"ELECTRICAL PROPERTIES OF SOME SINGLE CRYSTAL DODECABORIDES"

***

by

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SUMMARY

Previous work indicated that hot pressed $\beta$-AlB$_{12}$ was a semiconductor. Moreover, the simple electronic theory also indicates that $\beta$-AlB$_{12}$ should be a semiconductor, since there is one nonbonding electron per AlB$_{12}$-unit. For these reasons, we decided to measure the electrical properties of $\beta$-AlB$_{12}$ single crystals.

Single crystals of $\beta$-AlB$_{12}$ about 1 x 1 mm. size were grown from a copper melt at 1250°C. The melt technique coupled with slow cooling was used because of its advantages such as: simple set-up of the experiment; only easily available chemicals are required and it is a comparatively straight forward method still yielding crystals big enough for our purpose. Copper was used as a solvent, instead of previously used aluminum, because it allows crystal growth at higher temperatures.

However, the crystals of $\beta$-AlB$_{12}$ showed very high resistance at room temperature. From our measurements we conclude that the resistivity of $\beta$-AlB$_{12}$ is, at least, given as $\rho = 4 \times 10^7$ ohm.cm.

These results are inconsistent with the ones reported by Miss Khin for hot-pressed $\beta$-AlB$_{12}$ given as $\rho = 7600$ ohm.cm. or less. Since the hot pressing was done at about 800 - 900°C in graphite moulds with 97% AlB$_{12}$-powder, we think there is possibility that
lower borides or boron carbide are being formed, which are known to be good semiconductors.

We tried to dope \( \beta - \text{AlB}_2 \) by adding agents such as Mg, KMnO\(_4\), MgSO\(_4\), KH\(_2\)PO\(_4\), etc. to the melt. However, all these reagents either reduced the yield and size of the crystals or gave crystals of high resistance again. We think that molten copper keeps the impurities off. There is also a possibility that these doping agents get oxidized at 1250°C.

Hence, we conclude that \( \beta - \text{AlB}_2 \) has very high resistance at room temperature. This was also confirmed by checking the single and polycrystals of \( \beta - \text{AlB}_2 \) from Norton Co., Ontario and Cooper Metallurgical Association.

Boron carbide has been reported to be a semiconductor with \( \rho = 0.3 \) to 0.8 ohm. cm. for hot-pressed samples. Boron carbide being structurally related to \( \beta - \text{AlB}_2 \), we decided to study the electrical properties of its single crystals. These crystals were cut from a single melt grown crystal at Norton Co., Ontario. The resistivity of these crystals was measured by the Van der Pauw's method, which was very convenient for our crystal shapes.

Some of the crystals showed resistivity \( \rho = 0.50 \) ohm.cm. in agreement with the previously reported results. However, a few crystals showed
lower resistivity e.g. 0.13 and 0.20 ohm.cm.. The Hall mobility could not be measured and therefore is lower than 0.16 cm$^2$V$^{-1}$sec$^{-1}$. This is in agreement with the reported Hall mobility for pyrolytic boron carbide as 0.13 cm$^2$V$^{-1}$sec$^{-1}$.

We also studied the orientation of the boron carbide crystals by the Laue-method. The inclination of c-axis with respect to x-ray beam was determined. This was found to be 10° to 20° for normal resistivity samples (0.5 ohm.cm.) and 27° - 30° for the lower resistivity samples (0.13 to 0.20 ohm.cm.).

This indicates the possibility that the resistivity of $B_3C$ is orientation dependent.
CHAPTER I

INTRODUCTION
INTRODUCTION

In a world filled with lasers, masers, phosphors, ferrites, thermistors, transistors—and Xerox—there is no need to stress the practical importance of solid state devices. The solid state is a subject of major interest to students of chemistry. Many of the most imaginative scientists have made their marks in this field: Einstein, Debye, Wigner, Mott, Wagner, Pauling, Frenkel, and Schottky, are a few who immediately come to mind.

Crystals have been admired by man for their beauty and have been used as gems. However, the revolution of solid state devices in electronic technology has stimulated the study of semiconductor crystals. The structure and electronic properties of the crystals are being extensively studied. Due to the demand for high purity crystals, crystal-growth has become an important aspect of solid state chemistry.

HIGH TEMPERATURE SOLUTION GROWTH (1, 2)

This technique utilizes crystal growth from molten oxide fluxes or from liquid metals at temperatures of 600°C or more.
CHOICE OF SOLVENT:

Use of a single solvent or a mixture of solvents is also possible. An ideal solvent would:
(a) have a low volatility
(b) be easy to remove after growth
(c) be compatible with the crucible
(d) not react with the furnace atmosphere
(e) be cheap and non-toxic
(f) not form solid solutions or compounds with the material being grown
(g) not react with any of the reagents, to form crystals which would be similar in appearance or properties to those to be grown.

SLOW COOLING

The use of the slow cooling (1) technique is very common for producing small specimens, a few mm. on a side. The apparatus is a furnace with a temperature programmer and a crucible. A usual procedure is:
(Fig. I) Charge the crucible with weighed amounts of required materials. The crucible is then covered by a lid or an aluminum foil or by welding etc. whichever is suitable. The crucible is placed in the furnace and is heated to the maximum reaction temperature for some 12 to 24 hours. This is followed by slow cooling, usually
at a rate of 0.5° to 10°C per hour, to the desired temperature. Further cooling to room temperature is faster, generally at a rate of 100°C/hour. The crucible is taken out and treated with a suitable solvent, usually an acid or acids to dissolve the melt, separating out the undissolved crystals.

CONTROL OF NUCLEATION:

The average size of the crystals can be increased if the number of crystals growing is reduced. Nucleation can be initiated only in small regions by localized cooling. This can be achieved by blowing an air jet onto the crucible or by the use of an asymmetric heating arrangement.

To reduce the number of spontaneous nuclei, Hintzman and Muller-Vogt (3) have employed the oscillating temperature technique. This consists of a temperature oscillation (amplitude 20°) superimposed on a steady temperature decrease (2°/hour), as shown in Fig. II. Only the largest nuclei survive and grow, while the smaller ones redissolve during the peak part of the temperature oscillation cycle. These workers also reduced the area of nucleation by means of a platinum wire dipped into the flux, which in a platinum crucible would otherwise extend over the whole surface of the melt. By this technique they have obtained crystals of
rare-earth--phosphates, --arsenates, --vanadates etc.
having the dimensions 1 x 1.5 x 15; 3 x 0.5 x 7 mm. etc.

The slow cooling technique, thus, has advantages
of use of very simple apparatus, requires a minimum of
attention and still yields crystals of high purity and
large enough sizes necessary for research purposes.

DOPING (4)

In order to produce an appreciable concentration
of current carriers, a minute quantity of an impurity
is added to the pure substrate. This is known as
'doping'. Doping can be accomplished by different methods:

Diffusion (5)

A slice of semiconductor is exposed to a dense
vapour of the desired impurity. The impurity atoms
tend to diffuse into the solid (Fig. III).

Ion Implantation (5, 6)

It is a technique for introducing foreign atoms
into the surface layer of a semiconductor, by bombard-
ment of the solid with ions in KeV to MeV energy range.
Use of this technique affords the possibility of intro-
ducing a wide range of atomic species, thus making it
possible to obtain desired impurity concentrations accurately
positioned at particular sites (Fig. IV).
Neutron Irradiation

Exposure of a semiconductor to thermal neutrons often provides new carriers. Moreover, changes take place in mobility characteristics. The electrical properties of silicon and germanium have been studied after exposure to irradiation (7). Boron carbide is found to be a good host for neutron irradiation (8), being an extremely hard and high melting compound. During irradiation the center carbon atom of the chain of three carbon atoms, is selectively removed to an interstitial position. A boron atom can be introduced in this position to give $B_{12}C_{6}C_{6}$ or $B_{13}C_{2}$.

Crystal Defects

Grain - boundaries (9, 10)

A polycrystalline specimen can be defined as one composed of single crystal regions, separated by "grain boundaries". At the grain boundaries, the structures of one crystal do not fit precisely with those of adjacent crystals. It is usually easier for impurities to diffuse along the grain boundaries. The actual structure, hence, represents a layer of disturbed
crystallinity. The detailed atomic arrangement will depend on the angle of misfit between the boundary planes and hence on the relative orientations of the crystals on either side. The properties of metals and semiconductors are often affected by these grain boundaries. e.g. Plastic deformation and internal corrosion in metals are assisted by the presence of grain boundaries. Grain Boundaries and Electrical Properties of Semiconductors:

A grain boundary may have many effects on the electrical properties, depending upon the character of the bulk around it.

Tweet [11] has investigated grain boundaries in gold-doped germanium. He found that the grain boundaries produced a path of relatively low electrical resistance of temperatures below 100 K. The grain boundaries acted like a thin sheet of conducting material.

Pearson and others [12,13] have shown that the grain boundary is a p-type layer in the n-type germanium, forming an n-p-n structure. The p-layer of the grain boundary has been used as the base region of a junction transistor. However, characteristics of these transistors were poor.

In germanium, a low-angle grain boundary has been found [14] to behave as a recombination centre; that is,
a sharp decrease in the number of injected minority carriers is observed.

On the other hand, the grain boundary in ordinary germanium or silicon may act as an insulating or high resistance layer. Also the grain boundary, being a region of disorder, acts as a scattering region and lowers mobility.

In nickel oxide, the bicrystal conductance was found (15) as much as two orders of magnitude different than the crystal conductance, the boundary region was either more or less conductive than the bulk single crystal. These results could be explained in terms of increased grain boundary diffusion and segregation of impurities.

In advanced applications of semiconductors, it is generally desirable to work entirely with single-crystal material, especially since the grain boundary acts as a region of high recombination.

Twinning (10, 16)

The next-nearest-neighbour violation leads to a crystal imperfection described as 'twinning'. A twin is formed when a portion of the crystal lattice takes up a definite orientation related to that of the parent lattice in a particular way, the two parts remaining in intimate contact over their bounding surfaces. The
common plane across which the two parts of the lattice are reflected, is called the twinning plane (Fig. V, VI).

The energy of a twin is relatively low, since only a slight change in the diagonal atomic distances occurs with relatively little strain. A pure twin boundary, therefore, does not greatly influence carrier flow in semiconductors. In cases of undisturbed twins, no electrical effects of significance have been observed, not even in lifetime measurements of minority charge carriers. This structure-sensitive electronic magnitude is almost independent of twins in the path of the carriers if no doping gradient occurs.

However, in more complicated twinning configurations, lateral twin boundaries have a tendency to orient themselves in a complex manner and this produces strain. These lateral twin boundaries, therefore, are areas by which parameters like mobility and lifetime are affected.

In the well-known semiconductors like germanium and silicon, when twinning is present, generally other imperfections in the crystal are also present. Hence no direct results of the twinning effect on the electrical behaviour have been observed.
A horizontal muffle furnace for slow cooling. (after Brice, J. C., 1)

Temperature \( T \) in the melt as a function of time. Decrease of the mean temperature \( T \): 2°F/h. Amplitude of the temperature oscillation: 20°. Period: 8 min.

(after Hintzmann and Muller-Vogt, 3)

FIGURE III A furnace for doping by diffusion.
(after Carroll J., 5)
Fig. IV Schematic layout of ion implantation unit.
(after Mayer J. W., 6)

Fig. V Two-dimensional representation of twinned (black circles) and untwinned (open circles) parts of a crystal. The movement of the atoms into the twinned position is indicated by the arrows.
(after Rhodes R. G., 10)

Fig. VI Movements of atoms in the production of a twin.
(after Matare H. Y., 16)
CHAPTER II

ALUMINUM - BORIDE
HISTORICAL REVIEW

Boron forms one or more borides with most of the elements e.g. Be, C, Mg, Si, P, Ca, Sc, V, As, Cr, Mn, Y, Zr, etc. The Aluminum-Boron system has been studied by quite a few workers and the five phases reported (33, 36) so far are \( \text{AlB}_2 \), \( \text{AlB}_10 \), \( \alpha' \)-\( \text{AlB}_12 \), \( \beta \)-\( \text{AlB}_12 \), \( \gamma \)-\( \text{AlB}_12 \).

B. Jassonix (17) prepared \( \text{AlB}_2 \) in opaque hexagonal plates, while he prepared alloys of boron with various metals; however on heating with excess of boron, they went over into clear octahedral crystals.

Funk (18) prepared \( \text{AlB}_2 \) from a mixture of much \( \text{Al} \) and a small amount of B at about 1000\(^\circ\)C. According to him a mixture rich in B and a temperature of about 1500\(^\circ\)C, causes formation of \( \text{AlB}_12 \). At temperatures considerably below 1000\(^\circ\)C., \( \text{AlB}_12 \) is soluble in molten Al.

