Electron requirements of bonds in metal borides

Robert William Johnson
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ELECTRON REQUIREMENTS OF BONDS IN METAL BORIDES

by

Robert William Johnson

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Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean Of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1962
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I. INTRODUCTION

The element boron occupies a position in the periodic table which is on the borderline between metallic and non-metallic elements. Its physical properties resemble those of silicon more than those of its immediate neighbors, and the discontinuity of properties between boron and aluminum is almost without parallel in the other groups of the periodic table. Boron is a unique element in that every other element having fewer than four valence electrons per atom is metallic. From the position of boron next to carbon in the periodic table, one might expect it to offer an equally extensive and varied chemistry of covalent compounds. This expectation is being realized at the present time, at a pace accelerating with the increasing number of researchers in the field of boron chemistry.

The chemistry of boron has developed along three distinct paths. The first of these was concerned with boron compounds as they occur in nature, and those compounds which could be derived from them by reactions in air or in aqueous solution. Such compounds include borax, boric acid, and a long list of other compounds, all of which contain oxygen. The chemistry of all these acids, bases and salts represents the chemistry known from earlier periods in scientific history and has not seen any great development in more recent times.
The other two paths of development were started when reactions were carried out in such a way as to exclude oxygen from the reaction products. These two subdivisions are the boron hydrides and the metal borides, both of which began development around 1930. For both of these classes of compounds it soon became evident that the simple concept of covalent bonds that had been so successful in organic chemistry was quite inadequate to explain the compositions and structures observed.

The field of boron hydrides received its initial impulse from Stock (1), who prepared such compounds as $\text{B}_2\text{H}_6$, $\text{B}_4\text{H}_{10}$, $\text{B}_5\text{H}_9$ and many others. These and other related compounds were called electron deficient because not enough valence electrons were present to form covalent bonds between neighboring atoms in a manner consistent with the currently accepted bonding theory. Of course, the real deficiency was in the current theory, not in the number of electrons, which were quite sufficient to hold the molecules together. During the period following the discovery of these hydrides, most attention was focused on diborane, $\text{B}_2\text{H}_6$, and for a while the structure was the center of controversy. One group put forward evidence for a spatial arrangement of atoms like that of ethane, and another group took the position that the two boron atoms and four of the hydrogen atoms were arranged as in ethylene, the other two hydrogen atoms being in a double bond between the
boron atoms. The evidence of both groups was reviewed by Schlesinger and Burg (2) in 1942, who at that time regarded the question as undecided. Experimental evidence gathered in the following decade was decisive in favor of the ethylene-like model with its "hydrogen bridge" bonds. Such evidence came from electron diffraction, infra-red and Raman spectra, and specific heat studies. The bridge bond was found in other boron hydrides also, but only in the case of diborane could the "electron deficiency" be accounted for by bridge bonds alone. A great step forward came in 1954 when Eberhardt et al. (3) laid the theoretical foundation for two kinds of "three center" bonds based on the method of linear combination of atomic orbital (LCAO). The "open" three center bond is typified by the B-H-B bridge bond, and consists of a two electron bond shared by three atoms which lie along a somewhat curved path. The "central" three center bond consists of two electrons shared by three equidistant boron atoms. Their calculations showed that when the number of orbitals present was equal to the number of available electrons as in the hydrocarbons, the state of lowest energy is described by conventional or "two center" bonds. If there are fewer electrons than orbitals, the three center bonds are the more stable type. Thus the LCAO treatment not only explained the presence of three center bonds in the boron hydroxides but also explained their absence in organic compounds. In more
recent years the field has continued to expand, aided by the technique of nuclear magnetic resonance, a powerful tool for determining the structures of the new hydrides that are continually being discovered. The latest review of this part of boron chemistry was given by Lipscomb (4) in 1959. Early publications on the subject of borides (including elemental boron) are very few in number, but reach back almost a century. Perhaps the first borides discovered were AlB$_2$ and AlB$_{12}$ (5), which were reported in 1867. The next important advance was made by Moissan (6) who, in 1892, published an account of the preparation of amorphous boron by reduction of boron oxide by magnesium in a thermite-type reaction. Reports of boride preparations in the three decades that followed were almost as scarce as in the time before. In 1929 the preparation of some rare earth hexaborides by fused salt electrolysis was reported by Andrieux (7). Three years later the hexaboride structure was determined by Allard (8) and von Stackelberg and Neumann (9). It was then evident from the arrangement of boron atoms in the structure that the hexaborides were "electron deficient" too, in the same sense as were the boron hydrides. One important difference in the two cases is that three center bonds cannot be invoked to help explain the electronic structure of the hexaborides. In the two decades following Andrieux's paper many new borides were discovered and their structures determined by X-ray diffraction. The state of
knowledge of the subject at that time was well summarized in a review article by Kiessling (10) published in 1950.

A very unusual feature was found in most of the boride types whose structure had been solved. Distances between boron atoms were so small (1.5 - 1.9 Å) as to be explained only by the existence of covalent bonds between such atoms. Only at relatively metal-rich compositions were the boron atoms isolated from one another. Kiessling (10) described the typical borides as follows: (a) the $M_2B$ type, formed by Ta, W, Mo, Mn, Fe, Co, Ni crystallizes in a tetragonal structure of the CuAl$_2$ type, and the boron atoms, being separated from one another by 2.1 - 2.4 Å are considered isolated from one another. (b) The $MB$ type formed by Ta, W, Mo, Mn, Fe, Co, and other transition elements crystallizes in either the tetragonal or orthorhombic crystal systems. The boron atoms form zig-zag chains in the structure with a typical B-B distance of 1.80 Å. It is interesting to note for comparison that the monocarbides of transition elements usually have the cubic NaCl structure. One may suppose that the monoborides would also be cubic were it not for the tendency for B-B chains to form, destroying the cubic symmetry. (c) The $M_3B_4$ type formed by Nb, Ta, Mn and Cr has an orthorhombic structure. The boron atoms form double chains resembling a string of hexagons, as
A typical B-B distance along the length of a chain is 1.8 Å; the B-B distance across the chain is usually much shorter, about 1.5 Å and is suggestive of double bonds between such atoms. (d) The MB$_2$ type is formed by Mg, Al, and nearly all of the transition elements. Rare earth elements having an ionic radius less than that of Gd also form diborides, but these were unknown at the time of Kiessling's review. Nearly all of the diborides have the hexagonal AlB$_2$ structure, consisting of alternate layers of metal atoms and boron atoms. Each layer of boron atoms resembles a honeycomb,

![Honeycomb](image)

and B-B distances range from 1.71 Å for CrB$_2$ to 1.90 Å for YB$_2$. (e) The borides which form three dimensional boron frameworks are the types MB$_4$, MB$_6$ and MB$_{12}$. The MB$_4$ type was unknown at the time of the review, and the only known MB$_{12}$ type was UB$_{12}$. The structures of these are discussed and illustrated in a later section. The tetraborides have been reported for Be (11), Ca (12), the rare earths, U, and Th (13). The known hexaborides are formed by Ca, Sr, Ba, the rare earths and Th (10). Dodecarborides are now known
for U, Zn, Y, Dy, Ho, Er, Tm and Lu (14).

The first quantitative treatments of intra-boron bonding in borides appeared in 1954, with discussions of the hexaboride type by Longuet-Higgins and Roberts (15) and Eberhardt et al. (3), both using the LCAO method. The result of both treatments is that 20 electrons are required by each \( B_6 \) unit. The boron atoms supply three apiece, or 18, leaving two to be furnished by each metal atom. The conclusion was consistent with the report (7) that the electrical properties of the rare earth hexaborides seemed more metallic than those of the alkaline earth hexaborides. Also, Lafferty (16) had reported that the Hall coefficient of a sample of sintered \( \text{LaB}_6 \) corresponded to nearly one metallic type electron in the structure per lanthanum atom.

