1953

**Electrical properties of crystalline boron**

William Corr Shaw  
*Iowa State College*

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UMI
ELECTRICAL PROPERTIES OF 
CRYSTALLINE BORON 

BY

William Corr Shaw

A Dissertation Submitted to the 
Graduate Faculty in Partial Fulfillment of 
The Requirements for the Degree of 
DOCTOR OF PHILOSOPHY 

Major Subject: Physics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Dean of Graduate College

Iowa State College

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I. INTRODUCTION

A. Electrical Properties of Crystalline Boron

The electrical properties of crystalline boron have received relatively little attention in the literature. In Table 1 the elements which show the electrical properties of semiconductors are underlined. The number of extra underlines corresponds to the relative order of magnitude of the number of publications on the semiconducting properties of the element. (References 1, 2, 3, 4, 5.) (References are representative only.)

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Until recently, (Refs. 6, 7, 8) almost no papers had appeared considering boron in the light of modern solid state theory. This apparent neglect of boron is not due to lack of interest, but is due to the unavailability of sizeable single crystals of boron. All attempts to grow single crystals of boron larger than a few micrograms have so far failed. The difficulties in working with crystals this small are responsible, to a great extent, for the scarcity of publications on the semiconducting properties of boron.

In 1909, Weintraub (Ref. 9) studied some of the electrical properties of polycrystalline boron. Weintraub reported a reduction in resistance of one specimen, by a factor of $10^6$, when the specimen was heated to "beginning red". In 1913, Weintraub reported that the average resistivity of polycrystalline boron was about $10^6$ ohm cm and that impurities reduced this resistivity. Weintraub studied, and attempted to explain, the non-linear voltage current characteristics of his boron. He observed that the potential drop across a specimen of boron approached a maximum value, as the current through the specimen was increased. At higher currents the potential drop decreased. He used an empirical expression for the "breakdown voltage" which was based on a variation of resistance with temperature as $\exp(\alpha T)$, where $\alpha$ is a constant and $T$ is the
temperature in degrees centigrade. It is unfortunate that he did not try $\exp(\alpha/T)$, where $T$ is absolute temperature. This latter expression enters modern solid state theory and fits his data much better than the expression which he used.

In 1918, Lyle (Ref. 11) studied the "breakdown effect", first observed by Weintraub, and found the effect to be reproducible. He plotted resistance as a function of centigrade temperature and was able to relate the effective resistance of boron to the power input. In 1939, Bruce and Hickling (Ref. 12) made an oscilloscopic study of what they called the "gas discharge effect" in crystalline boron, but they made no attempt to explain the effect. In 1950, Shinn (Ref. 13) observed this same effect in samples of the crystals later used in the present work.

In 1943, Laubengayer and others (Ref. 14) reported their inability to observe large changes in the resistance of crystalline boron when the temperature was changed and they attributed Weintraub's results to impurities. This conclusion is contrary to present theories and it seems more probable that the samples tested by Laubengayer were impure.

The only reported studies of the semiconducting nature of crystalline boron, other than that of the present writer (Ref. 6), were made recently by Lagrenaudie (Refs. 7, 8).
Using Weintraub's data Lagrenaudie reported the intrinsic energy gap to be 1.2 electron volts. Using data on samples of boron which he collected from others, Lagrenaudie later reported the intrinsic energy gap to be 1.28 electron volts. On the basis of qualitative studies of thermoelectric and rectification effects, he reported that boron is a predominately p-type semiconductor. This latter observation was previously reported by the present writer. Lagrenaudie stated that in order to study these effects more carefully, it would be necessary to use single crystals of boron. The present work is concerned with single crystals.

B. Other Properties of Crystalline Boron

Boron, with atomic number 5, has an interesting positional relationship to the other monatomic semiconductors in the periodic table. Some elementary chemistry texts (Ref. 15) designate a line between boron (B) and tellurium (Te), as in Table 1, as the division between metals and non-metals. Most of the monatomic semiconductors lie within a narrow band parallel to this line.

Crystalline boron, though relatively brittle compared to diamond, is second only to diamond in hardness. Its almost jet black color appears sometimes to have a bluish to brownish cast. Facets on the minute single crystals are
clearly visible when viewed through a microscope of at least 30 power. Amorphorous boron is rapidly attacked, but the crystals are only slowly etched, by nitric acid. Crystalline boron is insoluble in hot strong alkalis or in hydrofluoric acid.

The crystal structure of crystalline boron is not simple. Hoard, Geller and Hughes (Ref. 16) have recently reported that the tetragonal unit cell contains fifty atoms. They describe the structure as follows: Forty-eight atoms are at the vertices of four nearly regular icosahedra. (A regular icosahedra has 20 equilaterally triangular sides.) The icosahedra are centered tetrahedrally and linked so that each boron atom has six bonds to the corners of a pentagonal pyramid. The two remaining atoms form only four tetrahedrally directed bonds to complete the network. According to Hoard, Geller and Hughes, the mean distance to the six nearest neighbors is between 1.75 and 1.80 Å. Weissenberg patterns and a density of 2.31 gm/cm³ were used in their analysis. Godfrey and Warren (Ref. 17) had previously reported an average minimum interatomic distance of 1.89 Å.

C. Preparation of Crystalline Boron

High purity polycrystalline boron was first prepared by Weintraub in 1909 (Ref. 9). Weintraub's method was modified slightly by Laubengayer and others in 1943 (Ref. 14).
In Laubengayer's process boron tribromide was reduced by hydrogen upon contact with a hot tantalum filament. Laubengayer reported growing some crystals slightly larger than one-tenth millimeter long.

Huibregste and Shinn in 1950 (Ref. 13) used the Laubengayer process in preparing the small quantity (about 0.5 gram) of boron crystals used in this work. These crystals were no larger than those previously grown but it is hoped that further attempts will be made to grow larger single crystals. However, in the present work a method was developed for mounting the microscopic crystals in a fashion suitable for electrical studies.

D. Objectives

1. Primary objective

The primary objective of this investigation was to gain information about the properties of the charge carriers in crystalline boron. The specific properties to be studied included the following:

1. Activation energies.
2. Densities.
3. Mobilities.

2. Secondary objectives

Secondary objectives included the following:


\(^1\)Reported by Shinn only.
crystals with four or more electrodes to make resistivity and Hall effect measurements possible.

2. Development of circuitry and techniques for measuring resistivities and Hall effects in small, high resistivity crystals.

3. Other pertinent observations and measurements which might contribute to an understanding of the electrical properties of crystalline boron.

Some of the terms used in the statement of objectives above will be defined and explained in the sections which follow.

E. Note on Units

The equations in the sections which follow are applicable to any self consistent system of units. (Refs. 18, 19, 20.) Examples of the many consistent systems of units are:

1. Electromagnetic cgs units.
2. Electrostatic cgs units.

The equations as stated are also applicable to any mixed system of units if the symbols are treated as quantities and not as pure numbers. When any mixed system of units is used, the units must be included with the numerical value when making substitutions for the symbols in an equation. The quantity, for which the equation is being
solved, will then be dimensionally correct but may not be in the desired units. If this quantity is not in the desired units, appropriate conversion factors must then be introduced. A convenient way of introducing such conversions is given in the following examples:

\[ 1 = \left[ 10^6 \text{ microns} / \text{meter} \right], \quad 1 = \left[ 10^4 \text{ gauss} / \text{weber} \right], \]

\[ 1 = \left[ 10^8 \frac{\text{gauss cm}^2}{\text{volt sec}} \right]. \quad (1) \]

Multiplication or division by the pure number one in any form does not change the value of a quantity. When the appropriate form of one is chosen, the units of any quantity may be converted to any other desired units having the same dimensions.

Many writers employ a mixed system of units and state their equations including only the numerical values of necessary conversion factors. Equations thus stated apply only to the particular set of mixed units chosen and the symbols must be treated as numbers corresponding only to the numerical values of the quantities in these units. These same writers frequently state or imply that the symbols represent quantities rather than numbers. The fact that this practice is common does not justify its use here.

Different mixed systems of units are used in this work. When computations are to be performed, simple examples
of the use of conversion factors will be given. However, the equations as stated in the simple theoretical development which follows are applicable to any system of units, consistent or otherwise. The symbols represent quantities, not pure numbers.
II. THEORY OF SEMICONDUCTORS

A. Energy Band Theory

1. Properties to be explained

Any satisfactory theory of semiconductors must provide an explanation for the properties which distinguish semiconductors from insulators and metals. Some properties which most semiconductors exhibit are as follows:

1. Room temperature resistivity in the range $10^{-2}$ to $10^{-8}$ ohm cm. (Authorities differ on the limits.)

2. Resistance which decreases with heating and which varies about exponentially with reciprocal absolute temperature through at least parts of the temperature range.

3. Decrease in resistivity with the introduction of small amounts of certain impurities.

4. Decrease in resistivity when exposed to certain kinds of light.

5. Hall and thermoelectric effects usually much larger than for metals.

6. Rectification when one of two metallic contacts is much smaller than the other.

The distinction between metals and semiconductors is clear except in the case of semiconductors containing a
relatively large amount of impurities. Impurities may cause a semiconductor to lose all of the properties listed above and cause it to behave like a metal. Hall and thermoelectric effects in metals are smaller than in most semiconductors but are sometimes easier to measure because of the lower resistivities of metals.

The distinction between semiconductors and insulators is not clear. Insulators show all of the properties listed except that the resistivities of insulators are higher. Some authorities (Ref. 21) class crystalline boron as an insulator. Hall and thermoelectric effects in insulators are larger than in semiconductors but are very difficult to observe because of the higher resistivities of insulators.

Ionic conductors may show most of the properties of semiconductors except that Hall effects have not been observed in ionic conductors. Ionic conductors also show polarization effects and the resistance and composition of an ionic conductor change with time as current flows.

2. The energy band concept

The simple energy band theory of solids provides reasonable explanations for most of the properties of semiconductors. Only enough of the energy band theory will be summarized here to serve as background for the
present experimental work. This summary will provide some logical basis for the equations to be used in the calculations. More refined treatment of the energy band theory will be found in the texts by Wilson, Sietz, Schockley, Mott and Gurney, and Wright (Refs. 22, 23, 24, 21, 25).

In the highly simplified discussion of solid state theory as applied to semiconductors which follows, electrons and atoms will be considered as particles, not waves. Approximate expressions will be derived in terms of simple average values of the velocities and energies of the electrons in a semiconductor. The results of approximate derivations will be followed by statements of the results of more nearly correct derivations where electrons are considered as waves and the Fermi-Dirac distribution of energies is considered.

In atomic theory atoms are assumed to have only discrete energy levels available for electrons. In the energy band theory of solids a crystal consisting of many atoms is assumed to have bands of allowed energy states. These bands may overlap or be separated by forbidden energy gaps. Isolated atoms have their own planetary electrons. However, in a solid the electrons in the bands are assumed to belong to all the atoms. The electrons have velocities and momenta characteristic of their energy states.

An idealized insulator or semiconductor has, at temperature absolute zero, an energy band completely filled
with electrons. This filled band is separated, from an empty band of higher energy levels, by a forbidden energy gap. Although the electrons in the filled band are moving, no preferred motion is possible. Therefore, an electric current, consisting of an excess of electrons carrying charge in some given direction, cannot flow. If sufficient energy is provided by an incident light photon, ionizing particle, or by thermal agitation, an electron may be lifted from the filled to the empty, or conduction, band. In the conduction band many energy states are available and the electron is considered as free to drift under the influence of electric or magnetic fields.

3. Electrons and holes

When a negatively charged electron is lifted into the conduction band, the energy state left empty in the formerly filled band is then ready for occupancy by another electron. Another electron in the filled band, moving in some preferred direction, may then fill the hole left in the filled band. This causes the hole to move in the opposite direction. If the hole is successively filled by other electrons moving in the preferred direction, the hole behaves almost like a positively charged electron. Thus two charged carriers moving in opposite directions, in an electric field, may result from the absorption of a
single quantum of energy equaling or exceeding the forbidden energy gap.

4. Effect of impurities

The presence of impurities or imperfections in the ideal crystalline solid may introduce isolated energy levels in the forbidden band. If an impurity level is normally occupied by electrons, it may serve as an electron donor to the conduction band. If the impurity level is normally unoccupied, it may serve as an acceptor of electrons from the filled band thereby creating mobile holes in the filled band. The electrons or holes in acceptor or donor levels are not mobile. Only one carrier results when an electron is lifted out of a donor or into an acceptor level.

B. Electrical Conductivity

1. Introduction

Electrical conductivity $\sigma$ in an isotropic material may be defined as the current density $i_x$ divided by the electric field $E_x$,

$$\sigma = \frac{i_x}{E_x}$$  \hspace{1cm} (2)

where $x$ is some chosen coordinate direction. If $i_x$ is
expressed in $\text{amp/cm}^2$ and $E_x$ is expressed in $\text{volt/cm}$, the units of $\sigma$ will be $(\text{ohm cm})^{-1}$.

In some solids, where more than one type of atom is present, the charged atoms, or ions, may move under the influence of an electric field. Conduction by such ions in a monatomic semiconductor is not probable and will not be considered here. Electrons and holes will be considered as the charge carriers which make conduction possible. These charge carriers have certain properties, including activation energies, numerical densities, and mobilities, which are of special interest. In the elementary mathematical treatments which follow these terms will be defined and their relation to conductivity will be explained. The results of more refined theoretical treatments will also be set forth for comparison and later use.

2. Activation energies of charge carriers

The activation energy of a carrier is the minimum energy required to place it in a band where the carrier can have a preferred motion. When impurities are not considered, the activation energy $E_g$ is the height of the forbidden energy gap between the filled band and the conduction band. A quantum of energy equal to $E_g$ is sufficient to provide both a mobile hole and a mobile electron. When impurities are considered, the activation energy $E_h$ or $E_e$
is respectively the height of an acceptor level above the filled band or the depth of a donor level below the conduction band. A quantum of energy equal to $E_h$ is sufficient to lift an electron from the filled band into an acceptor level thereby providing a mobile hole in the filled band. A quantum of energy equal to $E_e$ is sufficient to lift an electron out of a donor level into the conduction band where the electron is mobile.

There is evidence which indicates that activation energies are temperature dependent (Ref. 26, 27). For the present discussion $E_g$, $E_h$, and $E_e$ will be considered as constants.

3. Densities of charge carriers

In a semiconductor at any temperature other than absolute zero thermal fluctuations will provide some electrons with energy in excess of the energy gap $E_g$. This energy in excess of $E_g$ will maintain a certain average number of electrons in the conduction band. These free electrons in the conduction band may move almost at random. The paths of these free electrons will be limited by collisions in the crystal lattice or by falling back into holes. Holes may behave in a similar manner. In equilibrium, the rates of generation and recombination of electrons and holes must be equal.
Statistical considerations show that, when the energy gap $E_g \gg kT$, where $k$ is Boltzmann's constant and $T$ is absolute temperature, the number of quanta of thermal energy in excess of $E_g$ is proportional to $\exp(-E_g/kT)$. Hence, the rate of generating electron hole pairs is proportional to this exponential. From a principle like the law of mass action, the rate of recombination is proportional to the product of hole and electron densities, $n_h n_e$, where $n_h$ and $n_e$ represent respectively the numbers of holes and electrons per unit volume.

This reasoning leads to the expression

$$n_h n_e \sim \exp(-E_g / kT),$$

where the proportionality factor is negligibly temperature dependent by comparison with the exponential. In the case where the contribution of impurity levels is negligible, $n_h = n_e$ and the hole or electron density $n_c$ is

$$n_c \sim \exp(-E_g / 2kT).$$

A more complete theoretical derivation (Ref. 28) gives

$$n_c = (2) \frac{(2\pi m kT)^{3/2}}{h^3} \exp(-E_g / 2kT), \quad (3)$$

where $h$ is Planck's constant and $m$ is the mass of an electron.

The effective masses of carriers, $m_h$ and $m_e$ for holes and electrons respectively, are not necessarily equal
to \( m \). When the carrier density \( n_c \) is available from data on Hall effect, Equation (3) may be used to compute the geometric mean of the effective masses of the carriers by substituting the quantity \((\frac{m_h}{m_e})^{1/2}\) in place of \( m \).

