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Refractory Binary Borides, 17A

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TABLES

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I. A. Introduction

The wartime and post-war search for materials for high temperature applications has provided the major stimulus for recent studies of refractory binary borides. These investigations have revealed that many of the borides possess additional unusual chemical, electrical and thermal properties which make them attractive subjects for investigations less restricted in motivation. A few examples of these properties may be of interest. The electrical and thermal conductivities of ZrB₂ and TiB₂, for example, exceed by at least one order of magnitude those of the parent metals; the melting points of these borides are more than 1000° higher than those of the pure metals. The rare earth hexaborides include among their members some of the best thermionic emitters known.

Monoborides of arsenic and phosphorus show promise as high temperature semiconductors; higher borides of these non-metals, especially A₃B₉, are extraordinarily inert to chemical attack. The cubic form of boron nitride (Boronox™) is reputedly harder than diamond; it is of interest, too, for investigations of the bond structures of diamond-like compounds.

Serious recent work in this field began with the elegant series of investigations by Kiesling (1) in the late 40's and 50's. His work has been continued by Aronsson, Runquist, and others at Uppsala; in France, Bertaut and Blum have made major contributions; Samsonov and coworkers in the Soviet Union, and many workers in the United States are studying the borides. The literature of this field is impressive and is growing rapidly. Fortunately, several valuable review papers and compilations of crystal and physical data have been published within the past few years.

Probably the most comprehensive collection of crystallographic data dealing with borides is contained in Pearson's 'Handbook of Lattice Spacings and Structures of Metals' (2). X-ray and related measurements of more than
seventy five boride phases are summarized and comprehensive bibliographies accompany the text. Another valuable source is Hansen's "Constitution of Binary Alloys" (3). In addition to tabulations of x-ray data and bibliographical references, this work makes available in convenient form descriptions and critical commentaries on partial equilibrium diagrams for several metal-hydrogen systems.

"Refractory Hard Metals" by Schwarskopf and Kleffer (4) is somewhat dated in this rapidly changing field (it was published in 1953) but it does include detailed discussions of preparative methods and the physical properties of many borides as well as related carbides, nitrides and silicides. Schneider's recently published "Rare Earth Alloys" (5) contains a very complete and critical review of the crystal structures and the physical properties of the numerous rare earth borides. "The Constitutional Diagrams of Alloys: A Bibliography," published by the Institute of Metals (2nd ed., 1956) includes extensive listings of papers dealing with many boron-metal systems (6). Also useful are the review articles by Aronson (7). These include much material absent from prior publications as well as Tables of properties and very extensive lists of bibliographical references.

Two review articles by Sapsarev (8), unfortunately not yet available in English translation, serve as valuable guides to the earlier and relatively inaccessible Russian literature. The first, published in 1956, deals with the "Chemistry of Borides" (8a); the second, published in 1959, deals with "Borides of Rare Earth Metals" (8b), a field to which Sapsarev has contributed substantially.

I. B. Preparation of Borides

Industrial methods of preparation of refractory borides have been discussed in detail by Steinitz (9). Most of the borides can be prepared with varying degrees of difficulty and purity, in several ways. The reduction of metal oxides, using mixtures of carbon and boron carbide as combined reducing agents and sources of boron, has been widely used. Reduction of the desired metal oxide by other metals, including aluminum and calcium, has also been employed, although in these cases oxide residues are mixed with the product and these may be difficult to remove. When carbon is used, no oxide residues are left in the product. Fused salt electrolysis (10) is occasionally tried, though on a relatively limited scale. These and similar methods are usually intended primarily for industrial production at low cost.

For research purposes it is generally advisable to prepare the desired borides by the direct combination of finely divided boron and metal powders (in some cases the use of metal hydrides is more convenient). Preparations are carried out at elevated temperatures. Boron nitride crucibles (previously heated in hydrogen at about 1600°C to remove oxygen present in the B2O3 binder) are usually suitable; graphite crucibles may be used in some instances but carbon contamination must then be guarded against. Reactions are best carried out under purified hydrogen or in vacuum. If the starting materials are known to be free from oxygen, purified argon may be used in place of hydrogen.

For preliminary, exploratory work, arc melting on a water-cooled copper block (under argon) may be utilized. In general, heating by induction is preferred because of the superior temperature control possible with this method.

I. C. Classification of Boride Structures

Boron forms binary borides with a large number of metals and non-metals; their compositions range from B2H3 through B2H2 to some recently reported B70 phases. These cannot be classified simply in terms of the usual chemical or metallurgical rules.

In general, higher borides are formed by "large" metal atoms; smaller metal atoms tend to form metal rich borides. Kiesling (11) first commented on the striking tendency of boron atoms to form bonds with other boron atoms whenever possible. He classified the structures into four, partially overlapping, groups based primarily on the arrangement of boron atoms as follows:
1) borides with isolated boron atoms. These include the lower borides from $\text{Me}_2 \text{B}$ to $\text{Me}_3 \text{B}$. As the boron content increases there is a tendency for boron atoms to form isolated pairs, e.g. in $\text{Me}_2 \text{B}_2$ and $\text{Me}_3 \text{B}_4$.

2) borides with boron chains (single chains in $\text{MeB}$ and double chains in $\text{Me}_2 \text{B}$);

3) borides with two dimensional nets of boron atoms ($\text{MeB}_2$ and $\text{Me}_2 \text{B}_3$);

4) borides with three dimensional boron frameworks ($\text{MeB}_3$, $\text{MeB}_5$, $\text{MeB}_8$, and $\text{MeB}_{13}$).

In Section II the crystal chemistry of the borides will be discussed according to this scheme, followed by a description of binary borides of non-metals. The types of borides, classified according to the positions of the parent metals in the Periodic Table, will be discussed in Section III. Electrical, magnetic and other properties will be dealt with in Section IV.

The list of bibliographical references has been compiled primarily with an eye to usefulness for the general reader. It is not intended to be complete; references to early works have been omitted in many cases; others have been omitted because their reliability was open to doubt or because their contents have been dealt with adequately elsewhere.

II. Crystal Chemistry of Borides

A. Borides with Isolated Boron Atoms

The crystal structures of most of the compounds in this category are closely related (Table I). Aronson and Kungqvist (11) have discussed in detail the role played by "size" factors in cementite-type structures; similar considerations apply to other types discussed here. The radius ratios, $r_{\text{B}}/r_{\text{Me}}$, in all these phases exceed by a substantial margin the value (0.414) which should be most favorable for octahedral metal environments about the boron atom. It is pointed out that the radius ratios in these phases range from about 0.64 to 0.71 and exceed even the "ideal" values for the formation of trigonal prismatic "holes" for the boron atoms. Nevertheless, the metal atoms are generally
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</tr>
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<td>16.0</td>
</tr>
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</table>
arranged in the form of distorted triangular prisms about the boron atoms, rather than in the square anti-prismatic arrangements indicated by "else" factors.

Kissling (1) has noted the close relation between the $\text{Me}_2\text{B}$ and the $\text{Me}_2\text{B}$ structures. The former may be considered to be derived from the latter by omitting half the boron atoms. These phases will be discussed below.

In $\text{Me}_2\text{B}$, $\text{Me}_2\text{B}$, and $\text{Me}_2\text{B}$, the metal atoms are arranged in approximately close packed arrays with the boron atoms in the triangular prismatic "holes".

The metal atoms form slightly corrugated layers, with metal atoms at the corners of alternating triangles and squares in the layers (Fig. 1). Each metal atom has from eleven to twelve nearest metal atom neighbors; the boron atoms have six metal atom neighbors at the corners of their triangular prisms and three additional metal neighbors in triangular array about the central boron atom (Fig. 2).

In these structures the metal atoms form three-dimensional networks and the boron atoms are "interstitial". Boron to boron distances are large (i.e. 2.10Å or more) for adjacent occupied sites; in none of these phases are there any effective boron to boron linkages.

Arendso and Buggdvedt (11) have also noted that the metal to boron distances in borides of transition metals of Groups VII and VIII are anomalously short. In nickel and palladium borides the average metal to boron distance is 0.07Å less than the sum of the atomic radii, while in comparable borides of Groups IV to VI the average metal to boron distances exceed calculated values by about 0.03Å. The reasons for these differences are obscure but the effect is real.

In the series $\text{V}_2\text{B}_3$, $\text{Re}_2\text{B}_3$ and $\text{Pd}_2\text{B}_3$ for example, the metal atoms which belong to Groups V, VI and VII respectively, have almost identical radii for coordination number 12. In all three crystals the metal atoms lie at the corners of the usual triangular prisms about the boron atoms but the average short metal to boron distances decrease from 2.28Å in $\text{V}_2\text{B}_3$ to 2.23Å in $\text{Re}_2\text{B}_3$ and 2.17Å in $\text{Pd}_2\text{B}_3$. The authors suggest that the factors responsible for these anomalously short boron distances are, among other things, electron density effects and the presence of boron vacancy sites. In fact, the electron density of the boron vacancy sites may be sufficient to account for the anomalously short distances.
to metal distances may also furnish an explanation of the many differences between bortides of the platinum group metals and those of other transition metals.

Most of the Mo₆B compounds crystallize with the Cu₃Al₂ structure. In this structure sheets of tetrahedra of metal atoms form puckered layers; the metal atoms are at the corners of alternating squares and triangles within these layers (see Fig. 1). The boron atoms lie within the triangular prismatic or the square anti-prismatic holes between layers and have nine metal neighbors in the former case (as in Mo₆B), and eight in the latter (i.e., at the corners of square antiprisms). The Mo₆B structure may be visualized in terms of the Cu₃Al₂ type, from which alternate boron atoms have been omitted. The Mo₆B phases appear to have extended homogeneity ranges; possibly one limit is at the ideal formula Mo₂B.

Klessing (11) has noted that from a geometrical viewpoint the boron atoms may be considered to be arranged in strings within the metal lattices. Successive strings are far removed from one another (3.5 to 4.0A) but within a given string the boron-boron distances are close to 2.10A. These long distances apparently do not involve real boron-boron bonds, but the persistent string formations may be precursors of such bonds.

In Cr₂B₃ and the Mo₂Bₐ phases we note structures similar to those discussed above, except for the increasing tendency of boron atoms to link together in pairs. In V₃B₂, for example, the boron atoms form one short (1.99A) boron-boron bond. In these structures the isolated unit consists of a pair of boron atoms. Mo₂B crystallizes in the cubic, antifluorite structure in which no boron-boron contacts are possible (R = 8 = 3.30).

II. B. Bordides with Boron Chains

As the proportion of boron to metal atoms increases so do the possibilities for boron to boron linkages. The formation of boron pairs in V₃B₂ illustrates a trend which is continued into Mo₂Bₐ, Mo₂B and beyond. For example, in the orthorhombic modification of Mo₂B, two-thirds of the boron atoms form infinite zig-zag chains while one-third have no close boron contacts (9).

In this structure the boron atoms are present both as isolated atoms and as chains, whereas in the monoclinic polymorph all the boron atoms participate in the formation of infinite chains.

Most of the compounds with the Mo₆B composition belong to one of three structure types (Table II): the orthorhombic Fe₆B type, space group Pnna; the orthorhombic Cr₆B type, space group Ccm; and the tetragonal Mo₆B type, space group P4/mbm. Both Mo₆B and WB crystallize in the latter form at room temperature and transform to the Cr₆B type at elevated temperatures. The increase in crystal symmetry which usually accompanies a transformation from a low to a high temperature modification is absent here; there is actually a decrease in crystal symmetry from tetragonal to orthorhombic but this is offset in part by an approximately fifty percent reduction in cell size.

The three Mo₆B types are closely related to one another (Fig. 2). In all three the metal atoms are arranged at the corners of trigonal prisms. At the centers of these prisms are boron atoms, each bonded to six metal atoms and to two other boron atoms (in its chain).

In the Mo₂Bₐ compounds the metal atom arrangement is similar to that in other lower bordides except for the formation of double chains of boron atoms. These may be viewed as incipient two-dimensional boron nets, precursors of the Mo₂Bₐ structures. Klessing (13) had originally reported anomalously short boron-boron distances from one chain to another, but a recent careful structure analysis failed to reveal any significant differences among boron to boron bonds, either within or between chains (25).

The transition from the single boron chains of the Mo₆B phases to the double chains of Mo₂Bₐ is illustrated by Ru₁₁B₉, whose structure has been accurately determined by Asellus (88). Boron atoms in this crystal are of two
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<td>3.29</td>
<td>14.9</td>
<td>3.13</td>
</tr>
<tr>
<td>ReB₉</td>
<td>ReB₉</td>
<td>orthorhombic</td>
<td>Pmmn</td>
<td>h</td>
<td>3.29</td>
<td>14.9</td>
<td>3.13</td>
</tr>
<tr>
<td>Ta₂B₉</td>
<td>Ta₂B₉</td>
<td>orthorhombic</td>
<td>Pmmn</td>
<td>h</td>
<td>3.29</td>
<td>14.9</td>
<td>3.13</td>
</tr>
<tr>
<td>Wd₂B₉</td>
<td>Wd₂B₉</td>
<td>orthorhombic</td>
<td>Pmmn</td>
<td>h</td>
<td>3.29</td>
<td>14.9</td>
<td>3.13</td>
</tr>
</tbody>
</table>

**TABLE II:** Properties of Form Cusins

- **I:** Inorganic
- **M:** Metallic
- **C:** Covalent
- **S:** Ionic

**Notes:**
- **a:** Lattice parameter
- **b:** Lattice parameter
- **c:** Lattice parameter
- **c/a:** Lattice parameter ratio
- **Density:** Density of the compound
- **Ref.:** Reference number
types: one forms only two boron-boron linkages (i.e., single chains), the other forms three close boron bonds, two of which are involved in the formation of a bond chain, while the third serves to link two adjacent chains together.

In assessing the significance of various boron-boron or boron-metal distances often listed for these phases, it is important to bear in mind that in almost all cases the x-ray diffraction analyses yielded only metal atom positions. For the most part, boron atoms have been placed in "reasonable" positions on the basis of steric and symmetry considerations. Their locations are rarely known precisely. In many cases even the compositions of these phases are in doubt (see "Stoichiometry", Section IV).

II. C. Borides with Two-Dimensional Nets of Boron Atoms: MoB₂ and Mo₂B₄

These compounds include some of the best electric conductors, highest melting, hardest and most refractory of all the boride phases. Thirty well characterized members of this group are now known (Table III). Twenty-four are of the MoB₂ type. Their crystal structures are simple; the unit cells are hexagonal, the space group is $D_{6h}^{15}$, and there is one formula weight per unit cell. There are no variable atomic position parameters in this structure; the metal atom is at the origin of the unit cell $(0,0,0)$ and the boron atom lies along the long diagonal of the a a' section of the unit cell at $z = 1/2$, i.e., at 1/2, 2/3, 1/2 and 2/3, 1/3, 1/2 (Fig. 3). The metal and the boron atoms are arranged in alternate planar hexagonal layers perpendicular to "a". Each metal atom has six equidistant metal neighbors in its plane and twelve equidistant boron atoms, six in the layer above and six below the metal atom. Correspondingly, each boron atom has three closest boron neighbors in its plane and also forms six boron to metal bonds (Fig. 4).

