

# STRUCTURAL PRINCIPLES IN REFRACTORY BORIDES

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## ABSTRACT

The role of polyatomic groups in refractory borides is examined. Various arrangements of icosahedral boron groups are reviewed with emphasis on the crystal chemistry of these structures. It is demonstrated that formal presentation of lower borides in terms of tetrahedra (four metal atoms or two metal and two boron atoms) can be utilized to simplify understanding of these structures and to show relationship among structures that otherwise appear unrelated. It is shown that the  $M_2B_2$  configuration appears in a great majority of lower borides. Some principles on which these structures are built are described for the first time.

## INTRODUCTION

Many problems in identification of phases and variations in compositions of refractory borides can be traced to the lack of understanding of the role of polyatomic structural units in boron and related compounds. Thus, though a good quality boron was prepared at the beginning of the century<sup>1</sup> and even such complex compounds as  $C_2Al_3B_{48}$  have been identified<sup>2</sup> difficulties in distinguishing between boron, aluminium borides, aluminium boro-carbides etc.<sup>3,4</sup>, still seem to persist. Similarly, considerable amounts of work have been done since Moissan reported the existence of a boron carbide with the composition of  $B_6C^5$ , yet our recent work (unreported) indicates that the homogeneity range in the boron-carbon system has not yet been resolved. The consideration of stoichiometries, coordinations, electronic structure, nature of bonding, etc. have been applied to refractory borides with considerable difficulties and generally with less than satisfactory results. The difficulty arises from the facts that:

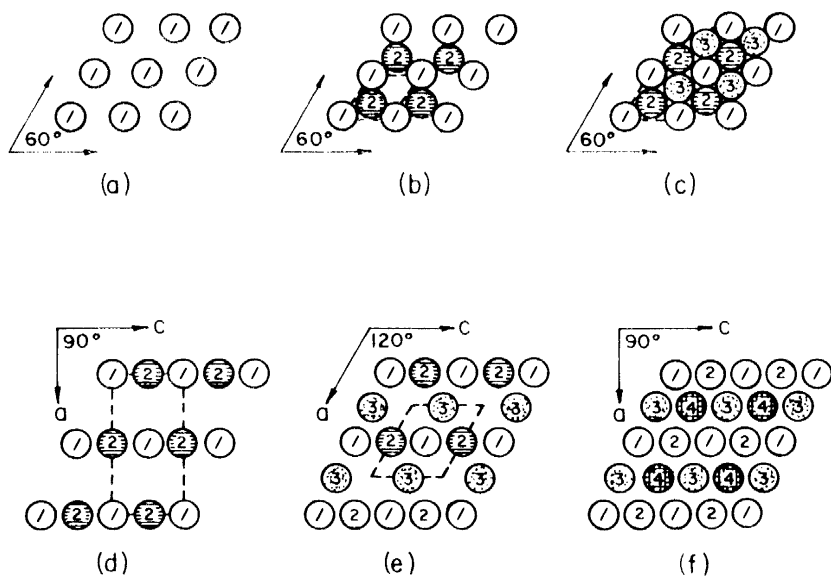
- (a) chemically different compounds are structurally closely related and produce similar x-ray patterns,
- (b) many structures may be stable only in the presence of impurities, and
- (c) many atomic positions show a tendency to partial occupancy<sup>6</sup>.

A helpful concept in the understanding of borides is based on the observation that boride structures can be described in terms of three-dimensional networks of polyatomic units with additional atoms being accommodated in the interstices among these groups. The variations in compositions and compounds can, thus, often be interpreted by either multiple or partial

occupancy of the interstitial sites by various atoms within the same structural framework. This concept is reviewed in this presentation with particular emphasis on the icosahedral  $B_{12}$  groups and the tetrahedral  $M_2B_2$  groups. Some aspects of the  $M_2B_2$  units are examined here for the first time.

### PACKING ARRANGEMENTS IN HIGHER BORIDES

The concept of packing in higher borides is based on the observation that quasi-spherical polyhedral groups of 12 or 84 boron atoms form three-dimensional arrangements which can be described in terms of stacking arrangements of closest packed layers of polyhedral units. There are in principle six basic models that can be derived in this manner by use of equal size spheres. The units may have coordination of eight, ten or twelve (referred to as primitive, close packed and closest packed arrangements, respectively). A coordination of eight is obtained by stacking the closest packed layers one above the other, so that each unit has only one close neighbour in the adjacent layers [see *Figure 1(a)*]. In the idealized case of equal size spheres, only one model can be classified in this group and is denoted as HP (hexagonal primitive arrangement). A coordination of ten is obtained by stacking the closest packed hexagonal layers in such a way that each unit has two close neighbours in each of the adjacent layers. In the idealized case of equal size spheres, three different models can be derived in this manner. These are: tetragonal close packing (denoted as TCP), composed of two different layers



*Figure 1.* Packing models that can be derived by stacking of closest packed layers of spheres. (a) HP - hexagonal primitive arrangement; (b) HCP - hexagonal closest packing arrangement; (c) CCP - cubic closest packing arrangement; (d) TCP - tetragonal close packing arrangement; (e) CPH - close packed hexagonal arrangement and (f) OCP - orthorhombic close packing arrangement.

[illustrated in *Figure 1(d)*]; close packed hexagonal arrangement (denoted as CPH), composed of three different layers [*Figure 1(e)*]; and orthorhombic close packing arrangement (denoted as OCP), composed of four different layers [*Figure 1(f)*]. A coordination of twelve is obtained by stacking closest packed hexagonal layers in such a way that each unit has three close neighbours in each of the adjacent layers. In the idealized case of equal size spheres, two different models can be derived in this manner and these are the well-known hexagonal closest packing (denoted as HCP) and cubic closest packing (denoted as CCP) arrangements illustrated in *Figures 1(b)* and *1(c)*, respectively.

The polyhedral atomic groups are not ideal spheres and hence the observed arrangements are as a rule somewhat distorted and often result in a change of symmetry of the unit cell. Thus, a variety of models can be derived from the six basic ones listed above. As has been proposed<sup>6</sup>, the specific model may be denoted simply by use of the capital letters describing the basic packing model. A numeral preceding these letters is used to describe the degree of multiplicity of the actual cell volume over that of the basic model and lower case letters following the capital letters to indicate the actual cell symmetry (r, t, o, etc. to indicate rhombohedral, tetragonal and orthorhombic symmetry, respectively). Use of this type of notation is illustrated in *Table 1* and the following discussion of  $B_{12}$  borides. Presence of  $B_{84}$  units rather than  $B_{12}$  is indicated by the lower case letter v immediately following capital letters, for example, 1/4CCPvr indicates a cubic closest packing arrangement of  $B_{84}$  units with a rhombohedral unit cell which has 1/4 of the normal CCP volume.

The  $B_{12}$  polyhedral groups with dimensions of 5.1 Å are considerably larger than single atoms so that interstitial openings present in these structures may accommodate not only individual but even groups of atoms. The atoms present in these interstitial openings can play a role in satisfying the steric and electronic requirements of the icosahedral units. For example, such atoms may provide crosslinking between the icosahedral boron groups and contribute to the bonding coordination of boron atoms<sup>28, 29</sup>. In addition, the interstitial atoms may act as electron donors to  $B_{12}$  icosahedra, which according to Longuet-Higgins and Roberts<sup>30</sup> require two additional electrons for stability. Since the interstitial openings are well-defined, it would appear a simple matter to define the stoichiometric compositions of  $B_{12}$  borides in terms of full occupancies of the interstitial sites. Unfortunately, as mentioned earlier, derivatives of  $B_{12}$  borides display, in general, a variable composition, which seldom can be explained in a simple manner. Perhaps the most serious complication is due to the ease with which higher borides form solid solutions between two members of an isotypic series. Some of the problems that have been observed and their consequences with respect to assignment of stoichiometry are discussed below.