These observations are in agreement with Hofman-Jeniche (19) who also investigated the crystal-structure of \( \text{AlB}_2 \)(20). The Unit-cell is hexagonal \((a = 5.00 \text{\AA}, c = 3.24 \text{\AA})\) with one molecule of \( \text{AlB}_2 \) per cell, Al being at the corners and boron at positions \((1/3, 2/3, 1/2); (2/3, 1/3, 1/2)\) forming a lattice similar to that of carbon in graphite.
The thermite (21) reaction was used by Lihl and Jenitschek which involves reaction of 750 gm Al; 420 gm. B$_2$O$_3$, 200 gm. Sulphur & 100 gm. KClO$_3$ followed by HCl-HNO$_3$ - treatment. The resulting AlB$_{12}$ was allowed to react with Al at 1350-1450° C, giving AlB$_2$.

Becher's (22) preparation involved heating Al and B in Argon or vaccuo in Al$_2$O$_3$- crucibles at 800° C. The product was found to contain AlB$_2$ and a phase AlB$_{30-45}$ the Debye-Scherrer diagram of which resembles that of P-AlB$_{12}$. AlB$_2$ is obtained by quick cooling from 1250-1450° to temperatures below 1000° C, whereas slow cooling often yields AlB$_{12}$. AlB$_2$ decomposes to Al and P-AlB$_{12}$ above 980° C.

Felten (23) prepared AlB$_2$ in very satisfactory yield from powdered B and Al in stoichiometric proportions, heated in a graphite tube in vacuum at 800° C.

According to P. Dubart (24) AlB$_2$, prepared from the elements at 800° C, on heating to 1000° C gives AlB$_{13}$ which probably is a mixture of P-AlB$_{12}$ and B.

Seretbyanskii et al (25) have studied the Al-B system products, prepared from the elements in a tube-furnace, from 600°-1400° C. According to them, AlB$_2$ is formed in the region 650°-950° C, with maximum yield at 800° C.
As the temperature is further increased above \(1000^\circ C\), only \(\alpha\)-AlB\(_{12}\) is formed regardless of the original composition; that is, the tetragonal modification \(a = 10.15 \ \text{Å}, \ c = 14.29 \ \text{Å}\).

This was further confirmed by Atoda et al (26) using DTA and X-ray techniques. They used mixtures of Al and B in molar ratios 1:2 and 1:12. In both cases AlB\(_2\) was the product between temperatures 600\(^°\)–1000\(^°\)C and \(\alpha\)-AlB\(_{12}\) was the further decomposition product above 1000\(^°\)C according to the equation: \(\text{AlB}_2 \rightarrow \frac{1}{6} \text{AlB}_{12} + \frac{5}{6} \text{Al}\). However, none of these workers found any \(\beta\) or \(\gamma\)-AlB\(_{12}\) or AlB\(_{10}\) phases.

These results differ in some respects from Serebryanskii et al. (27) who have presented a phase diagram involving a series of peritectic lines up to 2300\(^°\)C. They found \(\beta\)-AlB\(_{12}\), AlB\(_{10}\), \(\alpha\)-AlB\(_{12}\) phases successively in the products quenched at a series of increasing temperatures above 1400\(^°\)C. (Fig. VII)

\(\alpha\) and \(\beta\)-AlB\(_{12}\) were a topic of controversy in the literature with reference to their composition and structure. It was first believed that crystalline boron consists of diamond-like \& graphite-like crystals, the former having composition \(C_2\text{Al}_2\text{B}_4\). This light yellow crystalline compound was first made by Woehler (28) & Hanpe (29); however Diltz (30) improved the method. He used 100 gm \(\text{B}_2\text{O}_3\), 100 g S
200 gm. Al powder; CaC\(_2\) (instead of carbon) giving dark brown to metallic gray crystals with composition 6.07% Al, 15.80% B, 82.13%. Whether or not this was a definite chemical compound was not resolved at that time.

Later, Naray-Szabo (31) proposed that the diamond-like form has a carbon-content of only 0.7% and the true composition is Al\(_B\)\(_{12}\) with possible intergrowth of B\(_12\)C\(_3\) in the ratio 3:2. The structure is tetragonal or orthorhombic pseudotetragonal (a = 12.55, c = 10.18 Å) with the possible space group P 4/nnm. The "graphite-like" form has an AlB\(_{12}\) composition and the Laue-photographs showed monoclinic symmetry. However no conclusion could be drawn.

The true symmetry of the "graphite-like" boron was given by Halla and Weil (32) as tetragonal pseudocubic with a = 10.16, c = 14.28 Å with the formula AlB\(_{12}\), named henceforth as α-AlB\(_{12}\).

Kohn et al (33) have described the morphology of α-AlB\(_{12}\) as thin, hematite-like plates, which transmit wine red color in strong light. Prismatic and octahedral habits are also reported.

Kohn (34) has also reported a new phase, γ-AlB\(_{12}\). In color and general appearance it is similar to α-AlB\(_{12}\). The symmetry is orthorhombic a = 16.6, b = 17.5, c = 10.2 Å. This new phase was first observed along with the x-ray diffraction
patterns of \( \alpha \)-AlB\(_2\) in syntactic intergrowth. Geometrical transformation from the \( \alpha \)-unit-cell to that of \( \gamma \)-AlB\(_2\) is accomplished by alternate stacking of (101)\(_\alpha\) layers; thus there is a polytypic relationship between the two structures. The volume of the \( \gamma \)-unit cell is twice that of the \( \alpha \)-phase.

As noted previously, "diamond-like" boron was believed to be AlB\(_2\) with an intergrowth of B\(_4\)C. But according to Kohn and Eckart (35) this is \( \beta \)-AlB\(_2\) with an orthorhombic unit-cell \( a = 12.34 \pm 0.01 \) \( \AA \), \( b = 12.631 \pm 0.005 \) \( \AA \), \( c = 10.161 \) \( \AA \). Twinning was observed on the Weissenberg patterns.

The crystals are generally translucent amber with the color ranging from yellow to brown. The common crystal habits are bipyramidal and doubly terminated octagonal prisms. (Fig. X)

Matkovich et al (36,44), however, confirmed the formula \( \text{C}_2\text{Al}_2\text{B}_4\) previously reported by Hampe (23). X-ray analysis showed that \( \beta \)-AlB\(_2\) has two phases derived from a single high temperature phase with a composition \( \text{C}_2\text{Al}_2\text{B}_4\) which disproportionates on cooling. This high temperature phase was found to be tetragonal with \( a = 8.82 \) \( \AA \), \( c = 5.09 \) \( \AA \) at about 850\(^\circ\)C, with space group \( \text{P}4/\text{mmm} \) or \( \text{P}4/\text{n} \). The two phases into which it disproportionates are always in the same relative proportions both being ortho-
rhombic (1) \( a = 12.34 \text{ Å} \), \( b = 12.63 \text{ Å} \), \( c = 5.08 \text{ Å} \)

(space group \( \text{Cmma} \) or \( \text{C2ma} \)) (2) \( a = 6.17 \text{ Å} \), \( b = 12.63 \text{ Å} \),
\( c = 10.16 \text{ Å} \) (space group \( \text{Ammm}, A_{222} \), or \( A_{2mm} \)). The

dimensional similarity of the two phases permits their intertwining. The composition of these two phases
has not been established. They also say that the discrepency with the previous workers may be attributed to
the very small sample size (30 mgm.) used by Kohn et al (35) for their stoichiometric determinations.

Monoclinic \( \text{AlB}_{12} \) - Halla and Weil (2) have
described a monoclinic form of unit cell with two
alternative arrangements (33) given as

(1) \( a = 8.50 \text{ Å} \)
\( b = 10.98 \)
\( c = 9.40 \)
\( \beta = 110^\circ 54' \)

(2) \( a = 8.50 \text{ Å} \)
\( b = 10.98 \)
\( c = 7.37 \)
\( \beta = 143^\circ 29' \)

A striking similarity was observed with the cell
of elemental rhombohedral boron (37), if an alternative
cell is chosen for monoclinic \( \text{AlB}_{12} \). This relationship
between the pseudo-orthorhombic cell derived from the
triple hexagonal cell of \( \beta \) rhombohedral boron (\( a = 10.12 \text{ Å}, \beta = 65^\circ 28' \))

\begin{align*}
\text{Rhombohedral boron} & \quad \text{Monoclinic \( \text{AlB}_{12} \)} \\
ap & = 10.95 \text{ Å} \\
b & = 9.48 (10.95 \times \sin 60^\circ) \\
c & = 23.73 \\
3d_{100} & = 23.82 (= 3 \times 8.5 \times \sin 110^\circ 54') \\
\beta' & = 90^\circ 
\end{align*}

and monoclinic \( \text{AlB}_{12} \) is as above. If the monoclinic
phase is Al-boride it
obviously bears an extremely close relationship with \( \beta \)-rhombohedral elemental boron.

The alternative and more likely interpretation is that the phase described as monoclinic \( \text{AlB}_{12} \) is actually elemental B, which is also supported by Parthe and Norton (38).

\( \text{AlB}_{10} \) was first reported by Kohn et al in 1958 (33). They prepared crystals of \( \text{AlB}_{10} \) along with the other phases \( \text{AlB}_2 \), \( \alpha - \text{AlB}_{12} \) and \( \beta - \text{AlB}_2 \) by two different methods. The first one involved melting B (85-87% pure) with Al (99%) in ratio 2:1 in a aluminium oxide crucible. This crucible was placed in a graphite crucible and heated up to 1600-1700°C for 3-4 hours and cooled very slowly. The second method involved heating 40% Al, 46% \( \text{B}_2\text{O}_3 \) and 10% Sulphur in a fire-clay crucible covered with \( \text{KClO}_3 \).

\( \text{AlB}_{10} \) occurs as black, shiny crystals with pyramidal and tabular habits. The Unit-cell is orthorhombic with \( a = 8.881 \text{ Å} \), \( b = 9.100 \text{ Å} \), \( c = 5.690 \text{ Å} \); the probable space group is \( \text{B} \ 2/b 21/m 2/m \).

However, according to Matkovich et al (36), \( \text{AlB}_{10} \) can not be prepared by B and Al alone, but considerable quantities of carbon were required. A composition \( \text{C}_4\text{AlB}_{24} \) was indicated for it.
Matkovich et al (36) have also reported a lower boride \( \text{Al}_2\text{C}_4\text{B}_1 \) to \( 3 \) possessing a variable boron content. However, limits of composition or crystal structure have not yet been established.

All the higher Al borides have been synthesized by a number of workers.

Luetkenmeyer et al (39) used high temperature reaction of BN with Al. The vacuum evaporation of Al from BN crucibles produced AlB\(_2\) and probably AlB\(_{12}\) at the interface, as shown by metallographic studies. These Al-borides exhibit higher melting and decomposition temperatures.

Bliznokov et al (40) prepared Al-borides by vapour deposition. The gas phase contained pure AlBr\(_3\), BCl\(_3\) and H\(_2\). Crystals of \( \text{C}_4\text{AlB}_{24} \) were deposited on a graphite surface at 1400\(^\circ\) C to 1600\(^\circ\) C, carbon being supplied by diffusion from graphite. A binary compound of Al and B (\( \alpha \)-AlB\(_{12}\)) was prepared at temperatures greater than 1500\(^\circ\) C.

According to Bacher and Heidhard (41), at 1550\(^\circ\) C in presence of silicon, orthorhombic \( \beta \)-AlB\(_{12}\) is formed from Al and B in ratio 1:2 to 1:14, the amounts of Si being smaller than 0.2\%.

Al-dodecaboride was made by aluminothermic reduction
of B$_2$O$_3$ purified and analysed by Samsonov et al (42). Boron content was found to 82.5 - 82.8%. The crystals were tetragonal $a = 10.1 \pm 0.1$ Å, $c = 14.4 \pm 0.4$ Å.

Neronov et al (43) constructed a phase diagram for the Al-B system up to 1850°C and supported the existence of AlB$_2$, AlB$_{10}$ and $\alpha$ & $\beta$ AlB$_{12}$.

Neronov et al (43) also prepared Al-dodecaborides on a large scale from two different mixtures—-(1) B$_2$O$_3$ 1200 gm, CaSO$_4$ 600 gm, Al$_2$(SO$_4$)$_3$ 600 gm, Al-powder 1900 gm. (2) Na$_2$B$_4$O$_7$ 170 gm, B$_2$O$_3$ 1200 gm, CaSO$_4$ 860 gm, Al$_2$(SO$_4$)$_3$ 860 gm, Al-powder 2310 gm.

The above two mixtures were heated separately in an electric arc using graphite crucibles followed by HCl treatment. The AlB$_{12}$ crystals showed an Al:B ratio as AlB$_{12.7}$.

Matkovich et al (56) prepared Al-borides by different methods—

$\alpha$-AlB$_{12}$ was prepared by fusion of a mixture of 300 gm Al; 75 gm B in a BN crucible at 1700°C for 1 - 3 hours.