An LCAO treatment of the boron bonding in the \( \text{MB}_{12} \) borides was published in 1960 by Lipscomb and Britton (17). In addition, they proposed models for the electronic structure of the types \( \text{MB}_2, \text{MB}_4 \), and for \( B_{12}C_3 \) and elemental boron. Their publication is also a complete review of previous work on electronic structures of the higher borides (those of greater than 50 atomic percent boron). The experimental evidence cited by them supporting (or contradicting) the theoretical models is in all cases insufficient for adopting or rejecting the models, due to the lack of such evidence.
The present work was initiated in order to provide experimental evidence with which to evaluate the above mentioned models for the electronic structures of the boride types $\text{MB}_2$, $\text{MB}_4$, $\text{MB}_6$ and $\text{MB}_{12}$. (The models themselves will be described more fully in the discussion section.) All of the electronic structures reviewed by Lipscomb and Britton (17) have been derived by a procedure based on the LCAO method. For the borides the very scanty experimental evidence available to date tends to support the results given, but in the case of the tetragonal form of elemental boron the LCAO model (18) calls for many more electrons than would seem to be present. It is important to know whether the LCAO method can be successfully applied to boron-boron bonds in all situations. If such a procedure is supported by experimental evidence, a few of the many benefits to result are: (a) It will be possible to understand the bonding in a very large class of compounds, perhaps including ternary borides; (b) The knowledge might be extended to metal-rich borides which closely resemble many intermetallic compounds; (c) It may be possible to correlate electronic structure with melting point of refractory compounds, and thus lead to many new high temperature materials; (d) Using rare earth borides it should be possible to study the influence of metal ion size in borides on many properties, since the metal valence is a constant for most of the rare earths; (e) The electronics industry should
be able to find at least ten new semiconducting materials among the borides.

At the time the present work was begun, the boride type for which most experimental evidence had been gathered was the hexaboride. The evidence was not consistent, for if LaB$_6$ had one metallic electron per lanthanum atom as reported, the alkaline earths should have none, and be insulators or semiconductors. Samsonov and Grodshtein (19) however, reported the electrical resistivity of CaB$_6$ to be 123x10$^{-6}$ Ω-cm, barely higher than that of many metals. It appeared that if CaB$_6$ were truly a semiconductor, the reported resistivity must have been measured on a very impure sample. The Hall coefficient measurements on LaB$_6$ by Lafferty (16) and later by Samsonov (20) were open to question because the samples in each case were sintered powders prepared in the presence of La$_2$O$_3$ and carbon. Substitution of carbon or oxygen for boron in the lattice in small amounts would provide extra electrons over the amount presumed to be present.

The present work had the purpose of providing experimental criteria for judging the theoretical models of the four boride types mentioned earlier. One of the best ways to judge models such as these is to find out whether the boron atoms really have the number of electrons that the theory says they should have. It is implied in the theory that the electrons participating in boron-boron bonds are "bound" and
unable to move under the influence of an electric field unless somehow excited (by high temperatures for instance), and any metallic properties are to be accounted for by the presence of more valence electrons than are required by the boron atoms. Experimentally it is possible to determine whether the valence electrons are all bound, and if some are not bound it is often possible to determine the concentration of "free" (metallic) electrons. The former condition corresponds to semiconducting electrical properties, and in the other case the free electron concentration is often obtained directly from the Hall coefficient. These two types of electrical properties were measured on suitable borides. According to the proposed models (17) any of the four boride types would be a semiconductor if made from an alkaline earth metal. Previous experience had shown that all but the alkaline earth hexaborides would be very difficult to prepare in a form necessary for measuring electrical properties, so only the alkaline earth hexaborides were investigated for semiconductivity. The yttrium borides were chosen for Hall coefficient measurement, as the models for each indicated the presence of one free electron per yttrium atom. Yttrium was chosen because it is trivalent, forms the four boride types to be investigated, and the yttrium-boron phase diagram (21) was available.

The problems entailed in a Hall coefficient measurement
or the measurement adopted for probable semiconductors (determining the resistance-temperature relationship) were not unduly difficult, as methods for each have been published many times. The main obstacle to be overcome was the preparation of samples suitable for measurement. The borides presented an imposing challenge because of their very high melting points, extreme brittleness, and ease with which they are contaminated at temperatures required in their preparation. Single crystals were preferred for samples to be checked for semiconductivity, and were essential for Hall coefficient measurements on non-cubic borides because non-cubic solids usually show a distinct anisotropy. It was necessary to develop a new method for floating zone melting in order to obtain material of suitable form and purity.
II. EXPERIMENTAL DETAILS

A. Design of the Zone Melting Apparatus

The suitability of floating zone melting for preparing material for Hall effect measurements can be understood by consideration of the requirements of the samples to be measured and of the properties of the borides themselves. A sample for Hall effect measurement is usually in the shape of a flat rectangular slab, of a length about four times its width, and of any convenient thickness. During the measurement an electric current is passed down the length of the sample and electrical contacts along the edges enable a transverse voltage to be detected in a magnetic field. The current in the sample must be uniform, which requires that the sample be homogeneous and free from cracks and large voids. For substances which do not have a cubic crystal structure, the sample must be a single crystal suitably oriented with respect to the magnetic field. In general the purity requirements are not nearly as stringent for the metallic type substances as for the semiconductors.

Certain properties of the borides tend to severely limit the possible methods of preparation. All of the borides used in this study have melting points above 2000°C. Some of them are peritectic compounds. The only container that is known
to hold borides at their melting point without severe contamination is water-cooled copper. They are brittle, and cannot be mechanically deformed without cracking.

The method ultimately decided upon for preparation of compounds for Hall effect measurement was floating zone melting. That process is one in which a small molten zone is passed along a vertical rod, the melted portion held in place only by its own surface tension, with no crucible surrounding the rod. Principal reasons for this choice were: (a) Very slow rates of solidification of the boride could be achieved by controlling the traverse rate of the zone along the rod; (b) No crucible is required; (c) Mason and Cook (22) recently showed that peritectic compounds could be prepared by a slight modification of the zone melting. The condition (a) is most likely to result in large grains from which single crystals might be cut, and in any case give a non-porous homogeneous solid as required. The floating zone melting would have to be carried out under argon at atmospheric pressure to prevent serious change of composition that would occur if carried out in vacuo due to selective evaporation of yttrium or of boron. That requirement ruled out use of electron bombardment heating, making it necessary to develop a new method for floating zone melting.
1. **Apparatus**

The device which enables the necessary temperatures to be attained is called an eddy current concentrator, and is illustrated in Fig. 1. The one shown is a slight modification of the basic design published in 1940 by Babat and Losinsky (23). It fits inside of a conventional induction coil, but is separated from it by the quartz furnace tube. Its principle of action may be viewed as follows: The R.F. current in the induction coil, having a frequency of about 500 K.C. produces a certain definite amount of magnetic flux also alternating at 500 K.C. The penetration of the copper of the concentrator by the magnetic field at this frequency is of the order of $10^{-5}$ cm, and therefore negligible. The flux must therefore pass through some open space not blocked with copper, and a great deal of it consequently passes through the hole in the center. The magnetic field strength, being flux per unit area, is much increased over its value in the absence of the concentrator. Since the power developed in a conductor by an alternating magnetic field increases with the square of the field strength, the heating effect of a coil is greatly multiplied with the use of a concentrator.

The essential parts of the zone melting furnace are shown in Fig. 2. The tantalum plates to which the ends of the rod are wired have a V-shaped vertical groove bent into them, in which the ends of the rod lie. These grooves align.
Fig. 1. Eddy current concentrator, made of copper pieces soft soldered together. Scale 1:1
Fig. 2. Zone melting furnace. The vacuum system to which it is connected is not shown.
the rod so that it will pass through the center of the hole in the concentrator. The vertical tantalum wires shown connect the two plates together and slide through small holes in the concentrator as the rod is lowered. Under ordinary conditions of operation the entire rod is lowered at a chosen rate by means of a winch driven with a geared-down synchronous motor. However, the part of the rod above the molten zone can be moved independently of the lower part if desired. Such an adjustment is made, for instance, when the diameter of the molten zone needs changing.