## CRYSTAL CHEMISTRY OF $B_{12}$ BORIDES

### 1/4CCPr ( $\alpha$ -rhombohedral boron) derivatives

The 1/4CCPr series is based on a cubic closest packing of icosahedral units (see *Figure 2*) with a simple rhombohedral unit cell. The crystal chemistry

Table 1. Comparison of unit cell dimensions observed in  $B_{12}$  borides and those calculated from packing models of equal size spheres of 5.1 Å ( $B_{12}$  units) and 10.2 Å ( $B_{84}$  units) diameter

Packing model designation	Calculated			Observed $d(A)$	$(a/A)$	$(b/A)$	$(c/A)$	$(r/A)$	Conventional formula	Structural formula	Ref.
	$a(A)$	$b(A)$	$c(A)$								
CCP ( $B_{12}$ -cubo-octahedra)	7.2	—	—	7.408	—	—	—	—	$B_{12}Zr$	—	8, 9
	—	—	—	7.404	—	—	—	—	$B_{12}Lu$	—	
	—	—	—	7.473	—	—	—	—	$B_{12}U$	—	
	—	—	—	7.476	—	—	—	—	$B_{12}Tm$	—	
	—	—	—	7.484	—	—	—	—	$B_{12}Er$	$(B_{12})_4M_{14}$	
	—	—	—	7.492	—	—	—	—	$B_{12}Ho$	—	
	—	—	—	7.500	—	—	—	—	$B_{12}Y$	—	
—	—	—	7.501	—	—	—	—	$B_{12}Dy$	—		
CCP (cubo-octahedra)	5.1	—	7.2	5.22	7.3	7.35	—	—	$B_{12}Sc$	$(B_{12})_2M_2$	7
	(hexagonal presentation)	—	—	4.908	—	—	—	12.567	B	$B_{12}$	10
1-4CCP ( $B_{12}$ -icosahedra)	—	—	—	5.37	—	—	—	12.31	$B_6O$	—	11, 12
	—	—	—	5.984	—	—	—	11.850	$B_6P$	$B_{12}X_2$	
	—	—	—	6.142	—	—	—	11.892	$B_6As$	—	
	5.1	—	—	5.67	—	—	12.50	12.19	$B_{12}C_2$	$B_{12}C_2B$	
	—	—	—	5.63	—	—	—	12.29	$B_{12}C_2Al$	$B_{12}C_2Y$	
	—	—	—	5.65	—	—	—	12.35	$B_{12}C_2Si$	—	
	—	—	—	6.330	—	—	—	12.736	$B_{12}Si$	$(B_{12-n}Si_n)Si_2$	
	—	—	—	5.60	—	—	—	12.07	$B_4C$	$(B_{12-n}C_n)C_3B$	
	—	—	—	5.642	—	—	—	12.367	$B_{40}C_{14}Al$	$(B_{12-n}C_n)(C_{2-n}B_n)(B, Al)_n$	
	—	—	—	—	—	—	—	—	$B_{40}C_{14}Al$	—	
2HCPo ( $B_{12}$ -icosahedra)	8.8	8.3	5.1	8.89	9.10	5.69	—	—	$C_4AlB_{26}$	$(B_{12})_4C_9(AlB)_n$	5, 37

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Table 1—continued

Packing model designation	Calculated			Observed $a(A)$	$b(A)$	$c(A)$	Conventional formula	Structural formula	Ref.
	$a(A)$	$b(A)$	$c(A)$						
2TCP ( $B_{12}$ -icosahedra)	8.8	—	5.1	8.75	—	—	B	$(B_{12})_2B_2$	16
	—	—	—	8.82	—	—	$B_{48}C_2Al_3$ (800°C)	$(B_{12})_4C_2Al_4$	5, 17
	—	—	—	8.80	—	—	$B_{12}Be$	$(B_{12})_2Be_4$	18
	—	—	—	8.986	—	—	$B_{25}Ni$	$(B_{12})_2B_2Ni_2$	19
4TCP ( $B_{12}$ -icosahedra)	8.80	—	10.2	8.75	—	—	B	$(B_{12})_8B_4$	20
4TCPo ( $B_{12}$ -icosahedra)	6.2	12.5	10.2	6.17	12.63	10.16	$B_{48}C_2Al_3$	—	17
	12.5	12.5	5.1	12.34	12.63	5.08	—	—	
4HPo ( $B_{12}$ -icosahedra)	10.2	8.8	5.1	10.313	8.115	5.848	$MgAlB_{14}$	$(B_{12})_2B_8Mg_4Al_4$	21
	—	—	—	10.298	8.415	5.847	$NaB_{15}$	$(B_{12})_4B_8B_4Na_4$	38
1/4CCPvt ( $B_{84}$ -polyhedra)	10.2	—	25.0	10.944	—	—	B	$(B_{84})/(B_{10})_2B$	22
	—	—	—	10.98	—	—	$B_{32}Al$	—	23
	—	—	—	11.13	—	—	$B_{14}Si$	$(B_{84})/(B_{10-a}L_n)X$	
1/2CCPvt ( $B_{84}$ -polyhedra)	10.2	—	14.4	10.16	—	—	$\alpha AlB_{12}$	—	24
	—	—	—	10.12	—	—	B	—	25
	—	—	—	10.16	—	—	$BeB_6$	—	26
2HCPvo ( $B_{84}$ -polyhedra)	16.6	17.6	10.2	16.56	17.53	10.16	$\gamma-AlB_{12}$	—	27

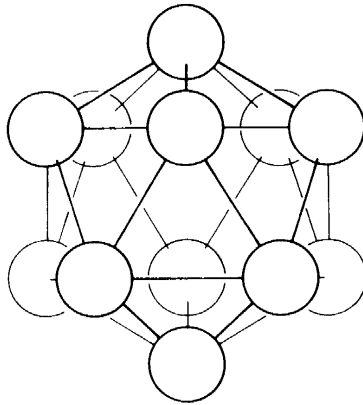


Figure 2. Twelve atoms occupying vertices of an icosahedron.

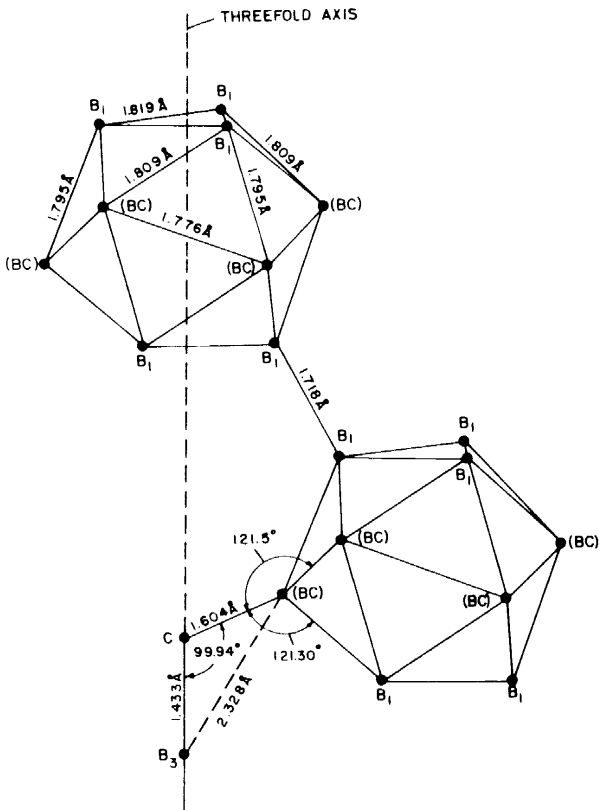


Figure 3. Interatomic distances in  $(B_{11}C_0)C_2B$ .

