Electron Requirements of Bonds in Metal Borides[*]

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Abstract—Electrical measurements have been made on CaB_6, SrB_6, BaB_6, YB_2, YB_4, YB_6, and YB_{12} for the purpose of testing models of the electronic structure of the boron atoms in the four boride types represented. The compounds CaB_6, SrB_6, and BaB_6 were found to be semiconductors. The Hall coefficients of YB_2, YB_6, and YB_{12} were measured and found to correspond to one free electron per yttrium atom in each compound. The Hall coefficient of YB_4 was also measured, but could not be interpreted because the free electron theory does not provide a theoretical value for comparison with experiment. The results are in agreement with the models proposed.

INTRODUCTION

The study of electron-deficient boron hydrides has benefited greatly from the application of the method of linear combination of atomic orbitals (LCAO) to the study of the bonds within the molecules. The increase in understanding has enabled many strange varieties of structure to be viewed within a coherent framework of one theory, and allowed

new compounds to be predicted, many of which were later found to exist.[1]
Many of the known borides are electron-deficient in the same sense as
are the boron hydrides, but are not as well understood as the latter.
The structure types which are electron-deficient are MB_4, MB_6, MB_{12},
some reported borides of unknown structure such as YB_{50},[2] and the
various forms of elemental boron. LCAO studies have been published
for MB_6,[3,4], MB_{12},[5] and elemental boron.[5,6] The recent discussion
by Lipscomb and Britton[5] covered all of the above boride types except
for YB_{50}, and in addition included MB_2, for which a bonding scheme
was suggested.

The present work was initiated in order to provide experimental
evidence with which to evaluate the models for the electronic structure of
the boride types MB_2, MB_4, MB_6, and MB_{12}. (The models themselves
will be described later.) The methods for experimentally testing the
LCAO models for the borides differ in principle from those which are
useful for boron hydrides. All of the electrons in boron hydride molecules
are considered to take part in the co-valent bonding, and a knowledge of
the composition and structure usually allows a fair test of the theoretical
model to be made. For the borides, metals of different valence often can
form the same boride type, so that one cannot assume that all valence
electrons are used for bonding in each case. The assumption that the
boride formed from the metal of lowest valence is the one for which all
of the metal atom electrons are needed for B-B bonds, is also open to
question unless reinforced with other information, because an iso-
morphous boride of a metal of yet lower valence may exist but be