Temperature control was achieved with the use of a Leeds & Northrup Rayotube radiation pyrometer, which indicates the temperature by the magnitude of the voltage developed by a thermopile within it. The voltage output was read on a 0-5 m.v. recorder, and was maintained within the necessary limits by manual adjustment of the R.F. converter. It should be pointed out that the true temperature cannot be read by this or any other conventional optical pyrometer because the correction for emmissivity is large, varies with the composition of the sample, the condition of its surface, and also generally changes on melting of the zone. However, the true temperature per se is not what was needed but rather some indication that the zone temperature lay in the desired temperature range indicated by the Y-B phase diagram (Fig. 3). In each case the temperature must be high enough for formation
Fig. 3. The Yttrium-Boron phase diagram (21)
of a liquid zone; that condition could be determined by visual inspection of the rod (through a high density filter). For incongruently melting compounds it was necessary in addition to stay below the temperature of decomposition. That requirement had to be handled indirectly: if a rod obtained from one run indicated that the zone temperature had been too high, the run was repeated, the voltage output of the Rayotube being maintained at a lower value.

B. Sample Preparation

1. Preparation of rods for zone melting

The yttrium borides were synthesized from yttrium metal (>99.9%) and boron pieces (>99%) of average diameter 3 mm. The necessary quantities of these elements were melted together in an arc melter under argon to form "buttons" weighing about 25 grams. The buttons were remelted into a trough in the water cooled copper plate to form rods about 1/4" in diameter and 4" long, of nearly circular cross section.

2. Procedure followed in a typical zone melting run

For each run, Mason and Cook's (22) zone leveling technique was employed. This method differs from ordinary zone melting in that the latter has a molten zone at the composition of the compound required and at a temperature
above its melting point, while the former uses a zone having a composition and temperature corresponding to a point on an adjacent liquidus line. The employment of zone leveling brings several advantages: First, if the liquidus line in question is relatively steep, it is much easier to maintain nearly constant temperature and zone size; secondly, peritectic compounds can be prepared by zone leveling but not by ordinary zone melting; third, a compound which exists over a range of composition will be produced with uniform composition by zone leveling, but not necessarily by ordinary zone melting.

Before a rod was mounted in the zone melting apparatus it was necessary to break it about one inch from an end so that material of different composition could be introduced. The pieces of rod were mounted in the holder with the break near the bottom, and the system assembled except for the quartz tube and induction coil. The calculated amount of extra material was then placed in the gap, and held there by the weight of the upper part of the rod. The quartz tube and coil were then put in place, the system evacuated to a pressure of 5-10x10^{-6} Torr, and the system outgassed by heating the rod to near 1700°C until the pressure dropped below 5x10^{-6} Torr. The rod was allowed to cool while spectrographically pure argon was admitted to the system. Heating was commenced until a molten zone was formed at the
location of the rod where the break had been. Lowering of the rod was begun at the rate of 0.2 inch per hour. While the run was in progress, both the rod and the recorder were observed every minute or two and adjustments made if necessary. The average run lasted six hours.

3. Preparation of the yttrium borides

\[ \text{YB}_2 \] According to the Y-B phase diagram (21) shown in Fig. 3, \( \text{YB}_2 \) melts congruently near 2100°C. Zone leveling runs were carried out with an yttrium-rich zone and also with a boron-rich zone, both at temperatures above 2000°C. The latter type of run always left crystals of \( \text{YB}_4 \) dispersed throughout the \( \text{YB}_2 \) such that no sample could be cut from it. The runs with an yttrium-rich zone deposited their elongated crystals, sometimes with yttrium in the grain boundaries. When this material was etched with 50:50 nitric acid, washed off and allowed to "age" for a week or two, it became very easy to cleave the crystals into flat elongated plates. X-Ray Laue patterns showed that the cleavage planes were the (001) planes of the hexagonal lattice. It was possible to use two such "splinters" for samples, although they were smaller than the size for which the sample holder was designed. (Any sample of length, width or thickness smaller than 1 cm., .2 cm., and .07 cm. respectively needed special adaptation to the sample holder.) These crystals were
the largest that could be obtained in the course of many zone leveling runs. The reason for the fine grained nature of the rods is unknown, but it could be due to an extraordinary sensitivity to impurities, or possibly the result of a phase transformation in the solid.

\[ \text{YB}_4 \] The ease of crystal growth in \( \text{YB}_4 \) is in direct contrast to the case of \( \text{YB}_2 \). One zone leveling run sufficed to produce a large grained rod. The run was carried out with an yttrium-rich zone at a temperature near 2600°C. It was found that the crystals in the rod could be cleaved along the \((001)\) planes of the tetragonal lattice. This cleavage together with spark cutting (to be described later) enabled a satisfactory sample to be obtained. Its length and thickness were less than the dimensions given above, for, although the rod contained large grains, their orientation was unfavorable for obtaining a full-sized sample.

\[ \text{YB}_6 \] This has a cubic structure, and for reasons given in the discussion section, it was considered necessary to obtain single crystals of a cubic material. The compound decomposes peritectically near 2600° and it can be seen from Fig. 3 that a boron-rich zone was the only kind possible. Zone leveling was carried out at a temperature close to the peritectic temperature, a fact that followed from the observation of some \( \text{YB}_4 \) crystals near the ends of the portion that had been melted. The only way that \( \text{YB}_4 \) could have been
formed in the presence of a boron-rich zone was by exceeding the peritectic temperature momentarily. A sample of standard size was cut from the rod with the spark cutter. By visual inspection of the sample it was estimated to contain only two or three grains.

\( \text{YB}_{12} \quad \) In all of the zone leveling runs on \( \text{YB}_{12} \), temperature control was very erratic. The evident reason for this behavior was that the zone absorbed much more power from the R.F. field when liquid than when solid, so that at any power setting the zone tended either to grow too large or to freeze. Manual power adjustments could not be made quickly enough to completely offset these tendencies, and there was no provision for automatic temperature control. In spite of this difficulty it was possible to obtain a sample of \( \text{YB}_{12} \) from one rod. The portion of the rod from which it was cut had frozen rapidly, and there is some evidence that a finely divided phase richer in boron was trapped with the \( \text{YB}_{12} \). The evidence concerning the amount and distribution of the second phase and its effect on the Hall effect measurement is discussed in later sections.

4. \textbf{Cutting samples for Hall coefficient measurement}

A brief description of the sample cutting is included because the method is of recent origin, and is probably the only method which will work for all of these borides. The machine used is a sparkcutter called the Servomet, manufac-
tured by Metals Research Ltd., Cambridge, England. In operation, a rapid series of high voltage D.C. sparks are created between the sample (positive polarity) and the tool, which is usually a piece of 1/32" brass sheet. The sparking takes place in a bath of kerosene. A servomechanism maintains a tool-sample distance such that sparks can repeatedly be formed but it prevents actual contact of the tool and work. This action is accomplished by a motor which moves the tool down toward the sample if the D.C. voltage rises above a certain value (as happens when sparking stops), and raises the tool if the voltage gets too low. If the tool is a flat sheet, the resulting cut is a groove slightly wider than the sheet thickness. Tubes can be used as tools for cutting out cylinders, and hollow tools of rectangular cross section can be fabricated for cutting out rectangular shapes. This type of cutting does not produce large stresses or temperature gradients in the material being cut as does cutting with abrasive wheels. Before the sparkcutter became available, some of the borides were cut with abrasive wheels, often resulting in fracture of the sample.