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of these derivatives has been reviewed earlier<sup>31</sup>. Since that time little new work has been carried out to clarify the nature of the interstitial atoms present in boron subarsenide, boron suboxide and boron subsulphide. The existence of a ternary system  $B_{12}C_2Al$  has been reported independently and almost simultaneously by Lipp and Roeder<sup>14</sup> and by our laboratory<sup>32</sup>. Lipp and Roeder<sup>14</sup> have also reported a new composition  $B_{12}C_2Si$  which appears to be closely related to  $B_{12}C_2Al$ . A detailed structure analysis of an aluminium borocarbide of composition  $AlC_4B_{40}$  has been reported by Neidhard *et al.*<sup>39</sup>. In our programme we have carried out a careful x-ray analysis of single crystals of rhombohedral boron silicide ( $SiB_{3-4}$ ) and boron carbide ( $B_{4-6.5}$ ). The boron silicide analysed for a composition of  $SiB_3$  and the structure was found to be in agreement with the findings of Magnusson and Brosset<sup>33</sup> where two silicon atoms are accommodated interstitially and lie along the threefold axis of the rhombohedral cell. The rest of the silicon partially substitutes for the icosahedral boron atoms at the bottom and top of the icosahedral triangles. This composition is consistent with a  $(B_{12-a}Si_a)Si_2$  stoichiometry where observed values of  $a$  vary between 1.0 and 1.5. Work on boron carbide crystals indicates that this compound resembles

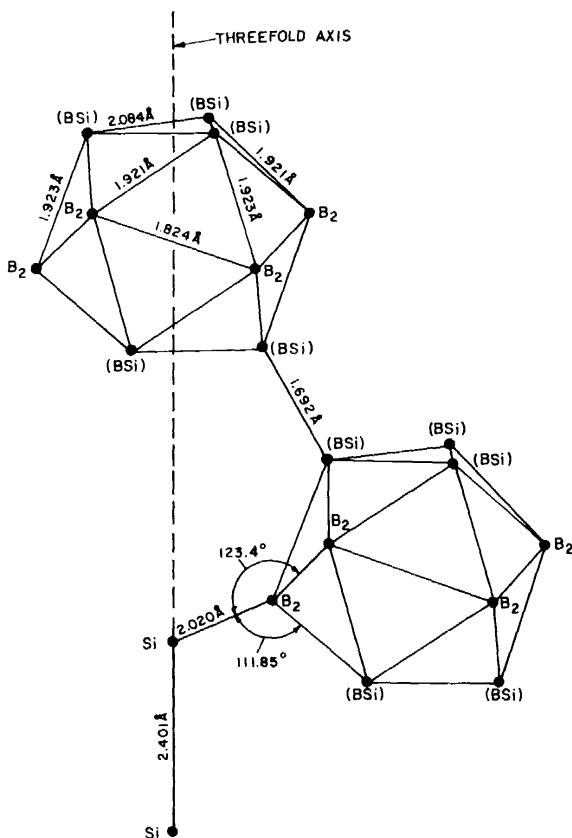
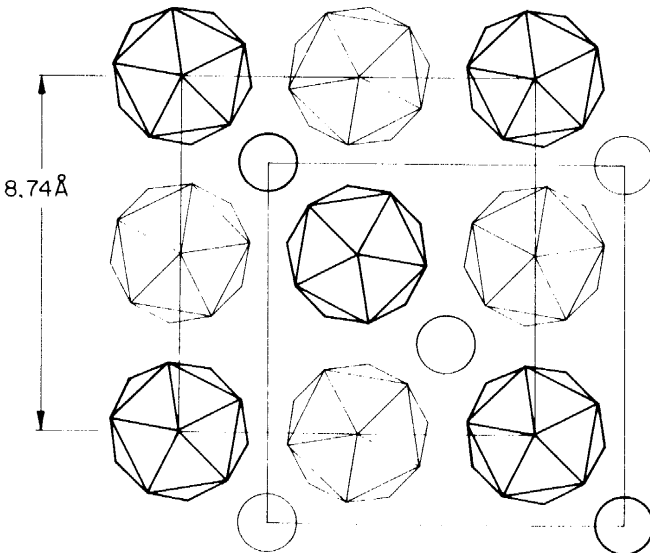


Figure 4. Interatomic distances in  $(B_{10.5}Si_{1.5})Si_2$ .

$\text{SiB}_3$  with carbon also substituting for icosahedral boron atoms but in a different position (see *Figures 3 and 4*). The interstitial opening accommodates two carbon atoms and one boron atom in a C—B—C arrangement. Existence of C—B—B linear and C—Al—B non-linear chains has been reported by Neidhard *et al.*<sup>39</sup> for  $\text{AlC}_4\text{B}_{40}$  [or  $(\text{B}_{12})(\text{C}_{2-x}\text{B}_x)\text{B}_{1-n}\text{Al}_n$ ]. Thus the composition of aluminium boron carbide may be written as  $(\text{B}_{12-a}\text{C}_a)(\text{C}_{2-x}\text{B}_x)(\text{B}_{1-n}\text{Al}_n)$ . These results lead to the conclusion that the commonly used formula of  $\text{B}_4\text{C}$  represents a solid solution of  $(\text{B}_6\text{C}_6)\text{C}_2\text{B}$  and  $(\text{B}_{12})\text{C}_2\text{B}$ . Therefore,  $\text{B}_{12}\text{C}_2\text{B}$  is the only stoichiometric compound in the rhombohedral phase of the boron-carbon system which has been observed<sup>34</sup>.  $\text{B}_{12}\text{C}_2\text{Al}$  and  $\text{B}_{12}\text{C}_2\text{Si}$  may also fall into this group and could be written as  $(\text{B}_{11}\text{Al})\text{C}_2\text{B}$  and  $(\text{B}_{11}\text{Si})\text{C}_2\text{B}$ , respectively. Thus, the compounds of the 1/4CCPr series can be designated by a general formula  $(\text{B}_{12-a}\text{L}_a)(\text{X}_{2-x}\text{B}_x)(\text{B}_{1-n}\text{Y}_n)$ . Interatomic distances in boron carbide and boron silicide are compared in *Figures 3 and 4*.

### 2TCP ( $\alpha$ -tetragonal boron) derivatives

The 2TCP derivatives are based on a tetragonal arrangement of  $\text{B}_{12}$  icosahedra which has differently oriented icosahedra at centres of all faces (see *Figure 5*). This isotypic series includes tetragonal boron,  $\text{BeB}_{12}$ <sup>18</sup>,  $\text{NiB}_{25}$ <sup>19</sup>,  $\text{C}_2\text{Al}_3\text{B}_{48}$  (high temperature phase)<sup>17</sup> and  $\text{AlBeB}_{24}$ <sup>40</sup> and was briefly discussed in an article by H. J. Becher<sup>35</sup>. In earlier work it had been shown that in tetragonal boron the two interstitial boron atoms were located in a twofold position<sup>16</sup>, even though two fourfold and one twofold openings were also available. In the case of  $\text{AlBeB}_{24}$ , it has been shown<sup>40</sup> that aluminium atoms are present in a fourfold position. With  $\text{NiB}_{25}$  it has been



*Figure 5.* Structure of tetragonal boron as viewed in the direction of the  $c$  axis. Two alternative unit cells are shown. The upper one has non-identical icosahedra at the centres of all faces and corresponds to the 2TCP model classification.

