the band gap was estimated to range from 0.17 to 0.28 eV, depending on composition. Undoped YCrB_4 was measured to have a maximum power factor of $6.0 \mu\text{W}/\text{cm K}^2$ at 500 K and Fe-doped YMoB_4 of $2.4 \mu\text{W}/\text{cm K}^2$ near 1000 K.

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1. Introduction

Intermetallic borides are attractive materials for a wide variety of applications, largely due to their exceptional hardness, high melting points, and chemical inertness at elevated temperatures. In particular, the more boron rich phases have attracted interest as potential materials for extremely high temperature (even up to 2000 K) thermoelectric power generation [1–3], due to their high temperature stability and to the complexities of their structures, which often result in hopping electron conduction and low thermal conductivity at such elevated operating temperatures. These compositions tend to be dominated by boron sub-structures that are invariably electron poor, necessitating the interposition of metal electron donors for stability [4,5]. Boron is trivalent and therefore classically capable of forming only three 2c–2e covalent bonds, leaving the remaining valence orbital unfilled. For this reason, a covalent boron network must resort to multi-centre bonding via cluster formation in order to achieve stability. These B–B covalent networks take a wide variety of forms: from icosahedra, as in the structures of $\beta\text{-B}$ [6], UB_{12} [7], MgAlB_{14} [8], and many other more complicated structures; to octahedra, as in the cases of

CaB_6 [9] and $\text{Th}_2\text{NiB}_{10}$ [10]; to polygonal layers; and to derivatives thereof.

Immediately following the discovery of superconductivity to 39 K in MgB_2 [11] there was a dramatic surge in experimental and theoretical investigation into the subject of the magnetic and electronic properties of the diborides, the structure of which consists of alternating metal layers and graphite-like layers of hexagonal boron sheets. Over the years, several surveys have been published on the electronic structures and thermal properties of the transition metal diborides with the AlB_2 structure, and the existence of a pseudo-gap was found to be a common feature among the entire series [12,13]. The diborides of tetravalent transition metals were found to exhibit the greatest thermal stability, which corresponded with the prediction of electronic structure calculations that the Fermi energies of these compounds sat at or near the minimum of that pseudo-gap, while the Fermi energies of higher and lower group transition metal diborides were predicted to fall above or below the minimum of the pseudo-gap, respectively. Due to the absence of a pseudo-gap in isostructural YHg_2 and HfBe_2 and its presence in AlB_2 , which certainly lacks any d-orbital hybridization, it was suggested that pseudo-gap formation is the result of multi-centre bonding within the B–B covalent network [10]. Moreover, this suggestion begs comparison to the somewhat analogous formation of the energy gap in the CaB_6 and UB_{12} systems, as was postulated by the symmetry-based electron counting models of the

* Corresponding author. Tel.: +1 434 924 6793; fax: +1 434 924 4576.

E-mail addresses: jws9n@virginia.edu, jwsimonson@gmail.com (J.W. Simonson).

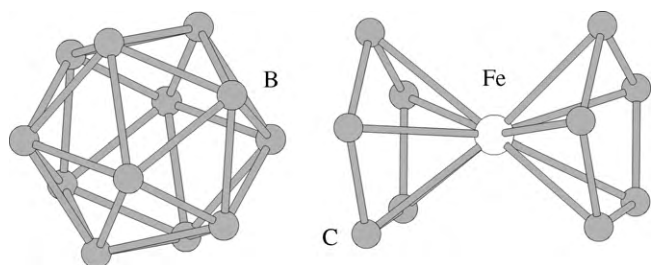


Fig. 1. Icosahedral borane molecule (left) and ferrocene molecule (right). The Fe atom is white, and the B or C atoms are gray. H atoms are omitted for clarity but are located radially outward from the B and C atoms.

early investigators of these compounds [4,5], i.e. that the so-called bonding orbitals of the polyhedral boron unit are fully occupied, the non-bonding orbitals are half occupied, and the anti-bonding orbitals are wholly unoccupied. The determination of the bonding nature of each orbital and the relative location of the HOMO–LUMO gap, however, is in general a nontrivial problem, and has only been solved analytically in the highest symmetry cases, those of the full icosahedral and full octahedral point groups [5,9].