5. **Preparation of CaB₆, SrB₆ and BaB₆**

If a material is to be checked for the semiconducting property by the usual method of measuring the change of electrical resistivity with temperature, the sample should be a single crystal. In that case the possibility of strange
electrical effects due to grain boundaries need not be considered. The sample must be very pure, since most impurities drastically affect the electrical behavior of semiconductors. On the other hand, the size and shape of the crystal are not critical. It is necessary only to be able to make four separate electrical contacts to it.

It is not possible to synthesize the alkaline earth hexaborides in an arc melter because the vapor pressures of the metals are too high. The reactions can be better carried out in sealed tantalum crucibles, although the highest temperature obtainable then is limited by the ability of the crucible to withstand its internal pressure. A crucible containing metal and boron could be welded shut in a helium atmosphere at no less than 1/2 - 1/3 atmospheric pressure with the available equipment. The trapped helium may then exert two atmospheres of pressure near 1500°C at which temperature the metal inside exerts about one atmosphere pressure. The temperature chosen for a given synthesis was the highest temperature considered safe for the crucible in question. The hexaborides of calcium and barium were prepared by heating a sealed tantalum crucible and reactants at 1000°C for 24 hours. The metal was at the bottom and powdered "amorphous" boron was contained in a smaller crucible in the upper part of the sealed crucible. At the end of the run the partially sintered boride product found in the upper crucible
was consolidated by arc melting. The product of arc melting contained boron as well as the hexaboride, but the latter could be distinguished from the former by its much higher electrical conductivity at room temperature. Hexaboride samples were selected for resistance vs temperature measurement if the entire surface of a fragment of an arc melted “button” showed electrical conductivity. These hexaboride samples were polycrystalline.

Single crystals of SrB$_6$ were obtained by the following procedure: Strontium metal in excess of that required for hexaboride formation, and boron which had been arc melted and crushed to powder were loaded into a 1/4" thick walled tantalum crucible, which was then welded shut under 1/2 atmosphere helium pressure. The tube was put into a vacuum resistance furnace and held for four hours with the bottom of the crucible near 1800°C and the upper part near 1650°C. The mechanism of crystal growth is the transfer of SrB$_6$ from the hotter region to the cooler, where it is less soluble and will precipitate. After the run, the crystals were freed from the excess strontium by dissolving away the latter with dilute acid. About six cubic shaped crystals were obtained, of about 0.2 mm on an edge.

6. Chemical analyses

Samples of the yttrium borides for spectrographic analysis were obtained from the rods from which the Hall
effect samples were cut. In the case of the alkaline earth hexaborides, the samples used for measurement were themselves analysed. The results given in Table 1 are of a semiquantitative nature. It is estimated that the total impurities in each case is less than 1000 ppm.

Table 1. Spectrographic analyses

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<td>ND</td>
<td>VFT</td>
<td>ND</td>
<td>T</td>
<td>VFT</td>
<td>ND</td>
<td>FT</td>
</tr>
<tr>
<td>YB₆</td>
<td>ND</td>
<td>T</td>
<td>VFT</td>
<td>ND</td>
<td>ND</td>
<td>VFT</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
</tr>
<tr>
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<td>ND</td>
<td>VW</td>
<td>ND</td>
<td>VW</td>
<td>T</td>
<td>ND</td>
<td>T</td>
</tr>
<tr>
<td>CaB₆</td>
<td>VW</td>
<td>T</td>
<td>FT</td>
<td>VW</td>
<td>ND</td>
<td>ND</td>
<td>VW</td>
<td>ND</td>
<td>T</td>
</tr>
<tr>
<td>SrB₆</td>
<td>T</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
</tr>
<tr>
<td>BaB₆</td>
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<td>FT</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>FT</td>
</tr>
</tbody>
</table>

aMeaning of symbols: W Weak
VW Very Weak
T Trace
FT Faint Trace
VFT Very Faint Trace
ND Not Detected

C. Measurements

1. Hall effect apparatus

The Hall coefficient $R_H$ for the geometry shown in Fig. 4 is defined by
Fig. 4. Hall effect sample, showing direction of magnetic field ($\vec{B}$), primary current ($\vec{I}$), Hall voltage ($\vec{V}$) and position of Hall voltage probes.
\[ R_H = \frac{E_x}{IB} \]  \hspace{1cm} (1)

where \( E_x \) = electric field in \( x \) direction, in volts/meter

\( I \) = current density, in amperes/meter\(^2\)

\( B \) = magnetic field strength, in webers/meter\(^2\)

If \( w \), \( t \) and \( i \) denote the width, thickness and current respectively, then

\[ E_x = \frac{V_x}{W} \quad \text{and} \quad I = \frac{i}{tw} \]  \hspace{1cm} (2)

where \( V_x \) = transverse voltage

and by substitution we obtain

\[ R_H = \frac{V_xT}{iB} \quad \text{or} \quad V_x = \frac{R_HiB}{t} \]  \hspace{1cm} (3)

In the present work the transverse voltage was not measured directly, but was balanced against a voltage arising from the \( iR \) drop along the sample. Thus

\[ V_y = iR \]  \hspace{1cm} (4)
where \( V_y \) = balancing voltage
\( R \) = a resistance to be determined below

Using the condition of balance that \( V_x = V_y \), we obtain

\[
R_H = \frac{iR}{B}
\]

Note that \( i \) does not appear here, so that the condition for balance is independent of the magnitude or direction of current flow, and alternating current may be used. Methods related to this one for Hall coefficient measurement may be found in a review by Jan (24).

The balancing operation is done with the 10-turn Helipot potentiometer connected as illustrated in Fig. 4. The sliding contact of the potentiometer is electrically equivalent to a movable probe contacting the sample. The Helipot is first set to a position of minimum voltage output for \( B = 0 \) (and therefore \( E_x = 0 \)). With a known magnetic field applied the new null point is found, corresponding to \( V_x = V_y \). The difference in helipot dial readings indicates what fraction of the slide wire has been traversed. That fraction times the total resistance \( R_T \) between the points of the double probe is the resistance \( B \) to be used in Equation 5. The final form of the equation is
The AC Hall effect apparatus is very similar to that used by Read et al. (25). It consists essentially of (a) an oscillator to supply a 95 cps AC current of up to 2.5 amperes to the sample, (b) a narrow band amplifier which amplifies the Hall voltage by a factor of about $10^7$, but is insensitive to frequencies more than 3 or 4 cps above or below 95 cps, (c) a magnet and power supply for fields up to 12.7 Kilogauss ($1.27 \text{ webers/meter}^2$), (d) a DC constant current supply, switch box and potentiometer for measuring $RT$, (e) an oscilloscope for viewing the output of the amplifier, (f) a sample holder, and (g) a balancing Helipot potentiometer. This method differs from Read et al.'s in that they measured $V_x$ directly, and used an extra AC signal (bucking voltage) to balance out a voltage in the Hall leads induced by the magnetic field of the primary current. The bucking voltage was not needed in the present arrangement because the design of the sample holder minimized the induced voltage to the point that no correction for it was needed.

The calibration of the magnet current vs. magnetic field strength was made with a Varian Fluxmeter, which utilizes nuclear magnetic resonance of protons or deuterons. The accuracy of the calibration is better than one part in $10^3$, so
the error in the field strength value is negligible compared with those of the other quantities in Equation 6 used to calculate $R_H$.

The sample holder is partially illustrated in Fig. 5. The primary current is led to the sample by a shielded coaxial cable, and even the sample and the slotted brass tube enclosing it approximate a coaxial configuration. This coaxial geometry minimizes the external magnetic field due to the primary current. The Hall voltage leads are also connected to a shielded cable with all of the conductors coaxial, thus minimizing the voltage induced by external fields. The standard size sample which will fit the holder without special adaptation is of length 9-12 mm, width 2-4 mm and thickness 0.5 - 1.2 mm.