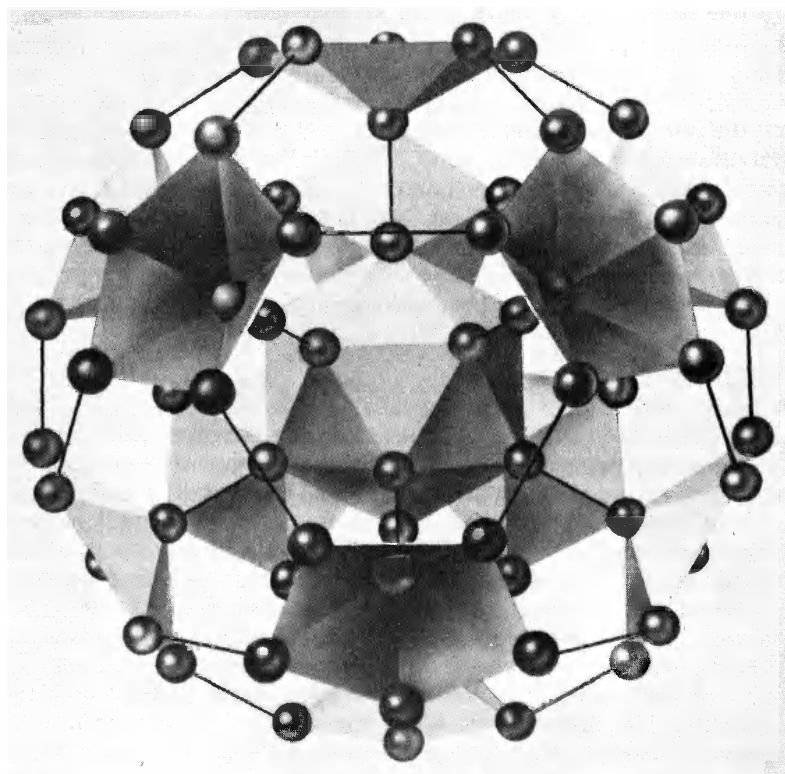


suggested<sup>19</sup> that the interstitial nickel and boron atoms occupy selectively two different sets of twofold interstitial positions in the structure. In the case of  $C_2Al_3B_{48}$ , the high temperature form is obviously a derivative of the 2TCP model. This was recently confirmed by Mattes *et al.*<sup>36</sup> It is suggested that this series corresponds to a  $(B_{12})_4C_2Al_4$  stoichiometry where the aluminium position is partially defective. In view of the above information a general formula for the 2TCP derivatives may be expressed as  $(B_{12})_4X_2Y_2Z_4$ .

It is interesting to note the ease with which these systems can convert from one to the other. Thus, Becher found that in reaction of  $BeB_{12}$  with  $BCl_3$  the four Be atoms are removed from the polyhedral framework while two boron atoms are inserted, apparently in different positions<sup>18</sup>.

#### 1/4CCPvr ( $\beta$ -rhombohedral boron) derivatives

It has been suggested that  $B_{14}Si$  and the so-called 'monoclinic'  $AlB_{12}$  were isotypic with  $\beta$ -rhombohedral boron<sup>29</sup>. This structure is based on a cubic closest packed arrangement of  $B_{84}$  units<sup>22</sup> (see *Figure 6*). There is a similarity



*Figure 6.* Ideal arrangement of boron atoms in the  $B_{84}$  polyatomic unit. The arrangement consists of a central  $B_{12}$  icosahedron and 12 pentagonal pyramids centred radially at the vertices of the central icosahedron. The 60 peripheral atoms occupy vertices of a truncated icosahedron (12 pentagonal and 20 hexagonal faces).

in the stacking arrangement of the  $B_{84}$  units in this isotypic series and of the  $B_{12}$  unit in the  $\alpha$ -rhombohedral boron series. In addition, the C—B—C interstitial chain in boron carbide bears a formal resemblance to the interstitial  $B_{10}$ —B— $B_{10}$  group in  $\beta$ -rhombohedral boron. In the case of  $B_{14}Si$  and monoclinic  $AlB_{12}$  it is suggested that the interstitial group consists of  $(B_7Si_3)$ —Si— $(B_7Si_3)$  and  $(B_6Al_4)$ —Al— $(B_6Al_4)$ , respectively<sup>23</sup>. A formulation for this isotypic series consistent with the above data would be  $B_{84}(B_{10-a}N_a)_2X$ . In this approach a group of atoms such as  $B_{10}$  is considered as an interstitial unit.

## 2HCPo derivatives

Only one member of this type has been described, namely  $C_4AlB_{24}$ <sup>5</sup>. This compound is based on a hexagonal closest packing of  $B_{12}$  units with an orthorhombic symmetry. The unit cell contains four  $B_{12}$  icosahedra. In  $C_4AlB_{24}$ , the eight carbon atoms occupy an eightfold position while two aluminium atoms appear to be randomly distributed among the two fourfold and a sixteenfold positions<sup>5</sup>.

It should be mentioned that  $C_4AlB_{24}$  converts on heating to a rhombohedral form of the  $1/4CCPr$  series, the formula of which may be written as  $B_{12}C_2Al_{0.25\ 0.75}$ <sup>32</sup>. This observation led Hoard and Hughes<sup>23</sup> to propose on the basis of stereochemical considerations the presence of a C—B—C chain in both the orthorhombic and the rhombohedral forms and then to reformulate the composition of  $C_4AlB_{24}$  as  $C_4AlB_{26}$ . In our work, we have observed compositions with a higher boron content ( $C_4AlB_{25}$ ), and subsequent simple crystal work by Perrotta *et al.*<sup>37</sup> leads to the approximate composition of  $C_4AlB_{26}$ . Accordingly four interstitial boron atoms could be present in the unit cell of this structure leading to the formulation  $(B_{12})_4C_8B_4Al_n$  and the series may be described by the general formula  $(B_{12})_4X_8Y_4Z_n$ .

## 4HPo derivatives

The compound,  $MgAlB_{14}$  with the structural formula of  $(B_{12})_4Mg_4Al_4B_8$  was first reported in this series<sup>21</sup>. The structure consists of a simple hexagonal arrangement of icosahedra with orthorhombic symmetry. The unit cell contains four  $B_{12}$  groups, eight additional boron atoms and up to eight metal atoms (see *Figure 7*). The interstitial boron atoms are accommodated in an eightfold position while magnesium and aluminium atoms are distributed among two fourfold positions. Both metal positions have been found to be partially occupied. The structure analysis indicated a tendency for some Al to be randomly distributed among the Mg positions. Another member of this series,  $NaB_{15}$  was reported by Naslain and Kasper<sup>38</sup>, with the structural formula  $(B_{12})_4B_4Na_4B_8$ . Assuming full occupancy of interstitial sites the general stoichiometry of  $(B_{12})_4X_4Y_4Z_8$  may be assigned to this series.