The simple geometry of the unit cell facilitates calculation of interatomic distances; the boron to boron distance $= \sqrt{3}$, the metal to metal distance, within a layer perpendicular to "a", is equal to the length of the "a" axis; the shortest metal to boron distance is $\left[\frac{a^2}{2} + \frac{b^2}{4}\right]^{1/2}$.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Amino Acid</th>
<th>Lattice Constants (Å)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₃⁺</td>
<td>P 6/m mm</td>
<td>a = 3.022, c = 3.222</td>
<td>2.47</td>
</tr>
<tr>
<td>Al⁺⁺⁺</td>
<td>= 3.099, c = 3.202</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Sc⁺⁺⁺</td>
<td>= 3.101, c = 3.171</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>Ti⁺⁺⁺</td>
<td>= 3.095, c = 3.162</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Zr⁺⁺⁺</td>
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<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Cr⁺⁺⁺</td>
<td>= 3.095, c = 3.056</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Nb⁺⁺⁺</td>
<td>= 3.095, c = 3.037</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Mo⁺⁺⁺</td>
<td>= 3.095, c = 3.037</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Ru⁺⁺⁺</td>
<td>= 3.095, c = 3.037</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Os⁺⁺⁺</td>
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</tr>
<tr>
<td>Rh⁺⁺⁺</td>
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<td>2.47</td>
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</tr>
<tr>
<td>Pd⁺⁺⁺</td>
<td>= 3.095, c = 3.037</td>
<td>2.47</td>
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</tr>
<tr>
<td>Pt⁺⁺⁺</td>
<td>= 3.095, c = 3.037</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Au⁺⁺⁺⁺⁺</td>
<td>= 3.095, c = 3.037</td>
<td>2.47</td>
<td></td>
</tr>
</tbody>
</table>

Note: The table lists the lattice constants and density for various compounds and amino acids.
Studies of numbers of compounds in which boron to boron bonds exist indicate that the "normal" boron radius is approximately 0.874, i.e., the "normal" boron-boron separation is 1.74A (1, 2). In the borides of the smaller metal atoms (e.g., Cu, Ag, Al, V, Cr, Fe) the length of the "a" axis is determined primarily by such boron-boron contacts. When $r_{ab}$ exceeds 1.55 A, the "a" axis expands (and with it, of course, the boron-boron distance). In $\alpha$-Be $r_{ab}$ = 1.505 A) the boron-boron separation is 1.83 A; in several recently prepared rare-earth and yttrium diborides (35) this distance exceeds 1.90 A. Clearly, in these phases the metal atoms are in contact and their separations determine boron to boron bond lengths.

The relatively rigid "graphitic" boron layers resist both compression and extension; in the case of $\alpha$-Be, the preservation of normal metal-metal distances in the "a" direction would lead to a boron-boron separation of only 1.52 A. The actual boron-boron separation is 1.65 A. Similarly, the diameter of the yttrium atom in the elementary state is 3.55 A, and the preservation of this metal-metal separation in $\beta$-Be would lead to a boron-boron distance of 2.05 A; the observed distance is 1.90 A.

The available evidence also suggests that the structure is much more tightly bonded in the "a" than in the "c" direction. The substitution of large metal atoms for smaller ones (by solid solution techniques) leads to such smaller changes in "a" than in "c" (30). The values of "a" for the 24 AlB$_2$-type compounds listed in Table III range only from 2.852 to 3.298 A. The corresponding range for "c" is 2.855 to 3.188 A. Also, coefficients: thermal expansion are generally larger in the "c" than in the "a" direction.

Elementary considerations of the sizes of metal atoms in $\alpha$-Be furnish a qualitative guide to an understanding of the variation of these c/a ratios.

Where the metal atoms are clearly not in contact, as in $\alpha$-Be and $\alpha$-$\text{B}_2$, the c/a ratio is close to unity. The small metal atoms fit loosely within the large interstices between the boron nets and close metal-metal approaches in the "c" direction are not impeded. In the case of the larger metal atoms, the "normal" increase in "a" is inhibited by the factors mentioned above; restrictions on lattice expansion in the "c" direction are weaker and the c/a ratio increases (up to 1.27 in UBe$_2$).

The variation of the lattice constants of $\text{NbB}_2$ and $\text{TaB}_2$ with boron content (1 c, 31) is interesting. These phases show wide ranges of homogeneity (comparable data are not available for other diborides). Kiesling (1 c) found that $a = 3.099$ and $c = 3.229$ A at the lower boron limit for $\text{TaB}_2$ (ca. 64 atomic percent boron). At the upper boron limit (ca. 72 atomic percent) $a = 3.057$ and $c = 3.291$ A. Similar results have been reported by Brewer (31) and others (30).

For $\alpha$-Be, Brewer found that at the lower boron limit (the exact homogeneity range was not reported) $a = 3.110$ and $c = 3.285$ A; at the upper boron limit $a = 3.085$ and $c = 3.311$ A. In both phases, however, the Me-Be distances remain substantially constant throughout the wide composition ranges; these are 2.94 A in $\text{TaB}_2$ and 2.76 A in $\text{NbB}_2$. The geometrical relation between d(Me-Be) and the lengths of "a" and "c" show that if d(Me-Be) remains constant, an increase in "a" must be compensated for by a decrease in "c" and vice versa; this is indeed observed.

In both cases "a" decreases as the boron content of the phase increases, and increases as the boron content decreases. In $\alpha$-$\text{B}_2$, when the boron content is in excess of the stoichiometric 66 2/3 percent, the boron layers are filled and the metal layers are only partially full: the converse is true when boron deficiencies exist.

In these borides, the "a" dimension is determined by the balance between the "stretching" forces due to metal atoms which have diameters larger than the "normal" 3.01 A, and strong cohesive forces within the boron network. When the boron content rises to 72 atomic percent (e.g., in $\text{TaB}_2$), the metal content is only 28 atomic percent and there are 0 vacancies or of every 36 available metal atom sites; this leads to a decrease in "a". Similar considerations apply to the increase in "a" when the boron content is decreased; d(Me-Be) is constant and the observed variations in "a" simply compensate for changes in "c".
It would be of interest to make similar measurements of the variation of lattice constants (and of the Re-B distances) with stoichiometry in other suitable diborides.

Most of the diborides are very stable phases, readily formed when appropriate amounts of metal and boron powders are mixed and heated. Among the transition-metal diborides, stability tends to decrease in going from Group IV to Groups VI and VII, as well as in going from lower to higher atomic numbers within a group. An interesting aspect of this stability trend is illustrated by the data in Table IV (30).

\( \text{MoB}_2 \) is stable above 1500°C and no \( \text{Wb}_2 \) phase with the \( \text{Alb}_2 \) structure has been reported. The stable room-temperature form of these phases has the assigned formula \( \text{MoB}_2 \) and the atomic arrangement differs substantially from that of the normal hexagonal \( \text{Alb}_2 \) type. Also, \( \text{MoB}_2 \) cannot be prepared as readily as most of the other transition-metal diborides. Kesslering (144) reported no evidence of \( \text{MoB}_2 \) in his study of the manganese-boron system but the compound was prepared subsequently by increasing the reaction temperatures to about 1500°C (29).

There is evidence that the \( \text{MoB}_2 \) that is formed dissociates if cooled slowly (37).

\( \text{ReB}_2 \) crystallizes in a structure closely related to both the \( \text{Alb}_2 \) and \( \text{Wb}_2 \) types (36). (This compound had been incorrectly assigned the formula \( \text{ReB}_3 \) by Aronsson, et al. (15)) The unit cell is hexagonal, the space group is \( \text{P}_6_3/mm \) and there are two formula weights of \( \text{ReB}_2 \) per unit cell. Simple geometrical considerations illustrate that the existence of planar boron nets in \( \text{ReB}_2 \) is unlikely. In the transition-metal diborides, the boron-boron separation in the planar boron nets ranges from 1.73 to 1.81 Å. A planar arrangement of boron atoms in \( \text{ReB}_2 \) would lead to a boron-boron separation of only 1.67 Å. This arrangement, however, would lead to Re-B separations of only 1.87 Å. The expected minimum distance of approach is 2.24 Å (\( r_3 = 0.87 \) Å and \( r_{\text{Re}} = 1.37 \) Å). These geometrical difficulties are avoided by the formation of puckered boron nets in which the boron-boron distance is 1.82 Å and the corresponding Re-B distance is 2.23 Å.

### Table IV - Melting Points of Transition Metals and their Diborides (30).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Melting Point (°C)</th>
<th>( \text{Wb}_2 ) Diboride</th>
<th>H.P. Diboride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1700</td>
<td>2920</td>
<td>1.62</td>
</tr>
<tr>
<td>Zr</td>
<td>1850</td>
<td>3050</td>
<td>1.57</td>
</tr>
<tr>
<td>Hf</td>
<td>2250</td>
<td>3280</td>
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</tr>
<tr>
<td>V</td>
<td>1735</td>
<td>2600</td>
<td>1.33</td>
</tr>
<tr>
<td>Nb</td>
<td>2550</td>
<td>3950</td>
<td>1.29</td>
</tr>
<tr>
<td>Ta</td>
<td>2990</td>
<td>3200</td>
<td>1.06</td>
</tr>
<tr>
<td>Cr</td>
<td>10-50</td>
<td>1900</td>
<td>1.02</td>
</tr>
<tr>
<td>Mo</td>
<td>2080</td>
<td>2100</td>
<td>0.95</td>
</tr>
<tr>
<td>W</td>
<td>3350</td>
<td>2200</td>
<td>0.97**</td>
</tr>
</tbody>
</table>

* "\( \text{MoB}_2 \) is stable above 1600°C.

** "\( \text{ReB}_2 \) has not been reported. The melting point shown is that of \( \text{ReB}_2 \). It is possible that \( \text{ReB}_2 \), like \( \text{MoB}_2 \), transforms to the \( \text{ReB}_2 \) structure near the melting point.
The boron coordination around each rhenium atom consists of two trigonal bipyramids joined at a common apex with their three-fold axes collinear and parallel to the c* axis (Fig. 5). Rhenium is at the common apex and the eight boron atoms are at the remaining vertices.

The structural relations among the closely related ReB2, ReB2, W2B2 and Mo2B2 structures are represented most clearly in terms of a notation due to Klessing (14). The sequence of approximately close-packed, planar, layers of metal atoms in the "c" direction is:

("normal") \[ \text{MoB}_2 : A - A - A - A \]
\[ \text{ReB}_2 : AB AB AB \]
\[ \text{W}_2 \text{B}_2 : AA BB AA BB \]
\[ \text{Mo}_2 \text{B}_2 : AA BB CC AA BB CC \]

Klessing denoted puckered boron sheets by K and planar sheets by H. The complete stacking sequence in the "c" direction is then:

\[ \text{MoB}_2 : AH AH AH \]
\[ \text{ReB}_2 : AK BK AK BK \]
\[ \text{W}_2 \text{B}_2 : AH AK BK AH \]
\[ \text{Mo}_2 \text{B}_2 : AH AK BK CH CK AH \]

Although the major features of the arrangement of metal and boron atoms in the Mo2B2 phases which Klessing postulated (14) are probably correct, there is some doubt concerning the stoichiometry of these phases. In a detailed study of the molybdenum-boron system (20), Steinits and co-workers could find no significant difference in boron content between Mo2B2 and MoB2. Their analyses indicated the boron contents of both phases to be slightly in excess of what was required for stoichiometric MoB2, but much closer to MoB2 than to Mo2B2. It is reasonable to conclude from this that "MoB2" is simply the high-temperature polymorph of "Mo2B2" and that both phases should probably be referred to as "diaborides".

Fig. 5. Environment of rhenium atom in ReB2.
A study of the Os-B and Ru-B systems by Kemper and Fries (33) bears on this point. When Os was heated with two parts of boron, the major phase formed was Os$_2$B$_3$. Heating two parts of Os with five parts of boron yielded Os$_2$B$_5$ as a minor phase together with a major unidentified phase. The assigned formulas in these cases are clearly only nominal.

A diboride of beryllium has been reported (19): the unit cell is hexagonal with $a = 9.77$ and $c = 9.55$ Å. The structure is complex and has not yet been completely analyzed.

Markovskii and Yezhovskii (38) have reported the preparation of diborides of Ca, Sr and Ba. No x-ray or other physical measurements were listed.

II. D. Borides with Three-Dimensional Boron Networks: MoB$_4$, W$_2$B$_6$, Mo$_2$B$_6$, MoB$_{12}$, MoB$_{20}$

1. MoB$_4$ : The existence and the composition of MoB$_4$ were established by Andreix in 1929 (10). Bertaut and Elsen carried out an x-ray diffraction study of this phase (39) and reported that the unit cell is tetragonal and contains four formula weights of MoB$_4$; the space group is $P_{4}^{3}3$ and $a = 7.006$, $c = 3.97$ Å.

These findings were confirmed by Zalikin and Tsyklotin (40) who reported on the synthesis and crystallography of the isostructural U$_2$B$_6$, Th$_2$B$_6$ and CeB$_6$. On the basis of a single-crystal analysis of Th$_2$B$_6$ they determined metal atom positions and reported that there is just room for 16 boron atoms in one unit cell if the atoms were assigned reasonable radii. The latter can be arranged in the structure in only one way. The atomic arrangement, viewed in projection down the "c" axis is shown in Fig. 6.

The thorium lattice consists of planar layers as shown, each thorium having five metal atom neighbors in its own layer. Between the layers are holes bounded by six thorium atoms as in MoB$_4$, i.e., with three thorium atoms "above" and three "below" the hole. There are four such holes in the unit cell and one boron atom goes into each. There are also larger holes bounded by eight thorium atoms at the corners of a square prism; there are two such "square" holes per unit cell and an octahedron of six boron atoms fits neatly in each of them, just as in MoB$_4$. These positions are clearly seen in Fig. 6.

The MoB$_4$ structure is thus a hybrid of MoB$_4$ and MoB$_{12}$, both in terms of composition and of structure. The boron atoms in adjacent holes, of either type, are in contact and form a continuous three-dimensional network. It was not possible to locate the boron atoms directly by x-ray diffraction methods; their positions were inferred on stereo grounds. The parameters were calculated by trial and error to make the B-B bonds as nearly equal in length as possible and to place the boron atoms as far from the thorium atoms as possible.

Tetaborides of most of the remaining rare-earth and related metals have since been prepared and lattice constants are shown in Table V.