The apparatus was checked by making a measurement on 99.999% pure copper and comparing the result with the value obtained by Chambers (26) on copper of the same purity. The average value found with this equipment was $R_H = -5.0 \pm 0.1 \times 10^{-11}$ meter$^3$/coulomb. The value given by Chambers is $R_H = -4.96 \pm 0.03 \times 10^{-11}$ meter$^3$/coulomb. The standard errors in the Hall coefficients of the borides are larger than that of the copper value, due primarily to the fact that the values of the fractional change in Equation 6 were generally much smaller for the borides than for copper.
Fig. 5. Hall effect sample holder
2. **Hall coefficients of the yttrium borides**

In assessing the total probable error of the measured Hall coefficients it is necessary to consider errors which arise from the measuring operation and errors originating from the condition of the sample. The standard errors listed with the coefficients are of the former type, and were calculated according to a method described by Topping (27), using the estimated probable errors in each of the three quantities appearing in the numerator of Equation 6. (The probable error in $B$ is negligible.) Sources of error of the second kind include impurities in solid solution, second phases, porosity, cracks and, in the case of compounds, departure from the expected stoichiometry. The possibilities of occurrence of such conditions are discussed below for each sample.

The first sample of $YB_2$ that was measured gave a very large standard error because of its irregular thickness and also because the value of the fractional change quantity was small and therefore poorly defined. The value of $R_H$ found for it was $-30.5 \pm 11.5 \times 10^{-11}$. A second sample obtained from the same rod was better in both respects, and for it $R_H = -20.5 \pm 2.5 \times 10^{-11}$. The latter sample showed no evidence of second phases, porosity or cracks. There is evidently no departure from stoichiometry for $YB_2$ for its measured density is very close to the value calculated from its ideal formula weight and lattice constants. Both of the
above Hall coefficients were obtained with the sample oriented with the c axis parallel to the magnetic field.

One sample of $YB_4$ was measured with the result that $R_H = -213 \pm 9 \times 10^{-11}$. The c axis of the crystal was oriented parallel to the magnetic field. The sample was of good quality, containing no cracks, porosity or second phases, but was smaller than the minimum size required by the sample holder. It was adapted for the sample holder by gluing it to a piece of bakelite which was constructed so that the sample-bakelite unit would fit snugly in the slot of the sample holder.

One sample of $YB_6$ was measured twice. For the second measurement it was turned upside down. The $R_H$ values found were $-44.7 \pm 2.2 \times 10^{-11}$ and $-44.6 \pm 2.4 \times 10^{-11}$. The only suspected error due to sample condition was that a defect lattice was thought to be possible, since the sample was deposited from a boron-rich zone, and the compound $LaB_6$ is known to form a defect lattice (12). However, $YB_6$ was found to have very nearly the ideal stoichiometry. This fact was determined by putting the measured density of the sample and the lattice constant into this equation:

\[
\text{formula weight per unit cell} = \frac{(\text{vol. of unit cell in } \text{Å}^3)(\text{density})}{1.6602}
\]  

(7)
The formula weight calculated in this way was 152.96; the value corresponding to ideal stoichiometry is 153.84. The difference in the two values lies within experimental error.

The one sample of YB\textsubscript{12} that was measured gave a value of $R_H = -108 \pm 15.4 \times 10^{-11}$. In addition to a rather large error in measurement, other errors are undoubtedly due to the condition of the sample. In the first place, it was found in the present work that YB\textsubscript{12} does not have the composition to be expected from its formula, but forms a defect lattice. That fact can be corrected for if the density of the YB\textsubscript{12} phase is known, and this point will be explored in more detail later on. A second difficulty is that although this compound has a density of 3.33 grams/cm\textsuperscript{3}, the density of the sample itself was found to be 3.11. This indicates that the sample contains a second phase, or is porous, or both. The second phase, if present, is that labeled YB\textsubscript{50} in Fig. 3, and is non-conducting at room temperature. Since the entire sample appears to be electrically conducting when tested with an ohmmeter, any second phase that is present must be finely divided. Juretschkte et al. (28) derived a relation which can be used to correct the Hall coefficient for porosity or for a finely divided non-conducting second phase:

$$R_m = \frac{(1 - 1/4 \, P) R_0}{1 - P}$$ (8)
where $R_m = \text{measured Hall coefficient}$

$R_0 = \text{corrected Hall coefficient}$

$P = \text{porosity}$

If the difference in density is due to porosity alone, the corrected Hall coefficient becomes $-103 \times 10^{-11}$. If it is assumed to be due entirely to a second phase, the corrected value is $-89 \times 10^{-11}$. Although the numerical accuracy of this measurement of YB$_{12}$ is less than that of the other borides, it nevertheless allows a conclusion to be drawn about the correctness of the theoretical model proposed for YB$_{12}$.

3. **Apparatus for resistance vs temperature measurement**

The available single crystals of SrB$_6$ were nearly cubic in shape and about 0.2 mm on an edge. A sample holder was needed which could maintain four separate electrical contacts at temperatures up to 1200°C. A design which proved successful consisted of a thoria disk 3/8" in diameter and 1/8" thick, through which a number of small holes were drilled. Four pieces of 5 mil tantalum wire were secured to the disk by threading them several times through the holes. Two of these wires were used to strap the crystal to the center of the disk and serve as potential leads. The other two were bent so as to push against opposite sides of the crystal, and were the current leads. The other ends of the four wires were
then connected to 20 mil tantalum wires which led through insulated vacuum seals to the outside of the vacuum furnace. When the holder was mounted in the furnace the sample was about 1/2" from the tip of the Pt-Pt 13% Rh thermocouple.

The resistance furnace used was part of a vacuum system in which a pressure less than 5 x 10^{-6} Torr could be maintained for furnace temperatures less than 1500°C. The heating element was made from strips of 2.5 mil tantalum sheet, and was surrounded by four concentric molybdenum radiation shields. The furnace contained very little ceramic material near the hot zone, so outgassing was kept to a minimum.

4. **Results of resistance vs temperature measurement of SrB_{6}, CaB_{6} and BaB_{6}**

The first few runs on SrB_{6} were done in an atmosphere of helium. The resulting resistance vs temperature curves exhibited only a positive slope from room temperature to 1000°C. When the run was repeated under a vacuum at 2 x 10^{-6} Torr, using a fresh crystal, a negative slope was observed between 725° - 1185°. The crystals heated in helium evidently became contaminated from it. It is not known whether the impurities were contained initially in the helium or were picked up in transferring it to the furnace. The question is not important, for the negative slope obtained under vacuum is enough to establish the fact
that SrB$_6$ is a semiconductor. Polycrystalline samples of CaB$_6$ and BaB$_6$ were run under helium, and negative slopes obtained. These were probably less susceptible to contamination than the SrB$_6$ sample because they were both much larger pieces.

All semiconducting materials, if they are pure enough, have a temperature range in which the resistivity decreases with increasing temperature. This is called the intrinsic range, and in it the resistivity $\rho$ can be represented by the equation

$$\rho = \rho_0 e^{\frac{\epsilon}{kT}}$$

where $\rho_0$ = a constant

$k$ = Boltzman's constant

$T$ = temperature, °K

$\epsilon$ = activation energy

Therefore, a plot of $\ln \rho$ vs $1/T$ should be a straight line of slope $\epsilon/k$. If $R$ (resistance) values are used instead of resistivity the slope will be the same. Plots of $\ln R$ vs $1/T$ are shown in Fig. 6. The $\epsilon$ values obtained from the slope are: CaB$_6$, 0.20 electron volts; SrB$_6$, 0.19 electron volts; BaB$_6$, 0.06 electron volts.

5. Other quantities measured in the present study

The lattice constants of many of the compounds were remeasured to check on published values. No serious
Fig. 6. Resistance-temperature behavior of the alkaline earth hexaborides
discrepancies arose. It should be mentioned that two widely different sets of lattice constants have been reported for YB₂ (21, 29). The smaller set (21) were found to be correct, since the theoretical density of YB₂ calculated from them is very close to the density measured in the present work. The correct set of lattice constants can be found in Table 2.