undiscovered. In the present work the method used for judging the proposed models is to find out whether the boron atoms have the requisite number of electrons suggested by the theory. It is implied in the theory that the electrons participating in B-B bonds are bound, and unable to move under the influence of an electric field unless somehow excited (by thermal energy 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 all of the valence electrons are bound, and if some are not bound it is often possible to determine the number of "free" electrons per atom. The former condition corresponds to semiconducting behavior, which is reflected in the electrical resistance-temperature relationship. In the latter case the free electron concentration is often obtained directly from the Hall coefficient. Accordingly, these two types of electrical properties were chosen for measurement on suitable borides. The proposed models[5] are such that any of the four boride types would be expected to 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 since 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 because information on the yttrium-boron phase diagram[2] was available (see Fig. 1).
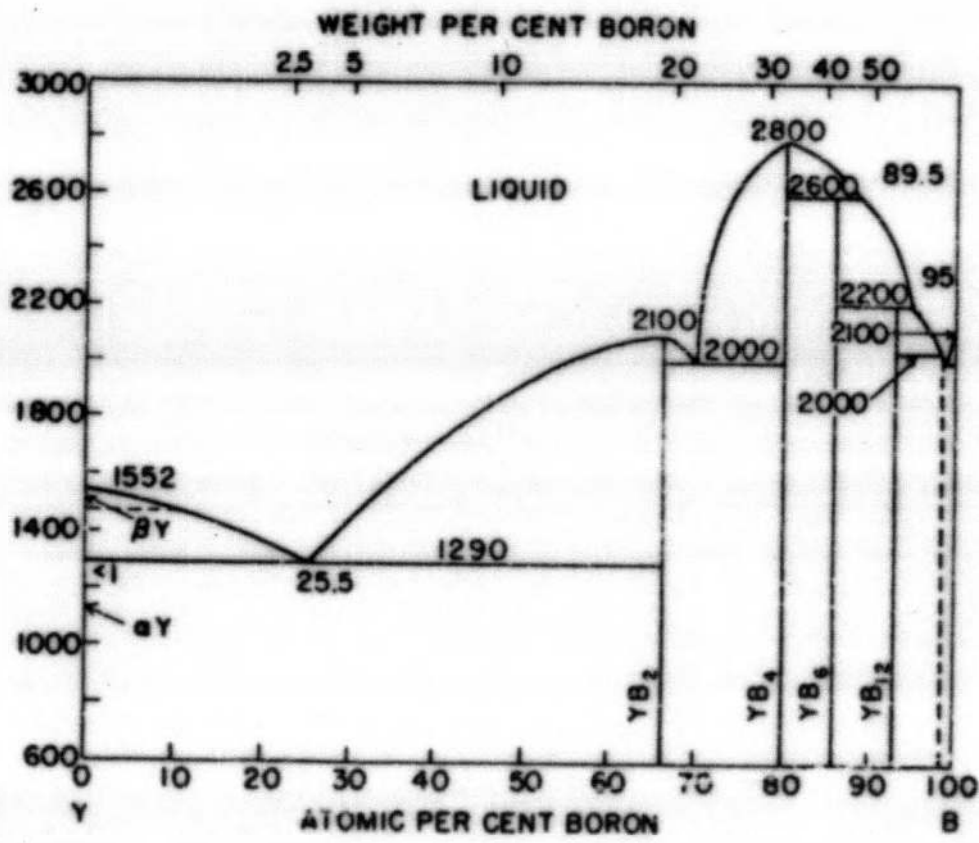
Fig. 1. The yttrium-boron system (see footnote 2).

The preparation of boride samples for Hall effect measurement is difficult 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. It was necessary to develop a new method for floating zone melting in order to obtain material of suitable form and purity. The details of that method are being published separately, and only the data obtained from the samples will be described here.

EXPERIMENTAL DETAILS

Sample Preparation

The method chosen for the preparation of the yttrium borides was floating zone melting. Some of the advantages to be gained by its use were: a) No crucible is required; b) Slow rates of solidification could be achieved by controlling the traverse rate of the zone along the rod; c) Mason and Cook[7] recently showed that single-phase bulk samples of peritectic compounds could be prepared by a slight modification of the zone melting procedure. (YB_6 and YB_{12} are peritectic compounds.) Condition b) is likely to result in large grains from which single crystals might be cut. The only previously described heat source for floating zone melting at the necessary temperatures (see Fig. 1) is electron bombardment, which was ruled out in this case by the fact that in the vacuum necessary for its operation the borides change composition

at temperatures near their melting points. The method that was developed in order to attain the necessary temperatures in an argon atmosphere used an induction coil coupled with a special type of RF step-down transformer called an eddy current concentrator.

The yttrium borides were synthesized from yttrium metal (99.9%) and boron pieces (99.0%) 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 g. The buttons were remelted into a trough in the water-cooled copper plate to form rods about 1/4 in. in diameter and 4 in. long, of nearly circular cross section.

For each run, Mason and Cook's[7] zone leveling technique was employed. This method differs from ordinary zone melting in that the latter has a molten zone of 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. In zone leveling, movement of the zone causes the compound in question to precipitate out of solution; in ordinary zone melting, solidification is by normal freezing. If the rate of zone travel is low enough, the compound will come out of solution on crystals already present instead of precipitating as separate crystals, and allow a single phase bulk sample of the compound to be grown. The zone will maintain its composition as it moves, since the material going into solution at one liquid-solid interface has the same composition as the compound coming out of solution at the other interface. The employment of zone leveling brings several advantages: first, if the liquidus line in question is

relatively steep, it is much easier to maintain constant temperature and zone length; second, 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.