Attempts to prepare SuB$_6$ by reactions of Su$_2$B$_4$ with amorphous boron have been unsuccessful (41). Initial efforts to prepare LaB$_6$ by similar reactions were also unsuccessful and this tetaboride could only be prepared by direct reaction of metallic lanthanum with boron (41). It is possible that a similar reaction between metallic europium and boron may be made to yield EuB$_6$.

Recently evidence for the formation of the isostructural CeB$_6$ was reported by Hamon and Johnson (47).

Fuchott (37) has reported that MoB$_4$ decomposes on slow cooling to yield MoB$_{12}$ plus a second phase. The latter appears to be MoB$_{12}$; x-ray powder data for this phase were listed; its structure is unknown.

Christian and Helgorsky (46) have discussed the preparation of MoB$_4$ and MoB$_{12}$. These are isomorphous, crystallizing in tetragonal unit cells with $a = 6.34$ and $c = 4.50$ Å. The unit cells contain four formula weights of MoB$_4$.

The MoB and W-B systems had been studied intensively by several groups previously and their failure to detect the tetaborides appears to be explained, in part, by Christian and Helgorsky's analysis of the thermal stability of MoB$_4$ and MoB$_{12}$.
### Table V. Tetragonal Tetroberides

<table>
<thead>
<tr>
<th>Metal</th>
<th>Lattice Constants (Å)</th>
<th>Density (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>7.11 6.41 0.576</td>
<td>2.07</td>
</tr>
<tr>
<td>Y</td>
<td>7.11 6.017 0.65</td>
<td>4.73</td>
</tr>
<tr>
<td>Th</td>
<td>7.255 6.113 0.66</td>
<td>8.45</td>
</tr>
<tr>
<td>U</td>
<td>7.975 3.979 0.662</td>
<td>9.76</td>
</tr>
<tr>
<td>Pa</td>
<td>7.19 4.014 0.655</td>
<td>9.39</td>
</tr>
<tr>
<td>La</td>
<td>7.30 4.17 0.591</td>
<td>5.88</td>
</tr>
<tr>
<td>Ce</td>
<td>7.325 4.090 0.586</td>
<td>5.72</td>
</tr>
<tr>
<td>Pr</td>
<td>7.00 4.17 0.692</td>
<td>5.71</td>
</tr>
<tr>
<td>Sm</td>
<td>7.219 4.102 0.580</td>
<td>5.38</td>
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<tr>
<td>Pm</td>
<td>7.124 4.070 0.587</td>
<td>5.12</td>
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<tr>
<td>Eu</td>
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<td>5.14</td>
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<tr>
<td>Gd</td>
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<td>6.00</td>
</tr>
<tr>
<td>Tb</td>
<td>7.20 4.029 0.586</td>
<td>6.60</td>
</tr>
<tr>
<td>Dy</td>
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<tr>
<td>Ho</td>
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<td>Er</td>
<td>7.071 3.997 0.555</td>
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</tr>
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<td>Tm</td>
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<td>7.10</td>
</tr>
<tr>
<td>Yb</td>
<td>7.01 3.90 0.571</td>
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<tr>
<td>Lu</td>
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<td>Hf</td>
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<td>4.80</td>
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<tr>
<td>Zr</td>
<td>6.34 4.50 0.71</td>
<td>4.40</td>
</tr>
</tbody>
</table>

![Diagram](image.png)

Fig. 6. Atomic arrangement in HfB₁₂ (projected along "a").
Pure MoB$_2$ and W$_2$B (prepared by heating the metals and boron in vacuum to 1400°C) dissociate at 1600°C to give Mo$_2$B$_3$ and MoB (and the corresponding tungsten compounds). In the presence of even small amounts of carbon, dissociation to the lower borides occurs at relatively low temperatures. It appears likely that previous investigators did not observe the tetraborides because of excessively high reaction temperatures or carbon contamination.

2. MoB$_2$: All the rare-earth metals, as well as calcium, strontium, barium, thorium, and plutonium form isostructural hexaborides (Table VI). The crystal structure was first determined by Stackelberg and Neumann (48). The unit cell is cubic and contains one formula weight of MoB$_2$. The space group is Pm3m; the metal atom is at the center of the cell with boron atoms arranged at the vertices of compact, regular octahedra, linked to one another by B-B bonds to form a three-dimensional boron network (Figs. 7, 8).

The three-dimensional nature of the boron network may be emphasized by considering the structure in terms of a cube, each of whose eight corners has been truncated by planes perpendicular to the body diagonals. The planes cut the cube edges about each corner at three points; in MoB$_2$ a boron atom is located at each of these points. The metal atom is located at the center of the large hole within the cube (Fig. 8). Each metal atom is coordinated to 21 boron atoms; each boron atom in turn forms four boron-metal bonds and five boron-boron bonds. Four of the latter represent intra-octahedral bonds; the fifth is a link to another octahedron. Although there is only one variable position parameter in this structure (i.e., boron atoms are at $x,y,z$ etc.), this has not been determined with precision by X-ray diffraction methods because of the difficulties associated with the location of light atoms in the presence of heavy metal atoms. Generally the boron positions have been established by assuming that all boron-boron bonds must be equal in length. This condition is
### TABLE VII: Properties of Members of the Family

<table>
<thead>
<tr>
<th>Metal</th>
<th>Lattice Const. (in Angstroms)</th>
<th>Density (g/cm³)</th>
<th>Coefficient of Linear Thermal Expansion (¹°C⁻¹)</th>
<th>Melting Point (°C)</th>
<th>ΔF₂</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>Ce</td>
<td>1.465</td>
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<td>6.2</td>
<td>2200</td>
<td>105</td>
<td>----</td>
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<tr>
<td>Sr</td>
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<td>6.6</td>
<td>2175</td>
<td>105</td>
<td>----</td>
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<td>Ba</td>
<td>2.006</td>
<td>6.7</td>
<td>6.9</td>
<td>2170</td>
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<td>----</td>
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<td>Sr</td>
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<td>6.2</td>
<td>6.2</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Sn</td>
<td>4.113</td>
<td>3.57</td>
<td>3.57</td>
<td>2170</td>
<td>123</td>
<td>----</td>
</tr>
<tr>
<td>Cu</td>
<td>4.115</td>
<td>4.00</td>
<td>4.00</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Ag</td>
<td>4.155</td>
<td>7.11</td>
<td>7.11</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>La</td>
<td>4.103</td>
<td>4.72</td>
<td>4.72</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Ce</td>
<td>4.101</td>
<td>4.99</td>
<td>4.99</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Pr</td>
<td>4.129</td>
<td>4.68</td>
<td>4.68</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Nd</td>
<td>4.135</td>
<td>4.68</td>
<td>4.68</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Sm</td>
<td>4.137</td>
<td>4.00</td>
<td>4.00</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Eu</td>
<td>4.140</td>
<td>4.00</td>
<td>4.00</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Gd</td>
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<td>4.55</td>
<td>4.55</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Tb</td>
<td>4.112</td>
<td>3.55</td>
<td>3.55</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Dy</td>
<td>4.110</td>
<td>3.55</td>
<td>3.55</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
<tr>
<td>Ho</td>
<td>4.111</td>
<td>3.55</td>
<td>3.55</td>
<td>2170</td>
<td>105</td>
<td>----</td>
</tr>
</tbody>
</table>

**Notes:**
- This value is probably incorrect.

### B: Tetragonal

<table>
<thead>
<tr>
<th>Lattice Constants (Å)</th>
<th>Density (g/cm³)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>4.248</td>
<td>3</td>
</tr>
<tr>
<td>Sr</td>
<td>4.250</td>
<td>3</td>
</tr>
<tr>
<td>Ba</td>
<td>4.255</td>
<td>3</td>
</tr>
</tbody>
</table>

*This is a subset of the tetragonal phase group.*
satisfied by setting the variable position parameter of a boron atom at:

\[ x = \frac{1}{2 + \sqrt{2}} = 0.293 \]

Careful x-ray diffraction or neutron diffraction studies are needed to check the validity of this assumption.

The rigidity of the boron network in \( \text{MeB}_6 \) is shown by the small coefficients of thermal expansion and by the narrow range of lattice constants of these phases. Although the diameters of the metal atoms in \( \text{MeB}_6 \) range from 3.55 to 4.45 Å (for coordination number 12), the lattice constants vary only from 4.096 to 4.268 Å; the three-dimensional boron network in the hexaborides resists stretching even more than did the planes of boron atoms in the diborides.

The boron network in \( \text{MeB}_6 \) is also a remarkably open one. The smallest radius of the "interstitial" holes which serve as sites for the metal atoms equals \( \frac{a}{2} \) and this dimension is substantially larger than the radii of any of the metals listed in Table VI with the exception of Be. As a result, the boron-boron distance in \( \text{MeB}_6 \) is increased from the "normal" 1.74 Å to 1.77 Å. In the other \( \text{MeB}_6 \) phases it ranges from 1.70 to 1.735 Å. It would be particularly interesting to establish the boron positions in \( \text{MeB}_6 \) precisely in order to ascertain whether all B-B bonds have been stretched uniformly or whether the elongation has been confined to the inter-octahedral bonds, leaving the octahedral dimensions unchanged.

A careful study of the effective atomic sizes of the rare-earth elements was carried out by Klamann and Howar (52). They found that, on proceeding from La to Lu, these elements with the exception of Eu and Yb showed a regular decrease in atomic size. The atomic radii of the two exceptions, Eu and Yb, are about 1/5 above the "normal" curve for the other rare-earth elements (Fig. 9). These anomalies are associated with the abnormal valencies of these metal atoms; while most of the rare-earth metals are effectively trivalent, Eu and Yb show a large amount of divalent character. The withdrawal of one electron from the outermost orbit to fill a gap in an inner one results in the observed increased sizes of these atoms.

**Fig. 9.** Dimensions of the rare earth metals and their hexaborides.
The dimensions of the \( \text{Nd}_2 \) unit cells (Fig. 9) show a similar, though less pronounced, anomaly in the case of \( \text{Eu}_2 \) and \( \text{Tb}_2 \). It appears, therefore, that the effective valence state of the rare-earth metals in the hexaborides is very much like that of the uncombined metals.

The sites of the rare-earth metal ions (\( \text{Nd}^{3+} \)) show no anomalies comparable to the above; these sizes decrease regularly from \( \text{La}^{3+} \) (1.061 Å) to \( \text{Nd}^{3+} \) (0.860 Å).

The lattice dimensions of the various \( \text{Nd}_2 \) and \( \text{Eu}_2 \) compounds listed in Tables V and VII also show a monotonic decrease with increasing atomic number of the metal and a distinction may therefore be drawn between the relatively "metallic" character of the \( \text{Nd}_2 \) compounds and the relatively "ionic" \( \text{Nd}_2 \) and \( \text{Eu}_2 \) compounds.

The cubic hexaborides require, as a necessary but not sufficient condition for structural stability, that the metal atoms be "large". The smallest of the metals crystallizing in this structure, \( \text{Nd}_2 \), has a radius of 1.72 Å for \( \text{C:N} \).

Hexaborides of relatively small metal atoms, (\( \text{Y}, \text{Dy}, \text{Cr} \)) have also been reported but these have complex structures which have not yet been solved. The dimensions of the \( \text{Nd}_2 \) phase are of some interest. These are almost identical (19) with those of \( \text{AlN}_2 \) (5) and the tetragonal polymorph of boron reported by Talley, Laplace and Post (94). Intensities of lines of the \( \text{Nd}_2 \) powder pattern differ significantly from those of \( \text{AlN}_2 \) but are not appreciably different from those of the tetragonal boron. The authors mention the possibility that \( \text{Nd}_2 \) may lie at one end of an extended homogeneity range which terminates in this tetragonal form of boron at the other end (19).

3. Metallic Dodecaborides: The first compound of this type, \( \text{NdB}_{12} \), was described by Bertaut and Bün in 1949 (29). The unit cell is cubic and contains four formula weights. The space group is \( \text{Pa}3 \). Stereo considerations, plus comparisons of observed and calculated intensities, indicated to Bertaut and Bün that the one variable position parameter in the structure, that of a boron atom, was \( x = \frac{1}{8} \). This leads to a highly symmetrical structure in which the metal atom
can be described as being at the centers of regular cube-octahedra with boron atoms at each of their twenty-four vertices (Fig. 10). Each boron atom is coordinated to two metal and five boron atoms. The structure may be visualised, alternatively, in terms of a modified NaCl-type structure with the metal atoms in place of the sodium and smaller cube-octahedral groupings of twelve boron atoms in place of the chloride ions (Fig. 11).

Subsequently the isomorphous ZrB12 was prepared; this phase is stable above 1600°C and could be prepared at room temperature only by quenching.

Surprisingly, in spite of the close similarity between Zr and Hf, HfB12 could not be prepared nor could dodecaborides of the other transition metals of Groups IV, V, and VI (56).

The large coordination number of the metal atoms in the MoB12 structure, together with the observed restriction of its synthesis to two of the largest of the transition-metal atoms, Zr and Hf, indicated that a necessary condition for the formation of this phase was the presence of metal atoms with large effective radii. The experiences with the Zr and Hf preparations also suggested that the siromium atom was near the lower limit of the permissible atomic size (the effective radii of Zr and Hf in the element are 1.585 and 1.575 Å respectively).

Post, Glaser and Moskovits (42) have described unsuccessful attempts to prepare dodecaborides of the rare-earth metals La, Ce, Pr, Sm, Gd and Yb. All of these have, in the element, effective radii exceeding 1.80 Å. In all of these preparations no borides were obtained with boron content higher than that corresponding to MoB12. More recently these preparations were repeated using boron and oxides of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb, Lu, Sc and Y (57). Only Dy, Ho, Er, Tm, Lu and Y* formed dodecaborides; the others did not. In apparent agreement with previous findings (42). However, when the reaction was carried out

*Seely (58) reported the preparation of YB12 shortly before LaPlace and Post.
using powdered metal in place of the metal oxide, it was found that TbB₁₂ and YbB₁₂ were also formed, although neither could be prepared from the oxides (39).

It is evident that the effective size of the metal atom plays a critical role in the formation of the dodecaborides. If we assume that the boron atoms are essentially spherical and that their radii are equal to half the B-B internuclear distances, then the radii of the "holes" inside the large cubo-octahedra of boron atoms about each metal range from 1.89 to 1.91 Å (Table VII). The rigid boron framework will not accommodate the larger rare-earth metal atoms whose effective radii (with twenty-four fold coordination) are appreciably greater than 1.91 Å.

The preparation of YbB₁₂ is particularly interesting in this connection. It will be recalled that the unit cell of YbB₁₂ is anomalously large, as is the radius of the Yb atom in the elementary state, whereas the dimensions of the TbB₁₂ unit cell are "normal". After their initial failure to prepare YbB₁₂, LabPace, Hinder and Post (37) explained this in terms of the anomalously large size of the Yb atom; it appeared that the effective radius of the Yb atom was larger than that of the available site in the dodecaboride lattice. It is evident that this "explanation" was premature, at least for YbB₁₂.