The density of carriers \( n_i \) provided by impurities depends on a smaller energy jump \( E_i \) and the density of impurities \( n_s \). When \( n_i \) is known from Hall effect data, an estimate of \( n_s \) may be obtained from the approximate formula

\[
n_s = n_i \exp\left(\frac{E_i}{kT}\right) .
\]

4. **Mobilities of charge carriers**

Carriers normally have randomly directed thermal velocities. In the simple approximate theory considered here, a carrier in a perfect crystal at absolute zero, has a mean free path limited only by the crystal boundaries. At any temperature above absolute zero the carrier is scattered by collisions with thermally displaced atoms. If the crystal is not perfect, the carrier is also scattered by imperfections in the lattice. Let \( \tau \) and \( \lambda \) be respectively the mean free time and mean free path between collisions. If a carrier, for example, a hole with a positive charge \( q_h = q \), and mass \( m \), is subjected to an electric field \( E_x \), it will have an acceleration \( a_x \) between collisions given by
If the carrier were an electron with negative charge $q_e = -q$, the acceleration would be in a direction opposite to that of $E_x$, but a positively charged carrier will be considered here for purposes of illustration. The velocity resulting from the acceleration $a_x$ will be superimposed upon the random thermal velocity during the time $\tau$. This intermittent acceleration between collisions will give the positively charged carrier a mean drift velocity $v_x$ parallel to $E_x$.

The mobility $\mu$ of a charge carrier is here defined as the absolute value of the quotient of mean drift velocity $v_x$ divided by the electric field $E_x$ causing the drift.\(^1\)

$$\mu = \left| \frac{v_x}{E_x} \right| \quad (5)$$

From elementary physics, the mean drift velocity may be written

$$v_x = a_x \tau / 2 \quad .$$

---

\(^1\) It is of interest to note that in derivations for mean free time, mean free path, and later for conductivity, Hall angle, and Hall voltage, the results could be made slightly more general if $\mu$ were defined as positive only for a positively charged carrier, and defined as negative for a negatively charged carrier. However, the derivation may be somewhat more simple using the definition given in Equation (5) above.
Thus, in terms of mobility,

$$\tau = 2 \mu m / q$$.

Taking the thermal energy of the carrier as

$$m v_t^2 / 2 = kT$$,

where $v_t$ is the mean thermal velocity, the mean free path may be written

$$\lambda = v_t \tau = 2 \left( \frac{2m kT}{q} \right)^{1/2} \mu / q$$.

Slightly more refined treatments, (Refs. 23, 24) where averaging is done in terms of the distribution of velocities, give

$$\tau = \mu m / q$$, \hspace{1cm} (6)

and

$$\lambda = \frac{3}{4} \left( \frac{2 \pi m kT}{q} \right)^{1/2} \mu / q$$, \hspace{1cm} (7)

where $\lambda$ is assumed constant and only thermal scattering is considered.

The temperature dependence of $\mu$ has been the subject of much experimental and theoretical effort. Simple theory considering only thermal scattering gives

$$\mu \sim (T)^{-1/2}$$, \hspace{1cm} (8)
When Conwell and Weisskopf (Ref. 29) considered impurity scattering, the result was much more complicated but still inadequate to explain experiment. (Ref. 30, 31) An empirical formula (Ref. 24), which fits some data on germanium fairly well, is

\[ \frac{1}{\mu} = a(T)^{-3/2} + b(T)^{3/2}. \]  

(9)

5. Dependence on carrier densities and mobilities

Conductivity has been defined in Equation (2). For positive carriers the current density is given by

\[ \mathbf{i}_x = n q v_x, \]  

(10)

where \( n \) is the numerical density of the charge carriers, \( q \) is the charge of each carrier, and \( v_x \) is the drift velocity previously mentioned. Then, for positive carriers, the conductivity is given by

\[ \sigma = n q \mu. \]  

(11)

---

1Typical values for the quantities in Equation (11) are as follows:

- \( n \) = \( 10^{22} \) electrons/cm\(^3\) for most metals and less than \( 10^8 \) carriers/cm\(^3\) for most insulators.
- \( q \) = \( 1.6 \times 10^{-19} \) coulomb/carrier (For holes \( q_h = q \).
  For electrons \( q_e = -q \).)
- \( \mu \) = 2 to 50 cm\(^2\)/volt sec for most metals, 0.1 to 4000 cm\(^2\)/volt sec for insulators and semiconductors.

If these quantities are expressed in the indicated units, \( \sigma \) is in \((\text{ohm cm})^{-1}\).
This expression also holds for negatively charged carriers if only absolute values of both charge and mobility are considered.

When more than one type of carrier is present, the resulting conductivities are additive giving for both holes and electrons,

\[ \sigma^r = q \left( n_h \mu_h + n_e \mu_e \right), \quad (12) \]

where all the quantities in the equation are positive.

6. Dependence on temperature and activation energies

If all sources on carriers are considered, Equations (3), (4), and (12) give

\[ \sigma^r = (\mu_h + \mu_e) S_g \exp\left(-\frac{E_g}{2 k T}\right) \]
\[ + \mu_h \sum_h S_h \exp\left(-\frac{E_h}{k T}\right) \]
\[ + \mu_e \sum_e S_e \exp\left(-\frac{E_e}{k T}\right), \quad (13) \]

where the summations are over all impurity sources of holes and electrons. The coefficients \( S_g, S_h, \) and \( S_e \) include constants from Equations (3) and (4). The temperature dependence of these coefficients or of the mobilities is slight compared to the exponential factors and will be neglected for the present discussion. The coefficients \( S_h \) and \( S_e \) are proportional to the numerical densities of
impurities.

The first term on the right in Equation (13) represents intrinsic conductivity and the second and third terms represent conductivities resulting from acceptors and donors respectively.

If the number of different types of impurities is few, then each individual term in Equation (13) usually has some range of temperatures where its contribution to the conductivity far outweighs the contributions of all other terms. In such a range where the $r$ th term has control,

$$ \sigma = \mu_r S_r \exp\left(-E_r/kT\right) + \text{other negligibly small terms.} $$

Then

$$ \ln \sigma = \ln \mu_r S_r - \left(E_r/k\right) \left(1/T\right). \quad (14) $$

Since $\mu_r$ is only slightly temperature dependent, the first term on the right in Equation (14) is almost constant. If $\ln \sigma$ is plotted against $1/T$, and if $E_r$ is constant in the temperature range considered, a straight line segment having slope $E_r/k$ should result. On such a plot, over a large range of temperatures, the result may be a series of almost straight line segments. The slope of each line segment yields the corresponding activation energy, $E_r$. Usually for these computations $T$ is expressed in °K, $k = 8.62 \times 10^{-5}$ ev/°K, giving $E_r$ in ev (electron volts).
Since in Equation (13)

\[ S_g > S_j, S_k \]

\[ E_g > E_j, E_k \]

at some low range of temperatures any contributing impurities present will have control. However, there must be some temperature above which the \( S_g \), or intrinsic, term takes and holds control. This temperature range is called the intrinsic range since here the behavior is intrinsic to the crystal and is not due to impurities.

C. Hall Effect

1. Introduction

In 1879, Hall (Ref. 32) observed that a conductor carrying an electric current, perpendicular to a magnetic field, exhibited a potential difference perpendicular to the direction of current flow and perpendicular to the magnetic field. This phenomenon is called the Hall effect. The Hall effect has since been used to investigate the electrical properties of many materials and has contributed more supporting evidence to modern solid state theory than any other single effect. A very elementary approach to the mathematical theory of the Hall effect will provide sufficient background for the present experimental study.
EQUIPOTENTIAL SURFACES AND HALL EFFECT
IN A CONDUCTOR WITH POSITIVE CARRIERS

(a) CONVENTIONAL CURRENT
IN +X DIRECTION. NO
MAGNETIC FIELD. EQUIPOTENTIAL SURFACES
PERPENDICULAR TO CURRENT FLOW.

(b) MAGNETIC FIELD
DIRECTED OUTWARD.
EQUIPOTENTIAL SURFACES TILTED WITH RESPECT TO CURRENT FLOW.

Figure 1. Equipotential Surfaces and Hall Effect

This figure illustrates a homogeneous isotropic crystal having a regular cross section through which a conventional current is flowing in the +x direction. In the absence of a magnetic field the equipotential surfaces are perpendicular to the direction of current flow. In the presence of a magnetic field the equipotential surfaces may become tilted in a manner depending upon the type, mobility and density of the charge carriers.
2 Dependence on carrier densities and mobilities

Figure 1 (a) illustrates the approximate distribution of equipotential surfaces in a crystal through which a conventional current is flowing from A to C in the absence of a magnetic field. The crystal is assumed to be homogeneous, isotropic, and regular in cross section. Probes B and D are situated at opposite edges of an equipotential surface so that no potential difference is observed between B and D. (In practice this arrangement is never quite possible geometrically and the resulting potential difference may be balanced out by an external voltage.) The electric field \( E_x \) gives rise to a mean current density,

\[ i_x = \frac{I_x}{A} , \]  

(15)

where \( I_x \) is the total current and \( A \) is the cross sectional area of the crystal.

Considering the charge carriers as positive, a magnetic field directed outward will deflect the carriers downward, causing a positive charge accumulation near D, and giving rise to a vertical field component \( E_y \). This vertical field component will cause the equipotential surfaces to be tilted as in Figure 1 (b). When equilibrium is reached, the upward force on a carrier due to the electric field \( E_y \) will just balance the average downward
force on the carrier due to its motion with mean drift velocity \( v_x \) in the magnetic field \( H_z \). Equating these forces,

\[
E_y q = H_z q v_x .
\]  

(16)

The Hall angle \( \theta \) is small and is taken equal to its own tangent giving \(^1,^2\)

\[
\theta = \frac{E_y}{E_x} = \frac{H_z v_x}{E_x} = \mu H_z
\]  

(17)

If \( w \) is taken as the width of the crystal between the probes \( B \) and \( D \), Equations (16), (5), (11), (2), and (15), give for the Hall voltage between these probes

\[
V_y = \left( \frac{1}{n q} \right) H_z I_x \left( \frac{w}{A} \right)
\]  

(18)

---

\(^1\) At this point it is interesting to observe that the dimensions of magnetic field strength are reciprocal to those of mobility. Using consistent units, \( \theta \) is then given as a pure number corresponding to radian measure. If mixed units are used, conversion factors may be required to get \( \theta \) in some easily recognizable angular measure. For example, if \( H_z \) is expressed in gauss, and \( \mu \) in cm\(^2\)/volt sec, division by the pure number one as given in Equation (1) will give \( \theta \) in radian measure.

\(^2\) With mobility defined as in Equation (5), and with \( q \) always positive, it is necessary to arbitrarily introduce negative signs in Equations (17), (18), and (19) when considering negatively charged carriers. It is also interesting to observe that these sign changes would have been automatic if \( q \) and \( \mu \) had been defined as negative for electrons.
If the crystal is rectangular in cross section with thickness $t$, the ratio $w/A$ reduces to $1/t$. If the crystal is cylindrical with diameter $d = w$, the ratio $w/A$ reduces to $\frac{4}{\pi}d$.

The coefficient of the directly measurable quantities, $H_z I_x (w/A)$, in Equation (18) is defined as the Hall coefficient $R_H$. When the Fermi-Dirac distribution of energies in metals is considered (Ref. 23), almost the same result as Equation (18) is obtained. (In this case the carriers are usually electrons and a negative sign must be introduced.) When the simple derivation of Equation (18) applies, the Hall coefficient is given by

$$R_H = V_y A / H_z I_x w = l / n q = \mu / \sigma$$  \hspace{1cm} (19)

Next consider both holes and electrons as carriers in the simple model used above. Holes, with charge $q_h = q$, moving with velocity $v_{hx}$, will be deflected downward as before. Electrons, with charge $q_e = -q$, moving in the opposite direction with velocity $-v_{ex}$, will also be deflected downward. The two effects will tend to cancel and a new field $E_y$ will be set up. In equilibrium this new field should satisfy the following relationship (neglecting recombination of holes and electrons in this idealized case).

$$E_y q = H_z (q) (v_{hx}) - H_z (-q) (-v_{ex}).$$
Manipulation similar to that used for obtaining Equations (17), (18), and (19) gives, on the basis of this simplified theory,

$$\theta = (\mu_h - \mu_e) H_z,$$  \hspace{1cm} (20)

and

$$R_H = \frac{1}{q} \frac{\mu_h - \mu_e}{\mu_h n_h - \mu_e n_e} = \frac{\mu_h - \mu_e}{\sigma}.$$  \hspace{1cm} (21)

Except in limiting cases, Equations (20) and (21) do not apply even for most metals and the problem must be considered more carefully (Ref. 23). Further discussion of the Hall effect in metals is not pertinent to the present problem, but Equations (20) and (21) were developed for comparison with the equations that follow.

When the Maxwell-Boltzmann distribution of energies, which applies approximately to most semiconductors, is considered, the following, more nearly accurate equation is obtained for the Hall coefficient in semiconductors. (Ref. 24)

$$R_H = \frac{3}{8q} \frac{n_h \mu_h^2 - n_e \mu_e^2}{(n_h \mu_h - n_e \mu_e)^2}.$$

$$\hspace{1cm} (22)$$
Equations (12) and (22) are frequently used for computing carrier densities and mobilities.\footnote{It is understood that consistent units, or appropriate conversion factors, must be used in all of these equations. A mixed system of units, using the cm, sec, volt, amp, coulomb, and gauss, requires the use of the conversion given in Equation (1).} These equations are most useful in the limiting cases. When acceptor impurities dominate, \( n_h \gg n_e \), and Equations (12) and (22) give

\[
n_h = \frac{3 \tau}{8 q R_H},
\]

(23)

and

\[
\mu_h = \left( \frac{8}{3 \tau} \right) R_H \sigma = \left( \frac{8}{3 \tau} \right) \left( \frac{\Theta}{H_2} \right).
\]

(24)

Similar equations, with appropriate changes in sign, apply when \( n_e \gg n_h \). In the intrinsic case, when \( n_h = n_e = n_c \),

\[
n_c = \frac{3 \tau}{8 q R_H} \frac{\mu_h - \mu_e}{\mu_h + \mu_e},
\]

(25)

and

\[
\mu_h - \mu_e = \left( \frac{8}{3 \tau} \right) R_H = \left( \frac{8}{3 \tau} \right) \left( \frac{\Theta}{H_2} \right).
\]

(26)

Studies by Johnson and others (Refs. 33, 34) indicate that the factor \( \left( \frac{8}{3 \tau} \right) \), which appears in Equation (22) and the succeeding equations, should be replaced by a factor depending upon the temperature and amount of impurity scattering. This is a third order effect and is
not usually considered in Hall effect measurements on semiconductors (Refs. 3, 5, 35, 36, 37).

The Hall coefficient $R_H$ is exponentially dependent on reciprocal temperature (decreasing in magnitude with increasing temperature). The temperature dependence of $R_H$ enters with reciprocal carrier density as in Equation (19), or with $1/\sigma$ as in Equation (21). The Hall angle $\theta$ is usually relatively temperature independent. The slow temperature dependence of $\theta$ enters with mobility as in Equation (17). At temperatures near the temperature where an impurity semiconductor becomes an intrinsic semiconductor, $\theta$ may exhibit a large temperature dependence.

D. Thermoelectric Effect

1. Introduction

Consider a circuit consisting of an electrometer $E$ connected by means of two lead (Pb) wires $P_1$ and $P_2$ to two points on some material $X$. Designate the connections, $P_1$ to $X$, and $X$ to $P_2$, as junctions $J_1$ and $J_2$ respectively. If junction $J_1$ is held at some fixed temperature $T_1$, and if junction $J_2$ is held at some temperature $T_2$ different from $T_1$, an emf may be noted at the electrometer $E$. This emf is called the Seebeck emf. The Seebeck emf consists of the sum of the emfs originating at the junctions and an emf originating within the material
as a result of the temperature gradient between the junctions.

Designate the potential drop across junction \( J_1 \) as \( V_1 \), considering \( V_1 \) as positive when the material \( X \) at \( J_1 \) is positive with respect to the metal \( P_1 \). In like manner, consider \( V_2 \) as positive when \( X \) at \( J_2 \) is positive with respect to \( P_2 \). Neglecting any emf originating within the material, the Seebeck emf is said to be positive if \( T_2 > T_1, V_2 > V_1 \), or if \( T_1 > T_2, V_1 > V_2 \). The Seebeck emf is negative in the reversed cases. A simple rule follows: If the material is more positive at the hot junction the Seebeck emf of the material (with respect to the reference metal) is positive.

The Seebeck emf between unlike metals is employed in temperature measurement and the metal to metal junctions are called thermocouples. When material \( X \), in the discussion above, is a metal, the reference metal, for purposes of comparison, is usually chosen as lead. When \( X \) is a semiconductor, the Seebeck emf is usually about one thousand times as large as when \( X \) is a metal, and the kind of reference metal used makes little observable difference.