The desired size and shape of a sample for Hall effect measurement was that of a flat rectangular slab of length, width, and thickness approximately 1.1, 0.3 and 0.1 cm respectively. The necessary cutting was done very satisfactorily with a Servomet sparkcutter (Manufactured by Metals Research Ltd., Cambridge, England). In the cases of YB_2 and YB_4 crystals could be parted by cleavage along 001 planes, and the shaping finished by sparkcutting.

Preparation of CaB_6, SrB_6 and BaB_6

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 atm pressure with the available equipment. The trapped helium
may then exert two atm of pressure near 1500°C at which temperature
the metal inside exerts about one atm 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 hr. 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 con-
ductivity 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 hexa-
boride 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 tantalum crucible with $\frac{1}{4}$" walls which was then welded
shut under 1/2 atm helium pressure. The tube was put into a vacuum

resistance furnace and held for 4 hr with the bottom of the crucible near 1800°C and the upper part near 1650°. 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.

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 analyzed. The results given in Table I are of a semiquantitative nature. It is estimated that the total impurities in each case is less than 1000 ppm.

TABLE I. Spectrographic analyses.

Sample	Cu	Fe	Mg	Si	Ta	Ti	W	Zn	Zr
YB_2	VFT[a]	VW	FT	VW	VW	FT	W	ND	T
YB_4	ND	T	ND	VFT	ND	T	VFT	ND	FT
YB_6	ND	T	VFT	ND	ND	VFT	ND	ND	FT
YB_{12}	T	FT	ND	VW	ND	VW	T	ND	T
CaB_6	VW	T	FT	VW	ND	ND	VW	ND	T
SrB_6	T	ND	ND	FT	ND	ND	ND	ND	FT
BaB_6	T	FT	FT	FT	ND	ND	ND	ND	FT

[a]Meaning of symbols:
W	Weak	FT	Faint Trace
VW	Very Weak	VFT	Very Faint Trace
T	Trace	ND	Not Detected

Measurements

The Hall coefficients were measured by an ac method very similar to that used by Read et al.[8] It consists essentially of a) an oscillator to supply a 95 cps current to the sample; b) a narrow band amplifier which amplifies the Hall voltage by a factor of about 10^7; c) a magnet and power supply for fields up to 1.27 webers/meter^2. The equipment includes accessories such as a constant current supply for measuring resistivity, and an oscilloscope for viewing the amplified Hall voltage. This method differs from that of Read et al. in that they measured the Hall voltage directly, whereas here the Hall voltage was balanced against part of the voltage drop along the sample, using a double probe on one side of the sample and a Helipot potentiometer for balancing. In practice, a Helipot setting was found corresponding to minimum gain at zero field. A reading was taken corresponding to a new null position with an applied field. The shift in null position is proportional to the Hall coefficient, which is given by

$$R_H = \frac{(\text{fractional change in null position})tR}{B} \tag{1}$$

where t = thickness of slab

R = resistance of sample between points of the double probe

B = magnetic field strength.

The magnet was calibrated with a Varian Fluxmeter, which employs the nuclear magnetic resonance of deuterons. This method of calibration is such that the error in B may be neglected.

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. in diameter and 1/8 in. 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 in. 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 5×10^{-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.

RESULTS

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,[9] using the estimated probable errors in each of the three quantities appearing in the numerator of Eq. (1). (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.

One sample of YB_6 was measured twice, with the sample inverted for the second measurement. 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.[10] However, YB_6 was found to have very nearly ideal stoichiometry. This fact was determined by putting the measured density of the sample and the lattice constant into the equation:

$$\text{formula weight per unit cell} = \frac{(\text{vol. of unit cell in } \mathring{A}^3)(\text{density})}{1.6602} \quad . \tag{2}$$

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_{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_{12} does not have the composition to be expected from its formula, but forms a defect lattice. A correction for this situation is considered later. A second difficulty is that although this compound has a density of 3.33 g/cm^3, the density of the sample itself was found to be 3.11. This indicates that the sample contains a less dense second phase, or is porous, or both. The second phase, if present, is that labeled YB_{50} in Fig. 1,

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.[11] derived a relation which can be used to correct the Hall coefficient for porosity or for a finely divided non-conducting second phase:

$$R_m = \frac{(1 - 1/4 \ P)R_o}{1 - P} \tag{3}$$

where R_m = measured Hall coefficient

R_o = corrected Hall coefficient

P = porosity.