$\gamma$-AlB$_{12}$ was prepared from 400 g. Al, 20 gm B in a zirconia crucible at 1400°C followed by slow cooling.

$\beta$-AlB$_{12}$ or C$_2$AlB$_{48}$ was obtained by fusion of 300 gm Al, 15 gm B; 0.50 gm C at 1400°C in a zirconia crucible for 8 hours and cooling at a rate of 100°C/hour. AlB$_{10}$ or C$_4$AlB$_{24}$ also was prepared by fusing 400 gm Al, 20 gm B
in a graphite crucible at 1400 °C for 6 hours.

**BORON POLYHEDRA IN HIGHER BORIDES**

The polyhedral structures of boron are well known. Those called "icosahedron" and "cubooctahedron" are most common.

The presence of an icosahedron was first established (45) in \( B_{12}C_3 \), existing in the form of \( B_{12}^- \) groups. This enabled the establishment of structures of the whole new rhombohedral boride series having similar structure, e.g. \( B_{12}C_3, B_{12}P_2, B_{12}S, B_{12}Si_2, \& \ B \) rhombohedral boron etc.

A different arrangement of \( B_{12}^- \) groups was first proposed by Bertaut and Blum in 1949 (46) giving rise to the series of dodecaborides displaying the new form, cubo-octahedron e.g. dodecaborides of the second half of the lanthanide series, Zr, U, Hf etc.

The \( B_{12}^- \) units may group together to form larger units acting as individual structural entities (49). This \( B_{84} \) unit is made of thirteen icosahedra, the central one surrounded by twelve half icosahedra. It is found in \( \alpha^- \) and \( \gamma^- \) AlB\(_{12} \). \( \beta^- \) Rhombohedral boron etc. (Fig. VII)

In the compounds of \( MB_{66} \) type a unit of 13-icosahedra has been observed e.g. YB\(_{66} \) (47) consists of a central icosahedron surrounded icosahedrally by 12-
icosahedra, forming a 156 atom unit. As a result of this geometry, the twelve outer icosahedra form a large icosahedron. This structure contains icosahedral packing to a higher degree than the \( B_{84} \)-unit in \( \beta \)-rhombohedral \( B \) (55) in which the outer 12 icosahedra are shared by the two central icosahedra. The remaining \( B \) atoms in \( YB_{66} \) are statistically distributed in channels that result from the above packing and form non-icosahedral cages. The yttrium atoms partially occupy sites in the channels.

Regular \( B_6 \)-octahedra are found in hexaborides such as \( CaB_6, BaB_6 \), etc.

**Aluminum-Borides**

All higher \( Al \)-boride structures are based on the principle that the \( B \)-polyhedra are joined to other \( B \)-polyhedra or \( B \)-atoms and \( Al \) occurs in the vacancies.

The close relationship between \( Al \)-borides and elemental \( B \) forms is remarkable e.g. Monoclinic \( AlB_{12} \) (32) \( (a = 8.50; b = 10.98; c = 9.40 \, \text{Å}; B = 110^\circ 54') \) and \( \beta \) rhombohedral \( B \) (37) \( (a = 10.12 \, \text{Å}, \alpha = 65^\circ 28') \) or \( \alpha \)-\( AlB_{12} \) \( (a = 10.16; c = 14.29 \, \text{Å}) \) and a new form (48) of tetragonal \( B \) \( (a = 10.12; c = 14.14 \, \text{Å}) \) or \( \beta \)-\( AlB_{12} \) \( (a/2 = 8.38; c/2 = 5.09 \, \text{Å}) \) and tetragonal \( B \) \( (a = 8.73; c = 5.03 \, \text{Å}) \).
\( \alpha - \text{AlB}_{12} \) has been classified (49) as cubic closest packing in terms of \( \text{B}_{84} \)-units. It has a tetragonal unit-cell with \( P_{4}^{2} \text{12}_{1}^{2} \) \( a = 10.16 \text{ Å}, c = 14.26 \text{ Å} \).

This requires presence of 16 \( \text{B}_{12} \) units/cell. However, on the basis of the density values only 14.4 such units can be present. This difference has been interpreted in terms of a defect structure. The deficiency of \( \text{B} \)-atoms can also be explained in terms of the \( \text{B}_{84} \)-units. A tetragonal cell of the above dimensions would accommodate 2 - \( \text{B}_{84} \) - units (equivalent to 14 \( \text{B}_{12} \)-units) in agreement with above mentioned requirement but in slight disagreement with the assigned space-group. As there is no defect packing of the \( \text{B}_{12} \)-groups known in any other \( \text{B}_{12} \)-borides, it appears more reasonable to assume the \( \text{B}_{84} \)-units.

A simple hypothesis (50) that correlates some of these problems is that \( \text{Al} \) substitutes for \( \text{B} \) in these structural types. Whether it does so at random or in certain preferred positions is not quite clear yet. This hypothesis, moreover, provides a reasonable basis for understanding the anomalous densities of \( \alpha - \text{AlB}_{12} \) and \( \text{AlB}_{10} \).

In \( \alpha - \text{AlB}_{12} \), the 14.4 formula weights per unit cell corresponds to 187 atoms, only a few percent less than
192 atoms which would be required for 16 \((B, Al)_{12}\) groups, or eight \((B, Al)_{10}\) plus eight \((B, Al)_{14}\) groups.

The covalent radius of B is \(5.1\) 0.88 A\(^0\) and that of Al is 1.26 A\(^0\). An Al-Al distance would probably greatly distort the structure, but the Al-B distance of 2.14 A\(^0\) is at least within the range of B-B distances found in boron hydrides and borides. Hence, the limited substitution of B by Al would not be unreasonable from the point of view of interatomic distances.

\(AlB_{10}\)

A similar problem arises while formulating the \(AlB_{10}\)-phase first reported by Kohn et al (33) with an orthorhombic unit-cell \((a = 8.83, b = 9.10, c = 5.69\) A\(^0\), Bb2m, Bbm2, or Bbmm space group) based upon four \(AlB_{10}\) in Bbm2. Unfortunately, the density of the crystal requires 5.2 \(AlB_{10}\) in the unit cell.

With the aid of above hypothesis (50) this discrepancy is explained by assuming four \((B, Al)_{14}\) groups or four \((B, Al)_{12}\) plus four \((B, Al)_{2}\) or four \((B, Al)_{10}\) plus eight \((B, Al)_{2}\), etc..

The crystal structure of \(AlB_{10}\) has been studied by Will (52, 53). However, as noted previously Matkovich et al (36) believed that \(AlB_{10}\) is rather \(C_4AlB_{24}\) whereas Perrotta et al (54) have
suggested that the AlB_{12} reported by Kohn et al (33) is actually C_{0}Al_{2.1}B_{51}.

\( \gamma \)-AlB_{12} is also classified (49) on the basis of the hexagonal closest packing of the B_{84} units. - and AlB_{12} have a common axis (10.16 Å) and the \( \alpha \)-axis of the \( \gamma \)-phase (16.56 Å) is 2/3 of the (101) \( \alpha \)-axis of \( \alpha \)-AlB_{12} (24.8) Å. This relationship is clearly that of the cubic closest packing and the hexagonal closest packing of the identical spheres. It can be concluded therefore, that \( \gamma \)-AlB_{12} represents an orthorhombic distortion of the hexagonal closest packing of the B_{84}-units.

C_{2}Al_{2}B_{48} (or \( \beta \)-AlB_{12}): This material described by Kohn et al (35) as a single phase, is now shown (36, 44) to exist at room temperatures as the two crystallographically related phases, "A and B". Both of these phases are classified (49) as tetragonal closest packing with 10 closest neighbours as shown in Fig. IX.

**The Electronic Structure of Borides and the Electrical Properties**

\( B_{12} \)-Icosahedron

The electronic treatment is also given to an icosahedron of the twelve B-atoms by Longuet-Higgins and Roberts (76). It is seen that there are thirteen bonding and seventeen antibonding orbitals within an
icosahedron. This demands twenty-six electrons for intra-icosahedral bonding.

This can be applied to boron carbide $B_{12}C_3$ structure, which consists of $B_{12}$ icosahedra and the linear $C_3$ chains linked together to form a giant rhombohedral molecule. Now each $B_{12}C_3$ unit contributes altogether forty-eight valence electrons to the crystal. Of these, sixteen are used to attach the carbon atoms to one another and to their surroundings and each icosahedron has to contribute six valence electrons to the covalent bonds which link it to the neighbouring six icosahedra. This leaves exactly twenty-six electrons to be disposed of and if these are confined to the thirteen bonding molecular orbitals of the icosahedron we obtain a closed shell structure. The closed-shell structure accounts for the extreme stability and hardness of the boron-carbide crystal.

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 (57). In applying it to the reciprocal lattice, the 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 $R_H$; as given by Johnson and Daane (58) may be calculated from equation—

$$R_H = \frac{1}{ne} \text{ m}^3/\text{C} \quad \text{---I}$$

where $n$ is the electron concentration $1/\text{m}^3$ and $e$ is the charge on the electron. 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 for $R_H$ for comparison with the experimental one except in very special cases.

**Aluminum-dodecaborides**

Aluminum dodecaborides which contain icosahedral groupings (36) of the boron atoms would be expected to be semiconductors on a similar argumental basis. There should be one electron excess after borrowing two electrons from the Al atom per formula weight.

Samsonov and Zhuravlev (42) have reported the electrical resistance of the tetragonal $\text{AlB}_{12}$ (probably the $\alpha$-phase) prepared by the alumino-thermic reduction as $\rho = 7.75 \times 10^5$ ohm.cm. at room temperature.

Golikova et al (59, 60) have studied the temperature dependence of electrical conductivity in $\alpha$-$\text{AlB}_{12}$ and
estimated the forbidden band-width as 2.5 ev. in the intrinsic conduction region. In the impurity conduction region the conductivity rose exponentially with rising temperature and the activation energies were 0.4 - 0.7 ev. for different impurity concentrations. This kind of temperature dependence of electrical conductivity and also of the thermoelectric power studied by the same authors indicates "hopping conduction", according to them. They have also mentioned that $\alpha$-AlB$_{12}$ had p-type conduction. The resistivity for the single crystals of $\alpha$-AlB$_{12}$ reported (64) is $\rho = 0.2 \times 10^5$ ohm.cm. at 400$^\circ$K. For different impurity concentrations the resistivity of $\alpha$-AlB$_{12}$ single crystals ranged (59) from $p = 10^1$ to $10^6$ ohm.cm. at 300$^\circ$K.

The previous work done by Dr. G. R. Finley and Miss Khin (61) was mainly on the hot pressed $\alpha$-AlB$_{12}$. The specific resistance value reported by them is $\rho = 117 \pm 20$ ohm.cm. (69). The Hall constant for the hot pressed blocks of $\beta$-AlB$_{12}$ was found to be $1.150 \times 10^{-6}$ m$^3$/C which leads to about 11 cm$^2$V$^{-1}$sec$^{-1}$ for the mobility and $4.3 \times 10^{15}$ cm$^{-3}$ for the carrier concentration.
Physical Properties of Aluminum-Borides

The previously noted five Al-boride phases namely $\text{AlB}_2$, $\text{AlB}_{10}$, $\alpha$, $\beta$ - and $\gamma$ - $\text{AlB}_{12}$ are characterized by their physical properties. These are high melting-points, extreme hardness ($\text{AlB}_2$ is an exception), high physical and chemical stability which enable their use as refractory materials.

The melting-temperature determinations were made by (62) placing single crystal specimens in a hot-pressed boron nitride crucible heated by an electrical resistance heating ribbon. The melting temperatures range from 1600° - 2500° C the $\text{AlB}_{10}$ being the highest melting phase.

The microhardness of the $\text{AlB}_{12}$ single crystals (yellow and red) determined by Cotter (63) ranged from 2400 - 2700 KHN. The vector hardness properties of Al-borides determined by the previous authors (62) are in satisfactory agreement with these values.

The temperature dependence of thermal conductivity and thermoelectric power has been studied by Golikova et al (59). The thermoelectric power ($\alpha$ $\mu$V/deg of $\alpha$-$\text{AlB}_{12}$ exhibited a continuous rise from 300° - 1800° K. The similar temperature dependence of thermal & electrical conductivity, according to them, indicates that $\alpha$-$\text{AlB}_{12}$ exhibits hopping conduction. The same coworkers in their recent publication (64) have given the thermoelectric
power ($\alpha$) $\mu W/\deg$ for the two single crystal specimens of $\alpha$-AlB$_{12}$, prepared by the same technological process as +510 and +480 at 400 K.

The thermal conductivity measurements with respect to temperatures are done on $\alpha$- and $\beta$-AlB$_{12}$ (59, 64). $\beta$-AlB$_{12}$ has a weak temperature dependence in the range of 0° - 400° K which may be attributed to its decomposition into two phases (36, 44) below 1100° K. The size of the sample precluded the measurements above 400° K. The thermal conductivity value (64) in $W/\deg \cdot \text{cm}$ is given as 0.105 at 300° K.