2. Thermoelectric power

Using the same notation as that used in the preceding discussion, let \( V \) designate the observed potential drop
between the two wires, or electrodes, P₁ and P₂. Let V be positive when P₂ is more positive than P₁. Then
\[ V = V₁ - V₂. \]

Thermoelectric power \( \frac{dV}{dT} \) may be defined as the temperature rate of change of the Seebeck emf.

\[ \frac{dV}{dT} = \frac{dV₁}{dT₁} = -\frac{dV₂}{dT₂}. \] (27)

Experimentally, the sign of the thermoelectric power \( \frac{dV}{dT} \) has been found to follow the sign of the Hall coefficient. A p-type semiconductor, in which positive carriers predominate because of higher density or mobility, has a positive Hall effect and a positive thermoelectric power. An n-type semiconductor has a negative Hall coefficient and a negative thermoelectric power. The thermoelectric power is useful in qualitative identification of semiconductors as p-type or n-type. Most elementary theories do not correlate quantitatively with experiments on thermoelectric power.

Some success at matching theory to quantitative data on the thermoelectric effect has been recorded (Refs. 4, 5, 7, 38, 39, 40, 41, 42, 43, 44, 45). Most of the writers on this subject do not quote quantitative results. Fukuroi, Tanuma and Tobisawa (Ref. 4) give quantitative data on tellurium which fits the following formula fairly well:

\[ \frac{dV}{dT} = \frac{k}{2q} \left( nₕ \muₕ - nₑ \muₑ \right) + 2T \left( \frac{\muₕ \muₑ}{2} \frac{d\muₕ}{dT} - \muₑ \muₑ \frac{d\muₑ}{dT} \right) \]
\[ \frac{nₕ \muₕ + nₑ \muₑ}{nₕ \muₕ + nₑ \muₑ} \] (28)
In the intrinsic range, Equation (21) reduces to

$$\frac{dV}{dT} = \frac{k}{2} \frac{M_h - M_e}{(M_h + M_e)} \left(1 + \frac{2 \epsilon}{kT}\right). \quad (29)$$

In the impurity range Equation (21) reduces to

$$\frac{dV}{dT} = -\frac{k}{2} \left(1 + \frac{2 \epsilon}{kT}\right). \quad (30)$$

In Equations (22) and (23), $\sigma$ is defined by

$$\sigma \sim \exp(-\epsilon/kT). \quad (31)$$

E. Other Effects

1. Rectification

When two metal connections to a semiconductor differ greatly in area (and contact resistance) the effective resistance between the two metal connections may differ with the direction of an applied potential difference. Elementary explanations of this rectification effect give the sign of the effect the wrong direction. Experimentally, the direction of easiest flow (least resistance) for a p-type semiconductor is when the semiconductor is positive with respect to the poorest (highest contact resistance) connection. The reverse is true for an n-type semiconductor.
2. Photoconductivity

If the resistance of a semiconductor shows a marked decrease in resistance when light is incident upon its surface, and if the decrease is not due simply to heating, the semiconductor is said to be photoconducting. Photoconductivity may be explained as the result of absorption of light quanta having energies equal to or greater than the activation energies of the carriers. Activation energies computed from photoconductivity data are always somewhat higher than activation energies computed from conductivity versus temperature data. This observation is explained by the Franck-Condon principle (Ref. 25).
III. EXPERIMENTAL

A. Introduction

A few measurements on micro-crystals have been made previously by others. Ordway (Ref. 46) measured thermo-electric effects in small crystals of refractory materials by means of a method similar to that used in this work. Busch, Wieland and Zoller (Ref. 3) used rather indirect methods for their measurements on grey tin. They used induced currents to estimate the conductivity and powder, packed into a rectangular space, for making Hall effect measurements. More direct methods were chosen for the present study, partly because the quantity of crystals available was so small, but principally because results obtained on single crystals are more significant.

The largest crystals used in this work had lengths of a few hundred microns. In order to make measurements directly on the individual single crystals, it was necessary to place electrodes on the crystals. Once the problems involved in mounting micro-crystals with several electrodes were solved, it was necessary to devise methods for making electrical measurements on the mounted crystals. Electrical measurements on the small, high resistivity, semiconducting crystals presented some special problems.

Resistivity and Hall effect measurements presented
fundamentally the same problem. Both required measurements of the relative potentials between electrodes, or probes, connected to the specimen. For resistivity measurements, the accuracy required in making measurements of relative probe potentials was not difficult to attain. For Hall effect studies, measurements of slight changes in potential were required, and these slight changes were more difficult to measure. In order to make resistivity measurements, it was necessary to consider the non-linear voltage current characteristics of crystalline boron. In order to make Hall voltage measurements, the low frequency electrical noise and drift which is characteristic of small, high resistivity, or semiconducting crystals, made a statistical approach to the problem necessary.

Measurements of thermoelectric, rectification and photoconductivity effects were relatively simple, after micromanipulative techniques had been developed.

B. Preparation and Testing of Specimens

1. Selection and treatment

a. Introduction. The boron crystals, which had been grown by Shinn (Ref. 13), were first inspected under a microscope. Fragments of the tantalum filaments, upon which the crystals had been grown, and some other foreign matter were observed mixed with the crystals.
The crystals themselves appeared as masses of trees and agglomerates. Hence it was necessary to clean the crystals, break up the masses, and sort out single crystals suitable for mounting.

b. Cleaning. Crystals were cleaned as follows: The crystals were placed in a 250 ml porcelain crucible. About 25 ml of 50 per cent KOH was added and the contents of the crucible were heated to about 200 °C for about 30 minutes. After cooling, the contents of the crucible were washed into a one liter graduate with distilled water. The graduate was filled with water and the crystals were allowed to settle for about 15 minutes. The diluted KOH solution was then decanted with the aid of a pipette. Care was taken not to draw off any of the crystals. About 10 ml of solution was allowed to remain in the graduate and the remaining solution was again diluted and decanted. After a third diluting and decanting operation, the residue was washed into a plastic beaker and again decanted. HF was then added to the crystals in the beaker and the beaker was placed in warm water for about 30 minutes. The diluting and decanting procedures were repeated and the crystals were washed again into the porcelain crucible. The entire process was repeated once more and after a final washing the crystals were placed in a petri dish and allowed to dry.
The cleaning treatment described above removed all visible traces of tantalum and other foreign matter. The crystals were kept covered except during sorting operations. Air borne dust settled on the crystals during such sorting operations under the microscope and made a later cleaning of some of the crystals desirable.

c. Breaking and sorting. The microscope and special lighting used in this work are shown in Figures 2 and 3. During the sorting procedure selected crystals were frequently lost from the field of view of the microscope as the result of slight disturbances. It was soon found that the masses of crystals could best be broken up, and selected crystals sorted out, when the crystals were kept immersed in water.

Ordinary jeweler's forceps were tried for sorting crystals, but hand control of the forceps was entirely inadequate. For some time, a small pipette consisting of capillary tubing drawn out to a point, was used for sorting crystals. Selected crystals were drawn up into the pipette and discharged into another petri dish. However, the selected crystal was usually accompanied by many undesirable crystals.

Finally the pneumatically controlled micro-forceps, shown in Figure 4, were made. These micro-forceps reduced the time required for sorting by a factor of at least 100.
Figure 2. Bausch and Lomb SSRKT-5 Microscope

Shadow free lighting is provided by four pen-light bulbs.

Figure 3. Microscope Light Fixture.

This fixture was made from 1/8 inch copper tubing, a 1/8 inch to 3/8 inch coupling, and a modified T joint and bracket. After forming and soldering, the assembly was chrome plated. Gummed paper insulation gives the sockets rigidity.
Explanation of Figure 4.

(1) Brass tube, 3/16 inch diameter, approximately 5 inches long, split longitudinally approximately one-half its length.

(2) Ends flattened and shaped to form points, and chromium plated for strength and hardness.

(3) Soft expansible rubber tube tied off at the end. Air pressure bulges this tube causing forceps points to separate.

(4) Tube to knee-controlled air valve. A leak in the air line permits the forceps to close when the valve is closed.

(5) Rubber bands (segments of soft rubber tubing), longitudinally adjustable in order to control the holding force of the points.

(6) Rubber stopper to support the forceps in a test tube in order to protect the points.
Figure 4. Micro-Forceps.

These pneumatically controlled forceps were used for sorting and handling microscopic crystals. See explanation on the preceding page for detailed description.
This very useful tool also greatly simplified other handling operations. A knee controlled air valve was used to open and close the forceps.

2. Crystalline nature and purity of specimens

   a. Optical and X-ray examination. Only those crystals which were obviously single throughout at least the major portion of the body, were chosen for study. Facets were clearly visible when the crystals were inspected under a microscope. In order to check the crystalline nature of the specimens, six sample specimens were prepared for x-ray study. The sample specimens were mounted at the ends of glass wool filaments with the aid of Duco cement diluted in nitrobenzene. (Microscopic amounts of Duco cement harden in about one second. Nitrobenzene retards setting.)

   Facets of mounted specimens were then studied qualitatively with an optical goniometer and the principal axes of the specimens were chosen and oriented with respect to holders. The principal axes of specimens were then mounted in, and parallel to, the x-ray beam and Laue photographs were taken. White molybdenum radiation was used. The crystals were small and the x-ray scattering coefficient of boron is low. For these reasons it was necessary to extend exposure times to three days in order to obtain observable x-ray patterns.
Figure 5 shows the Laue pattern obtained from one boron crystal. The absence of rings or multiplicity in the spots definitely verified that the specimens were not amorphous or polycrystalline. The apparent doubling of some of the spots in Figure 5 indicates that this particular single crystal may have twinned. Since this investigation was not concerned with anisotropy the possibility of twinning was not of special interest. Boron patterns are admittedly very difficult to analyze (Refs. 13, 15, 16) since boron has a complicated crystal structure. No attempt was made to analyze the x-ray patterns since this also was not an objective of this investigation.

b. Spectrographic examination. Spectrographic analyses of several samples of crystals were performed in order to check the purity of the specimens and in order to study the efficacy of the cleaning procedures.

Spectrographic carbon electrodes were prepared by pre-arcing. Samples were selected and deposited in the cupped ends of the electrodes using the micro-forceps of Figure 4. The samples prepared for spectrographic analyses were as follows:

1. Approximately 100 boron crystals similar to those used for measurements, but of undesirable shape. These had been previously treated with KOH and HF.
Figure 5. Laue Pattern from a Boron Crystal

This pattern was obtained from a small crystal mounted with long axis parallel to the x-ray beam. White molybdenum radiation was used with an exposure time of three days. This pattern indicates that the crystal was single though possibly twinned.
2. Fragments of the thin layer of polycrystalline and vitreous material which had been in direct contact with the tantalum filament. These fragments had been previously treated with KOH and HF.

3. Washed but untreated agglomerates and fragments equivalent in volume to sample 1 and 3.

4. Twenty-five drops of wash water, which had stood for several days on treated crystals, evaporated one at a time on the electrode.

The results of spectrographic analyses performed on the samples listed above are shown in Table 2.

Table 2. Results of Spectrographic Analyses

Entries are maximum parts per million; no entry if not detected. Ca, Cu, Mg, and Si were present in the electrodes and are not tabulated.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample Number and Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 Treated Crystals</td>
</tr>
<tr>
<td>Al</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1,000,000</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>100</td>
</tr>
<tr>
<td>Ni</td>
<td>100,000</td>
</tr>
<tr>
<td>Ta</td>
<td></td>
</tr>
</tbody>
</table>
The small amount of chromium detected in sample No. 1 is easily explained. This probably came from the micro-forceps which were used in sorting and handling the crystals. The tips of the forceps were hard chromium plated but crystalline boron is even harder than hard chromium. The trace of nickel is not so easily explained, but the indications are that it may have originated with the potassium hydroxide or hydrofluoric acid used in treating the crystals. Nickel did not appear in the untreated sample, No. 3.

No tantalum was detected in sample No. 1, but judging from the results on sample No. 2, it is still possible that some boron crystals may have had tantalum present as an impurity. This possibility must be considered in view of the deviations from typical behavior, displayed by a few crystals, when resistivity, Hall, and thermoelectric effects were studied.

C. Mounting Specimens

1. Mount design

a. Design requirements. One of the major experimental problems of this investigation was the development of a method for mounting microscopic single crystals with several electrical contacts. The necessity for extending measurements on the mounted crystals to high and low temperatures
made design considerations and choice of materials important. The requirements for the crystal mount were:

1. Mechanical stability.
2. Allowance for thermal expansion.
4. Resistance to oxidation, moisture, and chemical reaction between the materials composing the mount, over a wide range of temperatures.
5. Good electrical connections (not greater than 10 ohms between terminal and crystal).
6. Excellent insulation between connections (preferably greater than $10^{10}$ ohms).

b. Preliminary designs. Thirteen designs were tried before the arrangement eventually adopted was conceived. One of the preliminary designs is worthy of mention because it could probably be developed into a satisfactory arrangement.

A pyrex glass capillary tube about ten inches long was necked down, at a point about two inches from one end, to an inside diameter of approximately 0.1 mm. This was accomplished, without much reduction in outside diameter in the following manner. A one-fourth inch section of the tube was heated to softness. The tube was bent about 30° and the two cool segments were rotated simultaneously about their respective axes. This procedure caused the heated portion to flex in a continuous manner. When the inside diameter
appeared to be about to close, the tube was straightened while still rotating the cool segments. Small funnels were blown at the ends of the tube in order to facilitate the entrance of a crystal and the electrodes. Several of these tubes were made and crystals having diameters corresponding to the minimum inside diameter of the tubes were selected with the aid of the microscope.

A mount, adequate for resistance studies alone, was provided by placing a crystal in the narrow portion of one of these tubes and applying tapered tungsten wire electrodes to its ends under spring load. For Hall effect measurements it was necessary to apply contacts to the sides of a crystal. This was achieved as follows.

A tube was file marked for breaking at the neck. The long part of the tube to one side of this mark was wrapped with one layer of aluminum foil. The foil covered a two inch length of the tube at one side of the mark.

A semicylinder of glass, two inches long, was prepared by slitting tubing which would just fit outside of the capillary tube. Two drops of Sauereisen No. 7 cement (Ref. 47) were placed about one and one half inches apart in the semicylinder. The capillary tube was then laid in the semicylinder, file mark downward, so that cement was at each side of the mark, but not on the mark. The shorter part of the tube to one side of the mark then became cemented in the
semicylinder. The foil protected the tube at the other side of the mark from the cement while the cement formed a replica of the tube surface.

After the cement was set, the tube was broken at the file mark, in a manner to form a small overhanging lip. The lip assisted in relocating the parts in their former relative positions. Breaking was done by holding the thumbnail at a point not quite opposite the file mark. Most, but not all, of the aluminum foil was then peeled away. The longer part of the tube was replaced in its former position, was withdrawn about 0.03 mm by sliding in the ways formed by the remaining foil, and was fastened in place by the addition of cement at the edges of the semicylinder.

A crystal was then placed in the tube so that one end of the crystal was in each segment of the tube, and electrodes were applied to the ends of the crystal as previously described. Fine tungsten wires were then laid in the crack between the segments of the glass tube, and against the opposite sides of the crystal. The wires were then bent to lie alongside the tube, and were cemented in place. Connections were made by applying stripes of silver paint to the tube. The stripes were extended to terminals at the end of the tube remote from the crystal.

Difficulties encountered with this method of mounting were mostly due to two causes. These were:
1. Improper correlation of crystal size with capillary inside diameter.

2. Poor visibility, caused by internal reflections, in the vicinity of the break.

These difficulties were probably surmountable, but another approach to the problem appeared to offer a simpler solution, and led to the mount design finally adopted and developed.

c. Final design. Figure 6 is one version of the crystal mounting arrangement ultimately developed. This represents the results of many trial techniques and tests on materials. However, the figure shows the essential features embodied in this basic design. These features include:

1. The use of essentially L-shaped electrodes in order to facilitate spring loading of the contacts and to allow for differential expansion.

2. Spiral arrangement of the electrodes in order to obtain maximum separation between electrical connections to the crystal and to have the terminals on a macroscopic scale. (In the figure the fifth electrode, E, is an exception to this principle of spiral arrangement.)

3. The use of two flat ended electrodes as supporting members, one fixed to the base plate, and the other exerting sufficient elastic force on the
crystal to slightly imbed it in the ends of these electrodes.

4. The use of tapered (pointed or blade shaped) electrodes to obtain forcible contact at other selected points on the crystal.

5. The use of non-magnetic materials capable of serving as either good conductors or excellent insulators, as required, over a wide range of temperatures.