If the difference in density is due to porosity alone, the corrected Hall coefficient becomes -103×10^{-11}. If it is assumed to be due entirely to a second phase, the corrected value is -89×10^{-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}.

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 2×10^{-6} Torr, using a fresh crystal, a negative slope was observed between 725 - 1185°, evidently due to absence of contamination from the helium. It is not known whether the impurities were contained initially in the helium or were picked up in transferring it to the furnace. Polycrystalline samples of CaB_6 and BaB_6

were run under helium, and negative slopes obtained. These were probably less susceptable 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. In this intrinsic range the resistivity ρ can be represented by the equation

$$\rho = \rho_0 \rho^{\frac{\epsilon}{kT}} \tag{4}$$

where ρ_0 = a constant

    k = Boltzman's constant

    T = temperature, °K

    ϵ = activation energy.

Therefore, a plot of ln ρ vs $1/T$ should be a straight line of slope ϵ/k; the same slope will result if R (resistance) values are used. Plots of ln R vs $1/T$ are shown in Fig. 2. The ϵ values obtained from the slope are: CaB_6, 0.20 ev; SrB_6, 0.19 ev; BaB_6, 0.06 ev.

Other Quantities Measured in the Present Study

The lattice constants of many of the compounds were remeasured to check on published values. No serious discrepancies were observed. It should be mentioned that two widely different sets of lattice constants have been reported for YB_2.[2,12] Densities calculated from these lattice constants indicated the smaller set[2] to be correct. The correct set of lattice constants can be found in Table II.
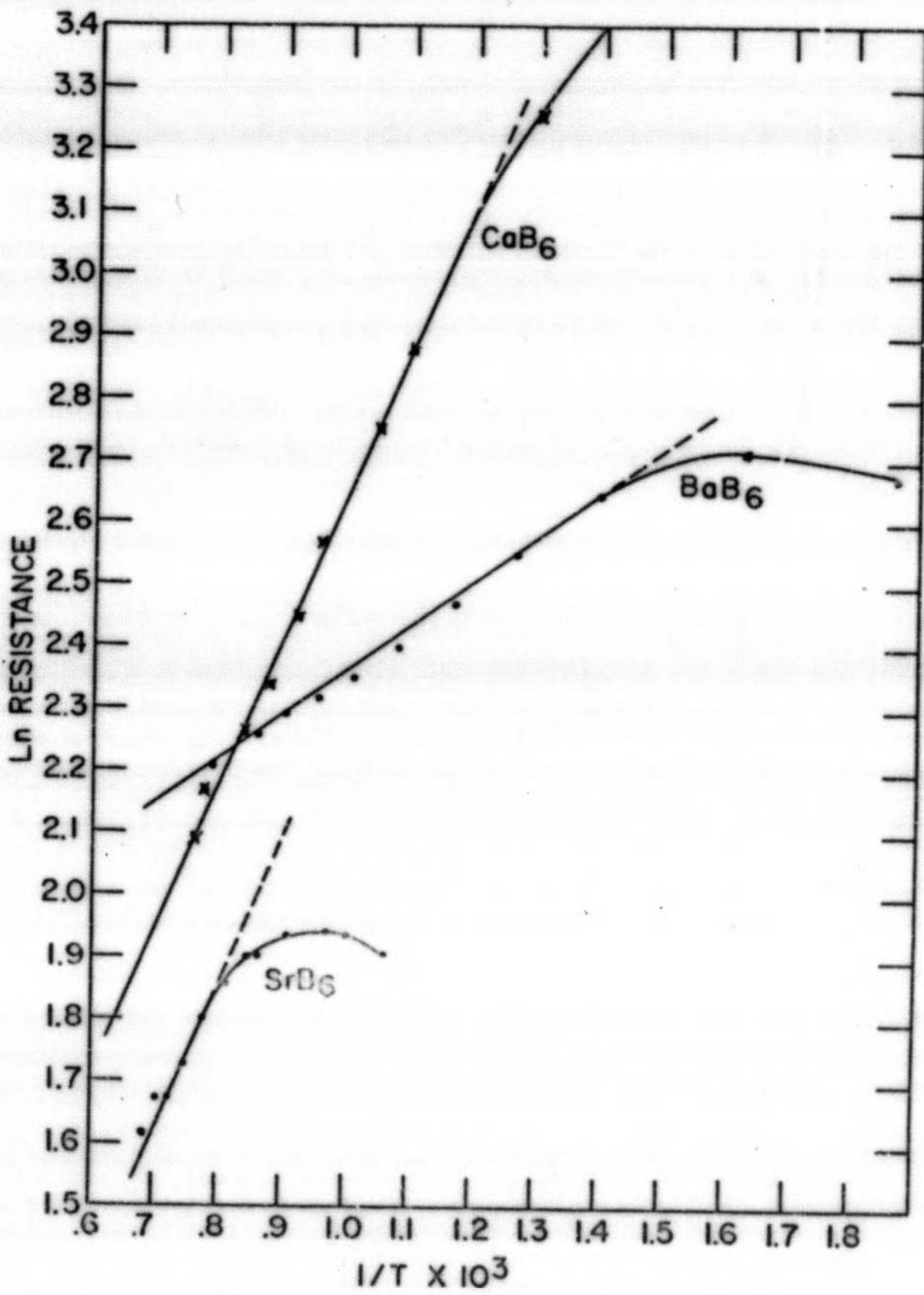
Fig. 2. Resistance-temperature behavior of the alkaline earth hexaborides.