The thermal conductivity of $\alpha$-AlB$_{12}$, however, decreases rapidly when the temperature is increased from 0° - 300° K although it varies for different samples. This value reached a minimum and was assumed (59) to be independent of temperature throughout the higher temperature range. The thermal conductivity values for the couple of $\alpha$-AlB$_{12}$ single crystal specimens given (64) are 0.031 to 0.043 $W/\deg \cdot \text{cm}$ at 300° K. According to them the thermal conductivity depends inversely upon the number of atoms per unit cell and the complexity of the crystal structure, only in the low temperature range (up to 300° K).
EXPERIMENTAL

Raw Materials: The raw materials used in the preparation of aluminum-boride, hexaboron phosphide \( B_6P \), \( MgAlB_{14} \) were as follows:

**Al** - Aluminum granules from ALCAN were 99.8% pure.

**B** - Boron granules from United Mineral & Chemicals 99.8% pure were ground to about 50 mesh in an iron mortar.

**Cu** - Copper filings were obtained from the machine shop.

**P** - Red phosphorus, amorphous was from Fisher Scientific Co., N.J.

Crucible - The crucibles used were thick walled Czerbide crucibles obtained from Weaver Material Service, Inc., New York. Czerbide, a proprietary SiC-base composition is extremely dense, has very high thermal conductivity, is non-wetted by many metals and is usable at low or high temperatures (55).

Preparation of B-AlB\(_{12}\)

The crystals up to 1 mm x 1 mm size were prepared in this laboratory by following this method—

A mixture of Al-granules, boron powder and copper filings in a ratio 4:1:7 (by weight) was placed in a Czerbide crucible covered with a thin aluminum foil.
It was then heated to 1250°C for about 12 hours in the Hotpack furnace (model 7761). This was followed by conventional slow cooling at a rate of 10°C/hour from 1250°C to 1100°C and further allowed to cool overnight on its own by turning the furnace off.

The melt, cooled to room temperature, was digested with hot concentrated nitric acid and hydrochloric acid repeatedly. The undissolved residue was washed, dried and examined under a binocular microscope.

The PRODUCT

The residue was a mixture of compounds including Al₂O₃, unreacted boron along with yellow-brown to dark reddish black crystals.

The crystals of \( \beta \)-AlB₁₂ could be easily separated because of their entirely different appearance from any of the starting materials. The typical crystals were yellow to deep amber showing bipyramidal habit (Fig. X) as described by Kohn et al (34, 62). The size ranged from 1/2 x 1/2 mm to 1 x 1 mm which was adequate for further electrical measurements.

The red and black crystals were probably \( \alpha \) and \( \gamma \)-AlB₁₂ phases.

It was found that copper is a very good solvent for Al-boride crystal growth. The previous attempts done on \( \beta \)-AlB₁₂ crystal-growth, by G.R. Finlay and
Miss Khin (61), did not give large enough crystals for further study. These were grown from an aluminum melt. The use of copper as a solvent enabled us to use high temperatures more easily the melting point of copper being higher (1083 °C) (66) than that of Al (660 °C). Moreover, copper gives crystals of high purity which is often difficult by any other solvent.

The larger size of the crystals is also attributed to a very slow cooling rate in a specific temperature range. As noted by previous workers (18, 19, 22, 24, 25, 26) and also according to our observations, AlB₂ phase is favoured in a rough range of 800 °C - 1100 °C. Hence the melt was allowed to cool at a rate of 10 °C/hour only in the range which favours formation of dodecaboride i.e. above 1100 °C. While it was cooled rapidly as the temperature approached AlB₂-phase range, from 1100 °C to below so as to give least chance for the aluminum-dodecaborides formed to decompose into AlB₂. Therefore our residue contained practically no AlB₂ phase.

Change of System Parameters

In all trials, Czermide crucibles were used, being most satisfactory. A Battersea-clay crucible was found to be attacked and hence was discarded thereafter.
Yellow-brass 65% Cu and 35% Zn (melting point 920°C) (66) was tried as a solvent in place of copper, however, it was not found desirable due to its lower melting point and higher vapour pressure, in spite of more homogenous melt.

It was found that the temperature of the reaction greatly affects the yield. This was consistent with the observations of earlier workers (18, 19, 22, 24, 25, 26). The temperatures up to 1150°C gave mostly thin, hexagonal, shiny crystals of $\text{AlB}_2$-phase and practically none of $\text{AlB}_{12}$-phases. As the temperature was further increased to 1250°C, the formation of dodecaborides was apparently favoured. In most of the cases, the yellow crystals of $\beta$-$\text{AlB}_{12}$ were also contaminated with red and black crystals which, we believe, are $\alpha$ and $\gamma$-$\text{AlB}_{12}$ phases.

Miss Khin (61) has reported that the best yield of $\beta$-$\text{AlB}_{12}$ crystals was obtained from a mixture of Al:B in a ratio of 4:1 by weight. Hence we used the same proportion of Al:B in most of our trials. The best proportion of all the three reactants, we found, was Al:B:Cu as 4:1:7. Any considerable increase or decrease in the amount of copper gave a poor yield. Some of our trials can be summarized as follows:
Table I  CRYSTAL GROWTH EXPERIMENTS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1 gm B + 4 gm Al + 15 gm yellow brass $\rightarrow$ heated at 1050°C for 10 hours.</td>
<td>gave shiny hexagonal AlB$_2$-crystals</td>
</tr>
<tr>
<td>2. 1 gm B + 4 gm Al + 9 gm brass $\rightarrow$ heated at 1120°C for 12 hours.</td>
<td>gave most of AlB$_2$ with a very few yellow crystals which were microscopic.</td>
</tr>
<tr>
<td>3. 1 gm B + 4 gm Al + 9 gm Cu-filings $\rightarrow$ heated at 1220°C for 11 hours.</td>
<td>gave a few AlB$<em>2$ crystals with large number of tiny Z-AlB$</em>{12}$ yellow crystals along with black crystals.</td>
</tr>
<tr>
<td>4. 1 gm B + 4 gm Al + 7 gm Cu $\rightarrow$ heated at 1250°C for 11 hours.</td>
<td>gave large number of brown crystals with increased size.</td>
</tr>
<tr>
<td>5. 1 gm B + 4 gm Al + 6 gm Cu $\rightarrow$ heated at 1250°C for 12 hours $\rightarrow$ Slowly cooled at a rate of 20°C/hr. from 1200-1040°C.</td>
<td>gave yellow, brown crystals of Z-AlB$_{12}$ with size increased twice or thrice than before, also quite a few AlB$_2$ present.</td>
</tr>
<tr>
<td>6. 5 gm AlB$_{12}$-powder (95%) + 7 gm Cu $\rightarrow$ heated at 1250°C for 15 hours $\rightarrow$ Slowly cooled at a rate of 10°C/hr. from 1250°C to 1150°C.</td>
<td>the residue did not contain any Al-boride at all.</td>
</tr>
<tr>
<td>7. 1 gm B + 4 gm Al $\rightarrow$ heated at 1250°C for 12 hours $\rightarrow$ Slowly cooled at a rate of 10°C/hr. from 1250°C to 1150°C.</td>
<td>the residue shows no Z-AlB$<em>{12}$-crystals at all. Black crystals were present, possibly $\gamma$-AlB$</em>{12}$ or AlB$_{10}$.</td>
</tr>
</tbody>
</table>
Boron Phosphide $B_6P$

Preparation of hexaboron phosphide $B_6P$, was attempted according to the U.S. patent by Hill D. E. (67). This was done by charging a 1/2"-diameter graphite crucible with 0.2250 gm. boron-powder (50 mesh) which was placed into one end of a 3/4" outside diameter quartz-tube. The other end contained red phosphor as 0.9905 gm in a quartz-boat. The quartz tube was then evacuated and sealed at both ends. This was heated in a high temperature furnace so that boron-powder was maintained at 1100 °C while the phosphorus-end was at 110 °C to volatilize and to maintain a phosphorus partial pressure of about 1000 micrometers of Hg. The temperature gradient was measured prior to the experiment using a Pt-10% Rh thermocouple.

The heating was continued for 24 to 26 hours. The phosphorus vapour was supposed to fill the entire tube at desired pressure and then react with the hot boron at the other end. However, no new crystals were observed at either end.

According to a private communication from Dr. A.K. Kuriakose, Norton Co., Niagara Falls (68), this can be attributed to the relatively low temperature of the boron end and larger particle size (50 mesh) of the boron-powder. The finer powder and the temperatures above 1200 °C would possibly yield the desired $B_6P$. There is also a possibility that an impervious BP layer is
produced through which the P-atoms did not diffuse. This is evident also from the phase-diagram given by Hill. However, a temperature of 1100 °C should give at least a low yield of B₆P, according to him.

The preparation of MgAlB₁₄ crystals was tried as described by Matkovich (69). A mixture of Mg, B, Al in atomic ratio of 1:2:14 was heated at 900 °C for 6 hours, cooled and treated with concentrated hydrochloric acid. A residue of small black crystals of MgAlB₁₄ was expected. However, we did not get any crystals at all by above method, as described by this author.

Our observation is that higher borides are formed at higher temperatures than 900 °C; generally at about 1200 °C or higher. The lower temperatures such as 900 °C often yield lower borides e.g. AlB₂ as in the case of aluminum borides. Hence we would expect MgAlB₁₄ crystals to form at 1100 °C or preferably higher temperatures. However, the author claims he got the crystals by the above method.

**X-ray Characterization of B-AlB₁₂**

A yellow, apparently a single crystal, prepared by the method described above, was picked up for x-ray analysis. The morphology was exactly as described by Kohn et al (34, 62). This shape of B-AlB₁₂ crystal (Fig.X) created some difficulties in finding a crystallographic axis. However, it was aligned about the C-axis, this
being comparatively easier to find. The oscillation and Weissenberg photographs of the $\beta$-$\text{AlB}_2$ crystal obtained are shown in Fig. XI a and XII.

As is evident from the x-ray photographs, the crystal was multiply twinned which tended to complicate the study. This observation is consistent with those reported by earlier workers (35, 44).

Kohn and Eckart (35) originally suggested one phase with the orthorhombic space-group Imma and the unit-cell dimensions $a = 12.34$, $b = 12.63$, $c = 10.16 \text{ Å}$ with observed twinning on (110) and (110).

Matkovich et al (44) proposed a combination of two phases with the space groups phase A Cmma (or C2ma) and phase B Ammm (or A222 or A2mm) and the unit cell dimensions $a = 12.34$, $b = 12.63$, $c = 5.08 \text{ Å}$ and $a = 6.17$, $b = 12.63$, $c = 10.16 \text{ Å}$ respectively. They observed that the generally weak reflections in planes with odd $l$ were singlets while as the reflections in the even layers ($l = 2n$) were doublets. Moreover, the body centered lattice requires that hk0 layer must conform to the condition that $h = 2n$ and $k = 2n$ and also requires that all layers conform to the condition that $h + k + l = 2n$. Hence in the case of the even layers ($l = 2n$) $h$ and $k$ must both be either odd or even. On the odd layers ($l = 2n + 1$) $h$ must be even when $k$ is odd and vice versa. However, they found the reflections
only those for which \( h \) is even and \( k \) is odd on odd layer. Whereas the reflections for which \( h \) is odd and \( k \) is even were systematically missing. They also observed twinning on (110) and (1\( \bar{1} \)0) faces.

However, a most recent investigation on \( \beta\)-AlB\(_{12} \) reported in Ph.D. thesis by Kunzmann Peter (70) again confirms the results of Kohn et al. According to him, the weaker reflections with \( h \) odd and \( k \) even on odd layers, which Matkovich et al (44) did not observe, could be seen on pictures with very long exposure times. He confirmed this with the aid of electron diffraction pictures taken from twinned crystals. Hence he concludes that the \( \beta\)-AlB\(_{12} \) system consists of a body centered phase with lattice parameters \( a = 12.54 \), \( b = 12.65 \) and \( c = 10.16 \, \text{Å} \) and possible space groups are Ima, I2ma.

Our observations are as follows:

The oscillation photograph shows alternate dark and light lines indicating a possibility of two components. The two axes \( c \) and \( c' \) could be calculated corresponding to these lines \( l \) and \( l' \) as shown in Fig. XIa. The Weissenberg photographs were taken corresponding to the \( c \)-axis.

Zero-layer Weissenberg showed systematic absences of \( h' \neq 2n \) and \( k' \neq 2n \). This observation is consistent with all the previous workers (35, 44, 70) and also
with the requirement for the body-centered lattice. The multiple twinning was observed on zero and even layers.