The arrangement shown in Figure 6 met all of the design requirements listed on Page 47 very well, with one exception. For studies above 500 °C, it was found that imbedding the crystal and the ends of the electrodes in a droplet of cement provided better stability. This procedure was not satisfactory for studies near room temperature since the cement tended to absorb moisture. The resistance of the cement was then less than that of the crystal. Imbedding (potting) the crystal was not always satisfactory when the mount was alternately heated and cooled since electrical contact with the crystal was then frequently lost.

In what follows, the methods used in preparing the components of the last models of the crystal mount will be described in detail. Variations from these methods, which were employed at earlier stages of the development, will be mentioned, where these variations might have merit in some different application.
Figure 6. Boron Crystal Mounted with Five Electrodes.

Tungsten electrodes in forcible contact with the crystal are cemented to a silica plate. Silver paint at A, B, C, D, and E provides connections.
2. **Mount materials**

   a. **Mount base.** The base of the mount shown in Figure 6 is a transparent fused silica plate (Ref. 48) one inch square by 1/16 inch thick. With the exception of a central area about 5/16 inch square, one surface of the plate was roughened by grinding in order to facilitate adhesion of the cement.

   b. **Cement.** Sauereisen No. 29 Low Expansion Cement (Ref. 47) was found to be the most satisfactory of several cements tried for securing electrodes to the plate. Some cements, while adhering well to silica, would expand when heated and break chips away from the plate. Some cements reacted with the electrodes at elevated temperatures. Sauereisen No. 29 had the best insulating properties and was least hygroscopic of the five cements considered. This cement, described as "zirconium base", consists of a powder and liquid to be mixed just prior to use. A setting time of about two hours was required until means for heating were devised which reduced this time requirement to about ten minutes. Cement was mixed on one face of a large rubber stopper with the aid of a toothpick which also served as applicator.

   c. **Electrodes.** Tungsten was chosen for electrodes because it is nonmagnetic, retains its elasticity at elevated temperatures, can be easily pointed, and is fairly immune to chemical attack. Tungsten oxidizes slowly in air
above 500 °C and for this reason attempts were made to plate the electrodes with some other more noble metal. Only chromium was successfully plated and, while this reduced oxidation, the tungsten was also embrittled. A coating of Sauereisen No. 78 cement was found to provide some protection and was used in a few cases.

**d. Current electrodes.** The large electrodes in Figure 6, electrodes A and C as designated at the edges of the plate, which support the crystal, will henceforth be referred to as current electrodes. In Figure 6 the current electrodes are 0.020 inch tungsten wire. The horizontal portion of electrode C is 3/32 inch long and the vertical part, mostly immersed in cement, is 9/16 inch long. The form of this electrode is more clearly illustrated in Figure 8, where the manner of fitting the electrode into its holder is also shown. Wire cutters or nippers were not used for cutting tungsten wire since these caused the wire to shred into separate fibers. Sheet metal shears were more satisfactory. Current electrodes were formed and the ends flattened by grinding as illustrated in Figure 7.

The use of gold caps over the flattened ends of the current electrodes was found to be desirable when mounting small crystals of softer materials such as antimony and germanium. Boron crystals seated well in tungsten alone when sufficient force was applied. The gold caps were made
Figure 7. Flattening the Ends of Current Electrodes.

The ends of current electrodes A and C of Figure 4 were flattened by grinding in this manner. This illustration also provides a view of the Bausch and Lomb SSRKT-5 microscope stand used in this work. With this versatile stand it was possible to swing and adjust the microscope in any desired position for the various phases of crystal sorting, electrode preparation, and mounting. During grinding operations the microscope objective was protected with a microscopic slide.
by rolling 0.010 inch wire between a microscope slide and a nail to a thickness of about 0.002 inch. A 1/16 inch length of this foil was then bent to form a U and molded over the end of the electrode with the aid of jewelers forceps. An example of gold capped electrodes is visible in Figure 22. Tungsten wire made square in cross-section by grinding the sides of a length of wire while it was held in a hacksaw frame, was used in some of the mounts.

e. Potential probes. Pointed electrodes (B, D, and E of Figure 6) were applied to the sides of a crystal for measuring relative potentials, or changes in potential, at certain points while a current flowed through the crystal. Three types of potential probes were tried. In the first versions the ends of the probes which contacted the crystal were blade shaped. These were prepared by holding 0.010 inch tungsten wire in a Vibro-Tool (Ref. 49) and laying a side of the wire against a fine honing stone. Tungsten wire, etched down to 0.0005 inch diameter, formed into a 1/16 inch semicircular loop and lightly spring loaded against a crystal, was also used.

The pointed potential probes, used in most of the crystal mounts, were prepared using the simple setup of Figure 8. Several techniques were tried and the one described here was found to be far the most rapid and reproducible.
Tungsten wire, 0.010 inch in diameter, was dipped in molten potassium nitrite at about 575° C. When the wire flashed red it was withdrawn steadily at about 1/4 inch per second. Three dips usually resulted in a sharp 15° point.

A dovetail slot in the end of the electrode holder engages the end of the electrode. This method of holding electrodes permitted withdrawal of the tool after the electrode was cemented in position. Wax on the tool prevented cement from adhering to the tool.
In a small stainless steel crucible (porcelain cracked when cooled and reheated) $\text{KNO}_3$ was heated so that the bottom of the crucible glowed a dull red (approximately $575 \, ^\circ\text{C}$). Tungsten wire, 0.010 inch diameter, was dipped in the molten salt to a depth of about one-quarter inch. The wire would then suddenly flash to bright red heat. Upon flashing there was a tendency to suddenly jerk the wire out, but a controlled steady withdrawal, taking about one second, gave the results desired. Repeating this process usually brought the end to a strong sharp $15^\circ$ point in a total of three dips. The angle of the point could be altered by varying the withdrawal rate.

**f. Terminals.** Connections to the electrodes were made by means of silver paint. The paint was applied at the outer ends of the electrodes and extended to the edges of the base plate. Terminal A was extended over the edge to the back of the plate in order to connect with the contact finger of Figure 21-(9).

Of several conducting paints tried, General Cement Silver Print No. 21-2 (Ref. 50) was most satisfactory. Silver paint connections withstood temperatures in excess of $900 \, ^\circ\text{C}$ and had resistances of about 0.1 ohm. Conducting paints and marking inks which tended to settle out were stored on a rotating tilted table shown in Figure 10.
Figure 10. Rotating Tilted Table.

Conducting paints and marking inks, which tend to settle out, were stored on this table.

Figure 11. Dentists' and Jewelers' Tools.

These tools were found to be especially useful in micromanipulative operations.
3. Mounting techniques

a. Tools and equipment. Some views of the microscope used appear in Figures 2, 7, and 13. A micro-forceps used in sorting crystals has been mentioned and illustrated in Figure 4. This tool found other applications in the adjustment and repair of crystal mounts, and in the thermoelectric measurements mentioned later. Figure 9 shows a tool, constructed for holding electrodes, which is also visible in later illustrations. The most useful tool for selecting crystals and handling while mounting, consisted of a tungsten probe tipped with a tiny droplet of rubber cement. Rubber cement was applied by just touching the tip of the tool to a drop of cement, and then dissolving away the excess in benzol.

Two Chambers micro-manipulators were used. The mechanism of this instrument is diagrammed in Figure 12 and its use is illustrated in Figure 13. This and other auxiliary equipment appears in later figures. A number of dentist's and jeweler's tools which were found to be especially useful are shown in Figure 11.

b. Procedure. Details of the mounting procedure can best be understood by a study of Figures 14, 15, and 16 and the accompanying explanations. Numbered items are there arranged in an order to give continuity to the procedure as well as to describe equipment and tools. The steps may also
Above diagram shows the working principle of the Micro-Manipulator. In "a," where the instrument is viewed from the side, screw "I" moves needle tip through vertical arc "y-z." In "b," where the instrument is viewed from above, screws "G" and "H" move the needle tip through the horizontal arcs "m-n" and "o-p."

Figure 12. Mechanism of the Chambers Micro-Manipulator

This diagram was duplicated from an E. Lietz, Inc. catalog (Ref. 51). This instrument was originally designed for biological applications. For the present work the tool holder (at X in this figure) was provided with an extension so that tools were held above the microscope stage as shown in Figures 13 and 14-(5). The working range at the tip of the tool was about one cubic millimeter.
Figure 13. Arrangement of Microscope, Stage, and Micro-Manipulators.

Here the micro-forceps of Figure 4 are supported at an angle above the stage by a buttonhook shaped extension. Motions in x and y directions are controlled respectively by the left and right hands. A transparent plastic box with slotted partitions for storage of mounted crystals appears in the left background.
be summarized as follows:

1. The surface of the base plate was ground as shown in Figure 15-(1) and electrode (2) was cemented in position as shown.

2. The base plate was positioned on the stage as in Figure 14, an electrode was placed in the holding tool as in Figure 9, and the tool was secured as shown in Figure 14-(8).

3. A crystal borne by the tool, Figure 14-(9), was manipulated into position between the electrodes Figure 15-(2) and (6) spring force was applied to the ends of the crystal and cement was applied at Figure 15-(7).

4. Additional probes were brought into position as shown in Figure 16 and cement was applied to give a result similar to Figures 17 or 6.

Figure 18 is a micro-photograph of crystal No. 47 of Figure 17. This exceptionally large crystal had a central single crystalline section 170 microns long. The ends were polycrystalline. The diameter was about that of a human hair. This crystal was used for conductivity measurements.
Explanation of Figure 14.

(1) Chambers micro-manipulator base plate altered to hold manipulators (2) and (3) in the position shown.
(2) and (3) Chambers micro-manipulators equipped with tool holder extensions (4) and (5).
(4) Tool holder extension (not visible in photograph) supporting tool holder (6).
(5) Buttonhook shaped tool holder extension supporting tool (8).
(6) and (7) Tool holders attached to tool holder extensions (4) and (5) and supporting tools (8) and (9).
(8) Electrode holder tool of Figure 9 secured in the tool holder (6). This tool is S shaped (in vertical plane) with ends flattened so the ends are parallel to the stage. The dovetail slot parallel to the plane of the tool, for holding potential probes, is visible at the outer end of the tool.
(9) Crystal pickup tool consisting of a glass tube supporting a pointed tungsten wire tipped with a small droplet of rubber cement. This tool is used in selecting the crystal to be mounted, transporting it to the stage, and locating the crystal between the current electrodes until the crystal is forcibly held by the current electrodes.
10) $X_1, Y_1, Z_1, X_2, Y_2,$ and $Z_2$, micro-manipulator controls
Explanation of Figure 14 (cont.).

for motions in indicated x, y, and z directions. Controlled motions are limited to approximately 1 mm in each direction.

(11) $Y_3$ Auxiliary control to obviate the uncertainty of y motion, due to elasticity in the $Y_2$ control, while applying force on the crystal in the $-x$ direction.

(12) Mechanical stage altered to hold a one inch square plate firmly, and equipped with auxiliary control $Y_3$.

(13) Microscope stage extended to the right in order to obtain clearance between the mechanical stage controls and the microscope objectives.

(14) Aluminum disk comprising the top of the stage heating unit. A 1/4 inch hole in the center of the disk permits substage illumination in the center of the field. A reverse wound chromel heating unit is cemented to the underside of the disk. This gives temperatures in excess of 100 °C for rapid setting of cement.

(15) Stage mount holder with electrical connections for checking crystal contacts, and effects of force and temperature, while crystal is under the microscope for observation.

(16) Micro-forceps stored in a test tube secured to the base plate in order to protect the points.
Figure 14. Arrangement of Stage, Micro-Manipulator, and Tools.

Chambers micro-manipulators (2) and (3) control the tools (8) and (9) while the crystal mount is held by the mechanical stage (12). See preceding and following pages for detailed description of the numbered items and mounting procedure.
Explanation of Figure 15

(1) Fused silica plate, one inch square, with surface roughened by grinding, except near the center, in order to facilitate adhesion of cement.

(2) Current electrode cemented to the silica plate prior to placing the plate on the stage.

(3) Cement applied to electrode (2) in a manner to prevent any flexure.

(4) Electrode holder tool spring loaded, using \( Y_2 \) control, against movable tool rest (5) so that \( y \) motion is then controlled by \( Y_3 \). The tool is holding electrode (6) in elastic contact with crystal (9).

(5) Tool rest consisting of a cone of brass shim secured by screw (10) to the mechanical stage (11). The tool rest bends at (10) in response to control \( Y_3 \). In order to remove the electrode holding tool from the electrode after the electrode is secured to the plate with cement, clearance is provided by retracting \( Y_3 \), thereby permitting the tool rest to be elevated by pivoting about the axis of screw (10).

(6) Electrode of 0.020 inch tungsten wire, with end ground flat, sprung into holding contact with the crystal by \(-x\) motion of the electrode holder tool (4) and cemented to the plate by (7).

(7) Cement holding electrode (6) to plate (1) leaving
Explanation of Figure 15 (cont.).

part of electrode free to maintain spring load.
Cement sets in ten to fifteen minutes when heated by the stage heater.

(8) Crystal pickup tool retracted from adhesive contact with the crystal.
Figure 15. Crystal Secured Between Current Electrodes.

This is a close-up view of the central portion of Figure 14. The crystal (9) has just been manipulated into position between the current electrodes using tool (8). Spring load was applied and cement deposited at (7). Details concerning the numbered items and procedures are given on the preceding pages.
Figure 16. Locating a Potential Probe.

Plate (1) has been rotated 180° from its former position as in Figure 15. The end of current electrode (2) was previously held by the electrode holder tool. The ends of tool (3) have been reversed and a potential probe (4) is being brought into position. After applying forcible contact, cement will be applied to the exposed shank of the probe.
Figure 17. Completed Crystal Mount for Conductivity Study.

After securing the potential probe of Figure 16, another probe was appropriately formed and secured in a similar manner. Additional cement and silver paint were applied to the outer ends of the electrodes and the mount was numbered with ceramic marking ink.
Figure 18. Microphotograph of Mounted Crystal.

This is crystal No. 47 of Figure 17. The central single crystalline portion of this exceptionally large crystal is 0.17 mm long.
D. Apparatus

1. Introduction

Several different setups of equipment were required for making electrical measurements on both the mounted and the unmounted boron crystals. Only a vacuum tube ohmmeter was required for simple qualitative measurements of rectification effects and photoconductivity. A heated tungsten probe, in addition to the microforceps and microscope, was required for qualitative measurements of thermoelectric effects. For quantitative thermoelectric measurements, it was necessary to construct heated thermocouples and controlling equipment, which were used in conjunction with potentiometers and an electrometer.

Special mount holders were required for Hall effect measurements and for resistivity measurements at low and high temperatures. A furnace was needed for heating a mounted crystal while it was held between the poles of a magnet. For resistivity measurements, it was necessary to develop a circuit for measuring the relative potentials of probes connected to a crystal. For Hall effect measurements, it was necessary to develop additional circuitry for amplifying and recording slight changes in relative probe potentials.
In order to select, construct and assemble the equipment it was necessary to consider several unique aspects of the problem. Because of their small size, the crystals were easily lost. The mounts were fragile and easily damaged. Because of the high resistivity of the crystals, static charge accumulations and capacity effects had to be suppressed. These effects necessitated complete shielding and choice of circuits that permitted grounding of most elements through relatively low resistances. Because of the small size of the crystals, the small area of contact with electrodes, the high resistivity and semiconducting behavior of the crystals, electrical noise in excess of Johnson noise presented serious problems (Refs. 52, 53, 54, 55). Noise exceeding the Hall voltages from boron necessitated equipment which permitted statistical analysis of Hall effect data.

It is interesting to note that approximately one ton of equipment was required for making measurements on a crystal weighing a few micrograms. This represents a weight ratio of about $10^{12}$.

2. Electro-mechanical components.

a. Equipment for thermoelectric measurements. Unmounted crystals were used in studies of thermoelectric effects. No special mount holders were required for
these studies. Preliminary measurements of thermoelectric effects were made using a tungsten probe heated by a small platinum coil. The coil was wound on the end of a 1/16 inch outside diameter alundum tube. The tungsten probe projected from the end of the tube. Micro-forceps were used to hold the crystal while it was touched with the heated probe. An electrometer was used to indicate the potential difference between the heated probe and the micro-forceps.