It has been found that all of the higher borides can be classified as derivatives of simple packing arrangements of  $B_{12}$  units. The stoichiometries within a given series can be expressed by a general formula denoting the interstitial atoms as X, Y and Z (each of which can assume values from zero to unity) and the substitutional icosahedral boron positions as L. A general description for stoichiometries of the five isotypic series may be listed as follows:

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1/4CCPr	Derivatives $(B_{12-a}L_a)(X_{2-x}B_x)(B_{1-n}Y_n)$
2TCP	Derivatives $(B_{12})_4X_2Y_2Z_4$
1/4CCPvr	Derivatives $B_{84}(B_{10-a}L_a)_2X$
2HCPo	Derivatives $(B_{12})_4X_8Y_4Z_n$
4HPo	Derivatives $(B_{12})_4X_4Y_4Z_8$

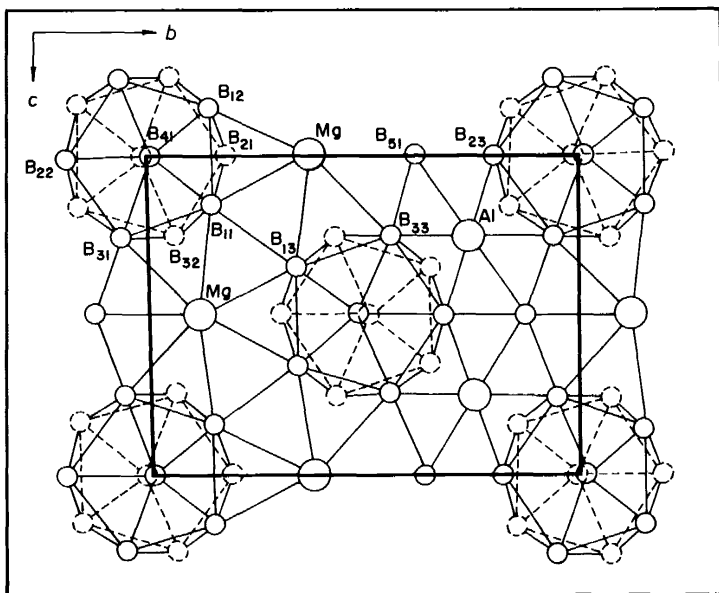


Figure 7. A layer of icosahedra in  $MgAlB_{14}$  with extra-icosahedral atoms. The atoms shown fall within  $x = \pm \frac{1}{4}$ .

## LOWER BORIDES

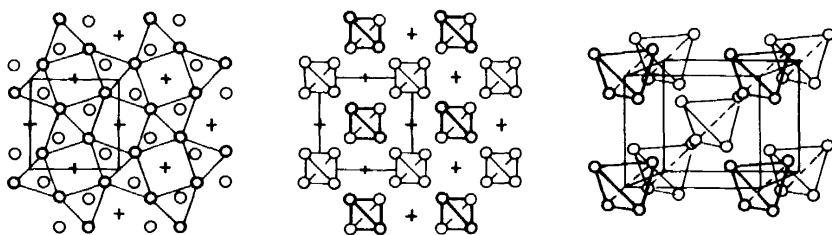
### Packing of $M_4$ tetrahedra

The polyatomic groups discussed in the preceding sections have a unique feature of appearing as closed cages clearly separated from each other. Separation of units is particularly pronounced when the external bonds of the polyatomic group are directed from the atoms away from the centre of the group. With the tetrahedral groups this is seldom the case and a complication arises from the fact that when two tetrahedra are in contact, the space between them is likely to be tetrahedral also. This coincidence results in alternative and apparently equivalent choices of tetrahedral units. Yet, one of the advantages of presenting a structure in terms of arrangements of polyatomic units is the clarity with which the structure can be visualized. Namely, the spatial relationship of atoms within the group is described separately, simplifying the description of the arrangements of these groups into periodic arrays. In the following discussions, this concept is utilized for the structures involving  $M_4$  and  $M_2B_2^*$  groups to simplify understanding, enable a comparison and

\*  $M_4$  represents a group of four metal atoms in a tetrahedral arrangement.  $M_2B_2$  represents a similar group consisting of two metal and two boron atoms.

bring out similarities between compounds that may otherwise appear unrelated.

It has been observed<sup>41</sup> that  $M_4$  tetrahedra presented as separate units often tend to pack in arrangements with ten closest neighbours. Tetragonal close packed and orthorhombic close packed examples are illustrated in *Figure 8* and *Figure 9* for  $Fe_2B$  and  $Mn_4B$  type structures, respectively. *Figure 8* shows a comparison of the usual presentation of the  $Fe_2B$  structure and its interpretation in terms of close packed tetragonal arrangement of the tetrahedral metal groups. A three-dimensional array of  $M_4$  groups is also shown to demonstrate the ease with which the atomic positions can be visualized. As may be observed, the  $M_4$  tetrahedral groups form a continuous framework of  $M_4$  tetrahedra where each  $M_4$  unit has ten identical neighbours in close contact. The square antiprismatic openings present between the units accommodate pairs of boron atoms.



*Figure 8.* Atomic arrangement in the  $Fe_2B$  structural type. Circles represent metal atoms and crosses represent boron atoms. (a) Conventional presentation of this structure projected on the (001) plane. Metal atoms are at  $z = \frac{1}{4}$  (heavy circles) and  $z = \frac{3}{4}$  (light circles). Boron atoms are at  $z = 0$  and  $z = \frac{1}{2}$ ; (b) Interpretation of the same projection in terms of tetrahedral groups of metal atoms; (c) Schematic three-dimensional view of the tetrahedral groups (boron atoms are not shown).

The structure of  $Mn_4B$ -type compounds, shown in *Figure 9* is based on orthorhombic close packed arrangement of metal tetrahedra. Though both the above structures have closest packed layers of tetrahedral groups, they [as illustrated in *Figures 1(a)* and *1(f)*] differ in the manner in which the layers are stacked. In the two types of packing, the unit cell dimensions can be derived by assigning the  $M_4$  group a quasi-spherical radius ( $R = 2r \sqrt{2/\sqrt{3}}$ ) and calculating the unit cell dimension by use of formulas:  $a = 2R \sqrt{2/\sqrt{3}}$  and  $c = 2R$  for tetragonal close packing and  $a = 2R \sqrt{3}$ ,  $b = 2a$  and  $c = 2R$ , for the orthorhombic close packing. Calculated and observed unit cell dimensions for this type of structure are compared in *Tables 2* and *3*.

Because simple dimensional analysis of these structures leads to tetragonal close packing with two structural units for  $Fe_2B$  and orthorhombic close packing with eight structural units for  $Mn_4B$ , the eight metal atoms in the former and the 32 metal atoms in the latter can be divided into groups of four atoms even before the structural units are identified as tetrahedral groups.

The boron atoms in both above structures are accommodated in the interstitial openings between tetrahedra. The presence of these atoms does not significantly affect the intertetrahedral distances. Consequently, in the calculation of the unit cell dimensions the role of the interstitial atoms has been

neglected. Though the presence of these atoms contributes to the stability of a particular phase, compounds of this type often have a variable composition due to partial occupancy of the interstitial sites. This is clearly the case in  $Mn_4B$  and  $Cr_4B$ . If all the openings were fully occupied with boron atoms the composition would correspond to the formula  $Mn_2B$  and  $Cr_2B$ .

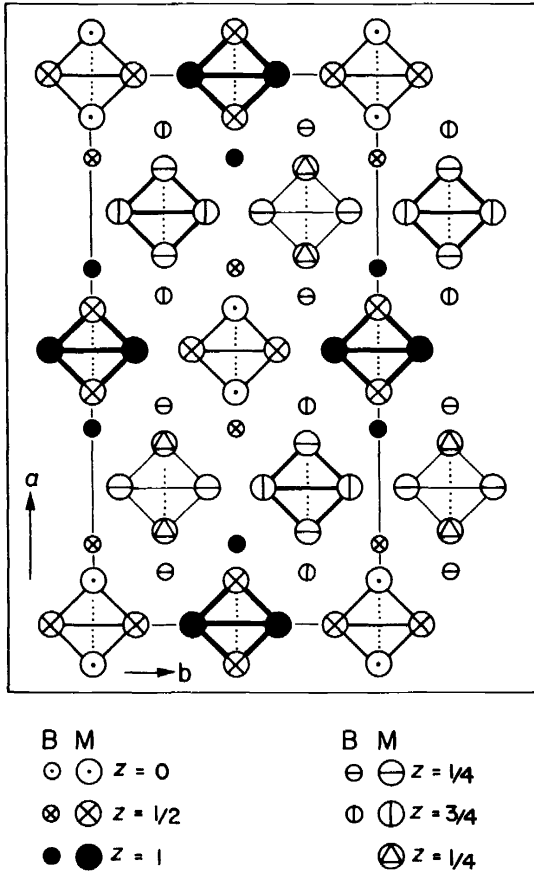


Figure 9. Structure of  $Mn_4B$  interpreted in terms of tetrahedral metals groups.