First layer Weissenberg, in our case, showed single twinning and reflections observed were those for which \( h \) is even and \( k \) is odd and also \( h \) is odd when \( k \) is even. This is in partial disagreement with Mathkovich et al (44), however it is consistent with the condition of \( h + k + 1 = 2n \) for the body centered cell.

We also noticed that the even layer Weissenberg photographs needed a very short exposure. An exposure of about two hours was quite enough. However, odd layer photographs needed at least seven hours exposure time. In practice, this fact created some troubles while taking the photographs. This clearly suggests that the even layer and the odd layer photographs correspond to two different components.

However, the "second layer Weissenberg" photograph would contain very weak or almost no reflections of second layer for the body centered cell, where as it can be well indexed as a first layer photograph for a C-centered cell if two components, one with it's \( c' \)-axis double than that of the previous one, are assumed to be present. All photographs showed tetragonal symmetry.

Mathkovich et al (44), who found twinning of the two A- and C- centered phases, made use of carbon
powder or a graphite crucible in the preparation of the Al-borides. This explains the presence of carbon in their composition. However, we did not use carbon in any form during the crystal growth of our B-AlB$_{12}$ crystals. Hence there is almost no chance of carbon being incorporated in our Al-B system and Matkovich's composition seems improbably in our crystals. Moreover, Matkovich did not find either phase body centered.

Above observations indicate a possibility of the presence of two polytypes, each component being twinned with itself.

The cell dimensions of one of the components from the oscillation and zero-layer Weissenberg photograph are $a' = 12.53$, $b' = 12.43$, $c' = 5.055\text{Å}$ with a C-centered cell.

The cell dimensions of the other component calculated from the first layer Weissenberg photograph are given as $a = 12.57$, $b = 12.58$, $c = 10.21\text{Å}$ with a body-centered cell.

However, no firm conclusion about the space groups could be drawn.

**Electrical Properties of B-AlB$_{12}$**

A suitable crystal prepared by the method described earlier was mounted on a non-conducting jig and resistivity measurements were tried using Van der Pauw's (105) theorem as described in detail for the boren-carbide crystals in chapter III.
However, the crystal did not show any measurable conductivity at all, indicating its high resistance. Attempts were made on several crystals, even after washing them by hydrofluoric acid to dissolve a possible oxide-film on the surface. The contacts were zotted to reduce any possible contact resistance, using an increasing power input up to 20 - 25 volts. However, the crystals still showed very high unmeasurable resistance.

A number of Al-boride single and polycrystalline samples obtained from different sources were also checked for conductivity, e.g. AlB$_{12}$ from Cooper Metallurgical Associates; a few AlB$_{12}$ samples from Norton Co., Niagara Falls, etc. However, none of them showed any measurable conductivity. The AlB$_{12}$-samples from Norton Co. included some grown from copper melts. Others were grown from Al melts.

**RESULTS AND DISCUSSION**

From our measurements we can calculate the lowest possible resistivity of R-AlB$_{12}$ crystals as follows:

Measurements of resistivity on one of the needle shaped crystal of R-AlB$_{12}$ showed the following results--

Length of the crystal = 0.1 cm.

Width and thickness of the crystal = 200 µ = 0.02 cm.

The width and thickness were measured by a high magnification calibrated microscope.
Our measuring circuit was such that we could use a maximum input voltage, over the crystal, of 100 volts and the maximum detectable current was $10^{-8}$ amperes.

However, we could not measure any change in current at all, therefore the minimum resistance of the crystal in the circuit, $R$, was--

$$R = \frac{V}{I} = \frac{10^2}{10^{-8}} = 10^{10}\text{ohms}$$

Hence, the minimum resistivity $\rho$ of the crystal can be calculated as:

$$\rho = \frac{R \times \text{Area}}{\text{Length}} \text{ ohm.cm}.$$  

$$= \frac{10^{10} \times (0.02)^2}{0.1}$$

$$= 0.0004 \times 10^{11}$$

$$\rho = 4 \times 10^7 \text{ ohm.cm}.$$  

Hence our calculations show the result that the resistivity of $\beta$-AlB$_{12}$ is at least $4 \times 10^7 \text{ ohm.cm}$.

An approximate number of carriers in $\beta$-AlB$_{12}$ can now be estimated assuming a mobility, $\mu$, of carriers as $1 \text{ cm}^2\text{v}^{-1}\text{sec}^{-1}$. This is a reasonable assumption since boron carbide has been reported (98,99) to have a mobility of the order of $0.13 \text{ cm}^2\text{v}^{-1}\text{sec}^{-1}$.

$$\delta^- = N e \mu$$

$$N = \frac{\delta^-}{e \mu}$$

$N$ = number of carriers per cm$^{-3}$

$\delta$ = conductivity ohm$^{-1}$cm$^{-1}$

$e$ = electronic charge = $1.6 \times 10^{-19}$ coulomb

$\mu$ = mobility of carriers cm$^2$v$^{-1}$sec$^{-1}$
\[ e = 4 \times 10^7 \text{ ohm.cm.} \]

in \( \beta\)-AlB\(_{12} \)

\[ \sigma = 0.25 \times 10^{-7} \text{ ohm}^{-1}\text{cm}^{-1} \]

\[ \mu = 1 \text{ cm}^2\text{v}^{-1}\text{sec}^{-1} \]

\[ N = \frac{0.25 \times 10^{-7}}{1.6 \times 10^{-19} \times 1} = 0.16 \times 10^{12} \text{ carriers/cm}^3 \]

The number of intrinsic carriers at room temperature, in \( \beta\)-AlB\(_{12} \) can be calculated as follows (71):

\[ N = 2^{27m_e^2kT} \frac{3/2}{h^2} \exp\left(-\frac{E}{2kT}\right) \]

In G.S.S. units—

\[ m_e = \text{mass of an electron} = 9 \times 10^{-28} \]

\[ k = \text{Boltzmann Constant} = 1.38 \times 10^{-16} \]

\[ h = \text{Planck's Constant} = 6.63 \times 10^{-27} \]

\[ E = \text{Energy gap for } \beta\text{-AlB}_{12} \text{ is taken as } 2.5 \text{ eV as was reported by Lagrenaudie (73) for Woehler's (28)} \]

"borocarbide".

Hence at room temperature an approximate number of carriers would be:

\[ N = 2^{\left(\frac{2 \times 3.14 \times 9 \times 10^{-28} \times 1.38 \times 10^{-16} \times 300}{43.56 \times 10^{-54}}\right)^{3/2}} \times \]

\[ \exp\left(-\frac{2.5 \times 1.6 \times 10^{-12}/1.33 \times 10^{-16} \times 2 \times 300}{2.5 \times 10^{19} \times e^{-48}}\right) = 2.5 \times 10^{19} \times e^{-48} = 2.5 \times 1.4 \times 10^{19} \times 10^{-21} \]

\[ N = 3.5 \times 10^{-2}/\text{cm}^3 \]

With this low value of number of carriers, there would not be any intrinsic conduction observed in...
\( p\)-AlB\(_{12}\) at room temperature. At higher temperatures intrinsic conduction would rise and could be calculated as—

\[
N = 2 \left( \frac{2 \times 3.14 \times 9 \times 1.38 \times 500 \times 10^{-44}}{43.56 \times 10^{-54}} \right)^{3/2} \times \\
(\exp^{-(2.5 \times 1.6 \times 10^{-12}/1.38 \times 10^{-16} \times 2 \times 500)}) \\
= (5.4 \times 10^{19}) \times e^{-29} = 5.4 \times 2.5 \times 10^{19} \times 10^{-13} \\
N = 1.35 \times 10^{7}/\text{cm}^3
\]

Similarly at \( T = 1000^\circ\text{K}\)

\[
N = 1.8 \times 10^{20} \cdot \exp^{-(2.5 \times 1.6 \times 10^{-12}/1.38 \times 10^{-16} \times 2 \times 1000)} \\
= 1.8 \times 10^{20} \times e^{-14.5} = 1.8 \times 5 \times 10^{20} \times 10^{-7} \\
N = 9 \times 10^{13} = 10^{14}/\text{cm}^3
\]

The resistivity of \( p\)-AlB\(_{12}\) might be measurable at high temperatures such as \( 1000^\circ\text{K}\), however, the sample has to be extremely pure.

From our calculations of number of intrinsic carrier, it is evident that any conductivity in \( p\)-AlB\(_{12}\) at room temperature should be extrinsic conductivity (caused by impurities). From the estimated value of the carrier concentration, the net number of electronically active impurities in our \( p\)-AlB\(_{12}\) is less than \( 0.16 \times 10^{12} \) carrier/cm\(^3\).

In order to observe any measurable conductivity, we tried to increase the impurity concentration by
doping the crystals by adding different reagents to
the melt before crystallization. The criterion for
selection of an impurity was the sufficiently small
ionic radius of one of the elements in a compound. The
atomic radius of Al is $1.43 \text{ Å}$ and the ionic radius is
$0.51 \text{ Å}$. The following ions have equal or smaller ionic
radii than that of Al:

- $\text{Mn}^{+7} - 0.46 \text{ Å}$,
- $\text{P}^{+5} - 0.35 \text{ Å}$,
- $\text{S}^{+6} - 0.30 \text{ Å}$,
- $\text{Se}^{+4} - 0.51 \text{ Å}$

These cations, whose ionic radii are equal or
smaller than that of Al, are more likely to be doped
than the larger ones. Thus the following chemicals were
used for doping—$\text{KMnO}_4$ (for $\text{Mn}^{+7}$); $\text{MgSO}_4$ (B.D.H. Laboratory
99.5% pure) for $\text{S}^{+6}$; selenious acid (Fisher Scientific
Co. 97% pure) for $\text{Se}^{+4}$, $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{MgNH}_4\text{PO}_4$ for $\text{P}^{+5}$,
etc. $\text{MgNH}_4\text{PO}_4$ was prepared from magnesium sulfate
and $\text{KH}_2\text{PO}_4$ as described by Vogel (72). The doping trials
are summarized in the table 2.

However, none of these doping agents worked. Most
of them either reduced the size and yield of $\text{J-ALB}_{12}$
crystals or gave crystals with very high resistance.
This was very surprising since in general most crystals
pick up impurities from reagents or crucible or atmosphere
during crystal growth. We do not understand why $\text{J-ALB}_{12}$
should not pick up impurities and not show extrinsic
conduction. The only explanation could be given as
melted copper keeps the impurities off, also a possibility that these doping agents get oxidized at 1250°C.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Doping Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Doping:</strong></td>
<td></td>
</tr>
<tr>
<td>1. Mg-ribbon</td>
<td>gave $\beta$-AlB$_{12}$ crystals with very high resistance, on increasing the amount of Mg the whole mass stuck to the crucible.</td>
</tr>
<tr>
<td>2. Charcoal powder</td>
<td>gave $\beta$-AlB$_{12}$ crystals of high resistance.</td>
</tr>
<tr>
<td>3. Mg-ribbon + Charcoal powder</td>
<td>yield of $\beta$-AlB$_{12}$ was reduced considerably, most of unreacted B-lumps were still present.</td>
</tr>
<tr>
<td>4. Na$_4$P$_2$O$_7$.10H$_2$O</td>
<td>Residue was very hard to dissolve in conc. acids. The residue obtained did not contain any AlB$_{12}$-phases, but only AlB$_2$ and unreacted boron.</td>
</tr>
<tr>
<td>5. MgNH$_4$PO$_4$.6H$_2$O</td>
<td>Reduced yield of $\beta$-AlB$_{12}$ crystals of very high resistance.</td>
</tr>
<tr>
<td>6. MgSO$_4$(Anhydrous) + Mg(ribbon)</td>
<td>Most of the mass stuck to the crucible. However, very few crystals of $\beta$-AlB$_2$ were obtained.</td>
</tr>
</tbody>
</table>
7. $\text{H}_2\text{SeO}_3$ (Selenous acid)  Black shiny crystals with an appearance similar to $\beta$-$\text{AlB}_2$ showed very high resistance.

8. $\text{KMnO}_4$  Shows microscopic black crystals with an appearance similar to $\beta$-$\text{AlB}_2$.

Previously reported resistivity for hot-pressed $\beta$-$\text{AlB}_2$ was 117 ohm.cm. (61). This is inconsistent with our observations on single crystal $\beta$-$\text{AlB}_2$.

These hot-pressed samples were prepared from 97% $\beta$-$\text{AlB}_2$ powder at about 800° - 900°C in graphite moulds. Our observation is that lower borides are formed in the range 800° - 1100°C. Hence there is a good possibility that lower borides of Al or of other impurities present could be formed e.g. ZrB$_2$, HfB$_2$, etc. Also a possibility of formation of boron carbide in the graphite mould cannot be overlooked. Most of these diborides and boron carbide are known to be semiconductors. Therefore, we think, that the conductivity of these hot-pressed samples does not represent the real conductivity of pure $\beta$-$\text{AlB}_2$.