Equipment for more exact measurements of thermoelectric effects was constructed and is illustrated in Figure 20. A diagram, not to scale, of the thermocouple and heater arrangement, appears in Figure 33(a) in conjunction with results on thermoelectric power. Two platinum-platinum-rhodium thermocouples were used to support and form electrical connections with the crystal being studied. Each of the thermocouples was located at the end of a two hole, 1/8 inch outside diameter alundum tube. The thermocouples were welded and formed under the microscope to a shape approximately as shown in Figure 33(a). Heating coils, consisting of six turns of platinum wire, were wound on the alundum tubes near the thermocouples. Copper wires were connected to the heating coils and the coils were coated with alundum cement. Both thermocouples and heating coil assemblies were fitted into
1/4 inch outside diameter alundum tubes so that the thermocouples projected from the ends of the tubes. The two leads from each of the thermocouples and the two leads from each of the heating coils extended from the other ends of the alundum tubes. These four leads from each assembly were wound in small spirals to allow some flexibility. The completed assemblies appear as the white pencil-shaped objects supported above the microscope stage in Figure 20.

In order to allow for thermal expansion, it was found necessary to support one of the thermocouple assemblies in the special fixture shown at the far right of Figure 20. This fixture permitted one of the assemblies to move longitudinally while the assembly was held rigid with respect to motion in other directions. Two parallel leaf springs attached to the opposite ends of a trapezoidal brass block served this purpose. This supporting fixture was attached to the right edge of the microscope stage as shown in Figure 20. The other thermocouple assembly was supported by one of the micromanipulator tool holders as shown at the left of the stage in the figure.

Vernier controlled variacs controlled the inputs to two 2.3 volt filament transformers which in turn supplied the heater currents. A switching arrangement provided for connecting either thermocouple to an automatic dial
The dial type potentiometer was used for indicating the temperatures at each end of a crystal supported between the two thermocouples. Cold junctions for each thermocouple were contained in the dewar flask shown at the left of the stage in Figure 20. The switching arrangement also provided for connecting the platinum elements of both thermocouples directly to a manually operated potentiometer. This manually operated potentiometer was used for measuring the thermoelectric emfs set up between the two platinum electrodes in contact with the crystal. An electrometer-galvanometer combination was used for indicating the null point. The platinum electrodes could also be connected to vacuum tube ohmmeter which was used for estimating the resistance of the crystal when both thermocouples were at the same temperature.

b. Equipment for low temperature studies. Because of the very high resistivity of crystalline boron at low temperatures, it was necessary to construct a special mount holder for low temperature studies. The requirements for this mount holder included the following:

1. Complete electrical shielding.
2. Protection from air currents which tend to set up static charge accumulations.
3. Resistance between leads greater than $10^{13}$ ohms.
Figure 19. Mount Holder for Low Temperatures.

Tungsten wires cemented in the ends of the glass tubes support the mount and connect to its terminals. A central glass tube carries a thermocouple.

Figure 20. Thermoelectric Measuring Equipment.

In this picture the microscope has been raised and swung away from the stage in order to make the heated thermocouples visible. Heater controls and the switching arrangement are contained in the box to the left.
A mount holder which satisfied these requirements was made. This mount holder permitted cooling the mounted crystal to low temperatures, and provided for direct connections to measuring instruments. The end of the holder, which held the mounted crystal, is shown in Figure 19 on the preceding page. The five glass tubes shown in the figure were each 1\(\frac{1}{4}\) inches long. The upper ends of these glass tubes were supported in a brass tube, 7 inches long, and 1-1/2 inches inside diameter. The contact leads, which supported the mount, were tungsten wires which were cemented in the glass tubes. The central glass tube carried a copper constantan thermocouple. A large test tube, also shown in the figure, was used to enclose the mount when it was immersed in the coolant. A mixture of trichloroethylene and dry ice was used as a coolant, and was contained in a dewar flask shielded with aluminum foil.

A megohmmeter was used for some resistance measurements at low temperatures. Most consistent results were obtained using an electrometer, with calibrated shunts, as an ammeter. The shunts used ranged from \(10^9\) to \(10^{12}\) ohms. The electrometer and shunt combination was supported directly above the mount holder and all leads were shielded.
c. Mount holder for high temperature studies. The requirements for resistance between leads in the high temperature mount holder were not as great as for the low temperature mount holder. Other requirements, however, made the construction of this mount holder more involved. Specific requirements for the high temperature mount holder included the following:

1. Complete electrical shielding.
2. Ability to withstand temperatures in excess of 700 °C.
3. Resistance between leads greater than $10^{10}$ ohms.

Three high temperature mount holders were constructed. The final version, which satisfied the requirements, is shown in Figures 21 and 22. The explanations which accompany the figures give details of the construction.

This mount holder provided individual shielding for each of the potential probe leads. A single shield served for both of the current carrying leads. Spacings were such as to provide maximum insulation between the potential leads. The Sauereisen cements were found to be inferior to alundum as an insulator so leakage paths through the cements were avoided.

d. Interpole furnace and auxiliary equipment. For study of Hall effect as a function of temperature, means for heating a mounted crystal while between the poles of
Explanation of Figure 21.

(1) Plug cast to fit the mouth of the interpole furnace shown in Figure 23-(5). The plug was cast of Sauereisen No. 1500 (vermiculite filler) and coated with Sauereisen No. 78 (alundum filler).

(2) and (3) "Super-nickel" tubes (negligibly magnetic), 3/8 inch O.D., individually shielding the potential probe leads. The middle sections of these tubes were slotted alternately from opposite sides approximately two-thirds through at intervals of 3/16 inch in order to minimize heat conduction.

(4) Tube similar to (2) and (3) shielding a pair of leads to the current electrodes.

(5) Copper heat dissipator for minimizing transfer of heat to the outer end of the holder where plastic insulated shielded cables connect to the tungsten leads.

(6) Ends of tubes (2) and (3) cut, flattened, and spot-welded to form a chamber for receiving the crystal mount, and coated with Sauereisen No. 78.

(7) Heavy coating of Sauereisen No. 78 on interior of chamber (6). A V-groove leads to the center of the chamber for the thermocouple (8).

(8) Platinum platinum-rhodium thermocouple lying in the V-groove of (7) with junction at centrally located apex of the V-groove.
(9) Fixed contact finger supported away from the cement by a small piece of alundum tubing. This contact is not visible in Figure 22 but is referred to there under (4).
Figure 21. Mount Holder for High Temperatures.

Shielded tungsten leads supported in alumnum tubes provide spring contacts to the mount terminals. Details of construction are explained on the preceding pages.
Explanation of Figure 22.

(1) End of a two hole alundum tube, 9-1/2 inches long by 1/4 inch in diameter. This tube was coated with silver paint excepting 1/2 inch from each end. The tube was supported at points about one inch from each end, in the tube of Figure 21-(3) with cement. Cement near the ends was avoided because of its inferior insulating properties.

(2) and (3) Contact fingers terminating the potential leads. These were made of 0.020 inch tungsten wire. The wire was formed to provide spring contact with the silver terminals of the mount which led to the potential probes. The tungsten leads were doubled back into the second holes of the alundum tubes and cemented for stability.

(4) Silver paint current electrode connection extended to the under side of the mount base plate in order to contact the fixed contact finger of Figure 21-(9).

(5) Contact finger spring loaded against the silver current electrode terminal in the foreground. This lead passed over the crystal through a small protecting tube. The small alundum tube is broken at two points (one visible) near the entrance to the shielding tube, Figure 21-(4). These breaks permit elastic flexure of the tungsten lead when changing crystal mounts.
Explanation of Figure 22 (cont.).

(6) Silver coated alundum tubes, 1/8 inch in diameter. These alundum tubes lie in the grooves between the metal tubes, Figure 21-(2), (4), and (3), allowing for additional leads. Similar alundum tubes, not visible, on the under side of the holder carry the thermocouple leads.
Figure 22. Close-Up View of Crystal Mount Holder.

Tungsten spring contacts connect to the silver terminals of the crystal mount. Gold capped, square cross section current electrodes were used in crystal mount No. 37 shown here.
a magnet were required. In order to apply the strongest possible magnetic field, it was necessary to keep the pole separation to a minimum. A furnace for heating mounted crystals was designed and constructed. This furnace allowed for a minimum pole spacing of one and one half inches. Unfortunately, the resulting maximum obtainable magnetic field of 7000 gauss was inadequate. In order to obtain stronger fields it was necessary to dispense with the furnace and resort to heating the crystal by means of the current flowing in the crystal.

The furnace was used extensively, however, for resistivity versus temperature measurements. Although other types of furnaces would have served this purpose as well, this interpole furnace will be briefly described. The furnace is illustrated in Figure 23-(5).

An oval shaped core for the heating element was constructed. A ten inch length of $3/4$ inch outside diameter, spirally grooved, alundum tubing was slit for a distance of two inches from one end. One of the semicylinders thus formed was cut free. This semicylinder was then cemented in a position, one inch radially outward from its former position, by the use of separators consisting of two one-inch square silica plates at each side. The remaining eight inches of alundum tubing served as a furnace support, and as a conduit for the heating current leads.
The core was reverse-wound with 18 turns of high temperature resistance wire and was coated with alundum cement. A box, which measured $4\frac{1}{4} \times 2\frac{3}{4} \times 1\frac{1}{4}$ inches, was made of 0.0014 inch molybdenum shim which had been corrugated to increase its strength. The heater was fitted into the box and the cavity between the walls of the box and the heater was filled with vermiculite. The assembled furnace was coated inside and out with Sauer-eisen No. 78.

Furnace power was supplied by a transformer capable of delivering 10 amperes at 20 volts. The transformer input was controlled by a variac. With mount holder inserted, the furnace provided a temperature of 900 °C when the power input was 193 watts. The power requirement was almost directly proportional to the temperature above room temperature.

e. Equipment for resistivity and Hall effect measurements. A good commercial potentiometer, with an electrometer galvanometer combination for finding the null point, would have been adequate for most resistivity measurements. Such an arrangement was used in a few preliminary resistivity measurements and in preliminary efforts to observe Hall effects. In order to investigate more fully the effective resistance of boron crystals under various conditions, and in order to study voltage current characteristics,
a potentiometer was required which was capable of handling more than 500 volts. In the method for measuring Hall voltages, which was eventually developed, it was necessary to accurately balance the potential of a probe connected to a crystal against another potential. A potentiometer, or potential divider, which satisfied these requirements was constructed.

The potential divider, amplifying and recording equipment and the magnet and magnet control equipment are shown in Figure 24 and described in the accompanying explanation. This equipment was employed in a circuit which was adapted to the study of voltage current characteristics, resistivity and Hall effects in high resistivity, electrically noisy crystals. A diagram of this circuit is shown in Figure 25.

3. Potential measuring circuit

a. Introduction. The circuit shown in Figure 25 is based on the circuit introduced by Evans in 1940 (Ref. 56). The Evans circuit was designed specifically for the study of Hall effects in high resistivity, semiconducting materials and since its introduction has been used by others (Ref. 57) for this purpose.

The principle of the Evans circuit may be most easily explained by referring back to Figure 1. In the Evans
Explanation of Figure 23.

(1) Crystal mount holder partially withdrawn from the mouth of the furnace. The mount holder is supported by two clamps attached to the tube carrying the current leads.

(2) Cannon connector (two prong) at the end of a two wire shielded cable leading from the current electrode connections.

(3) Amphenol connector (single prong) at the end of a single wire shielded cable leading from one of the potential probes. Another similar cable and connector is shown directly below.

(4) Thermocouple cold junction at the end of a shielded cable carrying platinum and platinum-rhodium thermocouple wires. The cold junction is in a slotted plastic protecting tube. Tip jacks, mounted in the dewar flask stopper, connect to the temperature measuring potentiometer.

(5) Interpole furnace. Outside dimensions of rectangular portion are 4-1/4 x 2-3/4 x 1-1/4 inches. See text for a more complete description.

(6) Power transformer supplying up to 20 volts, 10 amps, to the interpole furnace. Control is by a variac on the input. An A.C. ammeter is in series with the output.
Explanation of Figure 24.

(1) Shielded box for batteries supplying the crystal current.

(2) Power supply, Kepco Labs, 600 volt, 200 m.a., D.C., used in resistivity measurements and study of voltage current characteristics.

(3) Volt-ohmmist, RCA - Model WV-97A, used as a vacuum tube voltmeter for checking total voltage applied to the crystal and series resistance. This was also used for measuring crystal resistances approximately.

(4) Simpson meter, Model 260, used as a microammeter for approximate values of crystal current. This was not used in computing crystal resistance.

(5) Shielded box containing the potential divider, the series resistance, and the probe selector switch. A calibration chart for the potential divider lies on the table in the foreground.

(6) Electrometer, Keithley, Model 29, modified by adding output terminals. The rated input impedance was $10^{13}$ ohms. In use, this and other meters were placed at least six feet from the magnet and in its neutral plane.

(7) Galvanometer, Leeds and Northrup, No. 2430A, used on the electrometer output for preliminary checks on the probe potential balance.
(8) Amplifier, Liston-Folb, D.C. breaker, Model 10. The maximum gain was 80 DB. The gains used were 16 to 48 DB.

(9) Filter consisting of adjustable resistances, condensers, and chokes.

(10) Recorder, Brown Instruments. Another recorder, Model Y15 3x17(V)-x-9(V), which had additional damping and other controls, was actually used in place of the one shown in most of the work on Hall effects.

(11) Potentiometer, dial type, Brown Instruments, Model Y156x15V-X-(V), Range: 0-70.1 millivolts. This potentiometer was used for measuring furnace temperatures. A conversion chart (m.v. to degree C) is attached to the front panel.

(12) Electromagnet, Consolidated Engineering Company, Type No. 23-104A. The interpole furnace, and crystal mount holder, are in position between the poles of the magnet. The furnace power supply is at the bottom of the rack supporting (2), (6), (7), and (11).

(13) Magnet D.C. power supply and controls. This unit is mobile so that all control and recording equipment can be moved to a position more remote from magnet.
Figure 23. Interpole Furnace and Auxiliary Equipment.

Figure 24. Probe Potential Measuring Equipment.
method, the probe D, of Figure 1, is not used. In the absence of a magnetic field, as in Figure 1(a), the potential of probe B is balanced against an external potential which is equal to the potential of point O in the figure. The external balancing potential is obtained from a potentiometer connected across the current electrodes A and C of Figure 1. When the magnetic field is applied, as in Figure 1(b), the change in potential \( v \) of probe B, as indicated in the figure, may be measured by rebalancing the potentiometer. The potential change \( v \) (referred to as \( V_y \) or \( \Delta V \) in some later discussions) may also be measured with the aid of a calibrated null instrument which indicates directly the deviation from potential balance.

The Evans circuit permits grounding all circuit elements through relatively low resistances with the exception of the connection between probe B and an electrometer. This connection may be short and well shielded. This arrangement tends to minimize noise and drift resulting from pickup and static charge accumulations. However, the Evans single probe method, in the case of a perfectly symmetrical crystal, gives a Hall voltage which is only one half of the Hall voltage obtained when two probes are used. This disadvantage of the Evans method
may be outweighed by the advantage of better grounding especially in the case of a very high resistance crystal. The Evans method was found to be the most practicable in this work.

When random voltage variations due to electrical noise equal or exceed the voltage being measured, it is necessary to resort to statistical methods. A statistical method for accumulating Hall effect data was described by Pell and Sproull (Ref. 58) in 1952. The essential features of the method developed by Pell and Sproull are the following:

1. The magnetic field is periodically reversed.
2. Amplifiers and filters are used to build up the Hall voltage signal and the relative magnitude of electrical noise is kept to a minimum.
3. A chart recorder is used for accumulating a large quantity of data which can be subjected to statistical analysis.

These features of the Pell and Sproull method were incorporated in the circuit used in this work. Pell and Sproull reversed the magnetic field automatically by means of an amplidyne generator which supplied the field current. Manual methods of reversing the field current were used in this work.
b. Discussion. The circuit used in this work for the study of voltage current characteristics, resistivity, and Hall effects, is shown in Figure 25. This circuit makes use of the essential features of the circuits introduced by Evans, and by Pell and Sproull for Hall effect measurements. In addition, the circuit of Figure 25 is adapted to the study of voltage current characteristics and resistivity. The versatility of this circuit is due to the following additional features.

1. An adjustable, calibrated, resistance in series with the crystal serves as a standard for computing the current through the crystal and also serves to protect the crystal from current overloads.

2. A wide range, accurately calibrated, finely adjustable, potential divider permits precise balancing of the potential of a probe connected to the crystal.

3. A probe selector switch facilitates probe potential measurements without altering the crystal voltage or current.

A discussion of the circuit shown in Figure 25 follows. Reference back to Figure 24 and the accompanying explanation will provide additional details on the equipment and instruments used in the circuit.
PROBE POTENTIAL MEASURING CIRCUIT

Figure 25. Probe Potential Measuring Circuit.