Chretien and Laveant (60) have recently reported the preparation of GaB₁₂ and the indexing of the x-ray powder pattern of this phase. Soybolt (56) had previously reported that gallium does not react with boron. Efforts have been made to repeat this preparation of GaB₁₂ (61). It was found the "GaB₁₂" could be formed only when the procedure used by Chretien and Laveant was followed closely, i.e., when the ingredients were heated in vacuo in a silica tube. No reaction occurred when aluminum or boron nitride crucibles were used. A closer analysis of the "GaB₁₂" powder pattern revealed further that it is made up entirely of lines due to "B₁₂" and to Si(n). There is no reliable indication in the x-ray pattern that a new phase has been formed.
One additional group of dodecaborides should be mentioned: the AlB₁₂ compounds. Crystalllographic data for these phases are listed below in Table VIII (53). There is a striking similarity between the cell dimensions of \( \text{M} \) alpha AlB₁₂ and those of the tetragonal polymorph of boron mentioned in connection with \( \text{BeB}_6 \) (54). Dimensions, of the latter are \( a = 10.12, c = 14.14 \) A but the intensities of the lines of the x-ray powder patterns of the two phases differ significantly. It is likely that these three aluminum-boride phases bear close structural relationships to one another, but no complete crystal structure determination has yet been reported.

b. 

Hafnium Borides: Saybolt (58) reported the preparation of a cubic yttrium boride with an yttrium content of from 1 to 2 atomic percent. This may be the same phase reported by Lundin (95) as \( \text{YB}_70 \), but the latter states that the unit cell is tetragonal with \( a = 11.75 \) and \( c = 12.62 \) A.

LaPlaca (35) has reported the preparation of cubic borides of Ho, Tb, and Tb with compositions approximating \( \text{HoB}_70 \). His powder diffraction data indicate that the lattice is primitive and that the unit cell dimensions are all approximately \( 11.75 \) A. Preliminary single-crystal analyses of "Tb₇₀" by Kasper (62) reveal that the unit cell is cubic but that the true lattice constant is \( 23.59 \) A, rather than the \( 11.75 \) A indicated by powder data. These phases are remarkably hard and refractory; further work on them should be worth while.

II. E. Non-Metallic Borides:

1. \( \text{MoB}_2 \) (Isolated Boron Atom): Hexagonal boron nitride (50) is a highly refractory compound, widely used in high temperature technology. Although it is readily oxidized at 600-700°C to \( \text{B}_2 \) and \( \text{B}_2 \text{O}_3 \) by such oxidizing agents as carbon dioxide, water vapor and oxygen, it is extremely stable even at much higher temperatures in the proper atmosphere. In hydrogen it may be used above 2000°C without appreciable decomposition; in nitrogen still higher temperatures are permitted (63).
The similarity between hexagonal boron nitride and the isoelectronic graphite is emphasized by the widespread use of terms like "white graphite" or "white lambskin" for boron nitride. The crystal structures of the two compounds are very similar. Unit cell dimensions, in Å, are:

<table>
<thead>
<tr>
<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c/a</th>
<th>density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>2.46</td>
<td>6.736</td>
<td>2.73</td>
<td>2.26</td>
</tr>
<tr>
<td>Boron nitride</td>
<td>2.50</td>
<td>6.661</td>
<td>2.65</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Both structures contain planar hexagonal nets of atoms perpendicular to c, separated by a distance equal to half the length of c* in each case. In a careful investigation of the crystal structure of BN, Pease (64) demonstrated that it differs significantly from graphite. In the latter, atoms in successive layers are situated directly above the centers of hexagonal rings directly underneath; in boron nitride, hexagonal rings in successive layers are situated directly above one another, but the boron atoms in one layer are above the nitrogen atoms of the adjacent one, etc.

The similarity between boron nitride and graphite has led many investigators to speculate on the possibility of synthesizing a cubic, diamond-like boron nitride (63). This cubic modification, a typical cubic "III-V" compound, was finally synthesized by Wentorf (65) at high temperatures and pressures; the lattice constant is 3.615 Å compared with 3.567 Å for diamond.

The synthesis of the analogous cubic BP phase (cubso, sinoblande structure) has been reported by three groups of investigators (66, 67, 68). The compound is prepared by direct reaction of boron and phosphorus in sealed evacuated silica tubes at about 1000°C and by reactions between BCl₃ and either AlP or phosphorus plus hydrogen (69).

The isomorphous EAs phase can also be prepared by the direct union of boron and arsenic at 800°C (68). Efforts to prepare ESB were unsuccessful. It is interesting to note that Walker and Weiss (70) had predicted that both BP and EAs would crystallize in the cubic sinoblande structure. Lattice dimensions of the cubic EAs phases are:

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN</td>
<td>3.573</td>
</tr>
<tr>
<td>BP</td>
<td>4.538</td>
</tr>
<tr>
<td>EAs</td>
<td>4.777</td>
</tr>
</tbody>
</table>

BP and EAs decompose when heated above 1100°C; phosphorus and arsenic are lost, and higher borides, similar in structure to boron carbide and alpha boron, are formed (71). Williams and Bushwhack (69) have discussed the decomposition of BP and EAs and the formation of these higher borides.

2. The Boron Carbide Structure Type. The crystal structure of boron carbide is well known. It was first determined by Zhizhikov and Sevastiane (72) and confirmed shortly thereafter by Clark and Hoard (73). The unit cell is rhombohedral and contains one \( \text{B}_1\text{C}_3 \) structural unit. The boron atoms are situated at the vertices of a nearly regular, icosahedron which is linked together by B-B bonds to form a three-dimensional network. In each unit cell three carbon atoms are arranged linearly, parallel to the three-fold axis of the rhombohedral cell, in large holes formed by the approximately close-packed large boron icosahedra.

Recently, Docke and Kasper (74) described the crystal structure of "alpha" boron. To a good approximation this structure may be derived from that of boron carbide by the omission of the carbon atoms from the large interstitial holes in the latter. The arrangement of boron atoms at the vertices of the icosahedra and the linking together of these icosahedra to form a three-dimensional network are essentially identical in both structures.

Other recent work also indicates that the structure type once considered to be characteristic only of boron carbide is much more common than previously supposed (71). It occurs not only in "alpha" boron but also when atoms of many different kinds are present interstitially.
For example, Hatkovich (75) has reported preliminary results of an analysis of the crystal structure of \( \text{B}_{13}\text{P}_{2} \). Parr, LäPhee and Post (68) have reported the preparation of \( \text{B}_{13}\text{Al}_{2} \). The unit cell of this arsenide had been indexed originally (from powder data) on the basis of a C-face centered orthorhombic unit cell. Re-examination of the powder data has shown that the pattern could be

indexed equally well on the basis of the alpha boron type of rhombohedral cell, and a detailed comparison with the patterns of the phosphide and the carbide indicates that the rhombohedral indexing is correct. The ambiguity in indexing and the consequent assignment of two different crystal systems resulted from the fact that, to better than one part in 3000, the ratio \( d_{100}^2/d_{101}^2 \) was exactly 5/3000. As a result, different sets of indices fortuitously yielded equally good agreement between observed and calculated values of \( d^2 \).

A similar ambiguity in indexing was encountered in connection with the \( \text{B}_{13}\text{P}_{2} \) phase reported by Fastnach (76) who indexed the x-ray powder data on the basis of an orthorhombic unit cell with \( a = 6.20, b = 5.35 \) and \( c = 5.13 \) Å. Chemical analysis had indicated that the composition was close to \( \text{B}_{13}\text{P}_{2} \). This composition, however, taken in conjunction with the assumed orthorhombic unit cell, implied a calculated density which was less than the measured one. It was therefore assumed that the ideal composition of the new phase was \( \text{B}_{13}\text{P}_{2} \) which, together with the assumption that small amounts of \( \text{B}_{13}\text{Al}_{2} \) were present as impurities, led to satisfactory agreement between calculated and observed densities. However, just as in the case of the arsenide mentioned above, the x-ray powder pattern can be indexed more satisfactorily on the basis of a rhombohedral unit cell; the formula \( \text{B}_{13}\text{Al}_{2} \) leads to a calculated density of 2.65 compared with the observed value of 2.64 g/cm³.

In \( \text{B}_{13}\text{P}_{2} \) as in \( \text{B}_{13}\text{Al}_{2} \), whose pattern had also been indexed incorrectly on the basis of an orthorhombic unit cell, the ratio \( d_{100}^2/d_{101}^2 \) is exactly integral within the limits of experimental error. It is 1.50 in \( \text{B}_{13}\text{P}_{2} \) and 1.900

in \( \text{B}_{13}\text{Al}_{2} \). The structural significance, if any, of these unusual relationships is not clear.

A subsequent single crystal analysis of this boron-silicon phase (81) led to a modification of the \( \text{B}_{13}\text{Si}_{2} \) formula; the x-ray study, supported by chemical analysis and density measurements, indicated that the composition is actually \( \text{B}_{13}\text{Si}_{x} \).

The structure is described as similar to boron carbide, except that pairs of silicon atoms take the place of the linear chains of three carbon atoms in \( \text{B}_{13}\text{C}_{2} \); the remaining silicon atoms are statistically substituted for some of the boron atoms in the boron icosahedra.

It is interesting to note how recent studies confirm the original work on the silicon-boron system by Hoissan and Stock (84). They had reported two intermediate phases, \( \text{SiB}_{2} \) and \( \text{SiB}_{1.5} \). \( \text{SiB}_{2} \) has since been described by Adamsky (85) and Cline (86). Znuravlev (87) had previously reported that \( \text{SiB}_{2} \) is cubic with the \( \text{CaF}_{2} \) structure, but this is apparently incorrect. Adamsky and Cline both obtained single crystals of \( \text{SiB}_{2} \); both reported that it is orthorhombic and neither detected the cubic phase mentioned by Znuravlev. The other silicon boride reported by Hoissan and Stock, \( \text{SiB}_{1.5} \), is evidently the same as the \( \text{SiB}_{1.69} \) which Magnuson and Brozst have described.

A detailed x-ray diffraction analysis of the crystal structure of \( \text{B}_{13}\text{P}_{2} \) has been completed (82). Analysis of accurately measured single-crystal intensity data showed that in \( \text{B}_{13}\text{P}_{2} \) pairs of phosphorus atoms are arranged in “interstitial positions” parallel to the “c” axis, in the positions occupied by the linear chains of carbon atoms in \( \text{B}_{13}\text{C}_{2} \). The icosahedra in \( \text{B}_{13}\text{P}_{2} \), unlike \( \text{B}_{13}\text{Si}_{2} \), are made up of boron atoms only; there are no phosphorus substitutions. There is, however, considerable statistical disorder. The sites occupied by the pairs of phosphorus atoms are only 70% occupied; phosphorus atoms also occupy other available intericosahedral sites statistically. The composition indicated by the x-ray study and density and chemical analyses corresponds to one formula weight of \( \text{B}_{12}\text{P}_{1.4} \) per unit cell (i.e., the ratio of boron to phosphorus is very close to 13 to 2, but the contents of one unit cell include 12 boron and 1.8 phosphorus atoms on the average).
The synthesis of $\text{B}_2\text{S}$, similar in structure to $\text{B}_2\text{C}$, has also been described (85). It is very likely that additional representatives of this structure type will be found.

Crystallographic data for alpha boron and for the "boron carbide type" phases are listed in Table IX.

III. Metal-Boron Systems

A. Borides of the Alkali and Alkaline-earth Metals and Aluminum:

Binary borides of the alkali metals have not been reported.

Be-B: Beryllium boride phases corresponding to the approximate compositions $\text{Be}_2\text{B}$, $\text{BeB}_2$ and $\text{BeB}_3$ were first reported by Markovskii and co-workers (86). Subsequently $\text{Be}_2\text{B}$ was found to have the cubic CaF$_2$ structure with $a = 4.470$ Å (89). These findings have been verified by Sands and co-workers (19) who prepared and studied single crystals of $\text{BeB}_2$ and $\text{BeB}_3$, and in addition published a powder pattern of a reaction product labelled "$\text{BeB}_3$".

Markovskii, Konrashov and Markovskii (90) have reported the existence of a copper-colored beryllium-rich boride, designated as $\text{BeB}_2$ or $\text{Be}_2\text{B}_4$. All the lines of this phase are present in the Sands "$\text{BeB}_3$" pattern (18); the latter also contains, in addition to recognizable impurity lines, a number of lines due to an additional phase, possibly a second beryllium-rich boride.

Becker (91) has mentioned the preparation of $\text{BeB}_2$ but gave few details. This may be isomorphous with the Sands "$\text{BeB}_4$", enriched in boron.

Mg-B: The borides of magnesium have not been satisfactorily characterized. $\text{Mg}_3\text{B}_2$, once a favored example of a compound between a divalent metal and boron, does not exist. Russell and co-workers (26) reported that the boride phase in equilibrium with Mg (s) is $\text{MgB}_2$ (AlB$_2$ type). They found evidence for a tetraboride and two additional higher borides. The latter may correspond to the "$\text{MgB}_3$" and "$\text{MgB}_2$" phases reported by Markovskii and Konrashov (92). The thermal relations among the magnesium borides

<table>
<thead>
<tr>
<th>$\text{Mg}_n\text{B}_m$</th>
<th>$a$</th>
<th>$c$</th>
<th>$c/a$</th>
<th>$(d(001))^2$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{MgB}_2$</td>
<td>3.89</td>
<td>11.70</td>
<td>2.952</td>
<td>5.61</td>
<td>63</td>
</tr>
<tr>
<td>$\text{MgB}_3$</td>
<td>4.50</td>
<td>12.25</td>
<td>2.232</td>
<td>7.40</td>
<td>81</td>
</tr>
</tbody>
</table>

- Reference (71)
have been discussed by Christen (93). He found that MgB₂ can be prepared readily at 950°C but that it loses magnesium as the temperature is raised to 1300°C. As more and more magnesium is driven off a tetraboride, and when a hexaboride is formed and finally a phase designated as MgBₓ remains, where x varies from 6 to 17. None of the x-ray patterns, aside from that of MgB₂, has been indexed satisfactorily.

(Ca, Sr, Ba) - B: Calcium, strontium and barium form cubic MgB₂ phases. It has long been believed that these are the only borides formed by these metals, but a tetraboride of calcium with the UH₂ structure has recently been reported (97). Also, Markovskii and Evshina (36) state that diborides of Ca, Sr, and Ba were prepared by heating the metals with boron in argon at 900 - 1000°C. Unfortunately, x-ray diffraction analysis was not used; the products were never obtained pure and their formulas were established on the basis of chemical analysis of the products of hydrolysis in dilute HCl. Additional evidence for the existence of these diborides is needed.