### $M_2B_2$ -tetrahedra

When the polyatomic group contains two metal and two boron atoms the resulting tetrahedra are of lower symmetry than the  $M_4$  groups described above. The lower symmetry of this group simplifies the selection of the structural unit as it reduces the number of equivalent choices for the polyatomic group. Thus, using a suitable selection of the tetrahedral groups interesting similarities can be observed among otherwise diverse structures<sup>42</sup>. Such comparison is shown in Figure 10(a), (b) and (c) comparing the structures of

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Table 2. Comparison of calculated and observed unit-cell data in the Fe<sub>2</sub>B-type borides

Packing model: tetragonal close packing  
 Symmetry: tetragonal  
 Space group: *I4/mcm*

Compound	Metallic Radius <i>r<sub>m</sub></i> Å	Unit-cell dimensions				Reference
		<i>a</i>		<i>c</i>		
		Calc.	Obs.	Calc.	Obs.	
Cr <sub>2</sub> B	1.28	5.12	5.18	4.10	4.316	43
Mn <sub>2</sub> B	1.31	5.24	5.15	4.28	4.208	44
Fe <sub>2</sub> B	1.27	5.08	5.15	4.14	4.249	45
Co <sub>2</sub> B	1.26	5.05	5.016	4.12	4.22	46
Ni <sub>2</sub> B	1.24	4.97	4.988	4.06	4.244	47
Mo <sub>2</sub> B	1.40	5.60	5.534	4.58	4.735	48
W <sub>2</sub> B	1.40	5.60	5.564	4.58	4.740	49
Ta <sub>2</sub> B	1.46	5.84	5.774	4.77	4.864	50

Fe<sub>2</sub>B, V<sub>3</sub>B<sub>2</sub> and YB<sub>4</sub>. As may be observed, the V<sub>3</sub>B<sub>2</sub> structural type can be derived from the Fe<sub>2</sub>B structure type by replacing a metal pair in the tetrahedra with two boron atoms and replacing the interstitial boron pair by a single metal atom. Furthermore, when the single metal atom is replaced by a boron octahedron the resulting atomic arrangement is that of YB<sub>4</sub> structural type. In all three structures the structural framework is based on tetragonal close packing arrangement of the tetrahedron units. The extrapolyhedral atoms are thus regarded as interstitial. The occupancy of this interstitial position is compared in *Figure 11*.

The M<sub>2</sub>B<sub>2</sub> units are not quasi-spherical and the tetragonal close packing arrangement assigned to the above structures is based on analogy with the Fe<sub>2</sub>B structure rather than on a dimensional analysis of their unit cells<sup>42</sup>. For this and other reasons that will become apparent the concept of packing

Table 3. Comparison of calculated and observed unit-cell data in the Mn<sub>4</sub>B-type borides

Packing model: orthorhombic close packing  
 Symmetry: orthorhombic  
 Space group: *Fddd*

Compound	Metallic radius <i>r<sub>m</sub></i> Å	Unit-cell dimensions*						Ref.
		<i>a</i>		<i>b</i>		<i>c</i>		
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	
Mn <sub>4</sub> B	1.31	14.84	14.53	7.42	7.293	4.28	4.209	44
Cr <sub>4</sub> B	1.28	14.57	14.71	7.28	7.38	4.19	4.26	43

\*In this table the assignment of the *a* and *b* axes was reversed due to a non-conventional assignment of the axis by the original workers.

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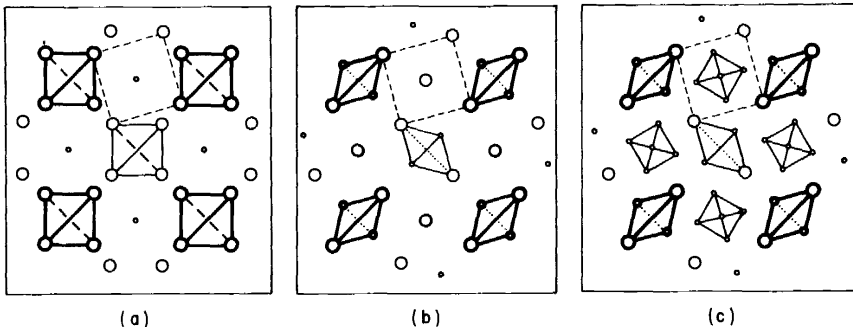


Figure 10. Comparison of the  $\text{Fe}_2\text{B}$ ,  $\text{V}_3\text{B}_2$  and  $\text{YB}_4$  structural types. Large circles represent metal atoms and small circles represent boron atoms. Dotted squares indicate interstitial openings. (a)  $\text{Fe}_2\text{B}$  structural type. A body-centred arrangement of  $\text{M}_4$  tetrahedra. Boron atoms are placed interstitially; (b)  $\text{V}_3\text{B}_2$  structural type. The same spatial arrangement of tetrahedra ( $\text{M}_2\text{B}_2$  in this case) as in (a) but the central and corner tetrahedra are differently oriented. Interstitial openings accommodate metal atoms in this structure; (c)  $\text{YB}_4$  structural type. The same arrangement of  $\text{M}_2\text{B}_2$  tetrahedra as in (b). Interstitial openings accommodate up to six boron atoms in the form of octahedra.

applied to some other  $\text{M}_2\text{B}_2$  structures would be of little useful significance. Yet, as mentioned earlier, the description of atomic arrangements in terms of the  $\text{M}_2\text{B}_2$  groups is utilized to bring out similarities among structures and demonstrate widespread existence of the  $\text{M}_2\text{B}_2$  tetrahedral configuration.

In the  $\text{V}_3\text{B}_2$  and  $\text{YB}_4$  type structures shown above the  $\text{M}_2\text{B}_2$  tetrahedra form chains along the  $c$ -axis direction by alternating boron and metal pairs

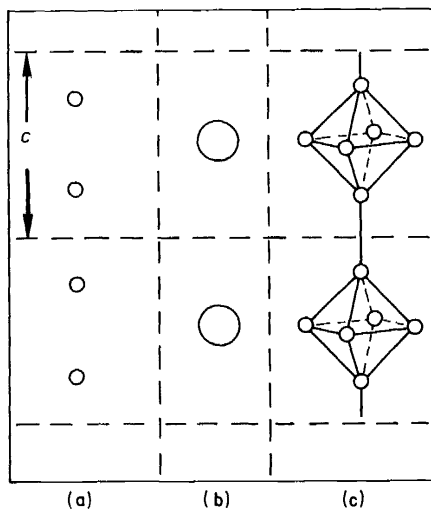


Figure 11. Comparison of the interstitial sites in (a)  $\text{Fe}_2\text{B}$ , (b)  $\text{V}_3\text{B}_2$  and (c)  $\text{YB}_4$ . In  $\text{Fe}_2\text{B}$  the interstitial sites accommodate two boron atoms along the fourfold axis (per unit-cell length). In  $\text{V}_3\text{B}_4$  and  $\text{YB}_4$ , the  $\text{M}_2\text{B}_2$  tetrahedra provide a larger opening which enables accommodation of four additional boron atoms in  $\text{YB}_4$  or a single metal atom in  $\text{V}_3\text{B}_2$ .