Resistivities of most of the borides are listed in Table 2. The values for the alkaline earth hexaborides depend entirely on the impurity contents of the samples. They are only approximate values since the sample dimensions were quite irregular. The relatively high values for these are characteristic of semiconductors.

To obtain resistivity values for the yttrium borides the only extra measurements necessary were those of the sample width and the distance of separation of the points of the double probe. The quantities R₁ and t were already measured for calculation of the Hall coefficient. The only extra samples measured were one of polycrystalline (unetched) YB₂ and a single crystal of YB₄ measured for current flow parallel to the c axis. The difference in the values for polycrystalline YB₂ and for the single crystal are believed to be related to purity rather than crystal orientation. It was mentioned earlier that etching had resulted in a kind of embrittlement of the YB₂ rod. If the embrittlement were caused by hydrogen entering the YB₂ lattice, then the resis-
tivity would be raised, even by very small amounts of hydrogen. On the other hand, the Hall coefficient would be affected very little by the presence of hydrogen in solution, since the coefficient depends only on the total number of free electrons in the case of \( \text{YB}_2 \). (This statement is justified in the discussion section.) The resistivity given for \( \text{YB}_{12} \) is probably too high also, because of the presence of voids or a non-conducting phase.
Table 2. Miscellaneous data for the borides studied

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Lattice constants, A</th>
<th>Resistivity, Ω-cm</th>
<th>Type of resistivity sample</th>
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</thead>
<tbody>
<tr>
<td>CaB$_6$</td>
<td>Simple cubic</td>
<td>4.1524±.0007</td>
<td>0.1</td>
<td>Polycrystalline</td>
</tr>
<tr>
<td>SrB$_6$</td>
<td>Simple cubic</td>
<td>4.197 ±.001</td>
<td>0.216</td>
<td>Single crystal</td>
</tr>
<tr>
<td>BaB$_6$</td>
<td>Simple cubic</td>
<td>4.2706±.0004</td>
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<td>---</td>
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<tr>
<td>YB$_2$</td>
<td>Hexagonal</td>
<td>3.298</td>
<td>3.843 (21)</td>
<td>Polycrystalline</td>
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<tr>
<td>YB$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YB$_4$</td>
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<td>7.111</td>
<td>4.017 (21)</td>
<td>Polycrystalline</td>
</tr>
<tr>
<td>YB$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YB$_6$</td>
<td>Simple cubic</td>
<td>4.103 ±.001</td>
<td>40.5±1.6x10^{-6}</td>
<td>Polycrystalline</td>
</tr>
<tr>
<td>YB$_{12}$</td>
<td>Face centered</td>
<td></td>
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III. DISCUSSION

A. Description of the Theoretical Model Used to Interpret the Results

As was stated in the introduction, the purpose of these measurements is to determine the number of bound electrons in the various types of borides so that a comparison could be made with the theoretical models proposed by Lipscomb and others. Use is made of the semiconducting property by saying that in the semiconducting borides all of the valence electrons of the boron atoms and of the metal atoms are bound, so that it is necessary to establish only that the boride in question belongs to the class of semiconducting materials. For the metallic type borides we need to find the number of "free" electrons and subtract that from the total number of valence electrons to find the number desired. Hence we need a means of converting the measured Hall coefficients into the number of free electrons per metal atom (or per unit cell). The equation to be used is based upon, and derived from, a particular model for conduction ("free") electrons. It is important to realize that this formula cannot be applied to every case, and in deciding whether or not it can be used in a particular case, we will choose criteria from the free electron theory of metals in the form in which it is currently
used (30).

A very brief outline of the pertinent part of the free electron theory will now be presented so that we can define the quantities needed to interpret the data. First of all, in a solid the electrons which are free to move under the influence of an electric field are assumed to have a wave length \( \lambda \) associated with them satisfying the DeBroglie relation:

\[
\lambda = \frac{\hbar}{\bar{p}}
\]

where \( \hbar = \text{Planck's constant} \) \hspace{1cm} (10)

\( \bar{p} = \text{momentum} \)

If the energy is given by

\[
E = \frac{1}{2} mv^2
\]

it can be shown that

\[
E = \frac{\hbar^2 |\vec{k}|^2}{2m}
\]

where \( \hbar = \frac{h}{2\pi} \) \hspace{1cm} (12)

\( \vec{k} = \frac{2\pi}{\lambda} \), called the wave vector

\( m = \text{mass of the electron} \)

Another result of the theory is that the electron can
have only certain discreet values for $\vec{k}$, thereby limiting the allowed values of $E$, since these are related by Equation 12. If the solid under consideration is a cube of side $L$, the allowed values of $\vec{k}$ are given by

$$\vec{k} = \frac{2\pi}{L} \vec{n}$$

where $|\vec{n}| = \sqrt{n_1^2 + n_2^2 + n_3^2}$, (13)

$n_1, n_2, n_3$ are integers

The next assumption of the theory is that the electrons are distributed among the possible energy states according to Fermi-Dirac statistics. This means that only two electrons may have one of the allowed $\vec{k}$ values, and at absolute zero the electrons occupy all such states up to a given energy value, above which the states are all empty. It is most convenient to regard the situation in terms of a three dimensional plot, in which the coordinate axes are the components of the wave vector in $x$, $y$ and $z$ directions in space. Thus a point $\vec{k}$ on the $k_x$ axis corresponds to a wave of wavelength $2\pi/k$ traveling in the $x$ direction, and it must be equal to one of the values $\frac{2\pi n_1}{L}$ given by Equation 13. It can be seen from Equations 12 and 13 that all $\vec{k}$ values of a given energy define a surface in this "$k$-space" which is approximately spherical. Therefore the electrons which occupy all states up to a given energy define a spherical surface,
called the Fermi surface. The volume of the sphere is such that \( \frac{N}{2} \) available states are contained within it, where \( N \) is the total number of electrons in the solid. Although this model is derived for a solid at absolute zero it remains a very good approximation at room temperature.

One more feature must now be added to the picture. The crystal in which the electrons move is a structure periodic in three dimensions and the electric potential due to the ion cores is therefore periodic. It is well known that waves moving through any periodic structure interact strongly with it when the wave length of the waves approaches the repeat distance of the structure. This phenomenon, which is responsible for diffraction of X-rays by crystals, is assumed to hold for the interaction of the wavelike electrons with the lattice, and the same equation, Bragg's Law, is used for both kinds of diffraction. The concept of the reciprocal lattice is also borrowed from crystallography, with slight modification. If \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) are the unit all axes, then the axes \( \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3 \) of the reciprocal lattice are given by

\[
\mathbf{b}_1 = \frac{2\pi (\mathbf{a}_2 \times \mathbf{a}_3)}{V}
\]

\[
\mathbf{b}_2 = \frac{2\pi (\mathbf{a}_1 \times \mathbf{a}_3)}{V}
\]

where \( V \) = volume of the unit cell

\[\text{(14)}\]
\[ \hat{b}_3 = \frac{2\pi(\hat{a}_1 \times \hat{a}_2)}{V} \]

The crystallographers leave out the factor $2\pi$. The reciprocal lattice is a lattice of points each of which represents a set of parallel planes in the real lattice. It can be shown (29) that with the above definition of the reciprocal lattice the condition for Bragg reflection is

\[ |\hat{n}|^2 = 2 \hat{k} \cdot \hat{n} \quad \text{where} \quad \hat{n} = \text{a vector from the origin (a reciprocal lattice point) to any other lattice point} \]

\[ \hat{k} = \text{wave vector} \]

The $k$-space discussed earlier is now put into the same plots as the reciprocal lattice, with a reciprocal lattice point at the origin of the $k$-space. The reflection condition expressed by Equation 15 is satisfied if the point for $k$ lies on any plane which is a perpendicular bisector of a reciprocal lattice vector $\mathbf{n}$. The smallest polyhedron enclosing the origin and made up of such planes defines the first Brillouin zone of the lattice. If the Fermi surface touches a zone boundary, the electrons represented by the places of contact cannot move through the crystal.
Equation 12 suggests that the number of \( \mathbf{k} \) values, and therefore the size of the Fermi sphere, depends on the size of the solid under consideration, but that is not the case. The first Brillouin zone can be shown to contain \( N \) states, or places for \( 2N \) electrons, where \( N \) is the total number of atoms in the crystal. Doubling the size of the crystal doubles the number of states, but also doubles the number of electrons with which to fill them. Therefore the position of the Fermi surface in the zone is independent of the size of the solid.