AlB₂: This system has been reviewed by Kohn (53). Crystallographic data are listed in Table VIII. The AlB₂ phase is the only aluminum boride whose properties differ significantly from those of boron. Its structure is well known but the others have not yet been determined. With the exception of AlB₂, the aluminum borides are high melting, very hard and extremely refractory.

Serebrovskii and Spalbaum (94) have reported an investigation of the aluminum-boron system. They prepared the diboride and found that it decomposed slowly to yield only the alpha AlB₂ phase. They found no signs of either AlB₁₀ or of the β or γ polymorphs of AlB₂. An investigation of the thermal relations among these phases is needed to resolve these apparent discrepancies.

B. Borides of Rare-earth Metals, Y and Sc:

These have been reviewed by Goetsch (5). Up to a few years ago only the hexaborides of a few rare earth metals had been reported. At present the rare-earth borides include compounds of the types RE₂B₁₀, RE₄B₁₀, RE₆B₁₂, RE₈B₁₂ and RE₁₀B₁₀ (the boron content of the latter has not been precisely determined).

Crystal data for diborides of Y, Sc, Gd, Tb, Dy, Ho and Er are included in Table III. The hexagonal Al₄B₁₀ and Y₄B₁₀ phases listed by Goetsch, with lattice constants of 3.83 and 4.45 for the former and 3.78 and 4.40 Å for the latter, are actually metal borides (MoB₂).

A number of rare-earth RE₈B₁₂ phases, with x varying from three to four, and with simple tetragonal structures, were described by the present author and co-workers several years ago (62). Subsequent investigations have indicated that these phases cannot be prepared in the absence of carbon and it is likely that the RE₈B₁₂ phases are borocarbides of unspecified, and possibly variable, boron and carbon content.

Yttrium and all the rare-earth metals, with the exception of europium, form stable tetragonal tetraborides. Yttrium, neodymium and the rare-earth metals also form cubic borides of the Ca₃C₆ type. Values of 4.36 and 4.035 Å have been reported for the lattice constant of ScB₆.

In either case (4.36 or 4.03) the lattice dimension is anomalously large; it is even larger than that of RE₆B₁₂ (4.268 Å), which is rather surprising in view of the relative sizes of the two metals in the elementary state (Rₓ = 1.60 Å; Rₓ = 2.16 Å).

Wide ranges of composition have been noted for REₓBₓ (41) and La₆B₁₂ (47) and similar homogeneity ranges may exist in other hexaborides. Powdered hexaborides have characteristic blue to blue-lavender colors; in general, they are good metallic conductors, extremely hard and high melting. Electrical and magnetic properties are discussed in Section IV.
The smaller rare-earth metals (atomic numbers 65 through 71) and Y form cubic dodecaborides (Table VII). These appear to be metallic conductors, but little else is known of their properties. The lattice constants of the rare-earth dodecaborides (Fig. 12) show no anomalies comparable to those of the hexaborides. In its tetraboride, as well as its dodecaboride, the effective valence of the ytterbium atom is +3; it appears to be in the +2 state in the hexaboride.

Borides, very rich in boron (approx. composition MeB<sub>7</sub>) have been reported for Y (95), Ho, Tb, and Tb (61). These are very hard and very refractory. It is very likely that this phase is also formed by other rare-earth metals.

C. Borides of Actinide Metals:

Thorium: Three intermediate phases are known: UBr<sub>2</sub> (31), UBr<sub>4</sub> (40), and UBr<sub>6</sub> (39). The U-US<sub>2</sub> eutectic is probably close to 1100°C (i.e., close to the melting point of uranium: 1130°C), (31) UBr<sub>4</sub> appears to be the highest melting uranium boride. A detailed analysis of the crystallography of UBr<sub>4</sub> and UBr<sub>6</sub> has been published by Weiss and Blum (104).

Th-Br: Only two intermediate phases are known: ThBr<sub>4</sub> (40) and ThBr<sub>6</sub> (49). The crystal structure of ThBr<sub>4</sub> was determined by Zalkin and Templeton (40) from single-crystal data. Its melting point is above 2500°C (31) compared with 2200°C for the hexaboride (105). The tetraboride of Y (melting point 2600°C) is also the highest melting of the many boride phases formed by that metal. Little is known of the melting points of the rare-earth tetraborides other than fragmentary data indicating that CeBr<sub>4</sub> melts at a lower temperature than CeBr<sub>6</sub> (31)) and the determination of these values would be worthwhile.

Pl-Br: Four intermediate phases have been reported (32). The cubic hexaboride has a wide homogeneity range; the lattice constant varies with composition from 4.115 to 4.140 Å. Both PuBr<sub>6</sub> and PuBr<sub>4</sub> were formed at 1200°C when the boron content of the reaction mix exceeded 70 atomic percent. The tetraboride is isostructural with UBr<sub>4</sub>. PuBr<sub>2</sub> could be prepared at 800°C but not at 1200°C. In PuBr<sub>2</sub> and UBr<sub>2</sub> the observed Mo-B distances exceed the calculated (contact*) values by .20 and .34 Å.
Figure 10. Unit cell dimensions of $\text{KNi}_2$ phases.
respectively, whereas in the transition-metal diborides this excess ranges from 0.05-0.08 Å. This may be associated with the anomalous long *a* axis in PuB$_2$ (1.90 Å) and UB$_2$ (1.99 Å) compared with the transition-metal diborides where the corresponding values range from 2.86 to 3.53 Å.

McDonald and Stuart (32) also report PuB (NaCl structure) with a = 4.92 Å. It is felt that the comments made below with respect to Ti, Zr, and Hf are applicable here also and that the presence of oxygen, nitrogen or carbon impurities may have stabilized the "monoboride" phase. It would certainly be worthwhile to re-examine these monoboride phases to establish whether any pure binary NaCl type monoborides exist, or whether all these are actually ternary or quaternary phases.

D. Borides of the Transition Metals of Groups IV, V, VI and VII: Ti-B: The solid solubility of boron in alpha Ti appears to be very large when its magnitude is estimated from changes of the lattice parameters of titanium-rich alloys (126). However, careful metallographic and analytical studies indicate that the solid solubility of B in alpha Ti is less than .05 weight percent between 750 and 1300°C and close to 0.1 weight percent at the eutectic temperature, 1670°C (97). The discrepancy is probably due to the presence of oxygen or nitrogen in the specimens studied by x-rays.

Titanium forms a stable monoboride (23) and a diboride (2). The former was examined by single-crystal methods and found to be orthorhombic (FeB type) with a = 6.12, b = 3.06, and c = 4.56 Å. It appears that the phase reported, on the basis of powder data, as tetragonal TiB$_2$ (96) (a = 6.11, c = 4.56) is actually this orthorhombic monoboride. The orthorhombic unit cell is pseudotetragonal (a = 2b) and this could readily lead to the observed misinterpretation of the powder data. The "NaCl-type" TiB$_2$ phase will be discussed under "Zr-B.

TiB$_2$ is extremely stable, an excellent thermal and electrical conductor, and it melts at 2900°C (30). The constitution diagram from 0-70 atomic percent boron has been published (97).

Zr, Hf-B: Cubic TiB$_2$, ZrB$_2$, HfB$_2$ and PuB phases with the NaCl structure have been reported frequently (56, 7, 8, 32). The evidence concerning these is often confusing but it appears that in most, or all of these, variable amounts of carbon, nitrogen or oxygen were present to stabilize the NaCl structure. It is probable that true binary NaCl type monoborides of Ti, Zr and Hf do not exist; a careful re-examination of the PuB preparation with rigorous exclusion of possible contaminants would be in order.

Zr, and Hf, like Ti, form very stable, hard and high-melting diborides. Their homogenity ranges appear to be narrow (30). ZrB$_2$ melts at 3050°C, HfB$_2$ at 3250°C (30). All these are excellent electrical conductors with reported resistivities of about 10 µohm-cm (4). These measurements were made on powdered specimens and the electrical resistivities of single crystals may be substantially smaller.

ZrB$_2$ is stable above 1600°C and melts at 2680°C (55, 98). Efforts to prepare the analogous diboride of Hf were unsuccessful. A tentative phase diagram of the Zr-B system has been published (98).

V-B: Four intermediate phases are known: V$_2$B$_2$ (22), VB (29), V$_3$B$_2$ (99) and VB$_2$ (2). There do not appear to be any stable higher borides of vanadium. The existence of at least one additional phase, possibly a high-temperature polymorph of V$_2$B$_2$, is indicated by observations of Hardy and Hama (107) on arc melted V-B specimens.

Nb, Ta-B: Tentative phase diagrams for the Ta-B, Nb-B and V-B systems have been published by Klafter and Bensevolov (108). Borides of the following types: Nb$_2$B$_2$ (22), NbB$_2$ (18, c), Nb$_2$B$_3$ (18, c) and HfB$_2$ are known. NbB, Nb$_2$B$_2$ (26) and TaB and Ta$_2$B$_3$ (10) have narrow homogenity ranges; the wide homogenity ranges observed in TaB and HfB$_2$ (18, c, 31) (and possibly in VB$_2$) have been discussed in Section II (diborides).

Klessinger noted that Ta$_2$B$_3$ (10) could never be obtained in pure form; it was always accompanied by either Ta (n) or TaB; the analogous Nb$_2$B$_3$ phase has not been reported.
Recent work by Leitman (110) helps to clarify this point. It was found that all the tantalum borides lose boron by evaporation at high temperatures.
Below 2000°C Ta_2B disproportionates to yield Ta_3B_2 plus Ta(B). Above 2160°C Ta_3B_2 in turn disproportionates to form Ta_2B and TaB. These reactions are indicated schematically in Fig. 13.

Leitman (110) has also noted that the composition of the "Ta_2B" phase is actually close to Ta_2.4B and "Ta_3B_2" is actually Ta_3.2B. The reaction with boron was found to yield TaB; TaB plus Ta(B) yielded TaB. No signs of "Ta_3B_2" were detected.

Cr_2B: "Cr_2B" has been described by Bertaut and Hulin (12), but Kiesling (1b) and Hupf (100) do not list Cr_2B as an intermediate phase in the chromium-boron systems. Cr_2B (12), CrB (1b), CrB (1b) and CrB (1b) have been reported by many authors. There can be little doubt about the existence of Cr_2B, CrB, and CrB, but there are differences of opinion about the conditions under which these phases may be prepared (7b). Hupf (100) has also reported a boron-rich compound, CrB, which had not been detected by earlier workers.

Elstroom (25) has subjected the crystal structure of CrB to a careful re-examination and found that the double boron chains previously described (1b) did exist, but that no anomalously short boron-boron bonds were present. Kiesling (1b) had reported such short bonds between boron atoms in adjacent chains.

The chromium borides are metallic, very hard and generally resistant to chemical attack. They dissolve in perchloric or hot sulfuric acid.

Mo-B: Kiesling (1a) first reported on the Mo_2B, MoB and Mo_2B_2 phases. In the course of examination of the Mo-B system (20), the Mo_2B_2 phase and two others, stable above 1600°C were discovered: β-MoB and MoB₂. It was observed that neither Mo_2B_2 nor MoB₂ have the ideal compositions indicated by their formulas; both had variable boron content, somewhat higher than that corresponding to the MoB₂ formula and lower than the Mo_2B₂ value.

![Phase relationships in the Ta-B system](attachment:image.png)
Kiesling did not observe borides richer in boron than \( \text{Nb}_2\text{B}_3 \).

Recently, \( \text{MnB}_2(\text{AlB}_2\text{ type}) \) was prepared \( \text{(56)} \) but it is evidently far less stable than most transition-metal borides. Fruchart \( \text{(37)} \) has reported that \( \text{MnB}_2 \) decomposes to \( \text{Mn}_2\text{B}_3 \) and \( \text{MnB}_6 \) on slow cooling. The powder pattern of the latter has not been indexed, but it is unlike that of other tetrahedrals.

**Re-B:** The tetragonal Re-B phase with \( a = 5.47 \) and \( c = 4.73 \) \( \AA \) which had been reported by Rosner et al. \( \text{(102)} \) has not been detected by subsequent investigations. Arendson \( \text{(103)} \) and co-workers have described the crystal structures of \( \text{Re}_2\text{B}_3 \) \( \text{(15,16)} \) and \( \text{Re}_4\text{B}_7 \) \( \text{(15)} \). The phase richest in boron appears to be \( \text{Re}_2\text{B}_3 \), whose crystal structure bears marked resemblances to those of \( \text{W}_2\text{B}_3 \) and \( \text{Mo}_2\text{B}_3 \) \( \text{(36)} \).

### 2. Borides of Metals of Group VIII:

**Fe-B:** Boron is only slightly soluble in alpha, beta or gamma iron: details of the phase diagram, at very low boron concentrations (0.001 to 0.025 wt. percent) are given by Hansen \( \text{(3)} \).

\( \text{Fe}_2\text{B} \) is tetragonal \( (\text{CuAl}_2\text{ type}) \). FeB appears to exist in two polymorphic modifications, Fruchart \( \text{(111)} \) found that the diffusion of boron into iron at 750°C to form the monoboride yields a new modification of \( \text{FeB} \); this transforms to the "normal" orthorhombic form \( \text{(Table II)} \) when it is heated above 1200°C. The direct reaction of iron with an equal part of boron at 1200°C also yields the orthorhombic modification (labelled \( \text{FeB} \)) by Fruchart.

**Co-B:** Co\(_2\text{B} \) \( \text{(2)} \) and Co\(_3\text{B} \) \( \text{(2)} \) exist in narrow homogeneity ranges. Runqvist \( \text{(13)} \) has reported a cobalt-rich boride, Co\(_8\text{B} \), with the cementite structure and this has been confirmed by Fruchart \( \text{(111)} \).

**Ni-B:** The nickel-boron system has been studied in detail by Runqvist \( \text{(21)} \) in the range of \( \text{Ni}_2\text{B} \) to \( \text{NiB} \). Single-crystal and powder methods were used. Intermediate phases are: \( \text{Ni}_2\text{B} \) \( \text{(cementite type)} \), \( \text{Ni}_2\text{B}_3 \) \( \text{(CuAl}_2\text{ type)} \), \( \text{Ni}_4\text{B}_3 \) \( \text{(orthorhombic)} \), \( \text{Ni}_6\text{B}_3 \) \( \text{(monoclinic)} \) and \( \text{NiB} \) \( \text{(CrB type)} \). \( \text{Ni}_2\text{B} \), \( \text{Ni}_3\text{B}_2 \) and \( \text{NiB} \) had been reported by...
others, but the two $\text{Ni}_2\text{B}_3$ phases had not been detected previously. The following two-phase regions were found: $\text{Ni}_4\text{B}_3$ plus $\text{Ni}_2\text{B}_3$, $\text{Ni}_2\text{B}_3$ plus orthorhombic $\text{Ni}_4\text{B}_2$, orthorhombic $\text{Ni}_4\text{B}_3$ plus monoclinic $\text{Ni}_2\text{B}_3$, monoclinic $\text{Ni}_4\text{B}_3$ plus $\text{Ni}_2\text{B}_2$. The orthorhombic $\text{Ni}_4\text{B}_3$ had a wide range of homogeneity; no such range was detected in the monoclinic form. The temperature ranges of stability of these two forms of $\text{Ni}_4\text{B}_3$ were not established. No borides richer in boron than $\text{NiB}$ were found.