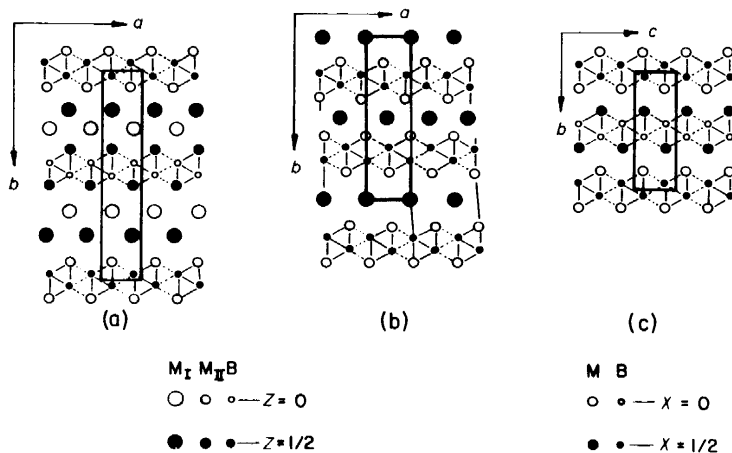


Figure 12. Different ways of stacking the  $M_2B_2$  layers. (All figures show the view of the MB—MB chains only.) (a) MoAlB structural type.  $M_2B_2$  tetrahedral layers are separated by two layers of aluminium atoms; (b)  $Mn_2AlB_2$  structural type.  $M_2B_2$  tetrahedral layers are separated by one layer of aluminium atoms; (c) CrB structural type. There is no metal interlayer between layers of the  $M_2B_2$  tetrahedra.

( $M_2—B_2$  type chains). In many structures the  $M_2B_2$  tetrahedra are also joined in a perpendicular direction forming the MB—MB type chains illustrated in Figures 12 and 14(a). The  $M_2B_2$  tetrahedra joined simultaneously in two directions form layers which may be variously stacked to result in a great variety of structures. In Figure 12(a), it is shown how the  $M_2B_2$  layers may be separated by two layers of metal atoms as is the case in MoAlB type

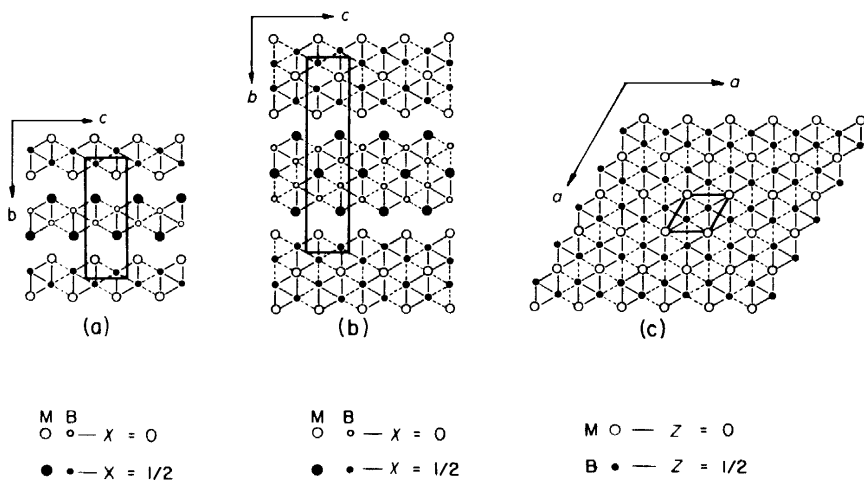


Figure 13. Comparison of MB and  $M_3B_4$  structural types. (a) CrB structural type. Separated  $M_2B_2$  tetrahedral layers; (b)  $Ta_3B_2$  structural type. Two  $M_2B_2$  layers condensed into a double ( $M_3B_4$ ) layer; (c)  $AlB_2$  structural type. Three-dimensional network of the  $M_2B_2$  groups.



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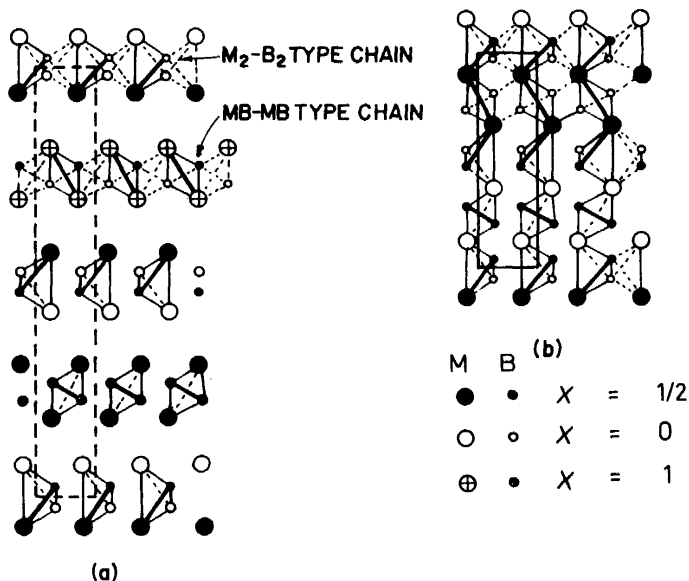


Figure 14. Comparison of MoB and IrB structural types. (a) MoB structural type (tetragonal). Separated  $M_2B_2$  layers are rotated by  $90^\circ$  from one layer to another. First row illustrates the  $M_2-B_2$  type layers while the second row illustrates the MB—MB type layers; (b) IrB structural type. Three-dimensional network of  $M_2B_2$  groups involving rotation of the  $M_2B_2$  units. This may be compared with the  $AlB_2$  structural type [Figure 13(c)] where the groups are not related.

structures. In  $Mn_2AlB_2$  type structures [Figure 12(b)] the  $M_2B_2$  layers are separated by one layer of metal atoms and in the CrB type structure [Figure 12(c)] there is no interlayer of metal atoms. Furthermore, two  $M_2B_2$  groups may be condensed into a larger group by sharing a metal atom. This may result in an  $M_3B_4$  composition [Figure 13(b)] while still further condensation of tetrahedra leads eventually to the  $AlB_2$  structure shown in Figure 13(c).

In the above examples all the structures have the same orientation of tetrahedral  $M_2B_2$  groups in all the layers. In some structures such as MoB (tetragonal form) the units are rotated by  $90^\circ$  from one layer to another as shown in Figure 14(a). Condensation of tetrahedra may occur in this case also and this leads to the IrB type structure illustrated in Figure 14(b). The  $M_2B_2$  tetrahedra appear also in a few other structures. The FeB structural type shown in Figure 15 is an additional example.

The widespread occurrence of the  $M_2B_2$  configuration (occurs in over 70 per cent of all known lower borides) indicates its stability. Depending largely upon the particular metal atomic size one or the other structure may be preferred, but the  $M_2B_2$  configuration appears persistently for metals within radius range from 1.24 Å to 1.80 Å.