$\alpha$-$\text{AlB}_2$, a crystal analogue of $\beta$-$\text{AlB}_2$, has been reported to be a semiconductor (59, 60), $\sigma = 5 \times 10^5$ ohm.cm.

Hence the number of carriers present, assuming $\mu = 1 \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$, would be:
\[ \sigma = \frac{1}{\delta} = 0.2 \times 10^{-5} \, \text{cm}^{-1} \text{ohm}^{-1} \]
\[ N = \frac{\sigma}{e\mu} = \frac{0.2 \times 10^{-5}}{1.6 \times 10^{-19} \times 1} \]
\[ N = 10^{13} \, \text{carriers/cm}^3 \]

The number of intrinsic carriers in \( \alpha\text{-AlB}_2 \) at 400°K can be calculated as:
\[ N = 2 \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} \times \exp \left( \frac{-E}{2kT} \right) \]
\[ = 2 \left( \frac{2 \times 3.14 \times 9 \times 10^{-28} \times 1.38 \times 10^{-16} \times 400}{43.56 \times 10^{-54}} \right)^{3/2} \times \exp \left( -\frac{2.5 \times 1.6 \times 10^{-12}/1.38 \times 10^{-16} \times 2 \times 400}{43.56 \times 10^{-54}} \right) \]
\[ = 3.8 \times 10^{19} \times e^{-36} \]
\[ = 3.8 \times 2.3 \times 10^{19} \times 10^{-16} \]
\[ N = 8.74 \times 10^{3} / \text{cm}^3 \]

Hence the number of carriers found in \( \alpha\text{-AlB}_2 \) is about \( 10^9 \) times more than would be found in a pure intrinsic sample. This indicates that the conductivity observed by Golikova et al \((59, 60)\) in \( \alpha\text{-AlB}_2 \) was extrinsic conductivity.

**Conclusions**

From our work on single crystals, we conclude that the resistivity of \( P\text{-AlB}_2 \) is at least \( 4 \times 10^7 \, \text{ohm} \cdot \text{cm} \) at room temperature.

Attempts at doping the \( P\text{-AlB}_2 \) crystals, by adding impurities to the melt, did not give crystals with increased conductivity.

The semiconductivity reported for hot-pressed \( P\text{-AlB}_2 \) does not represent the true conductivity of \( P\text{-AlB}_2 \).
Fig. VII Phase-diagram for Al-B system.
(after Serebryanskii et al, 27)

Fig. VIII Ideal arrangement of boron atoms in the B₄₄ polyatomic unit.
(after Matkovich et al, 49)
Fig. IX A comparison between (a) face-centered cubic, (b) body-centered cubic
and (c) tetragonal close-packed arrangements

(after Matkovich et al., 49)

Fig. X A crystallographic sketch of a common habit of $B-Al_H_x$. Crystal symmetry is
orthorhombic (pseudotetragonal). The pseudotetragonal nature is emphasized
by polysynthetic twinning on the (110) and (110) planes.

(after Kohn et al., 62)
Fig. XI

(a) Oscillation photograph
(\(\beta\)-AlB\(_{12}\))

(b) Zero-layer Weissenberg (1 hour exposure)
(\(\beta\)-AlB\(_{12}\))
Fig. XII (a) First-layer Weissenberg (7 hour exposure) 
$\beta$-AlB$_{12}$

Fig. XII (b) Second-layer Weissenberg (3 hour exposure) 
$\beta$-AlB$_{12}$
CHAPTER III

BORON - CARBIDE
Structure

As stated earlier, the presence of an icosahedron of $B_{12}$-atoms was first discovered (45) in boron carbide. Boron carbide is the parent or model-structure in the rhombohedral boride series.

The structure consists (49, 92) of nearly cubic closest packed icosahedra of $B_{12}$-atoms centered on the lattice points of a deformed face-centered lattice (Fig. XIII) bonded together along the diagonal of the lattice with a C-chain giving rise to the rhombohedral cell. Centered on each octahedral-interstice are the three C-atoms in a chain, the end C-atoms bonded to three B-atoms, one in each of the three closest icosahedra. The resulting structure is extremely hard and stable. The crystal structure of boron carbide has been studied by quite a few workers (74, 75, 45, 76) and is reviewed by Finley (77).

The central C-atom can be replaced by a B-atom giving a -C-B-C- chain in $B_{13}C_2$, by neutron irradiation. The other compounds in this series are $(3_4Si)_2$ or $B_{12}Si_3$, $(B_6Si)_2$ or $B_{12}Si_2$, $B_{12}S$, $B_{13}P_2$, $(B_6P)_2$ or $B_{12}P_2$ etc., and are summarized as follows:

Mathovich (78) and Cline et al (79) reported $B_4Si$ for the first time to be rhombohedral, isomorphous with $B_4C$ with three $B_4Si$ units/unit cell i.e. $B_{12}Si_3$, the three membered chain being formed by the 3-Si atoms.
However, Magnusson and Brosset (80) believe that the centre position remains occupied by boron and the third Si enters the boron icosahedra.

B$_6$Si has been described (81) as an orthorhombic structure resembling the structure of B$_4$C, having the chain of -Si-hole-Si-.

B$_{12}$S has been isolated (82) and shown to possess boron-carbide-type structure. The unit-cell is rhombohedral and the composition suggests the chain to be hole-S-hole. However (83), from a comparison with the other members of the series accommodation of sulphur in the central position requires a higher c/a axial ratio than B$_{12}$S displays. Thus partial occupancy of the two end positions by sulphur appears to be more consistent with the data.

B$_{13}$P$_2$ is reported (84) to be isomorphous with B$_4$C having a rhombohedral unit-cell with P-B-P chain and boron icosahedra.

LaPlaca et al (85) have reported a boron phosphide having the central site vacant. This phase was shown to have composition B$_6$P with two formula weights/unit cell giving a B$_{12}$P$_2$ rhombohedral unit. B$_6$P was also prepared by several methods by Hill (67). Boron oxide was first reported as B$_7$O of orthorhombic symmetry (86), this was corrected by LaPlaca.
et al (85') to a $B_{13}O_2$ composition with a rhombohedral symmetry. However, Rizzo (87') has proposed the composition of $B_6O$. It appears likely that this compound is a $B_{12}O_2$ in which oxygen occupies the two end positions of the chain in the rhombohedral cell.

Another boron arsenide with a composition of $B_{6-7}As$ was first reported by Williams and Ruehrwein (88'), and was shown to be isotypic with $B_{13}P_2$ belonging to the rhombohedral boride series. However, due to impurities and some variations occurring in the density measurements, it has not been determined whether the stichometry is $B_{13}As_2$ or $B_{12}As_2$.

Table 3

<table>
<thead>
<tr>
<th>Compound in rhombohedral Boride series</th>
<th>Rhombohedral cell with corresponding hexagonal cell dimensions in Å.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(B_4Si)<em>3$ or $B</em>{12}Si_3$</td>
<td>$a = 6.330, c = 12.736^{95}$</td>
</tr>
<tr>
<td>$(B_6Si)<em>2$ or $B</em>{12}Si_2$</td>
<td>$b = 18.267, c = 9.885$</td>
</tr>
<tr>
<td>$B_{12}S$</td>
<td>$\alpha = 67.56^{96}$, $a = 5.19$,</td>
</tr>
<tr>
<td></td>
<td>Hexagonal, $a = 5.80$, $c = 11.90$</td>
</tr>
<tr>
<td>$B_{13}P_2$ or $B_{12}PBP$</td>
<td>$a = 5.984$, $c = 11.85^{101}$</td>
</tr>
<tr>
<td></td>
<td>$a = 6.01$, $c = 11.72^{89}$</td>
</tr>
<tr>
<td>$(B_6O)<em>2$ or $B</em>{12}$O-hole-0</td>
<td>$a = 5.37$, $c = 12.31^{102}$</td>
</tr>
<tr>
<td></td>
<td>$a = 5.395$, $c = 12.342^{105}$</td>
</tr>
<tr>
<td>$B_{13}As_2$ or $B_{12}As_2$</td>
<td>$a = 6.142$, $c = 11.892^{90,91}$</td>
</tr>
<tr>
<td>$(B_4C)<em>3$ or $B</em>{12}C_3$</td>
<td>$\alpha = 65.18^{18}$, $a = 5.19$,</td>
</tr>
<tr>
<td></td>
<td>Hexagonal cell, $a = 5.60$, $c = 12.12$</td>
</tr>
<tr>
<td>$\beta$-rhombohedral boron</td>
<td>$\alpha = 5.057$, $c = 58.04^{1}$</td>
</tr>
<tr>
<td></td>
<td>Hexagonal cell $a = 4.908$, $c = 12.567$</td>
</tr>
</tbody>
</table>
Electrical Properties of Boron-Carbide

As discussed in the previous chapter, the electronic structure of boron-carbide, $B_{12}C_3$, described by Longuet-Higgins and Robert (56) is a closed shell one. It utilizes all 48 electrons available for bonding.

Boron-carbide is found to be a good semiconductor (93, 73). Electronic band structure given by Yamazaki (93) shows that the 48 electrons available per $B_{12}C_3$ unit, just fill the valence bands and the conduction bands are all empty. The energy gap between valence and conduction bands is calculated to be about 1 to 2.5 ev. between the zone boundary and the zone center. This explains the appreciable electric conductivity of this crystal.

J. Lagrenaudie (73) has reported boron carbide to be a semiconductor along with Al-dodecaborides.

Samsonov (94) found that boron carbide is a semiconductor, the width of the forbidden zone being 1.64 ev. This is within the range given by Yamazaki.

Samsonov and Sinel'nikova (95) also measured the activation energy $E$ from the temperature dependence of resistivity of hot pressed boron-carbide specimens, which is given as $E = 1.64$ ev.

The resistivity of hot-pressed boron carbide reported by Thompson (96) is 0.45 ohm.cm and by Finlay (97) is $0.3 - 0.8$ ohm.cm.
Recent studies on pyrolytic boron-carbide by
Neshpor et al (98, 99) showed the chemical composition
to be B - 78.5\%, C - 21.3\%, Fe - 0.2\%, Mn, Mg, Si, Al,
Ca, Cu, Cr, Ni, Ti, etc. being in extremely small amounts.
This indicates a small excess of boron over stoichi-
ometric composition (21.72\% C and 78.28\% B), hence a partial
replacement of carbon in the chain by boron is possible.
They found that boron carbide is an extrinsic p-type
semiconductor with $3.4 \times 10^{20}$ carriers/cm$^3$ in the tempera-
ture range 20$^\circ$ - 1000$^\circ$K. The activation energy of the
extrinsic current carriers was 0.22 eV. 'P-type' conduction
was probably by partial replacement of C-atoms in the
B$_{12}$C$_3$-composition by boron-atoms having lower valence.

Hall mobility reported by the above workers (98,99)
for pyrolytic boron carbide is 0.13 cm$^2$V$^{-1}$sec$^{-1}$, which
appears quite low compared with common semiconductors
like SiC or that of P-rhombohedral boron for which
$\mu = 55$ cm$^2$V$^{-1}$sec$^{-1}$ for p-type conduction (100) and
$\mu = 1$ cm$^2$V$^{-1}$sec$^{-1}$ for n-type conduction (101).

Properties and Uses

Boron-carbide is high melting, (melting point 2450$^\circ$C)
(96,97), extremely hard, and a good conductor of heat
and electricity. It is resistant (102) to strong alkali
and acids and in massive form resists oxidation by air
up to 600$^\circ$C.

The Knoop hardness reported (97) is 2800 k$_{100}$ kg/mm$^2$.
Microhardness reported by Thompson (96) is V.P.N.
4000 - 5000 kg/mm$^2$. 
Thermal conductivity reported by Deem and Lucks (103) is 0.065 C.G.S. units.

Based on its extreme hardness, boron-carbide is widely used for lapping and polishing purposes.

Boron carbide is used as a convenient base for the preparation of semiconductive resistors (104), which are useful as low-ohmic thermocompensators, being very stable to temperature changes and humid air.

Van der Pauw's Method

The method used for the measurements of specific resistivity is that of Van der Pauw (105). The significance of this method lies in the fact that the measurements can be made on a sample of arbitrary shape provided it has two flat parallel surfaces. The requirements for use of this theorem are --

1. The contacts should be at the circumference of the sample.
2. The contacts are sufficiently small.
3. The sample has to be homogenous in thickness.
4. The surface of the sample is singly connected, that is, the sample does not have isolated holes.
Our samples were boron carbide single crystals obtained from Norton Co., Niagara Falls, Ontario, which were in the form of flat plates with arbitrary shapes. Hence all above requirements are fulfilled.