We now list some conclusions (without proof) of the free electron theory outlined above: (a) If the Fermi surface touches a zone boundary some of the electrons may overlap into the next zone, that is, some electrons may have \( k \) values greater than those corresponding to the boundary (Equation 15). (b) If the lattice planes represented by that zone boundary contain a high density of atoms, the resulting strong tendency for reflection (avoidance of overlap) may be such that the Fermi surface is strongly distorted. Planes of low atom density may allow overlap with little distortion of the sphere. (c) If the Fermi surface is spherical and lies entirely within one zone, the Hall coefficient is given by

\[
R_H = \frac{1}{ne}
\]

where \( n = \) number of electrons/ meter\(^3\) and \( e = \) electronic charge in coulombs
\( R_H \) is negative for "good" metals, since \( e \) is negative for electrons. (d) If a zone is nearly full and the next higher zone empty (no overlap) the above formula may hold, with \( n/2 \) as the number of empty states in the zone, \( R_H \) becoming positive. (e) If more than one zone is occupied, the formula would not apply unless the effect of the electrons in one of the zones was completely dominant.

B. Interpretation of Results

1. \( \text{MB}_2 \)

The structure of \( \text{YB}_2 \) is simple hexagonal, with one yttrium atom and two boron atoms per unit cell. Each boron atom has three boron nearest neighbors coplanar with it at 1.9 Å. A plane of boron atoms would look like a sheet made up of hexagons, as illustrated in Fig. 7.

Lipscomb and Britton's model (17) for the diborides is one which is isoelectronic with graphite. Thus for each boron atom in a plane there are four electrons present in the B-B bonds. A diboride formed from a divalent metal would have exactly the number of electrons required for the B-B bonds, and \( \text{YB}_2 \) should have one free electron per Y atom.

The reciprocal lattice and Brillouin zone for \( \text{YB}_2 \) was constructed, and drawn to scale. A circle representing the projection of a Fermi sphere corresponding to one electron
Fig. 7. Crystal structure of four boride types, projected on the planes indicated. Filled circles represent boron atom positions, open circles metal atom positions. (The circles do not indicate atom sizes.) Dashed lines are drawn between covalently bonded boron atoms. Full lines enclose one face of a unit cell.
per yttrium atom was put into the drawing. The circle as drawn barely overlapped the zone boundaries in the direction of the c axis. Assuming that there is one electron per yttrium atom, free electron theory is not able to predict whether or not overlap will take place. However the theory does indicate the order of magnitude of the Hall coefficient for each possibility. If overlap occurs, the Hall coefficient should be much higher than that given by Equation 16. Without overlap the expected value is of the same order as that given by Equation 16. Using Equation 16 the calculated value of $R_H$ for one electron per yttrium atom is $-22.65 \times 10^{-11}$ meter$^3$/coulomb; the measured value is $-20.5 \pm 2.5 \times 10^{-11}$. This leads to the choice of a non-overlapping Fermi surface, as depicted in Fig. 8.

It was stated earlier that the sample was oriented with the c axis parallel to the magnetic field. With this orientation the electric and magnetic fields do not accelerate the electrons in the direction of the c axis. If the electrons had a component of acceleration in that direction some of them would undergo Bragg reflections at the zone boundary. That added feature would render the use of Equation 16 very dubious, in spite of non-overlap. For the orientation chosen, the question does not arise.

Having shown that the measured Hall coefficient of $YB_2$ is consistent with a choice of one electron per yttrium atom,
Fig. 8. Brillouin zone of YB₂, showing probable shape of the Fermi surface (not drawn to scale)
the expected result of alternative models should be indicated. The most likely alternative is a model in which each boron atom needs only three electrons instead of four, providing enough electrons for single covalent B-B bonds. In that case there would be three free electrons per yttrium atom. The corresponding Fermi surface in this case was found to completely enclose the first brillouin zone and lie in higher zones. The Hall coefficient for such a situation could be that given by Equation 16 only by sheer coincidence.

One more piece of evidence is available to support the conclusion that the boron layers are isoelectronic with graphite. Silver and Bray (31) measured some nuclear magnetic resonance effects in TiB$_2$ and ZrB$_2$, which are isomorphous with YB$_2$. They interpret their results as indicating a clear preference for the graphite electronic structure of the boron atoms in these compounds.

2. MB$_6$

The hexaboride case will now be treated instead of that of the tetraboride, because a discussion of the latter is easier with the hexaboride results in mind. The hexaboride structure illustrated in Fig. 7 is simple cubic. At each corner of the unit cell are six boron atoms arranged at the vertices of a regular octahedron. The nearest distance between boron atoms within an octahedron is the same as the distance between boron atoms on neighboring octahedra, 1.71 Å.
The metal atom is in the center of the unit cell.

Theoretical treatments by Longuet-Higgins and Roberts (15), Eberhardt et al. (3) and Yamazaki (32) all result in the conclusion that each boron octahedron requires 20 electrons, 18 from the boron atoms and two from the metal atom. Out of the total of 20 electrons, 14 supposedly form bonds within the octahedron and six go into external two electron covalent bonds to neighboring octahedra.

The above model is supported by the semiconducting nature of the alkaline earth hexaborides established in the present work. Strictly speaking the property was established only for SrB\(_6\) because the measurement was done on a single crystal; however the data for CaB\(_6\) and BaB\(_6\) are so similar to those for SrB\(_6\) that all can be regarded as semiconductors. There has been one previous report of semiconducting behavior of SrB\(_6\), by Eubank et al. (33). The \(\ln R\) vs \(1/T\) curve published by them corresponds to \(\epsilon = 0.51\) electron volts. (In the present work, \(\epsilon\) is found to be 0.19 electron volts.) Their results are hard to assess, since the sample they used was not well characterized with regard to purity. Their sample was made by reduction of Sr0 with boron, and if the reaction happened to be incomplete, the presence of free boron would have a strong influence on the resistance-temperature measurement, since boron itself is a semiconductor with \(\epsilon = 1.45\) electron volts.
A Fermi sphere corresponding to one electron per yttrium atom lies completely within the first Brillouin zone of \( \text{YB}_6 \) and we would therefore expect Equation 16 to be valid. The value of \( R_H \) thus calculated is \(-43.2 \times 10^{-11} \) meter\(^3\)/coulomb, which compares well with the measured value of \(-44.7 \pm 2.2 \times 10^{-11} \), and adds more weight to the evidence supporting the proposed model.

3. \( \text{MB}_4 \)

The tetraborides crystallize in the tetragonal crystal system. Each unit cell contains four metal atoms and 16 boron atoms. Twelve boron atoms are present as two octahedral configurations as are found in \( \text{YB}_6 \), and the remaining four link octahedra together in the basal plane, such that each of these four has three boron nearest neighbors. Two of the latter nearest neighbors belong to octahedra. In the \( c \) direction, octahedra are bonded directly to one another, as in \( \text{YB}_6 \).

The electron requirements of the boron atoms in this structure were derived by Lipscomb and Britton (17) as follows: The two octahedra in a unit cell are assumed to require 20 electrons apiece as in the hexaboride case. If the four non-octahedral boron atoms formed two-electron bonds with the nearest neighbors in octahedra and a four-electron bond with the non-octahedral nearest neighbor, then each of the four atoms in question require four electrons. This adds
16 electrons to the 40 from octahedra, making a total of 56 electrons per unit cell. Now it is easily seen that 48 electrons from the boron atoms leave two electrons to be supplied by each metal atom to make up the total of 56.