This circuit provides an accurately divided potential difference for balancing the potential of any probe chosen at P. Using a galvanometer G and a calibration chart of D and H, relative potentials of the probes can be accurately determined for resistivity measurements. Using A, F, and R, statistical analysis of slight variations of the potential due to Hall effect is possible.
The battery $B$ of Figure 25 was in a grounded metal box. The battery was used when making Hall effect measurements, but was replaced by a power supply when studying voltage current characteristics and resistivity. The voltmeter $V$ served as a reference both for computing relative probe potentials and for computing the current through the crystal. Slight errors in reading $V$ could thus introduce only second order errors (resulting from non-linear voltage current characteristics) into the resistance computations. Ammeter $I$ was used only for noting nominal values of crystal current. When the Hall voltages were being measured both $I$ and $V$ were removed from the circuit, in order to reduce pickup.

When the probe selector $P$ was in position 1, the corresponding potential drop across $S$ (and $I$) could be evaluated. From this potential drop the crystal current and the total crystal resistance could be computed. The difference between the potentials corresponding to positions 2 and 4 provided data for resistivity computations. The change in the potential balance at position 3, when the magnetic field was applied, gave the Hall voltage.

Several arrangements for finding the null point were tried. Of these the most satisfactory proved to be the high input impedance electrometer $E$ in combination with
the galvanometer G. The available current gain from the electrometer was about $10^9$. The sensitivity of the galvanometer was about $0.1 \mu$A/mm. The resulting maximum sensitivity of the combination was about $10^{-16}$ amp/mm. This combination was more than adequate for resistivity studies, but for Hall effect measurements it was necessary to use the amplified and filtered output of E. The recorder R was used for collecting Hall effect data.

The series resistance S was adjustable from zero to $10^8$ ohms by steps. The steps increased nominally by multiples of $10^{1/2}$. The potential divider, consisting of D and H, had a total effective resistance of about 116,000 ohms and provided means for dividing the applied potential into fractional parts of 0.00003. H was a ten turn helipot each turn of which was divided into 100 divisions. Readings were recorded to 0.1 division with an estimated error of $\pm 0.1$ division.

c. Calibration. Resistances having values specified to $\pm 1$ per cent and a helipot having linearity specified to $\pm 0.1$ per cent composed the elements S, D, and H of Figure 25. All the resistances were measured individually by means of a Wheatstone bridge and series combinations were checked. A plot of deviations from linearity of the helipot was prepared. These data were used in the preparation of calibration tables for the series resistance and
for the potential divider (considering both D and H). A summary of the analysis of the potential divider circuit shown in Figure 25 follows.

Let the resistances composing D of Figure 25 be $R_1, R_2, R_3, \ldots, R_n, R_{n+1}, R_{n+2}, \ldots, R_{11}, R_{12}$. Let $R_{n+1}$ and $R_{n+2}$ be the resistances straddled by H and let $R_h$ be the helipot resistance. Let $R_p$ correspond to that part of $R_h$ between its upper end and the pointer.

Then $R_n = \bar{R} + \Delta R_n$, where $\bar{R} = \frac{\sum_{i=1}^{12} R_i}{12}$,

and the total resistance $R_t = \frac{4}{R} \left\{ \frac{\delta_n}{2 + r + \delta_n} \right\}$

where $\delta_n = \frac{\Delta R_{n+1} + R_{n+1}}{R} < 0.01$,

and $r = R_h/\bar{R} \leq 10$.

Let the helipot dial reading be $s$ and let $\Delta s(s)$ be the measured deviation from linearity. Then let

$$\alpha = \frac{R_p}{R_h} = \frac{s + \Delta s(s)}{10}$$

and $\sigma_n = \sum_{i=1}^{n} \frac{\Delta R_i}{\bar{R}} < 0.01$. 
Take $V_p$ as the potential drop from the top of the potential divider of Figure 25 to the helipot pointer and $V_t$ as the total potential drop across the potential divider as indicated by the voltmeter.

The fractional potential drop is then

$$f = \frac{V_p}{V_t} = \frac{R}{R_t} \left\{ n + \sigma_n + \frac{a(2 + \delta_n)r}{(2 + \delta_n + r)} \right\}.$$  

This reduces to

$$f = C \left\{ N(n) + S(n, s) + s \right\}$$  \hspace{1cm} (32)$$

where $C = \frac{1}{60 + \frac{100}{r}}$, $S(n, s) = \Delta s(s) + \frac{31}{70} s \delta_n$, $N(c) = (5 + 10/r)(1+0.026 \delta_n)(n+ \sigma_n)$.

Equation (32) was used in the preparation of a table of $f$ values versus $n$ and $s$. Interpolation values were included. The mean interpolation value was a fractional value $f$ of 0.000142 per smallest division of the helipot dial. Readings were estimated to one tenth division. A potentiometer was used to check the calibration approximately.
E. Measurement Procedures

1. Introduction

The apparatus used in this work has been discussed in an order proceeding from simple equipment to the more complex. However, the procedures used in making measurements will be discussed in an order corresponding more closely to that of the theoretical development on pages 10 to 35. This order will also be used in the presentation and discussion of results.

Under the heading of resistivity the procedures used for measuring voltage current characteristics will be discussed first since it was necessary to consider these characteristics in order to determine resistance and resistivity. Procedures used for measuring resistance as a function of temperature will be discussed also under this heading since a method was developed for normalizing resistance versus temperature data so that this data could be used for indirectly evaluating resistivities. However, discussion of this normalizing procedure will be postponed until evidence for its validity can be presented in connection with results of the experiments.

Although qualitative studies of thermoelectric effects led to the discovery of the first boron crystal to show measurable Hall voltages, a discussion of the procedures
for measuring Hall effects more logically follows that of resistivity. Quantitative studies of thermoelectric effects served to supplement those on Hall effects as did also the less quantitative studies of rectification, forming and photoconductivity.

2. Resistivity

a. Voltage current characteristics. Some preliminary measurements of the voltage current characteristics of boron were made using a voltmeter connected directly across the ends of a crystal, and an ammeter and resistance in series with the crystal. A series resistance was necessary in order to protect the crystal from current overloads. The accuracy and ease of interpretation of measurements made by this method were not satisfactory. However, these preliminary studies served to indicate that the voltage current characteristics of crystalline boron were definitely non-linear and worthy of further study.

In order to make more detailed studies of voltage current characteristics the circuit shown in Figure 25 was used. A mounted crystal was placed in the holder as shown in Figure 22 and the holder was inserted in the furnace as shown in Figure 23. An initial set of measurements was then made at room temperature. The first
measurement of a set was usually made with a total applied voltage of about one volt. The series resistance was adjusted to a value approximately equal to that of the crystal. This was done as follows: with the probe selector switch in position 1 as shown in Figure 25, and with the potential divider set at a position $P_1$ corresponding to a fractional value $f_1$ of approximately 0.5, the series resistance was adjusted to a position most nearly corresponding to a balance as indicated by the electrometer $E$. The galvanometer $G$ was then connected to the output of the electrometer and the potential divider was adjusted accurately to the null point as indicated by the galvanometer and this position $P_1$ of the potential divider was recorded. The probe selector switch was then set to position 2 and the potential divider was readjusted to the null point and the value $P_2$ was recorded. In a similar manner the positions of the potential divider $P_3$ and $P_4$ corresponding to a potential balance with other probes connected to the crystal were found and recorded. This procedure was repeated using total applied voltages increased by multiples of approximately $10^{1/2}$ until the value of $P_1$ began to show a marked increase. The total applied voltage was then increased by smaller steps until the nominal current passing through the
crystal, as indicated by the ammeter I, approached a value considered to be unsafe for the crystal. When crystals were subjected to currents much in excess of 10 milli-amperes their conductivity characteristics usually were permanently altered. The maximum available voltage from the power supply was about 600 volts and it was usually possible to use this voltage safely when the crystal was at room temperature.

After a complete set of data had been obtained at room temperature the furnace current was turned on and set at about 1 ampere. Temperature equilibrium at about 50 °C in the furnace was usually reached in about 1 hour. The procedure described above was repeated and the furnace current was then reset to attain a temperature 50 to 100 degrees higher. Sets of data were thus obtained at successively higher temperatures until a temperature considered to be unsafe for the mounted crystal was approached. These studies were rarely extended to temperatures in excess of 450 °C since crystals were frequently damaged or their conductivity characteristics altered when heated to higher temperatures.

b. Room temperature resistivity. Based on a study of the voltage current characteristics of crystalline boron a method for accurately computing resistances at given ambient temperatures was developed. This method, which will
be described in some detail later, reduced the error in resistance computations from about ±10 per cent to about ±1 per cent. The final accuracy in computations of resistivity, therefore, was limited not by the accuracy of measurements of resistance but by the geometry of the crystals and the accuracy of measurements of the physical dimensions. The errors in measurement of the dimensions of the crystals used for direct computations of resistivity were estimated to be about ±10 per cent. On the basis of this estimate the error in the resulting values for room temperature resistivity was about ±20 per cent.

Indirect methods were used for estimating the resistivities of some crystals and these methods will be described in connection with the discussion of resistance versus temperature.

Data obtained on the voltage current characteristics of selected crystals at an ambient temperature of 25 °C were used for computations of room temperature resistivity. Crystals were mounted as shown in Figure 18 with two potential probes contacting the same side of a crystal and separated by a regular single crystalline segment. The resistance \( R_{24} \) of this segment of the crystal was used to compute the resistivity. An example of this computation will be illustrated in connection with other sample computations.
For a crystal having approximately circular cross-section, the length $l_{24}$ of the segment of the crystal between the two potential probes and the diameter $d$ of the crystal were required for resistivity computation. For a crystal having approximately rectangular cross-section, the length $l_{24}$, the thickness $d$ and the width $w$ were required. These physical dimensions of crystals were determined with the aid of calibrated microscope reticules. Two types of reticules were used. The square grid, shown in Figure 18, was used when microphotographs were taken. The calibration of this reticule was 0.132 millimeter per division as indicated in the figure. A linear reticule divided into 100 divisions was used when crystals were examined visually. The calibration of the linear reticule was 0.0134 millimeter per division. Both reticules were calibrated by comparison with a micrometer rigidly attached to the microscope stage. The dimensions of the crystals were recorded in terms of reticule divisions. For example, the dimensions of crystal No. 47, shown in Figure 18, were recorded as follows: $l_{24} = 1.3$ div, $d = 0.86$ div.

c. Resistivity versus temperature. The most complete set of measurements on resistivity versus temperature was obtained on crystal No. 47. After an initial study of the voltage current characteristics near room temperature had
been made, this crystal was potted in cement. A small droplet of Sauereisen No. 29 cement was mixed to a consistency somewhat thinner than that used for mounting probes and the crystal was covered with this cement. Measurements of the total resistance $R_{15}$ and of the segment resistance $R_{24}$ were made at temperatures up to $234^\circ$C. The crystal was then cooled to room temperature. These measurements were reproduced when the temperature was again raised and extended to $331^\circ$C. The crystal was again returned to room temperature. The final set of measurements on this crystal reproduced those previously made and extended the temperature range up to $549^\circ$C. Open circuits in the potted mount developed above this temperature.

All of the resistance measurements made on crystal No. 47 were performed according to the procedures described in connection with voltage current characteristics. The voltage current characteristics of the potted crystal were more nearly linear than those of the unpotted crystal. Resistances were computed in accordance with Ohm's law with data obtained when the total applied voltage was between 1 and 5 volts.

d. Resistance versus temperature. The procedure used to obtain the most complete set of resistance versus temperature data will be described. The crystal used in
this study was No. 46 shown in Figure 6. This crystal was originally mounted with five probes but after some preliminary room temperature resistivity measurements and some attempts to measure Hall voltages, contact with probe E, as indicated in Figure 6, was lost and this probe was removed. Resistance and resistivity data were obtained using the remaining probes.

It was found that the accuracy required in studies of resistance and resistivity versus temperature did not demand a complete investigation of voltage current characteristics since the voltage applied across the ends of the crystal was directly proportional to the current as long as this voltage remained less than about 5 volts. The first set of resistance versus temperature measurements made on crystal No. 46 were in the temperature range 25 to 150 °C. Measurements of probe potentials were made by the procedure described in connection with voltage current characteristics except that the applied voltage was kept at about 1.5 volts.

Measurements of the total resistance $R_{15}$ were also made simultaneously with the aid of a vacuum tube ohmmeter. The accuracy of the resistance measurements made with the ohmmeter when the resistance exceeded 80 megohms was not satisfactory. The calibrated error of the ohmmeter, when the resistance was less than 30 megohms was about $\pm 2$ per
cent and the resistance measurements made by the two methods agreed within 3 per cent.

A set of resistance measurements was taken while the temperature of the crystal was slowly increased for a period of 4 hours. Another set of resistance measurements was then taken while the crystal cooled to room temperature for a period of 2 hours. Data obtained while heating and cooling the crystal agreed within 5 per cent.

The next set of resistance versus temperature data on crystal No. 46 was obtained in the temperature range 25 to -80 °C. These measurements were made with the aid of an electrometer which was provided with a calibrated shunt and which was used as an ammeter in series with the crystal. Voltages of 10 to 30 volts, applied to this series combination, were measured with the aid of a vacuum tube voltmeter. The calibrated errors of this instrument were within ± 2 per cent. The crystal was placed in the holder as shown in Figure 19. A few grams of dehydrated silica gel (desiccant) were placed in the bottom of the large test tube, shown in Figure 19, before the mounted crystal and holder were inserted and sealed in the test tube. The electrometer and shunt combination were inverted and attached to the upper end of the holder. The dewar flask was filled about one third full of trichloroethylene and about 250 grams of dry ice was added. The dewar flask was
then raised into position beneath the test tube so that the test tube was not initially immersed in the coolant. Aluminum foil was wrapped around the dewar flask and extended to enclose the opening at the top. The aluminum foil and one side of the electrometer were connected to ground. The thermocouple was connected to an automatic dial type potentiometer. The readings of the voltmeter, the electrometer and the potentiometer were recorded while the temperature of the crystal slowly decreased. In order to accelerate the rate of cooling the dewar flask was periodically raised about 1/2 inch until a temperature of -79 °C was reached when the lower end of the test tube was immersed in the coolant. The dewar flask was then lowered by steps so that the test tube was withdrawn from the coolant. Measurements of resistance were continued while the crystal returned to room temperature. Above about -50 °C anomalous effects were observed. These effects might be explained as the result of moisture subliming from the walls of the test tube and condensing on the cooler crystal.

In order to extend resistance measurements to the highest possible temperatures crystal No. 46 was potted in cement as previously described in the case of crystal No. 47. In the case of crystal No. 46 contact between the crystal and potential probe B, as indicated in
Figure 6, was lost as a result of the potting operation. However, it was possible to continue measurements of total resistance.

Crystal No. 46 was then returned to the furnace and resistance measurements were made while the temperature was raised slowly to 750 °C. Resistance measurements below about 80 °C did not reproduce those previously made. It was verified by other experiments that this was due to the fact that the resistance of the cement in which the crystal was immersed was less than that of the crystal in this lower temperature range. Above 80 °C the resistance measurements previously made were reproduced within about 5 per cent. At 725 °C an open circuit through the crystal developed and it was clear that the crystal or crystal mount had undergone some chemical or physical alteration. Upon cooling the open circuit remained.

Similar sets of resistance measurements above room temperature were made on other crystals. The maximum temperatures attained with unpotted crystals were about 650 °C. Some resistance versus temperature measurements were made on unmounted crystals in conjunction with measurements on thermoelectric effects. Maximum temperatures attained in these cases were also about 650 °C. The ohmmeter was used in these latter measurements.
3. Hall effect

a. Preliminary measurements and attempts. The two probe method of studying Hall effects was used to measure the Hall voltages of a small crystal of antimony and a small crystal of germanium. These two crystals were approximately the same size as the boron crystals and were mounted in the same manner with the exception that gold caps were placed over the ends of the current electrodes. The circuit of Figure 25 was not used in the first set of measurements made on these crystals. The mounted crystals were placed between the poles of the magnet which supplied a magnetic field of 7,500 gauss. The voltage applied across the ends of the crystal was about 0.5 volts in the case of antimony and 5 volts in the case of germanium. Currents through the crystals were measured with an ammeter. A Leeds and Northrup drum type potentiometer was used for measuring Hall voltages between the potential probes at opposite sides of the crystal. A galvanometer was used for finding the null point.

With no magnetic field applied and with a known current passing through the crystal the potentiometer was balanced and its reading recorded. With magnetic field applied in each direction the potentiometer was re-balanced and the readings were recorded. This procedure
was repeated with crystal current reversed. Measurements on these crystals were made at room temperature only. The single probe method was later used for making Hall effect measurements on the antimony crystal and on several other germanium crystals. Results obtained by the two methods were in agreement within 20 per cent. The discrepancies could be attributed to errors in measurements of dimensions of the small, somewhat irregular crystals.