Rundqvist (21) has noted that this series of five nickel borides provides a striking example of the increasing tendency for boron-boron bond formation with increasing boron content, to which Kleckling had first drawn attention (16).

F. Platinum Metals-Boron

The borides of the platinum metals have been the subject of a series of investigations by Aronson and co-workers at the University of Uppsala (11, 15, 17).

Using powder and single-crystal x-ray techniques, they have determined the crystal structures of $\text{Rh}_2\text{B}_3$, $\text{Ir}_2\text{B}_3$ (and $\text{Ru}_2\text{B}_3$), and demonstrated that these are of the $\text{Th}_2\text{P}_2$ type (15). $\text{PtB}$ and $\text{Pd}_{1.5}$ were shown to have the hexagonal, anti-$\text{NiAs}$ structure, and $\text{IrB}$ was found, surprisingly, to crystallize with the $\text{Th}_2\text{P}_2$ structure.

Aecius has carried out a precise determination of the crystal structure of $\text{Ru}_{1.4}\text{B}_3$ (86) in which both single and double boron chains were found. Stenborg (14) has studied $\text{PtB}$ and $\text{Pd}_{1.5}$; the former has the orthorhombic cementite ($\text{Fe}_{3}\text{C}$) structure, the latter is monoclinic and isomorphous with $\text{Ni}_2\text{P}_2$.

Aronson has shown (15) that the "orthorhombic $\text{Rh}_2\text{B}_3$" described by earlier workers (16), was very probably $\text{Rh}_2\text{B}_2$. He also confirmed earlier observations (112) to the effect that the powder photographs of $\text{Rh}_{1.8}$ and $\text{Os}_{1.6}$ could be indexed on the basis of cubic unit cells (15).

Recent work by Kester and Pries (33) is of interest in this connection.

They studied the Os-B and Ru-B systems and reported the preparation of Os$_2$B$_2$ and Ru$_2$B$_3$ phases with the hexagonal $\text{AlB}_2$ structure, and Os$_2$B$_3$ and Ru$_2$B$_3$ with the $\text{W}_2\text{B}_3$ structure.

It will be noted (Table III) that $\alpha = 0$ in both Os$_2$B$_2$ and Ru$_2$B$_3$ and their powder patterns could, therefore, be indexed on the basis of relatively large cubic unit cells (112) but there can be little doubt that the hexagonal indexing is correct and that cubic $\text{RuB}$ and $\text{OsB}$ do not exist.

G. Borides of Gold and Silver:

Although the literature contains many statements to the effect that neither gold nor silver react with boron to form intermediate phases (3), Chworski (34) remained skeptical and has prepared the hexagonal diborides of both metals by direct reaction. There is a moral in this somewhere.
IV. Properties of Borides

Our knowledge of the properties of the refractory binary borides is scattered and fragmentary. The diborides and hexaborides have been investigated most intensively, but even for these phases the available data are generally inadequate and sometimes unreliable. Pure boride phases are difficult to prepare and their stoichiometry is often uncertain. As a result, inadequately characterized specimens have often been used for the determination of properties. Some efforts have been made to exclude data of doubtful validity from this Section. These cannot be wholly successful and the reader is urged to view the results reported here, particularly those dealing with impurity sensitive properties, as essentially tentative.

A. Stoichiometry:

Gross deviations of indicated compositions of borides from their accepted chemical formulas have been reported with disturbing frequency, usually when precise control has been maintained over the specimen composition, or when the latter has been subjected to careful chemical analysis.

Recently, Kemper and Friss (33) reported the preparation of RuB₂ and OsB₃ (AlB₂ type) and Ru₂B₃ and Os₂B₃ (H₂B₂ type). The osmium "diboride" phase was obtained when equal atomic proportions of boron and osmium were heated at either 1300 or 1685°C. When two parts of boron were heated with one of osmium at 1300°C, the product consisted mainly of "Os₂B₃" plus a minor amount of the "diboride". Similarly, when five atomic parts of boron were heated with two of ruthenium, the product consisted mainly of an unidentified phase, plus only minor amounts of the expected Ru₂B₃ phase.

Roof and Kemper (144) have recently reinvestigated the Os-B and the Ru-B systems in order to characterize the "unidentified phase" referred to above. Using single-crystal and powder x-ray methods they have shown that both Os and Ru form orthorhombic diborides of a previously unreported type. The space group is Pnam and the cell dimensions are:

<table>
<thead>
<tr>
<th>Boride</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuB₂</td>
<td>4.631</td>
<td>2.967</td>
<td>4.676</td>
<td>7.59</td>
</tr>
<tr>
<td>OsB₂</td>
<td>4.68</td>
<td>2.867</td>
<td>4.063</td>
<td>7.60</td>
</tr>
</tbody>
</table>

Similar deviations from the accepted chemical formulas have also been reported by Brewer and co-workers (31); they found that the composition of "Ta₅B₄" varied, without change of structure, from Ta₅B₄ to Ta₅B₄, and similar results are indicated for NbB₂.

A study of palladium borides revealed that the chemical composition of the phase conventionally labelled Pd₃B₂ is actually Pd₃.28B₂ and that the composition of Pd₂B₃ is Pd₂.₆₂B₂ (14). Aronsson (15) has described a boride phase with the composition IrB₄. This has the ThSi₂ structure and, in terms of that structure, almost 50 percent of the boron atoms are absent.

Kiesling (41) and Steinits (20) have found that the "Mo₂B₃" phase is deficient in boron; chemical analyses consistently indicated that the boron content ranged from 19.5 to 20.8 weight percent instead of the expected 22 percent.

A wide range of homogeneity has also been detected in LaB₆ (47). The boron content varies from 82.8 to 88 atomic percent, corresponding to compositions from LaB₆ to La₅B₅. The Mo₂B₃ phase described by Kiesling (41) is another example of a striking deviation from the ideal composition. This phase was described in terms of the Mo₂B₃ structure, from which half of the boron atoms are absent. There are indications that a continuous range of compositions from Mo₂B₃ to Mo₂B₃ can be prepared with the "Mo₂B₃" structure.

In the Eu-B system (19) the x-ray pattern of the EuB₂ is almost identical, with respect to intensities and "d" spacings, with that of one of the tetragonal polymorphs of boron (44). The suggestion has been made (19) that this Eu-B phase may have a range of homogeneity extending all the way from EuB₂ to pure (tetragonal) boron.

Similar results have been reported for boron carbide (138). This phase was found to be stable over a very wide range of composition, and it was concluded that very little significance could be attached to the "B₄C₆" formula usually assigned to it. The recent description of the alpha form of rhombohedral boron (94),
which is isostructural with boron carbide; lends added weight to the notion of
an extended range of carbon content in the latter, possibly from pure boron to $B_2C$.  

A detailed single-crystal structure analysis of $B_2P$ has recently
been completed (82). This substance, like boron carbide, is isostructural with
alpha boron. The composition of the crystal studied was found to be close to
$B_2P_{1.8}$ (i.e., there are twelve boron atoms and 1.8 phosphorus atoms in each unit
cell). The phosphorus sites in the structure are only partially and apparently
randomly occupied. It is very likely that similar ranges of composition will
be found in other representatives of the boron-carbide structure type (See Table IX).

Leitner and co-workers (109) have reported that $TaB_2$ has an actual
composition corresponding to $Ta_2B_3$ and that the composition of the phase generally
referred to as $TaB_2$ is closer to $Ta_2B_3$.  

As a more careful work is reported this list will expand. There is
fortunately, evidence that at least some of the binary borides possess narrow ranges
of homogeneity. The diborides of Group IV transition metals fall into this
category (93). Bick and Gille have found no detectable variation of lattice parameters
of rare-earth diborides with composition and the same appears to be true of the
rare-earth metal dodecaborides (37) and many of the lower borides (11). Nevertheless,
it is evident that the physical significance to be attached to chemical formulas
of many of the borides should be subjected to careful reappraisal. Where the
stoichiometry is either not established, or is open to question, it is probably
best to describe phases mainly in terms of structure types without attaching
undue importance to specific chemical compositions.

3. Chemical Reactivity:

Schwarzkopf has discussed the chemical properties of borides of Groups
IV, V, and VI metals (4). All are said to be readily decomposed by fusion in
molten alkali hydroxides or carbonates. All oxidize in air at elevated
temperatures, and show varying degrees of resistance to attack by mineral acids;
$TaB_2$ and $NbB_2$ are reported to be most resistant to such chemical attack. They
are unaffected by HCl and HNO$_3$ and are attacked only slowly by hot sulfuric and
hydrochloric acids.

Kasovskii and Kapotsovskaya (115) have also studied the chemical behavior
of a number of transition-metal diborides. With the exception of the Cr, Nb and Ta
compounds, all were reported to dissolve in cold nitric acid. CrB$_2$ dissolves in
hot nitric acid. $NbB_2$ and $TaB_2$ dissolve only in HF. $ZrB_2$ was said to be relatively
boor in its resistance to HCl, but ZrB$_2$ is not attacked by this reagent.

These findings agree only in part with those reported by Kevlesakaya
and Samsonov (113), who studied the resistance of borides of Ti, Zr, Nb, Ta, Cr, 
Mo and W to solutions of the common acid and alkali solutions. The diboride
of chromium was reported to be most soluble, and $TaB_2$ and $NbB_2$ the least soluble, in
pure acids. $TaB_2$ resists acid mixtures better. No$_2B_2$ is poorest in this respect.
Fusion with NaOH dissolved all the specimens.

Kiesling (1b), on the other hand, reported that the chromium borides
are resistant to solution in all the common acids except perchloric. Kiesling
and Liu (131) have studied the thermal stability of chromium, iron and tungsten
borides in the presence of ammonia at 1180°C. In all cases the borides
reacted to form boron nitride and a metal nitride. The
stability of chromium and iron borides in the presence of the ammonia was found to
increase with increasing boron content, indicating to the authors that strong boron-
boron bonds are present in the higher borides. The findings also indicated that
the strength of the metal to boron bond decreases with increasing atomic number
of the transition metal (See also Table IV).

Breuer and Haraldsen (127) found that ZrB$_2$, W$_2B$ and W$_3B$ are stable to
nitrogen at 1550°C. TiB$_2$ was found to react with nitrogen at that temperature to form
TiN, but was stable at 2000°C. The high-temperature reactions of carbon and nitrogen
with transition-metal borides indicated that the stablest of those studied were
the borides of Ti, Zr, Nb and Ta.

The lower borides of beryllium (e.g., Be₂B) are reported to be very poor
in their resistance to attack by oxygen, nitrogen and carbon at elevated tempera-
tures (114). Higher borides, such as BeB₂ and BeB₆ are generally stable up to
800-900°C. These results are consistent with the findings of another group that
the stability of beryllium borides in mineral acids increases with increasing
boron content of the compound (68).

Magnesium and aluminum diborides are readily soluble in dilute acids,
but the higher borides of both metals are substantially more resistant to chemical
attack (26, 53).

Veselka and Markovskii (142) have studied the chemical properties of
the alkaline-earth hexaborides and find that they are approximately as resistant to
chemical attack as the transition metal borides. They withstand attack by acids
and alkalies (except for nitric acid); they are stable in nitrogen gas at high
temperatures and do not react with carbon at temperatures up to 2000°C. At tem-
peratures above 600°C they oxidize rapidly in air, although even in this process is
apparently slowed by the formation of an adherent oxide film on the borides.

Brower and Haraldsen (127) found that the hexaborides of Ca and Th, and
the diborides of Zr, Nb and Ta, as well as all borides of Cr, are stable in
the presence of carbon up to the highest temperatures attained in their experiments.

C. Thermal and Mechanical Properties:

Coefficients of thermal expansion of diborides and hexaborides are listed
in Tables X and VI. The coefficients are generally very small, much smaller, in
most instances, than those of the pure metals. In only one case (the expansion of VB₂
in the c* direction) does the coefficient exceed 10 x 10⁻⁶ per degree. The
reported anisotropy of thermal expansion of this phase (i.e., VB₂) is extraordinarily
large (15.9 to 3.6); the measurements are very likely in error.

Published values of the heats of formation of various borides are
listed in Table X.

Leitner and co-workers (110) have calculated molar heats of formation
of several compounds, starting from the assumption that ΔH_f of ZrB₂ is close to
-71.7 kcal per mol. On this basis it was established that ΔH_f of Ta₂B₆,
Ta₃B₈, and Ta₅ all lie within the range -69.4 to -64.9 kcal., and that limits of
-22.7 to -51.7 could be set for TaB₂ and -20.0 to -26.0 for W₂B₃.

There is considerable uncertainty regarding the correct value of ΔH_f
of TiB₂. Brower and Haraldsen (127) had reported -71.4 kcal., and Samsonov has
recorded a value of -70.0 kcal. (6a). Williams (128) has repeated and refined
some of his earlier work on TiB₂ and has reported that ΔH_f = -68 ± 5 kcal per mol.

The elastic constants of TiB₂ have been measured by Gilman and Roberts (135).

These are:

| C | 10¹² dynes/cm² | 4.9 |
| 00 | 3.04 | 2.5 |
| 01 | 3.42 | 4.1 |
| 02 | 3.83 | 3.2 |

The Debye characteristic temperature of 10³K has been computed from these
values of the elastic constants (135). This may be compared with a Debye tempera-
ture of 990 ± 30K computed from single-crystal x-ray diffraction data (141). The very
high value of the Debye temperature is consistent with other known properties of the
material, e.g., its very high melting point and its great hardness.