Thus, four spring loaded tungsten contacts were made along the circumference of the flat boron-carbide crystal. The current was passed between an adjacent pair of contacts while the voltage across the other was measured. The measurements were repeated by reversing the current and voltage polarity both. This gave four voltage and current readings for one combination of the pairs. This was repeated for the rest of the three cyclic combinations to give sixteen current and voltage readings. Thus 4 different resistances $R_1$, $R_2$, $R_3$ and $R_4$ were obtained from these voltage to current ratios. These were reduced to two, $R_1$ and $R_2$ by averaging out $R_1$ and $R_3$ and $R_2$ and $R_4$ respectively.

The specific resistivity in such a case is given by Van der Pauw as

$$\rho = \frac{d}{(2\ln 2)}(R_1 + R_2)f(R_1/R_2) \text{ ohm}\cdot\text{cm}$$

Where $d$ is the thickness of the crystal in cms., voltage and current are measured in millivolts and milli-ampere respectively, the function $f(R_1/R_2)$ is given by Van der Pauw in graphical form.
Electrical Measurements

The crystal under consideration was glued on a jig using very small amounts of "Lepages" glue. The jig consists of a plastic plate of dimensions 2 x 2 inches. The four copper-plates of side 1/2" are fixed at the four corners of the plastic plate by means of #4-40NF brass screws.

The tungsten electrode was then bent to shape as shown in Fig. XIV with a pair of tweezers. The doubly bent loop structure provides the necessary spring action for electrical contact with the crystal.

These tungsten electrodes are soldered to the metal pieces on the corners of the jig by a hot-dip method. The soldering alloy is allowed to melt using a soldering-iron which is coated on the tungsten wire so as to provide a firm, good electrical contact between the tungsten wire and the metal piece. The four leads from the corners are connected by means of a wire to the crystal socket. The contacts between the four tungsten leads and the crystal were made by placing the tungsten points at the sides of the crystal mechanically.

Tungsten Microelectrode Preparations

Four tungsten wires used for the electrical contacts with the crystal, were fabricated by the method described by Cool and Crawford (106). This method is simpler than most methods published so far and yet yields an electrode of good quality.

A 0.625 cm. diameter carbon rod was pushed through
the bottom of a 50 ml. polyethylene beaker to a distance of about 2.5 cm. and sealed in place with an epoxy cement. A 7.5 cm square piece of thick plexiglas with a hole drilled in the center was used as a cover. This cover had an alligator clip to hold a piece of wire in the hole properly. The carbon rod and alligator clip were connected to the secondary of a 6.3 V ac, 1A transformer, which, in turn, was powered from a variable voltage source.

The beaker was filled with a solution which was 70% 8-10M NaOH and 30% 5N NaOH. A 5 cm length of tungsten wire (127 u in diameter) was lowered 6-7 mm into the solution and held in place with the alligator clip. The wire and the carbon rod would be vertically aligned and their tips were about 1.8 cm. apart. A 6.3 V ac potential was then applied across the alligator clip–carbon rod connections. A vigorous bubbling in the area of the immersed wire would be immediately obvious. For obvious reasons, this procedure should be carried out under a fume hood, even though the NaOH should eliminate the production of significant amounts of HCN. The electrode was left immersed and the 6.3 V ac potential applied until the vigorous bubbling ceases. The cessation of bubbling, although not complete will be sudden and an apparent event to any observer. At this
point, the applied voltage was turned off, the variable voltage supply setting was changed, and a polishing potential of 0.8 V ac was applied across the secondary of the 6.3 V ac transformer for 15 - 20 seconds. The etched electrode was then removed and rinsed in the following solutions, in order:
(i) saturated Na$_2$CO$_3$, (ii) 1% acetic acid, (iii) 95% alcohol and (iv) xylene. This gives an electrode with a tip diameter between 0.5 and 2.0 µm. The entire etching procedure takes about 2 minutes.
"Zotting" is the process for reducing the resistivity between the contacts and the crystal by discharging a capacitor.

The tip of a tungsten electrode often gets oxidized in air and hence contains a layer of tungsten-oxide on the surface. This layer of oxide or particles of glue or dust on the surface of the crystal are burnt off by discharging a capacitor over the contacts to give a contact between clean surface of crystal and the tungsten wire.

The capacitor discharge network is shown in Fig.XVI. The function switch selected one of the pair 1 and 3 or 2 and 4 for zotting and then resistances of the zotted leads can be measured. The discharge energy can be selected in three ranges. The "zotting" is done in such a manner that the contact resistances become minimum.
EXPERIMENTAL

Electrical Measurements on Boron Carbide Crystals

The single crystals used for the electrical measurements were taken from a batch prepared from the melt in a resistance furnace at Horton Co., Chippawa, Ontario. They had separated in irregular shapes, up to 10 mm. in maximum dimension, along apparent grain boundaries. Single crystals from this batch have previously been studied by Tucker and Senio (8) and by Silver and Bray (107).

Crystals from this batch, known to be of good quality and high purity and very close to stoichiometric $\text{B}_{12}\text{C}_3$, were cut and sectioned into slabs by Mr. Tarno Roopma at the Geology Dept., Brock University. Since there are no visible external faces, these slabs were randomly oriented sections.

RESULTS AND DISCUSSION

The resistivity of the two hot-pressed specimens was found to be 0.90 and 0.56 ohm.cm., in reasonable agreement with the reported range (96, 97) of $\rho = 0.3 - 0.8$ ohm.cm. However, the contacts appear to be rectifying, particularly for D9531 sample. This can be attributed to inhomogeneity and presence of grain boundaries which are always present in hot-pressed samples. Each grain boundary disturbs the periodicity
VANDER PAUW MEASUREMENT

Hot Pressed Crystal Boron Carbide  Thickness (b) 0.230...cm  Date .................

Particulars  D 9489

<table>
<thead>
<tr>
<th></th>
<th>Resistivity ρ</th>
<th>A. C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Voltages in mV, currents in mA)</td>
<td>A.C. frequency</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i_{12} +9.4...</td>
<td>i_{12} +9.0...</td>
<td>i_{21} -8.2...</td>
</tr>
<tr>
<td>v_{34} =2.15...</td>
<td>v_{43} +2.11...</td>
<td>v_{34} +2.25...</td>
</tr>
<tr>
<td>i_{23} +5.7...</td>
<td>i_{23} +5.6...</td>
<td>i_{32} -5.2...</td>
</tr>
<tr>
<td>v_{41} =13.0...</td>
<td>v_{14} +13.0...</td>
<td>v_{41} +12.1...</td>
</tr>
<tr>
<td>i_{34} +13.0...</td>
<td>i_{34} +13.2...</td>
<td>i_{43} -13.5...</td>
</tr>
<tr>
<td>v_{12} -3.00...</td>
<td>v_{21} +2.9...</td>
<td>v_{12} +3.1...</td>
</tr>
<tr>
<td>i_{41} +13.6...</td>
<td>i_{41} +13.6...</td>
<td>i_{14} -13.5...</td>
</tr>
<tr>
<td>v_{23} =28.4...</td>
<td>v_{32} +28.5...</td>
<td>v_{23} +28.0...</td>
</tr>
</tbody>
</table>

R_1/R_2 9.174  f(R_1/R_2) 0.715  (R_1+R_2) 2.44  f x (R_1+R_2) 1.745  (Average)

A.C. Calibration ...........
..............................
..............................

ρ = 2.266 x b x Average = 0.909 ....... Ωcm.

Thermocouple (mV) ............  Temp. °C ............  1/T .............
### VANDER PAUW MEASUREMENT

<table>
<thead>
<tr>
<th>Particulars</th>
<th>D 9531</th>
</tr>
</thead>
</table>

#### Hot Pressed Boron Carbide

<table>
<thead>
<tr>
<th>Thickness (b)</th>
<th>0.240 cm</th>
<th>Date</th>
</tr>
</thead>
</table>

#### Resistivity $\rho$

(Voltages in mV, currents in mA)

<table>
<thead>
<tr>
<th>$i_{12}$</th>
<th>$v_{34}$</th>
<th>$i_{23}$</th>
<th>$v_{41}$</th>
<th>$i_{34}$</th>
<th>$v_{12}$</th>
<th>$i_{41}$</th>
<th>$v_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-1.0...$</td>
<td>$+3.1...$</td>
<td>$-0.5...$</td>
<td>$+2.9...$</td>
<td>$-0.5...$</td>
<td>$+2.9...$</td>
<td>$-1.0...$</td>
<td>$+7.7...$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$i_{21}$</th>
<th>$v_{34}$</th>
<th>$i_{32}$</th>
<th>$v_{41}$</th>
<th>$i_{43}$</th>
<th>$v_{12}$</th>
<th>$i_{14}$</th>
<th>$v_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+10...$</td>
<td>$-2.9...$</td>
<td>$+5...$</td>
<td>$-3.6...$</td>
<td>$+6...$</td>
<td>$-1.8...$</td>
<td>$+12...$</td>
<td>$-5.9...$</td>
</tr>
</tbody>
</table>

#### A.C. Calibrations

- $R_1/R_2 = 1.536$
- $f(R_1/R_2) = 0.984$
- $(R_1+R_2) = 1.052$
- $f \times (R_1+R_2) = 1.0557$  (Average)

A.C. Calibration

- $\rho = 2.266 \times b \times \text{Average} = 0.5630$ $\Omega \text{cm}$

Thermocouple (mV)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$1/T$</th>
</tr>
</thead>
</table>

Table No. 5
**VANDER PAUW MEASUREMENT**

Table No. 6...

Crystal Barcon-Carbide-A Thickness (b) 0.051 cm Date

Particulars Single Crystal

<table>
<thead>
<tr>
<th>Resistivity $\rho$</th>
<th>A. C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Volts in mV, currents in mA).</td>
<td>A.C. frequency</td>
</tr>
<tr>
<td>$i_{12}$ = 20.....</td>
<td>$i_{12}$ = 19.....</td>
</tr>
<tr>
<td>$v_{34} = 54$.....</td>
<td>$v_{43} = 53$.....</td>
</tr>
<tr>
<td>$i_{23} = 12$.....</td>
<td>$i_{23} = 12$.....</td>
</tr>
<tr>
<td>$v_{41} = 20$.....</td>
<td>$v_{14} = 16$.....</td>
</tr>
<tr>
<td>$i_{34} = 13$.....</td>
<td>$i_{34} = 13$.....</td>
</tr>
<tr>
<td>$v_{12} = 45$.....</td>
<td>$v_{21} = 41$.....</td>
</tr>
<tr>
<td>$i_{41} = 26$.....</td>
<td>$i_{41} = 23$.....</td>
</tr>
<tr>
<td>$v_{23} = 37$.....</td>
<td>$v_{32} = 34$.....</td>
</tr>
</tbody>
</table>

$R_1/R_2 = 2.0637$ | $f(R_1/R_2) = 0.957$ | $(R_1+R_2) = 4.3875$ | $f \times (R_1+R_2) = 4.1988$ (Average)

A.C. Calibration

$\rho = 2.266 \times b \times \text{Average} = 0.4652 \ \Omega \text{cm}$

Thermocouple (mV) Temp. °C $1/T$


VANDER PAUW MEASUREMENT

Table No ... 7 ...

Crystal Boron Carbide-B Thickness (b) 0.089 cm Date .................

Particulars Single Crystal

<table>
<thead>
<tr>
<th></th>
<th>Resistivity ρ</th>
<th>A. C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Voltages in mV, currents in mA)</td>
<td>A.C. frequency</td>
</tr>
<tr>
<td>i_12 -15......</td>
<td>i_12 -15......</td>
<td>i_21 ±16......</td>
</tr>
<tr>
<td>v_34 +26......</td>
<td>v_43 -25......</td>
<td>v_34 -29......</td>
</tr>
<tr>
<td>i_23 -11......</td>
<td>i_23 -11......</td>
<td>i_32 ±12......</td>
</tr>
<tr>
<td>v_41 +7......</td>
<td>v_14 -7......</td>
<td>v_41 ±7......</td>
</tr>
<tr>
<td>i_34 -8......</td>
<td>i_34 -8......</td>
<td>i_43 ±8......</td>
</tr>
<tr>
<td>v_12 ±14......</td>
<td>v_21 -14......</td>
<td>v_12 -13......</td>
</tr>
<tr>
<td>i_41 -9 ......</td>
<td>i_41 -9 ......</td>
<td>i_14 ±10......</td>
</tr>
<tr>
<td>v_23 ±11......</td>
<td>v_32 -11......</td>
<td>v_23 -10......</td>
</tr>
</tbody>
</table>

R_1/R_2 1.9822... f(R_1/R_2) 0.961... (R_1+R_2) 2.6548... f x (R_1+R_2) 2.5513... (Average)

A.C. Calibration ...........

...........................

ρ = 2.266 x b x Average = ................. Ωcm.

Thermocouple (mV) ........... Temp. °C ............ 1/T ............
VANDER PAUW MEASUREMENT

Table No ... 8 ...

Crystal: Boron Carbide-C
Thickness (b): 0.05 cm
Date: .........................