The stability of the  $M_2B_2$  groups may be taken as an indication of strong internal bonding between the atoms of this group. Accordingly, assuming that the atoms of the  $M_2B_2$  groups are in close contact and that, consequently,

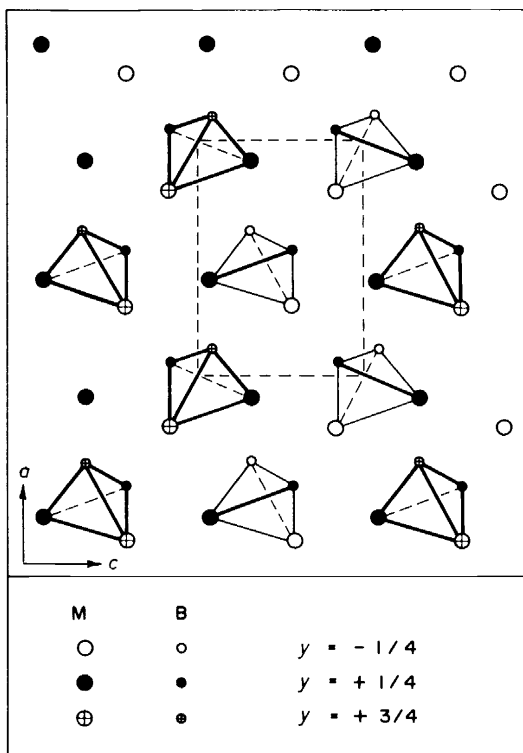


Figure 15. Structure of FeB interpreted in terms of  $M_2B_2$ -tetrahedra.

boron pairs are always at a right angle with respect to the metal pairs, the geometry of the chains is defined and the periods of the  $M_2B_2$  chains and the MB—MB chains [see Figure 13(a) for illustration] can be calculated by the following formulas:

$$M_2-B_2 \text{ period} = \sqrt{8r_m r_b} \quad (1)$$

$$MB-MB \text{ period} = 4r_m r_b / \sqrt{r_m^2 + r_b^2} \quad (2)$$

where  $r_m$  and  $r_b$  represent the atomic radii for metal and boron atoms respectively. The calculated and observed values for various structures are compared, with excellent agreement, in Tables 4 and 5.

As may be observed from equation (2) the MB—MB period becomes equal to the metal diameter ( $2r_m$ ) when  $r_m/r_b = \sqrt{3}$ . In that case the metal atoms form closest packed layers and the consequence is the  $AlB_2$  type structure [see Figure 13(c)] with hexagonal symmetry. With the boron atom radius of 0.9 Å, the metal radius ideal for this structure is 1.56 Å. In fact, as shown in Table 6, this structure occurs with metals with atomic radii from 1.32 Å to 1.80 Å. In order to comply with the above  $r_m/r_b$  requirement both boron-boron and metal-metal distances undergo adjustments by up to  $\pm 8$  per cent

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Table 4. Calculated and observed periods in the MB—MB type tetrahedral chains

Structural type	Compound	$r_m$	Direction of chain (axis)	Chain period		Ref.
				Calc.	Obs.	
		Å		Å	Å	
CrB (Orthorhombic)	TaB	1.46	<i>c</i>	3.06	3.16	50
	NbB	1.46	<i>c</i>	3.06	3.17	50
	MoB	1.40	<i>c</i>	3.03	3.08	48
	WB	1.40	<i>c</i>	3.03	3.06	55
	VB	1.36	<i>c</i>	3.00	2.97	56
	CrB	1.35	<i>c</i>	2.99	2.93	54
	NiB	1.24	<i>c</i>	2.91	2.93	51
MoB (Tetragonal)	MoB	1.40	<i>a</i>	3.03	3.11	49
	WB	1.40	<i>a</i>	3.03	3.12	49
FeB (Orthorhombic)	FeB	1.27	<i>b</i>	2.93	2.94	51
	MnB	1.31	<i>b</i>	2.97	2.98	44
	CoB	1.26	<i>b</i>	2.93	3.04	51
	TiB	1.47	<i>b</i>	3.07	3.06	52
Ta <sub>3</sub> B <sub>4</sub> (Orthorhombic)	Ta <sub>3</sub> B <sub>4</sub>	1.46	<i>c</i>	3.06	3.13	50
	Nb <sub>3</sub> B <sub>4</sub>	1.46	<i>c</i>	3.06	3.14	50
	V <sub>3</sub> B <sub>4</sub>	1.36	<i>c</i>	3.00	2.99	53
	Cr <sub>3</sub> B <sub>4</sub>	1.35	<i>c</i>	2.99	2.95	54
	Mn <sub>3</sub> B <sub>4</sub>	1.31	<i>c</i>	2.97	2.96	44

 Table 5. Calculated and observed periods in the M<sub>2</sub>—B<sub>2</sub> type tetrahedral chains

Structural type	Compound	$r_m$	Direction of chain (axis)	Chain period		Ref.
				Calc.	Obs.	
		Å		Å	Å	
CrB (Orthorhombic)	TaB	1.46	<i>a</i>	3.24	3.28	50
	NbB	1.46	<i>a</i>	3.24	3.30	50
	MoB	1.40	<i>a</i>	3.18	3.16	48
	WB	1.40	<i>a</i>	3.18	3.19	55
	VB	1.36	<i>a</i>	3.13	3.06	56
	CrB	1.35	<i>a</i>	3.12	2.97	54
	NiB	1.24	<i>a</i>	2.98	2.97	51
MoB (Tetragonal)	MoB	1.40	<i>a</i>	3.18	3.11	49
	WB	1.40	<i>a</i>	3.18	3.12	49
Ta <sub>3</sub> B <sub>4</sub> (Orthorhombic)	Ta <sub>3</sub> B <sub>4</sub>	1.46	<i>a</i>	3.24	3.29	50
	Nb <sub>3</sub> B <sub>4</sub>	1.46	<i>a</i>	3.24	3.30	50
	V <sub>3</sub> B <sub>4</sub>	1.36	<i>a</i>	3.12	3.03	53
	Cr <sub>3</sub> B <sub>4</sub>	1.35	<i>a</i>	3.12	2.98	54
	Mn <sub>3</sub> B <sub>4</sub>	1.31	<i>a</i>	3.07	3.03	44
V <sub>3</sub> B <sub>2</sub> (Tetragonal)	V <sub>3</sub> B <sub>2</sub>	1.36	<i>c</i>	3.12	3.03	57
	Nb <sub>3</sub> B <sub>2</sub>	1.46	<i>c</i>	3.24	3.28	57
	Ta <sub>3</sub> B <sub>2</sub>	1.46	<i>c</i>	3.24	3.29	57

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Table 6. Calculated and observed unit-cell dimensions in the  $\text{AlB}_2$  type isotypic series

Compound	$r_m$	Calc.	Obs.	Ref.
$r_m/r_b > \sqrt{3}$	Å	Å	Å	
$\text{UB}_2$	1.80	3.14	3.99	61
$\text{YB}_2$	1.80	3.30	3.84	62
$\text{GdB}_2$	1.80	3.31	3.94	63
$\text{TbB}_2$	1.77	3.28	3.86	63
$\text{DyB}_2$	1.77	3.29	3.84	63
$\text{HoB}_2$	1.76	3.27	3.81	63
$\text{ErB}_2$	1.75	3.28	3.79	63
$\text{LuB}_2$	1.74	3.25	3.74	64
$\text{ScB}_2$	1.62	3.15	3.52	65
$\text{MgB}_2$	1.60	3.08	3.52	66
$\text{ZrB}_2$	1.60	3.17	3.53	51
$\text{HfB}_2$	1.58	3.17	3.47	67
$r_m/r_b < \sqrt{3}$				
$\text{TiB}_2$	1.47	3.03	3.29	51
$\text{NbB}_2$	1.46	3.09	3.31	51
$\text{TaB}_2$	1.46	3.09	3.24	51
$\text{AgB}_2$	1.44	3.00	3.24	58
$\text{AuB}_2$	1.44	3.14	3.52	58
$\text{AlB}_2$	1.43	3.01	3.26	59
$\text{MoB}_2$	1.40	3.06	3.10	51
$\text{VB}_2$	1.36	3.01	3.06	51
$\text{CrB}_2$	1.35	2.97	3.07	51
$\text{OsB}_2$	1.34	2.98	2.87	60
$\text{RuB}_2$	1.32	2.85	2.86	60

of their normal values. As may be expected from equation (2) only those metals that have atomic diameter smaller than 1.56 Å form chain type  $\text{M}_2\text{B}_2$  layers as presented in Tables 4 and 5.

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