To address the lack of a formal solution to the bonding scheme of more complex systems, a set of electron counting rules, commonly referred to as Wade's rules, was developed in the 1970s to predict the formation of new molecular structures and to determine the stability of polyhedral boranes via the method of molecular orbitals [14]. In the past decade, Wade's rules for assigning electron occupancy to simple boron sub-clusters have been subsequently generalized to include macro-polyhedral boranes, metallocenes, and organometallic molecules under the heading of the so-called "mno rule" [15]. The "mno rule" postulates that the number of occupied molecular orbitals, N , in a cluster with deltahedral geometry – such as a borane or carborane – is given by the sum of m , n , and o , where m is the number of polyhedra in the cluster, n is the number of vertices, and o is the number of single-vertex-sharing condensations. The more familiar Wade $n+1$ rule merely treats a special case with one polyhedron ($m=1$) and no condensations ($o=0$). As an example, consider the single icosahedral borane molecule in Fig. 1, in which a boron atom is located on each vertex of a regular icosahedron with a covalently bonded hydrogen atom oriented radially outward. Such a cluster is referred to as *closo* or "closed" to signify that it lacks no deltahedral vertices. In this example, the molecular unit includes one polyhedron, twelve vertices, and no condensations, yielding $N=1+12+0=13$ orbitals below the HOMO–LUMO gap. Some 26 electrons are therefore required for stability, but only 24 are available; each of the 12 boron atoms provides two electrons to skeletal bonding while their remaining electron is dedicated to the formation of a 2c–2e classical covalent bond with hydrogen. As a result, two additional electrons are needed for structural stability of the cluster. It bears mention that this result is identical to that obtained from the computationally rigorous Longuet–Higgins' technique, which results in the analytical solution of the energies of the borane molecular orbitals in the I_h point group [5].

For an example more appropriate to the discussion of bulk layered borides, consider the sandwich molecule ferrocene in Fig. 1 – the structure of which consists two co-parallel open (so-called *nido* to signify the lack of one vertex) cyclopentadienyl (C_5H_5) rings located on opposite sides of a central condensed vertex occupied by an iron atom. In this case, there are two polyhedra, a total of eleven occupied vertices including that of iron, one condensation at the iron site, and two unoccupied vertices, yielding $N=2+11+1+2=16$. Each carbon atom contributes three electrons to the total count, and as is analogous to the boron case above, the fourth is bonded with hydrogen. A covalently bonded iron atom contributes two electrons, for a total of 32 electrons, perfectly filling

those orbitals below the HOMO–LUMO gap and providing insight into why $Fe(C_5H_5)_2$ is stable while other isostructural cyclopentadienyl complexes such as chromocene or cobaltocene are far more reactive due to a lack of electrons or the occupation of anti-bonding states, depending on the metal atom.

With Jemmis' *mno* rule able to predict the stability of stability of macro-polyhedral molecules with high accuracy, only a few steps must be taken to apply this construction to bulk intermetallic compounds. It is well known that stability in a molecular system is achieved by filling molecular orbitals to the brink of the HOMO–LUMO gap. Therefore the assumption is made herein that an equivalent situation occurs in a crystalline solid when a sufficient number of electrons serves to position the Fermi energy exactly at the cusp of a band gap or pseudo-gap. A validation of this assumption is presented in Section 4 of this work via comparison of the predictions of an electron counting rule for bulk compounds with the results of published electronic structure calculations and transport measurements. This generalized *mno* rule is shown to provide a simple and easy-to-use tool to enable quick screening of potential thermoelectric materials that fit the necessary structural motif and to offer a gateway into explanation of their electronic properties. The alloys presented in this work are an example of the results of such a screening.

It is important to note, however, that the expansion of electron counting rules from molecules to crystalline solids is far from a novel idea in general. Indeed, even a book has been recently published on the subject, addressing several methods of counting skeletal electron pairs and cluster valence electrons. The book also covers the generalization of these molecular orbital models to crystalline systems either by examination of cluster analogues or via the Zintl–Klemm concept [16]. A more in depth discussion of Wade's rule for molecular and cluster systems, as well as of *closo*, *nido*, and *arachno* boranes is presented in its early chapters. Of particular relevance to the bonding of crystalline borides is the discussion of the stability of the rare earth hexaborides and of GdB_4 , neither of which can be explained by naive application of the Zintl–Klemm approach. In addition to that text, during the review process for this article, the authors of the present work were made aware of a recent publication that outlines the relationship between electron and valence counting rules and the structural arrangements and stabilities of cluster, chain, and ring compounds, including the layered borides $YCrB_4$, $ThMoB_4$, and Y_2ReB_6 [17]. Rather than using the *mno* rule as a starting point, the article discusses the bonding of such systems via consideration of several possible oxidation numbers of the boron networks and the critical examination of electronic structure calculations based on these possible states. Overall, the methods of generalization presented in these two sources offer insight into the bonding of boron- and carbon-based compounds that is complementary to what can be learned by the procedure described in the remainder of this article.

As mentioned above, there has been a great deal of work published on transitional metal diborides, but several ternary alloys with similar structures have not yet been as thoroughly investigated. The current study of electron counting in some of these systems, however, has suggested their potential for thermoelectric application. Consider for example the $YCrB_4$ -type compounds. While the structure of AlB_2 consists of alternating layers of metal atoms and boron hexagons, the boron network of the $YCrB_4$ structure type is instead built of pentagons and heptagons to accommodate metals of varying sizes [18]. It forms for over 100 different compositions [19]. LMTO calculations performed as part of an ongoing search for superconductivity in layered borides have shown $YCrB_4$ in particular to be a semiconductor with a narrow band gap of about 0.05 eV, with the states near the gap being of predominantly Cr-d character and with significant d-orbital hybridization [20]. More recently, alloys with the $YCrB_4$ structure

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