The above model derives partial support from the fact that CaB$_4$ (12) and BeB$_4$ (11) have been reported to exist and be isomorphous with all of the other tetraborides. MgB$_4$ has also been reported to exist (11), but no structure data given. If semiconductivity were established for one of these the model given above would be confirmed. Unfortunately, it is not possible to settle this as the electrical properties of these compounds are apparently unknown. As was stated in the introduction, previous experience with alkaline earth-boron systems indicated that it would be very difficult to prepare crystals of the tetraborides suitable for measurement. Such an approach was not taken in the present work because it did not offer a reasonable chance for success.

When the reciprocal lattice for YB$_4$ was constructed and a Fermi sphere corresponding to one electron per yttrium atom drawn in, it was found that the sphere overlapped into four zones. One would therefore not expect Equation 16 to apply. Certainly the number obtained from Equation 16, $-31.8 \times 10^{-11}$, does not even approximate the experimental value of $-213 \pm 9 \times 10^{-11}$. There is no straightforward way to obtain a calculated value for $R_H$ for comparison with the experimental
value. The most that can be said is that the Fermi surface as drawn does not contradict the measured value. (It might, for instance, if all of the zones occupied were nearly full, which would lead one to expect a positive instead of a negative value for $R_H$.)

It should not be supposed that the present work lends no support to the proposed model for $YB_4$. The octahedral boron configurations were shown to require 20 electrons apiece in the hexaborides and there is no reason to suppose that the situation would be different for tetraborides. The non-octahedral boron atoms are similar to those in $YB_2$ in that they have three coplanar boron nearest neighbors. This similarity of environment of the atoms in the two structures argues in favor of similar electron requirements, i.e. four electrons per atom. If the analogies described hold true then the electronic structure of the proposed model would appear valid.

4. $MB_{12}$

The Bravais lattice of the dodecaborides is face-centered cubic (33). The structure can be regarded as being built up of $B_{12}$ units having boron atoms at the vertices of a cube-octahedron (a polyhedron having six square faces and eight equilateral triangular faces, and resembling a cube with the corners cut off). The metal atoms are located in large interstices formed when the $B_{12}$ units pack together.
The electron requirements calculated by Lipscomb and Britton (17) for this structure are the following: Bonds internal to the polyhedron require 26 electrons. All bonds between polyhedra contain two electrons apiece, one from each polyhedron. Thus 38 electrons are required, and since the boron atoms supply only 36 of these, the remaining two must come from the metal atom.

One would expect to find that the composition of the YB\textsubscript{12} would be that calculated from the formula. In the present work, that was found not to be the case, as the theoretical density of YB\textsubscript{12} is 3.442 grams/cc.; the measured value is 3.33. A boride sample of the theoretical composition of YB\textsubscript{12} was heated to just below the peritectic temperature for an hour, after which only two phases were present, YB\textsubscript{6} and YB\textsubscript{12}. It is reasonable to assume that the true composition is more boron-rich than the theoretical one because not all of the possible positions are occupied by yttrium atoms. This is thought to be related to the facts that metal atoms larger than yttrium do not form a dodecaboride, and when smaller metal atoms form this compound the lattice constant is smaller (14). (For YB\textsubscript{12}, a = 7.500 Å; for ZrB\textsubscript{12}, a = 7.408 Å.) If the lattice must stretch to accommodate the yttrium atoms, then there may be no energy difference in putting in more than a certain number of them, and no "driving force" for a reaction. On the assumption of
a defect lattice, the formula weight per unit cell was calculated from the lattice constant and measured density. The formula weight corresponds to 3.68 yttrium atoms per unit cell.

According to the proposed model, if there were four yttrium atoms per unit cell, four free electrons per unit cell would be present. The Fermi sphere corresponding to that electron concentration lies entirely within the first Brillouin zone. Since there are actually fewer electrons available, Equation 16 should still be valid. A value of 3.68 yttrium atoms per unit cell corresponds to an electron concentration of 3.05 electrons per unit cell. The calculated Hall coefficient in that case is $-86.5 \times 10^{-11}$. The experimental value had to be corrected for non-conducting porosity, but since it is unknown whether voids or a boron phase is present, the corrected value could lie anywhere in the range from $-89 \pm 15 \times 10^{-11}$ to $-103 \pm 15 \times 10^{-11}$. This degree of agreement between observed and calculated Hall coefficients is sufficient to verify the proposed model, for the following reason: an alternate model of a different electron requirement would have at the very least one more or one less energy level per polyhedron of 12 boron atoms, or a difference of two electrons. If it required two more, then there would not be sufficient valence electrons; if it required two fewer electrons, there would be 11.05 free electrons per unit cell.
instead of 3.05. The Hall coefficient corresponding to the former number is \(-26.4 \times 10^{-11}\).

C. Possible Direction of Future Work on Borides

The present work is believed to contribute to the study of borides in two respects. First, the practice of using samples prepared by powder metallurgy techniques can be avoided because zone melting provides material of higher quality in nearly all respects, and is capable of yielding single crystals in some cases. The current literature of experimental solid state physics reveals that the meaningful measurements can come only from samples which are well characterized with regard to purity and physical form. A corollary of that statement is that measurements of anisotropic properties should be made on single crystals. Perhaps the quality of measurements made on borides can now be raised toward the level of the measurements on other materials studied in the field of solid state physics and chemistry.

The second contribution of this work is that it justifies a greater confidence in the LCAO method as a means of describing the electronic structure of a large number of boron-containing materials. A great deal of progress may be expected in any field for which there is a workable theory.
On the practical side, many new compounds may be predicted, and some of their properties estimated, and presently known compounds may be better exploited for their useful properties. On the theoretical side, the knowledge gained in one field can often be extended to neighboring fields. For example, the LCAO method might be applied to the beryllium atoms in MBe$_{13}$ type compounds. The structure of these (35) is reminiscent of those of some borides, since there are icosahedral groups of Be atoms in the structure. These groups have a Be atom in the center in contrast to boron icosahedra, in which there is no central atom. Other neighboring fields are ternary metal-boron compounds with Be, C, N, O, or Si; and some classes of intermetallic compounds. The number of compounds involved is greater than 1000. There is a good possibility that bonding concepts arising from the LCAO method will eventually allow the field of "electron-deficient" materials to be as well developed as is that of organic chemistry.
IV. SUMMARY

A new method for floating zone melting by induction heating has been developed. It has been used for preparation of samples of YB_{2}, YB_{4}, YB_{6} and YB_{12} for Hall effect measurement. The samples of YB_{2} and YB_{4} were single crystals, and the other two polycrystalline.

The Hall coefficient of each compound was measured; the single crystal samples were oriented with the c axis of the crystal parallel to the magnetic field. The results for YB_{2}, YB_{6} and YB_{12} agree within experimental error with theoretical values calculated with the assumption that in each of the three borides there is one free electron per yttrium atom. The free electron theory does not offer a means of calculating a theoretical value for YB_{4}. On the basis of structural similarities between YB_{4} and YB_{6}, and also between YB_{4} and YB_{2}, it is suggested that in YB_{4} there is also one free electron per yttrium atom.

Resistivity versus temperature data were obtained for a single crystal of SrB_{6}, and for polycrystalline samples of CaB_{6} and BaB_{6}. The results establish that these are semiconductors.

All of the above measurements were made in order to judge the correctness of certain proposed models for the electronic structure of borides of the types MB_{2}, MB_{4}, MB_{6}.
and $\text{MB}_1$. The models had been derived by application of the method of linear combination of atomic orbitals (LCAO) to the boron-boron bonds in each structure. The measurements made in the present work are in agreement with the proposed models in each case, and so not only are the specific models supported thereby, but also the principle of applying the LCAO method to many related materials tends to be justified.
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