TABLE II. Miscellaneous data for the borides studied.

Compound	Structure	Lattice constants, Å a	c	Resistivity, Ω-cm	Type of resistivity sample
CaB_6	Simple cubic	$4.1524 \pm .007$		0.1	Polycrystalline
SrB_6	Simple cubic	$4.197 \pm .001$		0.216	Single crystal
BaB_6	Simple cubic	$4.2706 \pm .0004$		---	---
YB_2	Hexagonal	3.298	3.843^2		
YB_4	Tetragonal	7.111	4.017^2	$39 \pm 2.6 \times 10^{-6}$	In basal plane
				$28.5 \pm 1.3 \times 10^{-6}$	In basal plane
YB_4				$31.3 \pm 1 \times 10^{-6}$	Parallel to c axis
YB_6	Simple cubic	$4.103 \pm .001$		$40.5 \pm 1.6 \times 10^{-6}$	Polycrystalline
YB_{12}	Face centered cubic	$7.500 \pm .001$		$94.8 \pm 2.7 \times 10^{-6}$	Polycrystalline

Resistivities of most of the borides are also listed in Table I. 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.

DISCUSSION

For the purpose of interpreting the results of the Hall coefficient measurements, the "free" electrons in these compounds are assumed to behave in the same manner as do the conduction electrons in a metal, as described by Ziman.[13] In applying it to the borides, the reciprocal lattice and first Brillouin zone is constructed, and a spherical Fermi surface placed in the center of the zone. The radius of the sphere corresponds to the expected electron concentration. If it happens that the sphere lies completely in the first Brillouin zone then the expected Hall coefficient may be calculated by

$$R_H = \frac{1}{ne}$$

where n = electron concentration, $1/\text{meter}^3$

e = change on the electron, coulombs.

If a large part of the sphere falls into higher zones, this formula does not apply, and there is no satisfactory way to obtain a calculated value of R_H for comparison with experiment, except in very special cases. If a small overlap into higher zones is indicated, the true Fermi surface may not be represented by the sphere, since such a representation neglects the Bragg reflection of electrons at the zone boundary, and

the more likely surface is one which overlaps much less than indicated, or does not overlap at all. An example of such a situation is found with YB_2, and is discussed below.