The two probe method and procedures similar to those described above were used in unsuccessful attempts to measure Hall effects in several boron crystals. When an electrometer was substituted for the galvanometer and connecting leads were more carefully shielded, some indications of Hall voltages were observed. Erratic behavior of the electrometer due to electrical noise originating in the crystal and pickup in other circuit elements made exact measurements impossible. Apparatus designed for measuring Hall effects in low resistivity specimens by alternating current methods was also tried. Both the single and two probe methods were used in these attempts. Some indications of Hall voltages were again observed but the measurements were still erratic and irreproducible.

b. Measurements on boron. The single probe method and the circuit shown in Figure 25 were employed in all successful Hall effect measurements on crystalline boron.
The most complete set of these measurements was obtained on the low resistivity boron crystal No. 104 and the procedures used in obtaining this set of measurements will be described.

The interpole furnace was not used but the mounted crystal in the holder alone was inserted between the poles of the magnet. A maximum magnetic field strength of 18,000 gauss was obtained when the pole spacing was reduced to 7/16 inch. The voltage applied across the crystal, the current through the crystal and the relative potential of the Hall probe in contact with the side of the crystal were measured by the methods previously described. The galvanometer G of Figure 25 was used to find the null point. The probe selector switch was first set in position 1 and then in position 3. After balancing the relative potential of the Hall probe (position 3) the output of the electrometer was switched to amplifier A of Figure 25. With amplifier gain set at a relatively low value adjustments of the filter F and the recorder R were then made in order to bring the recorder pen to a position near the center of the tape. The filter and recorder were kept in adjustment as amplifier gain was increased by steps to the maximum usable value. The amount of usable gain was limited by electrical noise and drift as indicated by the recorder pen. Greater stability could usually be obtained
by waiting several hours before starting measurements.

With amplifier gain set at the maximum usable value the recorder tape was calibrated. This was done by slightly changing the setting of the helipot dial $H$ of Figure 25 so that the recorder pen made a trace near one edge of the tape. The tape was annotated to show the corresponding setting of the helipot dial. The helipot dial was then reset so that the pen made a trace near the opposite edge of the tape which was also annotated to show the corresponding helipot setting. This procedure was repeated a total of five or seven times. The entire calibration procedure was usually repeated after each set of measurements.

From the calibration data a factor was computed for converting divisions of the recorder tape to microvolts. This was done in the following way. The sum of the absolute values of the changes in helipot settings in turns (of the dial) was divided by the sum of the absolute value of the changes in recorder pen positions in divisions (of the tape). By means of the helipot dial calibration factor and the total voltage $V_t$ this quotient was converted into a factor directly relating the divisions on the recorder tape to Hall voltage. This procedure gave only half as much weight to the initial and final calibration setting as to the intermediate settings but tended to compensate
for any drift prevailing during calibration of the recorder tape. The resulting conversion factor differed for each set of measurements. The entire width of the recorder tape (250 divisions) usually corresponded to 10 to 100 millivolts.

After the preliminary calibration the recorder pen was again adjusted to center, if no prevailing drift was observed, or to one side in order to allow for a prevailing drift. The magnet current was turned on and left on for 40 seconds while the recorder tape was marked. The magnet was then turned off and the field current was allowed to fall to zero. The magnet current was then reversed and left on for another 40 seconds. This reversing procedure was repeated an average of 60 times for each run. In order to get usable data, 400 repetitions were sometimes required. With the exception of the first five preliminary runs on crystalline boron approximately one half of the data for each run were taken with crystal current reversed.

In the analysis of the Hall effect data the tape record for the first 20 seconds of each 40 second interval was not used. Transient effects due to switching the magnetic field were often present in this first portion of the record. The mean value of each of the second 20 second intervals was compared with the average of the
corresponding mean values for the preceding and following intervals when the magnetic field was in the opposite direction. The differences thus obtained, properly signed, were tabulated in terms of divisions of the recorder tape. Mean values of these differences and their standard errors were computed and converted to Hall voltages. The single probe method used in these measurements gives Hall voltages, resulting from the application of a magnetic field, one half as large as those given by the two probe method. In order to compensate for this the Hall voltage recorded was that resulting from the reversal of the magnetic field. The statistical formulae used in these computations and an example will be presented later.

Figure 26 shows a sample of the recorder tape record obtained from one run while making Hall effect measurements on crystalline boron. The photograph at the left in Figure 26 shows a strip of the 12 inch wide recorder tape which included a preliminary calibration and 26 readings. The photograph at the right is a closer view of the last portion of the tape shown at the left. In Figure 26 the notes originally written on the tape in pencil have been inked in for the sake of clarity. Lines originally drawn on the tape with red and green pencils have been inked in as solid and dashed lines respectively. Additional explanatory notes have been added and the tape has been
The portion of tape at the left shows a record of Hall effect data. Section (A) was for calibration. The pen trace in the other sections shows the effect of noise and drift. A closer view of (F) is at the right.
divided into sections which were given letter labels in order to facilitate explanation.

The section of tape shown in Figure 26 was specifically chosen to illustrate certain features of the procedures employed in taking Hall effect data. The data recorded on this strip of tape will be used later in a synthetic example designed to illustrate the statistical methods used in computing Hall voltages and their standard errors.

The section of tape at (A) in Figure 26 was used for a preliminary calibration. The four short traces at the right of the page and the three at the left correspond to settings of the potential divider as annotated on the tape. The initial trace at the right corresponds to the notation \( P_3 = 7/3.66^4 \). The number 7 of this notation indicates the setting of the potential divider \( D \) of Figure 25 and the number 3.66\(^4\) indicates the setting in turns of the helipot \( H \). The last figure was estimated between divisions of the helipot dial. Only the last three figures of the remaining six calibration annotations were recorded.

After calibration the recorder pen was returned to the center of the tape and the magnet was turned on. The notation \( G \) on the tape corresponds to a green pilot light which indicated the direction of the field. After
an initial period of 60 seconds the magnet was turned off, the current through the field coils was permitted to return to zero and the magnet was turned on in the opposite direction. The notation R on the tape corresponds to a red pilot light which indicated the new direction of the field. This procedure was repeated through the sections labeled (B) and (C) of the recorder tape. The deflection of the pen at a point between sections (B) and (C) was believed to be due to some spurious effect and the corresponding readings were discarded.

At the end of section (C) of Figure 25 the recorder pen started to move off of the right margin of the tape. By this time it was believed that a prevailing drift to the right had been noted so the recorder pen was returned to the left margin by manual adjustment. The first two readings of section (D) proved to be too near the left margin and were discarded. The recorder pen was reset to a point more distant from the left margin and several additional readings were made. In section (D) the direction of the prevailing drift appeared to reverse and at the end of this section the pen was reset at the right margin. The sequence of readings through sections (E) and (F) was then obtained.

A closer view of the final section (F) is shown at the right in Figure 26. In this view the record made by
the recorder pen is more readily visible. This view may be used to illustrate the methods employed in the analysis of the data provided by the tape record. The limits of the 40 second intervals are indicated by the short horizontal lines separating the sequence of letters G and R which indicate the direction of the magnetic field. A representative point was chosen in the second half of each 40 second interval and was circled. Points corresponding to a given direction of the applied magnetic field were joined by straight lines. In the figure the points corresponding to a direction of the magnetic field indicated by G are joined by dashed lines. The points corresponding to the direction of the magnetic field indicated by R are joined by solid lines. The horizontal distance in recorder tape divisions between each point and the line joining the preceding and following points, was measured and recorded at the right edge of the tape. In this way each point was compared with the graphical average of the preceding and following points. This procedure, of course, gave half as much weight to the initial and final readings of the sequence as to the remaining points in the sequence.

An example of a measurement of 10 divisions on the recorder tape is indicated near the center of section (F) of Figure 26. In the case of this record all readings obtained when the dashed line was to the left of the solid
line, are indicated as negative. This sign corresponds to the sign of the Hall voltage.

From each run as described above one value of Hall voltage corresponding to given values of magnetic field strength and crystal current was obtained. With crystal current held constant runs were made using different magnetic field strengths. Similarly, with the magnetic field held constant runs were made using different crystal currents. After accumulating a quantity of Hall effect data on Crystal No. 104 this crystal was placed in the furnace and a study was made of its resistance versus temperature behavior. The resulting data were used for estimating the temperatures of the crystal from its effective resistance at various values of crystal current. The resistance data were also used for estimating resistivity in a manner to be described later.

Less extensive studies of Hall effect were made on two other boron crystals. One run only was made on each of the crystals, Nos. 23(b) and 40. Crystal No. 40 was a high resistivity crystal and an exceptionally long run was required in order to obtain usable Hall effect data.

4. Thermoelectric effect

a. Qualitative measurements. Preliminary qualitative measurements of thermoelectric effects were made on 14
germanium crystals and about 250 boron crystals. The germanium crystals were all of macroscopic size but the procedures used were essentially the same as those used on the boron crystals. In the case of boron a petri dish containing the dry unmounted crystals was set on the microscope stage. The micro-forceps and the heated tungsten probe previously described were mounted in the micro-manipulator tool holders. The micro-forceps were connected to one terminal of the electrometer and ground. The tungsten probe was connected to the other terminal of the electrometer by means of a shielded cable.

While the crystals were observed under the microscope the petri dish was moved until a selected crystal was located under the tips of the micro-forceps. The micro-forceps were opened, lowered and closed on the selected crystal. The tungsten probe was then brought into contact with the crystal. The current through the tungsten probe heater was increased slowly until the platinum wire of the heater glowed a bright orange. While the temperature of the tungsten probe was increased, thermoelectric emfs as indicated by the electrometer were observed. In some cases the tungsten probe was readjusted to contact a different point on the crystal and the procedure was repeated.

In the case of crystals showing behavior in any way exceptional the electrometer was disconnected and an
ohmmeter was used to make an approximate measurement of resistance between the unheated tungsten probe and the micro-forceps. After making observations most of the boron crystals were placed off to one side of the petri dish. Two boron crystals which showed unusual thermoelectric behavior and which had unusually low resistances, were set aside in another petri dish. These crystals were assigned Nos. 103 and 104.

b. Quantitative measurements. Quantitative measurements were made on two germanium crystals and four boron crystals. In this case the apparatus of Figure 20, previously described, was used. A petri dish containing the crystals to be studied was set on the microscope stage beneath the tips of the thermocouples of Figure 20. The micro-forceps were used to pick up and locate a selected crystal between the tips of the thermocouples as shown in the diagram of Figure 33-(a). Runs were made on one of the boron crystals both while mounted longitudinally as shown in the diagram and while mounted laterally between the thermocouples.

The temperature $T_2$ of thermocouple No. 2, as indicated by the dial type potentiometer, was set and held within 2 degrees of a chosen temperature. Thermocouple temperatures were adjusted by means of the heater controls shown at the left in Figure 20. The temperature $T_1$ of
thermocouple No. 1 was then adjusted to some temperature lower than $T_2$. This adjustment usually necessitated several readjustments of the heater controlling $T_2$. The platinum elements of both thermocouples were then connected to the manually operated potentiometer and a measurement of the thermoelectric emf between these elements, or electrodes, was made and recorded. The temperature $T_1$ was then readjusted to a higher value, while holding $T_2$ constant, and another measurement of the emf between the platinum electrodes was recorded. This procedure was repeated for successively higher values of $T_1$ until $T_2$ could no longer be held constant. When $T_1$ was raised to a value exceeding $T_2$ by more than about 200 °C it was usually not possible to hold $T_2$ to its original constant value even when its heater current was reduced to zero. $T_2$ was then reset to a value approximately 100 °C higher than its previous value, and the entire procedure was repeated. For the case $T_1 = T_2$ the resistance of the crystal between the platinum electrodes was measured with the aid of an ohmmeter. This was done for each value of $T_2$. Maximum temperature used was about 650 °C. When this temperature was approached the platinum electrodes appeared to soften and crystals tended to become imbedded in the electrodes. Boron crystal No. 103 which had displayed unusual thermoelectric behavior was lost in this
manner. A quantitative study of thermoelectric effects in crystal No. 104 was not made.

For each value of $T_2$ thermoelectric emfs were plotted as a function of $T_1$. Values of thermoelectric power equal to the slopes of the resulting family of curves for each crystal were computed and tabulated. The mean values of these slopes, properly signed and corresponding to selected temperatures, were plotted as a function of temperature.

5. Other effects

a. Rectification. Relations between contact resistance and the direction of applied emf were studied on five boron crystals. An ohmmeter, which applied a voltage of 1.5 volts was connected across all combinations of electrodes in contact with a mounted crystal. Indicated values of resistance for positive and negative directions of the current were tabulated in a two way table which illustrated the relation between contact resistance and the direction of the applied emf.

b. Forming. The term "forming" refers to a technique frequently used with germanium transistors. Forming is done in order to stabilize the point contacts by a process which may be micro-welding. A condenser discharge or the output of a spark or Tesla coil is usually used. Forming
experiments with boron crystals were done using an automobile spark coil and condenser, a micro-switch, and two dry cells. Without any connections to the other contacts of a crystal, a given contact was formed by connecting it to the high voltage terminal of the spark coil and several pulses were applied. When other electrodes were connected to the low voltage side of the coils, the reaction was so violent that the electrodes were dislodged.

Forming experiments were carried out on the five mounted crystals used in the experiments on rectification. The mount of one of the crystals was destroyed, but after forming, the rectification experiments described above were repeated on the remaining four crystals.

c. Photoconductivity. Rough measurements of photoconductivity were made on eight mounted crystals. The current electrodes of a mounted crystal were connected to an ohmmeter which applied a voltage of 1.5 volts. The crystal was alternately exposed to radiation and relative darkness and changes in the indicated resistance were noted. X-ray, ultraviolet and visible white radiation were used. In the case of visible white radiation, which caused the largest changes in indicated resistance, a 75 watt tungsten light bulb was used. The bulb was placed at a distance of approximately 4 inches from the crystal. Additional measurements were made with a 2 inch layer of
water interposed between the light and the crystal. Measurements were also made with the crystal immersed in carbon tetrachloride.

F. Computations

1. Notation

In the calculations involving voltage current characteristics, resistance and resistivity, and Hall and thermoelectric effects, the following notation and units were used in recording the data.

\[ l_{24} \] : length of a segment of a crystal between probes 2 and 4. (Microscope reticule divisions = div)

\[ d \] : diameter, or thickness, of a crystal in a direction perpendicular to the surface of the mount. (div)

\[ w \] : width of a crystal where the cross section of the crystal was essentially rectangular. (div)

\[ t \] : time.

\[ t_r \] : room temperature. (°C)

\[ I_f \] : furnace current. (amp)

\[ c \] : thermocouple emf as indicated by an automatic potentiometer. (mv)
T_f or T_a: furnace temperature or ambient temperature in the neighborhood of a crystal. (°C)

T_1 and T_2: temperatures of the thermocouples used in thermoelectric measurements. (°C)

V_t: voltmeter reading indicating total potential drop across crystal and series resistance. (volt)

I_x: nominal crystal current as indicated by a microammeter. (μA)

R_s: series resistance. (ohm or megohm)

I_H: magnet current. (±, amp)

D_H: separation of magnet poles. (inch)

H_z: magnetic field strength. (gauss)

P_1, P_2, . . .: null settings of the potential divider corresponding to different probe selector positions.

f_1, f_2, . . .: fractions of the total potential drop corresponding to P_1, P_2, . . .

V: thermoelectric emf as measured by a manually operated potentiometer, with sign taken as positive when the platinum electrode at the lower temperature was more positive. (mv)
The values for fractional potentials, magnetic field strength, series resistance, and furnace temperature were obtained directly from calibration tables. In a few cases resistance versus temperature data were plotted directly.

The following additional notation and units were used in computations based upon the above data.

\( V_{15} \) or \( V_x \): potential drop across a crystal between probes 1 and 5 including the potential drop across the contacts. (volts)

\( \Delta V_3 \) or \( V_y \): Hall voltage, average change in potential of probe 3 due to a reversal of the magnetic field. (±, μv)

\( I_x \): crystal current as computed from the potential drop across \( R_s \).

\( R_{15} \) or \( R_x \): total resistance between probes 1 and 5 including contact resistances. (ohm or megohm)

\( R_{24} \): resistance of the segment of a crystal between probes 2 and 4, not including contact resistances. (ohm or megohm)

\( \rho \): resistivity, reciprocal conductivity \( 1/\sigma \). (ohm cm)

In the analysis of voltage current characteristics and in the discussion of indirect methods of determining resistivity, some additional notation applicable to these
specific arguments will be introduced as required.