Particulars: Single Crystal

<table>
<thead>
<tr>
<th>Particulars</th>
<th>Resistivity $\rho$</th>
<th>A. C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Voltages in mV, currents in mA)</td>
<td>A.C. frequency</td>
</tr>
<tr>
<td></td>
<td>..........................</td>
<td>...................</td>
</tr>
<tr>
<td>$i_{12}$ 16</td>
<td>$i_{12}$ 16</td>
<td>$i_{21}$ 16</td>
</tr>
<tr>
<td>$v_{34}$ 10</td>
<td>$v_{43}$ 6</td>
<td>$v_{34}$ 7</td>
</tr>
<tr>
<td>$i_{23}$ 10</td>
<td>$i_{23}$ 10</td>
<td>$i_{32}$ 10</td>
</tr>
<tr>
<td>$v_{41}$ 17</td>
<td>$v_{14}$ 14</td>
<td>$v_{41}$ 14</td>
</tr>
<tr>
<td>$i_{34}$ 15</td>
<td>$i_{34}$ 15</td>
<td>$i_{43}$ 16</td>
</tr>
<tr>
<td>$v_{12}$ 10</td>
<td>$v_{21}$ 6</td>
<td>$v_{12}$ 7</td>
</tr>
<tr>
<td>$i_{41}$ 31</td>
<td>$i_{41}$ 30</td>
<td>$i_{14}$ 32</td>
</tr>
<tr>
<td>$v_{23}$ 42</td>
<td>$v_{32}$ 37</td>
<td>$v_{23}$ 36</td>
</tr>
</tbody>
</table>

$R_1/R_2 = 2.6571$, $f(R_1/R_2) = 0.223$, $(R_1+R_2)_1 = 915.2$, $f \times (R_1+R_2)_1 = 7.677$. (Average)

A.C. Calibration

..........................
..........................

..........................

$\rho = 2.266 \times b \times \text{Average} = 0.2003$ Ωcm

Thermocouple (mV) ......... Temp. °C ............. $1/T$ .............
**VANDER PAUW MEASUREMENT**

<table>
<thead>
<tr>
<th>Crystal Boron Carbide-D Thickness (b)</th>
<th>0.990 cm</th>
<th>Date</th>
<th>Particulars</th>
<th>Single Crystal</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Resistivity ρ</th>
<th>A. C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Voltages in mV, currents in mA.)</td>
<td>A.C. frequency</td>
</tr>
<tr>
<td>i₁₂ ±.22.....</td>
<td>i₂₁ ±.23.....</td>
</tr>
<tr>
<td>v₃₄ ±.9.4.....</td>
<td>v₄₃ ±.9.9.....</td>
</tr>
<tr>
<td>i₂₃ ±.19.....</td>
<td>i₂₃ ±.19.....</td>
</tr>
<tr>
<td>v₄₁ ±.4.4.....</td>
<td>v₄₁ ±.4.6.....</td>
</tr>
<tr>
<td>i₁₃ ±.19.....</td>
<td>i₁₃ ±.19.....</td>
</tr>
<tr>
<td>v₁₂ ±.8.8.....</td>
<td>v₁₂ ±.8.9.....</td>
</tr>
<tr>
<td>i₄₁ ±.22.....</td>
<td>i₄₁ ±.22.....</td>
</tr>
<tr>
<td>v₂₃ ±.5.4.....</td>
<td>v₂₃ ±.5.3.....</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R₁/R₂ 1.7838</th>
<th>f(R₁/R₂) 0.972</th>
<th>(R₁+R₂) 0.9484</th>
<th>f x (R₁+R₂) 0.6302. (Average)</th>
</tr>
</thead>
</table>

A.C. Calibration ............

........................................

ρ = 2.266 x b x Average = ....0.1255............. Ωcm.

<table>
<thead>
<tr>
<th>Thermocouple (mV)</th>
<th>Temp. °C</th>
<th>1/T</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of the lattice. Impurities and gases are transported along grain boundaries. Oxygen may be adsorbed on the surface of the grains in the form of negative ions or as an oxide layer. Oxide layers having a high resistivity can reduce the conductivity of the solid. This might be a reason for slightly high resistivity 0.90 ohm.cm. of D9489 sample.

The resistivity of two crystals A and B was found to be 0.48 and 0.52 ohm.cm., in agreement with the reported range of 0.3 - 0.8 ohm.cm..

The resistivity of two more crystals, C and D was found somewhat lower than so far reported. It was 0.20 and 0.13 ohm.cm..

The resistivity of crystals E and F could not be measured due to drifting voltages.

In case of these single crystals also, the contacts were found to be rectifying. The rectification occurred inside probably because of inhomogeneity and non-uniform concentration of impurities and of contact problems.

We were not able to measure any significant Hall effect on any of these crystals, at all. With the increased input voltage, drifting of the output voltage also increases and the small Hall voltage can not be distinguished from noise.
This indicates that boron carbide has very low Hall mobility. The electrical circuit, we used, could detect a minimum Hall voltage of \(10^{-6}\) volts and the magnetic field applied was about 2.4 kilogauss. We could not measure any change in voltage, hence the maximum mobility, \(\mu\), of carriers can be calculated as follows:

Hall coefficient \(R_H = \frac{\Delta v \times b}{B \times I} \times 10^5 \text{ cm}^3/\text{coulomb}\)

\(\Delta v = \text{change in voltage in millivolts}\)

\(I = \text{current in milliamperes}\)

\(B = \text{magnetic field in kilogauss}\)

\(b = \text{thickness of the sample.}\)

We take average \(b = 0.050\) cm. and average \(q = 0.50\) ohm.cm. for boron carbide.

We assume change in voltage \(\Delta v\) to be minimum as \(1 \times 10^{-3}\) millivolts for 10 milliampere current. (For SiC, this \(v = 0.10\) millivolts for \(I = 10\) milliamperes.)

\[R_H = \frac{10^{-3} \times 0.05}{6.6 \times 10} \times 10^5\]

\[R_H = 0.076 \text{ cm}^3/\text{coulomb}\]

Therefore, mobility, \(\mu\), is given as---

\[\mu = \frac{R_H}{q} \frac{\text{cm}^2}{\text{volt} \cdot \text{sec}^{-1}}\]

\[= \frac{0.076}{0.50}\]

\[\mu = 0.16 \frac{\text{cm}^2}{\text{volt} \cdot \text{sec}^{-1}}\]
Our calculations show that the mobility of the carriers in boron carbide is $0.16 \text{ cm}^2\text{v}^{-1}\text{sec}^{-1}$ or less.

This is consistent with the reported mobility for pyrolytic boron (98, 99) carbide as $0.13 \text{ cm}^2\text{v}^{-1}\text{sec}^{-1}$.

The number of current carriers in our boron carbide, hence can be calculated as:

\[ \sigma = Ne \mu \]

\[ N = \frac{\sigma}{e \mu} \]

\[ \sigma = 0.5 \text{ ohm} \cdot \text{cm}. \]

\[ \zeta = \frac{1}{\sigma} = 2 \text{ ohm}^{-1}\text{cm}^{-1} \]

\[ N = \frac{2}{1.6 \times 10^{-19} \times 0.13} \text{ carrier/cm}^3 \]

\[ = 9.6 \times 10^{19} \]

\[ N = 10^{20}/\text{cm}^3 \]

The number of intrinsic carriers in boron carbide at room temperature can be calculated as follows (71):

\[ N = 2 \left( \frac{2 \pi m_e kT}{\hbar^2} \right)^{3/2} \exp^{-E/2kT} \]

Average $E$ for boron carbide is $1.64 \text{ eV}$.

\[ N = 2.5 \times 10^{19} \times \exp^{-\left(1.64 \times 1.6 \times 10^{-12}/1.38 \times 10^{-16} \times 2 \times 300\right)} \]

\[ = 2.5 \times 10^{19} \times e^{-32} \]

\[ = 2.5 \times 1.3 \times 10^{19} \times 10^{-14} \]

\[ = 3.25 \times 10^{5}/\text{cm}^3 \]

By comparing this value with the calculated number of carriers in our samples as $N = 10^{20}/\text{cm}^3$ it is evident that these crystals have extrinsic conductivity.
This observed number of carriers in our samples, although in agreement with the reported concentration (98, 99) of $3 \times 10^{20}$ carriers/cm$^3$ for pyrolytic boron carbide, appears to be higher than usual semiconductors. However, the observed resistivity (0.50 ohm.cm.) is quite high compared with the usual semiconductors e.g. SiC having $\xi = 0.035$ ohm.cm. has an approximate carrier concentration $2.3 \times 10^{17}$ carriers/cm$^3$. Hence the only way the higher carrier concentration can be explained in boron carbide is by assuming the mobility of carriers lower than that of SiC. This justifies our observation of low mobility in boron carbide 0.16 cm$^2$v$^{-1}$sec$^{-1}$ or less (mobility of carriers in SiC is about 900 cm$^2$v$^{-1}$sec$^{-1}$).

However, samples C and D showed still lower resistivity 0.13 and 0.20 ohm.cm.. To explain this only on the basis of impurity contents, one has to assume still higher number of carriers in these samples. Such a high concentration of carriers is uncommon in usual semiconductors.

The electrical resistivity may be dependent on crystal orientation, because boron carbide has a non-cubic symmetry. Therefore, we have studied orientation in these crystals by conventional Laue back-reflection method (108, 109).
Orientation of Boron Carbide Crystals by Laue Method:

The procedure can be summarized as follows:

The Laue photographs were obtained by mounting the crystal with its flat surface perpendicular to x-ray beam. The stereographic projections were drawn from these photographs and angles between important zones and poles were measured. The interplanar angles were calculated for the ideal boron carbide crystal using the equation for a hexagonal system:

\[
\cos x = \frac{2}{3a^2} \left( 2h_1h_2 + 2k_1k_2 + h_1k_2 + k_1h_2 \right) + \frac{l_1l_2}{c^2}
\]

\[
\left( \left( \frac{4}{3a^2} \left( h_1^2 + k_1^2 + h_1k_1 \right) + \frac{l_1^2}{c^2} \right) \left( \frac{4}{3a^2} \left( h_2^2 + k_2^2 + h_2k_2 \right) + \frac{l_2^2}{c^2} \right) \right)^{1/2}
\]

The inclination of C-axis with respect to x-ray beam projection for boron carbide \( c/a = 2.167 \).

The orientations are:

- Crystal A: 22°
- Crystal B: 11°
- Crystal C: 29°
- Crystal D: 27°

Orientation of crystal E could not be measured, since it didn't show single spots of reflection, indicating the possibility of a polycrystalline sample.

Discussion

As previously noted, the resistivity measurements could not be done on sample E. From its Laue-photograph,
it shows the possibility of a polycrystalline sample. This may explain the above observation. Grain boundaries are known to affect the resistivity in several ways.

Crystals A and B, which have almost equal resistivities, had the inclination of C-axes inclined between 10° and 22°. This indicates that the resistivity of boron carbide single crystals remains almost constant in the above range of inclination.

Crystals C and D having lower resistivities 0.20 and 0.13 ohm.cm. showed an increased inclination up to 27° - 30°. This indicates the possibility that the electrical resistivity of boron carbide is orientation dependent. Moreover resistivity when C-axis is parallel to the direction of current, $\rho_{\parallel}$, is less than when it is perpendicular to the direction of current $\rho_{\perp}$.

Conclusions

The boron carbide crystals prepared from a melt at Norton Co., Ontario, have resistivities in the range of 0.13 to 0.52 ohm.cm.

The Hall mobility in these crystals is 0.16 cm$^2$V$^{-1}$sec$^{-1}$ or lower.

The samples with the resistivity of about 0.50 ohm.cm. have a high concentration of carriers about $10^{20}$/cm$^3$, hence the conductivity is extrinsic conductivity.
The resistivity of boron carbide single crystals may be orientation dependent and $\rho_{\parallel}$ is less than $\rho_{\perp}$, if $\rho_{\parallel}$ is measured along the c-axis.
Fig. XIII. Rhombohedral unit cell
(after Thompson, 92)

Whisker assembly for the ceramic cartridge..............FIG.XIV

Crystal mounted on non-conducting jig.......................FIG.XV
Leads 13 and 24 respectively are turned to ZOT, followed by resistance check.

**4 POLE : 6 POSN SW. ROTARY. L&N. LOW NOISE**

![Diagram](image)

( Rack mounted with crystal input, 5 pin female conn. in 12 and 34; see config.)

.................FIG. XVI
Table 10
Angles Between Crystallographic Planes
For The Boron Carbide Hexagonal System

\((c/a = 2.167)\)

<table>
<thead>
<tr>
<th>(h_1k_1l_1)</th>
<th>(h_2k_2l_2)</th>
<th>Angle in Degrees</th>
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Fig. XVII POLLE DIAGRAM: for Boron Carbide $c/a = 2.167$
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