$\underline{MB_2}$. The structure of YB_2 is simple hexagonal, with one yttrium atom and two boron atoms per unit cell. Each boron atom has three boron nearest neighbors co-planar with it at 1.9 Å. A plane of boron atoms would look like a sheet made up of hexagons, as illustrated in Fig. 3.

Lipscomb and Britton's model[5] 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 YB_2 should have one free electron per Y atom.

The reciprocal lattice and Brillouin zone for YB_2 was constructed, and drawn to scale. A circle representing the projection of a Fermi sphere corresponding to one electron 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 Eq. (5). Without overlap the expected value is of the same order as that given by Eq. (5). Using Eq. (5) the calculated value of

MB$_2$ (OOI PLANE)

MB$_4$ (OOI PLANE)

MB$_6$ (IOO PLANE)
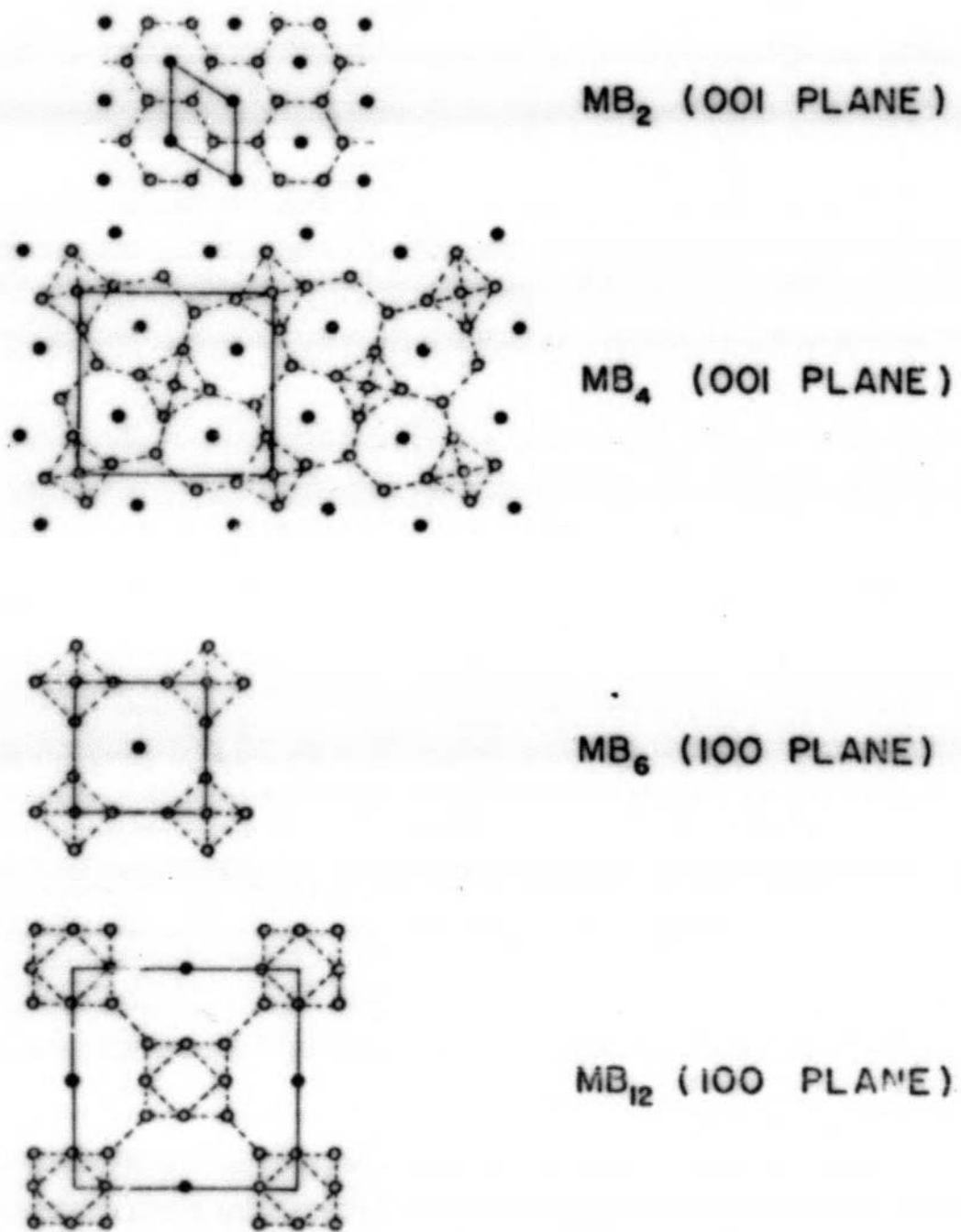
MB$_{12}$ (IOO PLANE)