The X-ray data for TiB₂ have also been analyzed to yield values of the
root-mean-square amplitudes of thermal motion of the boron and titanium atoms.
At 300K these are:

<table>
<thead>
<tr>
<th>Material</th>
<th>Parallel to &quot;c*&quot; (in A)</th>
<th>Perpendicular to &quot;c*&quot; (in A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.064 ± 0.003</td>
<td>0.067 ± 0.003</td>
</tr>
<tr>
<td>Ti</td>
<td>0.064 ± 0.001</td>
<td>0.052 ± 0.001</td>
</tr>
</tbody>
</table>

The similarities between the amplitudes of motion parallel to and perpendicular to
"c*", and between the coefficients of thermal expansion in the different directions,
reflect the pseudo-isotropic character of TiB₂ (141).
### Table 2: Properties of Transition-Metal Borides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Microhardness (kg/mm²)</th>
<th>Coefficients of Linear Thermal Expansion (x 10⁻⁵)</th>
<th>ΔHf (kcal/mole)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB₂</td>
<td>27000</td>
<td>5.6</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>VN</td>
<td>2070</td>
<td>3.6</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>CrB₂</td>
<td>1800</td>
<td>6.0</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>2200</td>
<td>5.6</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>NbB₂</td>
<td>2200</td>
<td>5.6</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>MoB₂</td>
<td>1200</td>
<td>7.6</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>WeB₅</td>
<td>2250</td>
<td>7.2</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>HfB₄</td>
<td>2900</td>
<td>5.4</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>TaB₄</td>
<td>2500</td>
<td>5.2</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>WₓBₙ</td>
<td>2850</td>
<td>5.5</td>
<td>0.6</td>
<td>140</td>
</tr>
</tbody>
</table>

* (116) reports α = 5.73 x 10⁻⁶/°C, (distomeric)  
** (128) has reported ΔHf of TiB₂ = -50 ± 5 kcal/mole

---

D. Magnetic Properties:

The magnetic properties of transition-metal borides have been studied by Kukushkin and Prokopenko (119). Twenty alloys, ranging in composition from 5 to 72 weight percent of boron, were prepared. Four Mn-B phases were detected, of which only MnB was ferromagnetic. The spontaneous magnetisation rose sharply at 37 percent boron and reached a maximum at 50 percent boron. The MnB phase could be detected when more than 33 percent of boron was present. The spontaneous magnetisation of MnB at room temperature is 800 ± 2 gauss cm, suggesting its possible use as a magnetic material. The ferromagnetic Curie temperature of MnB is 289 ± 4°C.

The magnetic susceptibility of Mn-B alloys reached a maximum at 220-240°C; a second maximum was observed at 285-295°C when more than 32 percent boron was present.

Prochazek (111) has studied the iron-boron system. He found that both Fe²B and Fe₃B are ferromagnetic with Curie temperatures of 742 and 399°C respectively.

Lundqvist, Nayers and Westin (128) have measured the paramagnetic susceptibilities of a number of monocarbides over a wide range of temperatures. V₃B, Cr₃B and Mo₃B are paramagnetic and were investigated in the temperature range 100°C to 800°C. MnB, Fe₃B and Co₃B are ferromagnetic and were studied from their respective Curie points to 800°C.

VB and Cr₃B are strongly paramagnetic. Their susceptibilities decrease markedly between 100 and 300°C and show little variation above the latter temperature. The susceptibilities are accurately described by Weiss-Curie relations as follows:

\[
\chi_{VB} = \frac{29 \times 10^{-3}}{T + 220} \text{ emu}
\]

\[
\chi_{Cr₃B} = \frac{2.6 \times 10^{-3}}{T + 950} \text{ emu}
\]

MnB manifests very weak, temperature independent, paramagnetism (\(\chi = 4.0 \times 10^{-5} \text{ emu} \cdot \text{g}^{-1}\)). This is interpreted in terms of a filled d band; the slightly positive susceptibility is attributed to conduction-band paramagnetism.

The ferromagnetic Curie temperatures reported by Lundqvist, et al, for MnB and Fe₃B (370 and 390°C) are in fair agreement with values reported previously (362°C (119) and 381°C (117)).
Juratschke and Steinitz (136) have measured the magnetic susceptibilities of a number of transition-metal diborides; all are weakly paramagnetic except for ZrB₂ which is diamagnetic.

Magnetic properties of various hexaborides are listed in Table XI. These are particularly useful as guides to the effective valence states of the metal atoms in those compounds. The data indicate that all the metals listed, with the possible exception of Sm, are in the +3 state in the hexaborides. For example, the calculated moment for Ca₄⁺ is zero, and in view of the fair agreement between the observed moments (2.31 and 2.30) and that calculated for Ca₄⁺, we may exclude the tetravalent configuration from consideration. In the case of Sm, the experimental moment in the hexaboride is approximately halfway between the values calculated for Sm⁺³ (1.60) and Sm⁺⁴ (3.65).

The indicated Yb⁺³ configuration in the hexaboride is puzzling. The anomalously large size of the YbB₆ unit cell has been attributed to the effective divalent character of Yb in the hexaboride. This hypothesis appears to be ruled out in view of the close agreement between experimental values of the magnetic moments and those calculated on the assumption that the Yb ion is in the +3 state (i.e., 4.50 vs 4.50 for Yb⁺³). However, the analysis of Hall effect and resistivity measurements indicates that there are only 0.65 conduction electrons per metal atom in YbB₆ (Table XIV). The latter may be reconciled with the notion of divalent Yb in YbB₆ if the assumption is made that each metal atom contributes two electrons to the boron lattice to stabilize the latter (see "Bonding" below). Measurements of the effective magnetic moments of the Yb atom in YbB₆ may help to resolve this apparent contradiction.

Coles and co-workers (117a,b) have reported antiferromagnetic behavior in GeB₆ at low temperatures; a distinct maximum in the magnetic susceptibility plotted against the absolute temperature occurs at 14K. Direct interactions among the metal-ion cores are considered unlikely in view of the large metal-metal distances (4.10 Å). The observed effect was attributed to indirect antiferromagnetic

### Table XI - Magnetic Properties of Hexaborides

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\mu_{\text{exp}})</th>
<th>(\mu_{\text{calc}})</th>
<th>(\Theta_p (°C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>YB₆</td>
<td>0</td>
<td>0</td>
<td>(\approx) (\approx)</td>
</tr>
<tr>
<td>LaB₆</td>
<td>0</td>
<td>0</td>
<td>(\approx) (\approx)</td>
</tr>
<tr>
<td>CaB₆</td>
<td>2.91</td>
<td>2.90</td>
<td>2.56</td>
</tr>
<tr>
<td>PrB₆</td>
<td>(\approx)</td>
<td>3.37</td>
<td>3.62</td>
</tr>
<tr>
<td>NbB₆</td>
<td>3.02</td>
<td>3.04</td>
<td>3.66</td>
</tr>
<tr>
<td>SmB₆</td>
<td>(\approx)</td>
<td>(\approx)</td>
<td>1.60</td>
</tr>
<tr>
<td>GeB₆</td>
<td>4.11</td>
<td>(\approx)</td>
<td>(\approx) (\approx)</td>
</tr>
</tbody>
</table>

- *Exhibited* refers - Opic behavior from about 350 - 750°C; susceptibilities were measured in those temperature ranges and extrapolated to 25°C.
- **Exhibited** non-Ams-Curie behavior; the susceptibility rose with increasing temperature.

\(\mu\) = magnetic moment in Bohr magnetons

\(\Theta_p\) = paramagnetic Curie temperature.
interactions among the 4f ions which are assumed to take place via the conduction electron which is present for each 4f atom (117b).

Only one investigation of the magnetic properties of a higher boride has been reported. Bertaut and Blum (49) established that VB_12 is diamagnetic.

2. Electrical Properties:

This Section will be concerned mainly with the electrical properties of various transition-metal diborides and rare-earth and alkaline-earth hexaborides, i.e., with the only groups that have been studied systematically. Only scattered bits of information are available concerning other borides; these will be dealt with first.

Johnson and Imes (97) noted that LaB_6 is metallic in appearance, and is presumably an electronic conductor, but gave no numerical details. Fruchart (111) reported that Ni_3B is metallic, with a resistivity of 25.5 microhm-cm. The resistivity of 65-percent dense VB is 65 microhm-cm; extrapolation to 100 percent density indicates that the fully dense material should have a resistivity of about 35-40 microhm-cm (26). Resistivities of 64 microhm-cm have been reported for both MoB and CrB (4).

MoB becomes superconducting at 6K (145); of the large number of borides whose possible superconductivity has been investigated, only TaB_2, NbB and NbB show superconductivity at temperatures greater than 1.28K (107).

The ther oelectric coefficients of various monoborides have been measured by Lundqvist et al at several temperatures (132). Their results are listed in Table XII. The indicated ther oelectric powers of these materials are low and none shows great promise for ther oelectric applications, but the data are useful for studies of electron properties. These results, in conjunction with the magnetic data for these phases, to which reference has been made above, have been interpreted as indicating that the properties of a boride of composition M_B, where z is the atomic number of the metal, may be correlated with those of the pure metal of atomic number z + 1 (132).

<table>
<thead>
<tr>
<th>Compound</th>
<th>0°C</th>
<th>20°C</th>
<th>100°C</th>
<th>250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrB</td>
<td>-0.6</td>
<td>-0.6</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>NbB</td>
<td>+6.8</td>
<td>+6.8</td>
<td>+6.6</td>
<td>+6.5</td>
</tr>
<tr>
<td>FeB</td>
<td>-6.8</td>
<td>-6.4</td>
<td>-1.9</td>
<td>-0.7</td>
</tr>
<tr>
<td>MoB</td>
<td>+4.0</td>
<td>+3.5</td>
<td>+4.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

* Reference (132)
Hall constants, resistivities and thermoelectric coefficients of various transition-metal diborides are listed in Table XIII. The data reported by Lyov, Nemchenko and Samonov (125) are the most recent; agreement with comparable values reported some years previously by Juretschke and Steinits (136) is surprisingly good. In general, measurements of impurity sensitive properties, such as electrical resistivity, show a wide scatter; in column 7b we have listed resistivity values assembled by Aronson (7b) which are considered to represent the limits within which the correct values may be expected to fall. Variation of porosity of the sintered polycrystalline specimens used for these measurements and the probable presence of impurities in many of them are the chief causes of the wide ranges reported. The resistivities determined by Juretschke and Steinits were corrected for porosity effects.

Data in the column headed "(146)" in Table XIII were published more than thirty years ago by Hoers. Although the compounds were identified only as "borides", the magnitudes of the resistivities and the similarities between the melting points listed by Hoers and those given in Table IV, leave little room for doubt that the phases referred to were actually diborides. Impurities, in the form of the pure metals, oxides, free boron or other boride phases, could only have raised the indicated resistivities and lowered the melting points.

The usefulness of single-crystal measurements should be pointed out again here. Those would represent measurements on relatively pure, single phases, would yield information on the anisotropy of the resistivities, would make possible more reliable magnetic and thermoelectric measurements, and would eliminate grain boundary effects.

In comparing the results reported in (125) with those of (136) (Table XIII), the remarkably good agreement among the Hall constants in the two sets of data should be noted. All the transition-metal diborides have negative Hall constants (with the possible exception of MoB₂); both sets of measurements indicate very large negative magnitudes of R for diborides of Group IV metals and much smaller magnitudes for the others.
TABLE XII: Electrical Properties of Transition Metal Dichorides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref: 125</th>
<th>Ref: 136</th>
<th>Ref: 7b</th>
<th>Ref: 146</th>
</tr>
</thead>
<tbody>
<tr>
<td>TaB₂</td>
<td>-17.8</td>
<td>14</td>
<td>-3.1</td>
<td>-24</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>-17.6</td>
<td>17</td>
<td>1.1</td>
<td>-20</td>
</tr>
<tr>
<td>HfB₂</td>
<td>-17.0</td>
<td>12</td>
<td>---</td>
<td>-17</td>
</tr>
<tr>
<td>VB₂</td>
<td>-1.1</td>
<td>16</td>
<td>---</td>
<td>-1.1</td>
</tr>
<tr>
<td>NbB₂</td>
<td>-2.1</td>
<td>34</td>
<td>-1.4</td>
<td>-1.0</td>
</tr>
<tr>
<td>TaB₂</td>
<td>-2.2</td>
<td>37</td>
<td>-3.1</td>
<td>-2.7</td>
</tr>
<tr>
<td>CrB₂</td>
<td>-1.1</td>
<td>21</td>
<td>-0.8</td>
<td>-1.1</td>
</tr>
<tr>
<td>MoB₃</td>
<td>+0.1</td>
<td>25</td>
<td>+5.2</td>
<td>+0.5</td>
</tr>
<tr>
<td>W₂B₅</td>
<td>-1.7</td>
<td>33</td>
<td>+3.2</td>
<td>-1.6</td>
</tr>
</tbody>
</table>

R = Hall coefficient in cm. per coulomb (x 10⁴)

$\rho$ = Resistivity in microhm cm.

$\alpha$ = Thermoelectric coefficient in microvolts per degree.
Juratschke and Steinits interpreted their data on the basis of a model whose electrical conductivity is mainly due to electrons in one energy band. The large negative Hall constant of the Group-IV metal diborides then implies that in these compounds there is a small fractional number of conduction electrons in this band. The band is nearly empty; it is either separated by an energy gap from the next lower one or overlaps another band slightly. In the diborides of Group-V and VI metals the band then fills to the extent of about one additional conduction electron per unit cell. (Juratschke and Steinits made detailed measurements of a large number of solid solutions between TiB₂ and V₄B₆, and between V₄B₆ and Cr₄B₆, in addition to the pure phases listed in Table XIII.) The Hall constants in the diborides of the Group-V metals are negative but their values are closer to "normal" if there is about one electron per unit cell in the conduction band in these compounds. The mobilities of conduction electrons in the Group-IV compounds are in the range 200-300 cm²/V·sec.; these values decrease by factors of about fifty in the Group-V and VI compounds.

It is suggested (136) that the band structures in these diborides are very similar to those of the parent metals, and that the three valence electrons of each boron atom participate in the occupation of the metal d bands. This leads to a lowering of the centers of gravity of these bands, both in an absolute sense and relative to the next higher band. In TiB₂ the 3d band would be effectively filled by the six boron electrons and would overlap with the 4s, giving a small number in that band. This model accounts in a remarkably simple way for many aspects of the Hall data, for the electrical resistivity of the pure TiB₂, V₄B₆ and Cr₄B₆ phases and the solid solutions among them, and for the weak ferromagnetism observed in these compounds. Some less satisfying aspects of the Juratschke-Steinits model will be discussed in the next section, under "Bonding."

The thermoelectric coefficients and the temperature dependence of the coefficients of transition-metal diborides and their solid solutions have also been measured (149). Results are shown in Figs. 14, 15. These indicate a systematic change of thermoelectric power with composition of the solid solution, but cannot be explained on the basis of the simple one-band model postulated by Juratschke and Steinits (136) to explain their measurements of Hall constants and electrical resistivities. (It should be noted that the specimens used for these thermoelectric measurements were the same ones used previously by Juratschke and Steinits.)

The electrical properties of the rare-earth and alkaline-earth borides have been investigated in detail by Paderno and Sanzoni; in two comprehensive papers (129, 130) these authors have listed not only their own findings but also large amounts of data from other sources. Selected portions are presented in Table XIV.

From room temperature to about 800°C, and possibly higher, these phases all behave like metallic conductors. The relatively high resistivity of the alkaline-earth hexaborides, particularly Ca₆B₁₀, is in agreement with a qualitative observation made by Lafferty (105) as well as with a theoretical prediction made by Longuet-Higgins (137).

The electrical properties of the hexaborides have also been studied by Lafferty (105). Considerable attention was devoted to La₆B₁₀ which, because of its low work function and high thermal stability, shows considerable promise as a thermionic electron emitter for high-temperature applications. It was found that when the material is heated to a sufficiently high temperature, metal atoms at the surface begin to vaporize. Because of the strength of the metal-boron bonds, the rate of vaporization is low; Lafferty's measurements indicate that the latent heat of vaporization of lanthanum from lanthanum boride equals 169 kcal. per mole, an unusually high value. The metal atoms which are vaporized are rapidly replaced by diffusion from the bulk. At this stage, no appreciable vaporization of boron atoms occurs and the boron framework remains intact. Unlike oxides and other ionic compounds, the La₆B₁₀ structure is stable over a wide range of composition; as many as one-fourth of the metal atoms may be lost without causing the collapse of the structure.
Fig. 14. Thermoelectric power of sintered TiB₂ vs. Constantan. (dε/dT vs. T)

Fig. 15. Thermoelectric power of sintered FeB vs. Constantan. (dε/dT vs. T)
<table>
<thead>
<tr>
<th>Metal</th>
<th>Resistivity (microhm cm)</th>
<th>Hall Coeff. ( N(10^3) )</th>
<th>Thermal Coef. of e. res. ( \times 10^5 )</th>
<th>Mobility of carriers ( \text{cm}^2/\text{volt sec.} )</th>
<th>Number of conduction electrons per atom ( 10^7 )</th>
<th>Thermal Coeff. of elect. res. ( \times 10^5 )</th>
<th>Work Function (Electron volts)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>222</td>
<td>-91.0</td>
<td>-32.8</td>
<td>461.0</td>
<td>0.05</td>
<td>+1.16</td>
<td>---</td>
<td>121</td>
</tr>
<tr>
<td>Sr</td>
<td>111</td>
<td>-75.3</td>
<td>-30.7</td>
<td>66.0</td>
<td>0.06</td>
<td>+0.53</td>
<td>---</td>
<td>123</td>
</tr>
<tr>
<td>Ba</td>
<td>77</td>
<td>-37.3</td>
<td>-26.2</td>
<td>74.7</td>
<td>0.03</td>
<td>+0.08</td>
<td>---</td>
<td>124</td>
</tr>
<tr>
<td>Y</td>
<td>40</td>
<td>-4.6</td>
<td>+0.5</td>
<td>1.0</td>
<td>0.02</td>
<td>+0.02</td>
<td>---</td>
<td>125</td>
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<tr>
<td>La</td>
<td>15</td>
<td>-5.0</td>
<td>+0.1</td>
<td>3.1</td>
<td>0.00</td>
<td>+0.02</td>
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<td>126</td>
</tr>
<tr>
<td>Ce</td>
<td>20</td>
<td>+0.2</td>
<td>+0.3</td>
<td>13.2</td>
<td>1.08</td>
<td>+0.06</td>
<td>---</td>
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</tr>
<tr>
<td>Pr</td>
<td>20</td>
<td>-0.3</td>
<td>+0.6</td>
<td>1.92</td>
<td>1.02</td>
<td>+0.02</td>
<td>---</td>
<td>128</td>
</tr>
<tr>
<td>Nd</td>
<td>20</td>
<td>+0.3</td>
<td>+0.0</td>
<td>22.0</td>
<td>1.00</td>
<td>+0.03</td>
<td>---</td>
<td>129</td>
</tr>
<tr>
<td>Sm</td>
<td>207</td>
<td>+15.5</td>
<td>+7.6</td>
<td>0.74</td>
<td>2.86</td>
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<td>Eu</td>
<td>85</td>
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<td>-17.7</td>
<td>99.3</td>
<td>0.99</td>
<td>+0.30</td>
<td>---</td>
<td>131</td>
</tr>
<tr>
<td>Gd</td>
<td>45</td>
<td>-4.4</td>
<td>+0.1</td>
<td>9.6</td>
<td>0.96</td>
<td>+0.40</td>
<td>---</td>
<td>132</td>
</tr>
<tr>
<td>Tb</td>
<td>27</td>
<td>+4.6</td>
<td>+1.1</td>
<td>12.5</td>
<td>0.96</td>
<td>+0.30</td>
<td>---</td>
<td>133</td>
</tr>
<tr>
<td>Yb</td>
<td>47</td>
<td>-35.0</td>
<td>-23.5</td>
<td>17.9</td>
<td>0.95</td>
<td>+0.33</td>
<td>---</td>
<td>134</td>
</tr>
<tr>
<td>Th</td>
<td>15</td>
<td>-2.0</td>
<td>-0.6</td>
<td>9.7</td>
<td>1.00</td>
<td>+0.38</td>
<td>---</td>
<td>135</td>
</tr>
</tbody>
</table>

* Obtained by extrapolation to zero porosity (121).
Lafferty (105) reported 27 microhm cm.
As a result, the LaB$_6$ surface retains its activity and remains essentially unchanged throughout the heating process and does not show the rapid deterioration characteristic of metal and oxide surfaces under comparable conditions.

Diffusion of metal atoms to the surface continues until the hexaboride structure collapses and is replaced by that of pure boron. It is clear that, if Lafferty's picture is correct, the final melting point must be that of pure boron. Lafferty found that the melting points of the hexaborides of Ca, Sr, Ba, La, Ce and Th, all lie within the range 2230 ± 40°C (Lafferty's measurements). This was interpreted as implying that in all these cases the recorded melting point was that of essentially pure boron.

The electrical resistivity of LaB$_6$ varies from about 25 microhm·cm at 20°C to 120 microhm·cm at 1600°C (102). Pederson, et al. (121) reported similar results; they found that the resistivity changes from 18 microhm·cm at room temperature to 140 microhm·cm at 2000°C. Over this range the thermal coefficient of resistivity is 0.06 microhm·cm/deg; the comparable coefficient for metallic lanthanum is 0.216 microhm·cm/deg.

P. Bonding:

It is convenient to classify the many theories of interatomic bonding in refractory borides in terms of the types of electron transfer assumed to take place when the bond is formed. Keesling (12) and Juretschke and Steinits (136) and others consider that the formation of these bonds is accompanied by the transfer of electrons from the boron to the metal atoms. Opposed to this is the view expressed variously by Pauling (150), Longuet-Higgins and Roberts (147, 148), Lipscomb (143) and Samsonov (137, 139) to the effect that the bonding process involves the transfer of electrons from the metal to the boron atoms.

The latter position appeals strongly to those who look upon the formation of a boride primarily as a chemical process, and who interpret interatomic bonding in terms of ionization potentials, relative electro-negativities and bonding orbitals with calculable electron requirements.

This point of view has been adopted by Johnson and Deane (147) who studied phase relationships in the lanthanum-boron system and examined critically the available electrical and magnetic data for LaB$_6$. The great hardness and the high melting point of that compound were cited in support of the view that its outstanding structural feature is the strong and relatively rigid boron network. They found that the lanthanum hexaboride phase is stable from LaB$_6$ to LaB$_{7.8}$ (it is probably more useful to refer to the latter as La$_{0.76}$B$_6$). This wide range of homogeneity was explained in terms of the electron requirements of the boron network and the availability of such electrons in the valence band of the metal atom. Calculations by Longuet-Higgins and Roberts (148) and by Lipscomb and Britton (143) indicate that two electrons must be transferred to each boron octetatom in the hexaboride structure to ensure its stability. In stoichiometric LaB$_6$, there is therefore one "excess" valence electron for each lanthanum atom. Lafferty (102) has actually interpreted his Hall constant measurements in terms of the presence of one such negative current carrier for each lanthanum atom in (presumably stoichiometric) LaB$_6$. From this point of view a deficiency of metal atoms can be tolerated, so long as enough electrons are made available to the boron network. A lower limit of La$_{0.69}$B$_6$ is theoretically possible, with each lanthanum atom contributing all three valence electrons to the boron net; at that composition the phase would presumably be an electrical insulator. Actually, the observed lower limit occurs at La$_{0.76}$B$_6$, a limit which may be determined by the onset of mechanical instability in the boron lattice due to the large number of metal atom vacancies.

The authors have utilized similar considerations to explain the variation of the lattice constants of EuB$_6$ with composition. In this phase, which also has a wide range of homogeneity, all the Eu atoms would be expected to be in the +2 state at the stoichiometric composition, at which point the lattice constant should be a maximum (See Fig. 9). As the relative amount of Eu is decreased (i.e., in the presence of a relative excess of boron), the electron requirements of the boron network can be satisfied only by the conversion of Eu atoms from the +2 to the +3
state. In the latter state the effective size of the metal atom is decreased, resulting in the observed decrease in the lattice constant.

Sansonov and co-workers (50, 104, 137) have for some time emphasised the importance of low values of the first and second ionization potentials of the metal atoms for the formation of stable binary borides. It is assumed that electron transfer takes place from the relatively electronegative metal atoms to the electron-poor boron atoms. Nashor and Sansonov (50) postulate that in the hexaborides each metal atom must transfer ten electrons to the boron network. Their empirical analysis of the ionization potentials of the metals indicates that such transfer is unlikely to occur if the first ionization potential of the metal exceeds 6.6 to 6.8 electron volts, or if the second exceeds 11.5 to 12 electron volts. The failure of metals like Ca, Sn, Zn, Ga, Sn and Pb to form borides is ascribed to the high ionization potentials of these metals and their consequent inability to transfer electrons to the boron lattice (130). Vacancies in an inner electron shell are also stressed as a necessary condition for the formation of borides. It is pointed out that there are no alkali metal borides nor any borides of B subgroup metals. It is difficult, however, to reconcile this argument with the acknowledged stability of alkaline-earth and aluminium borides with the existence of gold and silver diborides. In some of these metals (i.e., alkaline earths, aluminium, gold and silver) are there unfilled inner electron shells, and in the case of both gold and silver the ionization potentials exceed by a large margin the limits mentioned by Nashor and Sansonov.

Loquet-Higgins and Roberts have used the method of localized molecular orbitals to determine the electron requirements of boron icosahedra in boron carbide (147) and of boron octahedra in the hexaborides (146). Both types of boron networks were found to be electron deficient, requiring electrons from outside sources for stability.

Lipson and Britton (143) extended this work and have outlined a valence theory of the structures of the higher borides. It is assumed that the boron framework may be isolated into polyhedra connected by localized bonds. The molecular orbitals of individual polyhedra are then investigated, and the electron requirements for bonding in these polyhedra are considered to be satisfied by transferring electrons from the relatively electronegative metals to the boron framework until the bonding orbitals of the latter are filled. Excess metal valence electrons, if any, are responsible for the observed metallic properties.

Lipson and Britton have computed the bonding requirements of the groups of twelve boron atoms arranged at the vertices of cubo-octahedra in NaB\textsubscript{12}; the method used is similar to that used by Loquet-Higgins and Roberts for boron icosahedra (147). In the cubo-octahedra of the dodecaborides each boron atom forms four internal and one external bond to other boron atoms. An LMBO molecular orbital approach indicates that thirteen internal electron pair bonds are formed by each group of twelve boron atoms. The latter can furnish thirty-six valence electrons but, of these, only twenty-four are available for internal bonds. Twelve additional valence electrons are needed for the twelve external bonds. There is an overall deficiency of two electrons and these are furnished by the metal atom. If the metal were divalent the dodecaboride would be an insulator, or at best a poor conductor. In \textit{Dh}\textsubscript{12} the metal atom has four valence electrons and the compound is metallic; considerations of this sort may be used to account for metallic properties in the rare-earth dodecaborides.

Similar calculations indicate that each \textit{Rg} octahedral group in \textit{Dh}\textsubscript{6} needs twenty electrons to satisfy its bonding requirements (fourteen for seven internal orbitals and six more for six external bonds). The six boron atoms can furnish only eighteen and the deficiency is made up by the metal. On this basis it would be expected that the alkaline-earth hexaborides would be insulators. Although
precise data for highly purified specimens are not available, the data in Table XIV do indicate that CaB₆ has the highest resistivity of all the hexaborides with SrB₆ and BaB₆ not far behind.

These modified molecular orbital techniques have also been applied to the tetraborides and the diborides. On the basis of Lipson and Britton's calculations the former require fifty-six electrons for the boron-boron bonds in each unit cell. The sixteen boron atoms can only furnish forty-eight; the metal atoms contribute eight (two each).

The treatment of the diborides is based on NiB₆ as a closed shell prototype of the transition-metal diborides. Magnetism is assumed to form a doubly charged positive ion within the boron framework; the transfer of two electrons to the boron atoms makes these isoelectronic with graphite. The excess valence electrons of the transition metals account for their metallic properties.

This approach, as the authors emphasize, is far from complete in its present form. It is oversimplified and arbitrary in its description of "isolated" boron polyhedra, but it does appear to represent the beginnings of a unified picture of bonding in these borides. It does not, however, account for the instability of most Group-III metals to form borides; it ignores the presence or absence of unfilled inner orbitals in the metal atoms; and it does not account for observed trends in the electrical, magnetic and other properties of the di- and hexaborides.

The alternative picture of the bonding process in borides, i.e. that in which electron transfer is assumed to proceed from the boron to the metal lattice, has been presented clearly and persuasively by Ikeda and Imai (17). In discussing borides as interstitial phases, evidence based on crystal structure analyses and magnetic measurements is brought forth in support of the view that the interstitial boron atoms act as electron donors; in the diborides, the electrons are believed to be taken up by the incomplete d shells of the transition-metal atoms. Jureitschke and Steinits (136) have taken a similar position. Their simple model (See Section IV, D) in which it is assumed that the three valence electrons of each boron atom participate in the occupation of metal d bands, accounts satisfactorily for the electrical resistivity and Hall constants of various transition-metal diborides. These explanations have been limited thus far to the transition-metal diborides. They are far from satisfactory in their present form, despite their successful application to the interpretation of electrical and magnetic measurements. For example, it is difficult to reconcile the assumed transfer of three electrons from each boron atom to the metallic bands with the known relative electronegativities of the two types of atoms. It is also difficult to accept the statement of Jureitschke and Steinits that "the principal role of the boron atoms is the stabilization of a simple hexagonal metallic structure without any pronounced boron to boron bonds". A careful analysis of the lattice constants of the diborides and the higher borides indicates, to the present author at least, that the boron networks play a very important part in these structures and that boron to boron bonds must be extremely strong. Additionally, the model proposed by Jureitschke and Steinits is a first approximation; a more refined treatment of the problem would necessarily have to take the boron bands into consideration, and in so doing may avoid some of the difficulties of the simpler treatment.


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