Fig. 3. Crystal structure of the four boride types, projected
on the planes indicated. Open circles represent boron
atom positions, filled circles metal atom positions.
Dashed lines are drawn between co-valency bonded
boron atoms. Full lines enclose one face of a unit cell.

R_H for one electron per yttrium atom is -22.65×10^{-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.

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 Eq. (5) 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, 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 co-valent 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 Eq. (5) 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[14] 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-like electronic structure of the boron atoms in these compounds.

$\underline{MB_6}$. 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. 3 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,[4] Eberhardt et al.[3] and Yamazaki[15] 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 it would appear reasonable to regard these as semiconductors also. There has been one previous report of semiconducting behavior of SrB_6, by Eubank et al.[16]

The ln R vs 1/T curve published by them corresponds to $\epsilon = .51$ ev. (In the present work, ϵ is found to be .19 ev.) 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 SrO 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 $\epsilon = 1.45$ ev.

A Fermi sphere corresponding to one electron per yttrium atom lies completely within the first Brillouin zone of YB_6 and we would therefore expect Eq. (5) to be valid. The value of R_H thus calculated is -43.2×10^{-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.

$\underline{MB_4}$. The tetraborides crystallize in the tetragonal 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 YB_6, and the remaining four link octahedra together in the basal plane, such that each of these four has three boron nearest neighbors (see Fig. 3). Two of the latter nearest neighbors belong to octahedra. In the c direction, octahedra are bonded directly to one another, as in YB_6.

The electron requirements of the boron atoms in this structure were derived by Lipscomb and Britton[5] 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[10] and BeB_4[17] have been reported to exist and be isomorphous with all of the other tetraborides. MgB_4 has also been reported to exist,[17] but no structure data given. If semiconductivity were established for one of these the model given above would be confirmed.

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 Eq. (5) to apply. Certainly the number obtained from Eq. (5), -31.8×10^{-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 tetra-borides. The non-octahedral boron atoms are similar to those in YB_2 in that they have three co-planar 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.

$\underline{MB_{12}}$. The Bravais lattice of the dodecaborides is face-centered cubic.[18] 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[5] 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_{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_{12} is 3.442 g/cc; the measured value is 3.33. A boride sample of the theoretical composition of YB_{12} was heated to just below the peritectic temperature for

an hour, after which only two phases were present, YB_6 and YB_{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.[19] (For YB_{12}, a = 7.500 Å; for ZrB_{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, Eq. (5) 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 -86.5×10^{-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 -26.4×10^{-11}.

SUMMARY

It has been shown in the present work that the models for the electronic structure of the boron atoms in MB_2, MB_4, MB, and MB_{12} are consistent with the observed electrical properties of certain compounds representative of these types. This outcome justifies a greater confidence in the LCAO method as applied to B-B bonds in these and other co-valent structures, and suggests the possibility that a workable theory based on the LCAO method may be at hand in the near future for understanding other kinds of refractory compounds such as carbides, nitrides, and silicides, in addition to those based on boron.

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Fig. 1. The yttrium-boron system (see footnote 2).

Fig. 2. Resistance-temperature behavior of the alkaline earth hexa-
borides.

Fig. 3. Crystal structure of the four boride types, projected on the planes
indicated. Open circles represent boron atom positions, filled
circles metal atom positions. Dashed lines are drawn between
co-valency bonded boron atoms. Full lines enclose one face of
a unit cell.

END