The following values of certain universal constants will be used in the computations.

\[
\begin{align*}
    h & : \text{Plank's constant, } 6.62 \times 10^{-27} \text{ erg sec.} \\
    k & : \text{Boltzmann's constant, } 8.62 \times 10^{-5} \text{ ev/°K} \\
    N & : \text{Avogadro's number, } 6.03 \times 10^{23} \text{ molecules/mole.} \\
    q & : \text{absolute value of electronic charge, } 1.60 \times 10^{-19} \text{ coul/carrier}
\end{align*}
\]

Other notation which has been previously introduced, and the units which will be used in expressing these quantities are the following.

\[
\begin{align*}
    \epsilon & : \text{activation energy as defined by Equation (31). (ev)} \\
    E_g & : \text{intrinsic energy gap, equal to } 2\epsilon \text{ in the intrinsic range. (ev)} \\
    R_H & : \text{Hall coefficient as defined by the first part of Equation (19). (cm}^3{/coul)} \\
    n_h, n_e, n_c, \text{ and } n_t & : \text{numerical densities of holes, electrons, either type of carrier, and total of both types of carriers respectively. (carriers/cm}^3{)} \\
    \mu_h \text{ and } \mu_e & : \text{mobilities of holes and electrons as defined by Equation (5). (cm}^2{/volt sec)}
\end{align*}
\]
2. Additional formulae

Additional formulae, which have not been previously stated, and which relate some of the quantities listed above, are as follows:

\[ V_{15} = V_x = (1 - f_1) V_t \quad \text{(33)} \]
\[ I_x = f_1 V_t / R_s \quad \text{(34)} \]
\[ R_{15} = R_x = (1 - f_1) R_s / f_1 \quad \text{(35)} \]
\[ R_{24} = (f_4 - f_2) R_s / f_1 \quad \text{(36)} \]

\[ A = d w, \text{ for a crystal which is rectangular in cross section} \quad \text{(37)} \]
\[ A = \pi d^2 / 4, \text{ for a crystal which is circular in cross section} \quad \text{(38)} \]

\[ \rho = R_{24} A / l_{24} \quad \text{(39)} \]

Equation (39) is the defining equation for resistivity expressed in the notation used in these calculations. It should be noted for future reference that \( R_{24} \) does not include contact resistances, while \( R_{15} \) does, and that \( \rho \)
is directly proportional to $R_{24}$. The proportionality factor depends only upon the geometry of the individual crystal being considered.

Some additional statistical formulae were used in the analysis of Hall effect data (Refs. 59, 60, 61). These formulae, the notation and some statistical terminology are given and briefly explained below. Some of the formulae and the statements concerning them are only approximately true.

The mean (arithmetic mean or average) $\bar{X}$ of a group of data consisting of $N$ items is given by

$$\bar{X} = \frac{\sum X_i}{N}$$

(40)

where the summation is performed over the $N$ values of the individual items $X_i$. The standard deviation (root mean square deviation) $S'$ of the individual items from the mean is given by

$$S' = \left( \frac{\sum x_i^2}{N} \right)^{1/2} = \sqrt{\frac{\sum (X_i - \bar{X})^2}{N}}$$

(41)

where the summations are as above and $x_i = X_i - \bar{X}$. The latter expression of Equation (41) is more easily adapted to machine computation.

The standard deviation $S'$ has several interesting properties. However, the standard error $S$ is of more interest in the present application. The standard
deviation is a measure of the variation of the individual items from the mean and is ideally independent of \( N \).
The standard error is a measure of accuracy of the mean of \( N \) items, supposedly chosen at random from a very large number of items, as compared to the true mean \( M \) of all the items. The standard error decreases as \( N \) increases. An estimate of the standard error is given by

\[
S = \frac{S}{(N - 1)^{1/2}}.
\]

Equation 42

Frequently when \( N \) is larger than 10 or 20, \( N^{1/2} \) is used in place of \( (N - 1)^{1/2} \) in Equation 42.

For practical purposes it may be considered that the probability is about two to one that the true mean \( M \) lies within the limits set by \( \bar{X} \pm S \). A more nearly accurate statement is that the probability that \( \bar{X} \) lies within \( M \pm S \) is 0.6827. The probability that \( \bar{X} \) lies within \( M \pm 2S \) is 0.9545 and within \( M \pm 3S \) is 0.9973.

Another commonly used measure of the accuracy of a mean of \( N \) items as compared to the true mean \( M \) is the probable error \( P \). It is usually considered that the probability is about one to one that the true mean lies within \( \bar{X} \pm P \). The probable error \( P = 0.674 S \). The probable error is frequently computed by methods less well founded in statistical theory than those used in computing the standard error. In the present work the standard
error is used in preference to the probable error.

The standard error $S_c$ of a sum or difference is given approximately by

$$S_c = \left( \sum S_i^2 \right)^{1/2}, \quad (43)$$

where each $S_i$ is the standard error of a term in the sum or difference and the summation is performed over all the values of $S_i$ involved.

The fractional standard error $s$ is given by

$$s = S / \bar{X}. \quad (44)$$

The fractional standard error $s_c$ of a product or quotient is given approximately by

$$s_c = \left( \sum s_i^2 \right)^{1/2}, \quad (45)$$

where each $s_i$ is the fractional standard error of a term in the product or quotient and the summation is performed over all the values of $s_i$ involved.

3. Sample calculations

Some sample calculations specifically selected and adapted for the purpose of illustration are given below. With the exception of example No. 3 all of the examples are based on actual computations performed in this work. Conversion factors equal to the pure number one are enclosed
These factors do not change the value of quantities but are introduced to convert given units to desired units. Some additional calculations will be illustrated in less detail later. When the actual routine calculations were performed some simplifications of the procedures illustrated here were employed.

Example No. 1. - Resistivity of crystal No. 46 at 25 °C.

Given: Microscope reticule calibration

\[ 1 \text{ div} = 0.0132 \, \text{cm}. \]

Segment length,

\[ l_{24} = 0.35 \, \text{div}. \quad (\text{div} = \text{microscope reticule division}) \]

Diameter,

\[ d = 0.96 \, \text{div}. \quad (\text{cross section approximately circular}) \]

Fractions of total potential drop,

\[ f_1 = 0.139, \quad f_2 = 0.275, \quad f_4 = 0.464. \]

Series resistance,

\[ R_S = 110 \, \text{megohm}. \]

Compute: resistivity \( \rho \).

Solution: From Equations (36), (38), and (39)

Segment resistance,

\[ R_{24} = (f_4 - f_2)R_S / f_1. \]
Cross sectional area, 
\[ A = \pi d^2 / 4 \] 

Resistivity, 
\[ \rho = R \frac{A}{l} \] 

Substituting and introducing appropriate conversion factors 
\[ \rho = \frac{(f_1 - f_2) R \pi}{4 f_1 l} d^2 \] 
\[ = \frac{(0.189)(110 \text{ megohm}) \pi (0.96 \text{ div})^2}{(4) (0.139) (0.85 \text{ div})} \] 
\[ \cdot \left[ \frac{0.0132 \text{ cm}}{\text{div}} \right] \cdot \left[ \frac{10^6 \text{ ohm}}{\text{megohm}} \right] \] 
\[ = \frac{(1.89)(1.10)(9.6)^2(1.32)(\pi)(10^5) \text{ohm cm}}{(4) (1.39) (8.5)} \] 
\[ = 1.7 \times 10^6 \text{ ohm cm} \] 

Example No. 2. - Intrinsic energy gap for crystal No. 46. 

Given: Crystal resistance, 
\[ R_x = 5200 \text{ ohm at 658 °K}, \] 
\[ R_x = 52 \text{ ohm at 981 °K}. \] 

(Values obtained from smoothed curves.)

Compute: Energy gap \( E_g \) .

Solution: From Equation \( (31) \) 
\[ R_x \sim \rho = 1/\sigma \sim \exp(\varepsilon /k T), \]
whence

\[ E_g = 2 \epsilon = \frac{2k \Delta \ln(R_x)}{\Delta(1/T)} \]

\[ = (2)(8.6 \times 10^{-5} \text{ ev/°K})(2.3) \log(5200/52) \]

\[ = \frac{(1/658 \text{ °K}) - (1/981 \text{ °K})}{(1/658 \text{ °K})} \]

\[ = 1.6 \text{ ev} \]

Example No. 3 – Hall voltage and standard error from data of Figure 26.

Given: Recorder tape data from Figure 26
Calibration data from tape is as follows:

<table>
<thead>
<tr>
<th>Helipot Setting (turns)</th>
<th>Tape Record (divisions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.664</td>
<td>212</td>
</tr>
<tr>
<td>3.636</td>
<td>15</td>
</tr>
<tr>
<td>3.661</td>
<td>220</td>
</tr>
<tr>
<td>3.638</td>
<td>42</td>
</tr>
<tr>
<td>3.662</td>
<td>226</td>
</tr>
<tr>
<td>3.634</td>
<td>31</td>
</tr>
<tr>
<td>3.660</td>
<td>217</td>
</tr>
</tbody>
</table>

Helipot calibration,

fraction of total voltage = 0.0142/turn.

Total voltage across potential divider,

\[ V_t = 50.0 \text{ volts} \]
Compute: Hall voltage $V_y$ and standard error.

Solution: Sum of the absolute values of changes in helipot settings in turns:

\[ 3.664 - 3.636 = 0.028 \]
\[ 3.661 - 3.636 = 0.025 \]
\[ 3.661 - 3.638 = 0.023 \]
\[ 3.662 - 3.638 = 0.024 \]
\[ 3.662 - 3.634 = 0.028 \]
\[ 3.660 - 3.634 = 0.026 \]

\[ \sum \quad 0.154 \cdot \]

Sum of the absolute values of changes in recorder pen position in divisions:

\[ 212 - 15 = 197 \]
\[ 220 - 15 = 205 \]
\[ 220 - 42 = 178 \]
\[ 226 - 42 = 184 \]
\[ 226 - 31 = 195 \]
\[ 217 - 31 = 186 \]

\[ \sum \quad 1145 \cdot \]

Calibration factor,

\[ l = \frac{0.154}{1145} \text{ turn} \cdot \frac{0.0142}{\text{turn}} \]
From Equation (40) and Figure 26 the mean
\[ \bar{X} = \frac{1}{N} \sum X_1 = -2.19 \text{ div} \]

From Equation (41) the standard deviation,
\[ S' = \left( \frac{1}{N} \sum X_1^2 - \bar{X}^2 \right)^{1/2} = 4.55 \text{ div} \]

From Equation (42) the standard error,
\[ S = S'/(N - 1)^{1/2} = 0.91 \text{ div} \]

The Hall voltage and standard error,
\[ V_y = (-2.19 \pm 0.91) \text{ div} \sqrt{95.5 \mu v/\text{div}} \]
\[ = (-209 \pm 86) \mu v. \]

Example No. 4 - Hall coefficient of crystal No. 104
at 24 °C
Given: Crystal thickness,
\[ d = 1.02 \text{ div} \text{ (cross section approximately rectangular)} \]
Magnetic field,
\[ H_z = 18,000 \text{ gauss}. \]

Crystal current,
\[ I_x = 18.7 \mu \text{a}. \]

Hall voltage,
\[ V_y = -100 \mu \text{v}. \]

Compute: Hall coefficient \( R_H \)

Solution: From Equation (19)

\[
R_H = \frac{V_y d}{H_z I_x} = \frac{-100 \mu \text{v}}{(18,000 \text{ gauss})(18.7 \mu \text{a})}
= \frac{(1.02 \text{ div})}{10^6 \mu \text{v} \cdot \left[ \frac{0.0132 \text{ cm}}{\text{div}} \right]}
\cdot \left[ \frac{10^8 \text{ gauss cm}^2}{\text{volt sec}} \right] \cdot \left[ \frac{10^6 \mu \text{a}}{\text{amp}} \right] \cdot \left[ \frac{\text{amp sec}}{\text{coul}} \right]
= - \frac{(1.02)(1.32)(10^3)}{(1.8)(1.87)} \frac{\text{cm}^3}{\text{coul}}
= -400 \text{ cm}^3/\text{coul}.

Example No. 5 - Mobility and density of electrons in
crystal No. 104 at 24 °C.
Given: Hall coefficient,
\[ R_H = -400 \text{ cm}^3/\text{coul} \]

Resistivity,
\[ \rho = 610 \text{ ohm cm} \]

Crystal assumed to be in impurity range.

Compute: Mobility \( \mu_e \) and density \( n_e \).

Solution: From Equation (24)

\[ \mu_e = \left( \frac{8}{3} \pi \right) \left( -\frac{R_H}{\rho} \right) \]

\[ = \frac{(8)(400 \text{ cm}^3/\text{coul})}{(3 \pi)(610 \text{ ohm cm})} \]

\[ = \frac{8}{3 \pi} \text{ ohm cm} \text{ coul} \text{ volt sec} \]

\[ = \frac{8}{3 \pi} \text{ cm}^2 \text{ volt sec} \]

\[ = 0.6 \text{ cm}^2/\text{volt sec} \]

From Equation (23)

\[ n_e = \frac{3 \pi}{8} q R_H \]

\[ = \frac{3}{8} \pi \left( \frac{1.6 \times 10^{-19} \text{ coul/electron}}{1.6 \times 10^{-19} \text{ coul/electron}} \right) (400 \text{ cm}^3/\text{coul}) \]

\[ = 1.8 \times 10^{16} \text{ electrons/cm}^3 \]
Example 6 - Standard error of Hall coefficient and mobility values computed in examples No. 4 and 5.

Given: Hall voltage = $(100 \pm 20) \mu \text{v}$.

Calculated mean Hall coefficient = $-400 \text{cm}^3/\text{coul}$.

Calculated mean mobility of electrons $= 0.6 \text{ cm}^3/\text{volt sec}$.

Estimated fractional standard error in measurement of thickness of crystal $= \pm 20$ per cent.

Estimated fractional standard error in extrapolating calibration curve for magnetic field $= \pm 10$ per cent.

Estimated fractional standard error in evaluation of resistivity of crystal $= \pm 40$ per cent.

Other statistical errors assumed small by comparison.

Compute: Standard errors of Hall coefficient and mobility.

Solution: From Equation (144)

Fractional standard error of Hall voltage

$= \pm 20 \mu \text{v}/100 \mu \text{v}$

$= \pm 20$ per cent.
From fractional standard errors of Hall voltage, thickness and magnetic field, and Equation (45) fractional standard error of Hall coefficient

\[ \frac{\Delta R_H}{R_H} = \pm (0.20)^2 + (0.20)^2 + (0.10)^2 \sqrt{2} \]

\[ = \pm 30 \text{ per cent.} \]

Standard error of Hall coefficient

\[ \frac{\Delta R_H}{R_H} = \pm (0.30) \text{ (400 cm}^3/\text{coul)} \]

\[ = \pm 120 \text{ cm}^3/\text{coul}. \]

Fractional standard error of mobility of electrons

\[ \frac{\Delta \mu}{\mu} = \pm \left( (0.30)^2 + (0.40)^2 \right)^{1/2} \]

\[ = \pm 50 \text{ per cent.} \]

Standard error of mobility of electrons

\[ \frac{\Delta \mu}{\mu} = \pm (0.50) (0.6) \text{ cm}^2/\text{volt sec} \]

\[ = \pm 0.3 \text{ cm}^2/\text{volt sec}. \]
IV. RESULTS AND DISCUSSION

A. Introduction

One of the principal difficulties encountered in this work on small, single crystals was the frequent loss or damage of the mounted crystals. Reproduction and rechecking of some of the results on individual crystals was often impossible owing to slight physical alterations in the mounts or changes in physical properties of the crystals after they had been subjected to high temperatures. In order to compensate for this difficulty and gain confidence in the results obtained on individual crystals, it was necessary to make measurements on a large number of crystals. In a few cases, notably crystals No. 23(b), 30, 46, 47 and 104, it was possible to obtain reproducible and relatively complete data from several mutually independent experiments.

Table 3 is a partial summary of experiments performed on twenty five of the more than fifty crystals mounted for study. This summary is presented in the form of a check list showing what type of experiments were performed on each of the twenty five crystals. With the exception of six germanium crystals and one antimony crystal, all of the crystals are described as typical, almost typical or
<table>
<thead>
<tr>
<th>Voltage</th>
<th>Experiments performed</th>
<th>Total number of crystals tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>X</td>
<td>18 almost typical</td>
</tr>
<tr>
<td>28</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>18</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>3</td>
<td>X</td>
<td>22(a) typical</td>
</tr>
<tr>
<td>6</td>
<td>X</td>
<td>22(b) low res.</td>
</tr>
<tr>
<td>3</td>
<td>X</td>
<td>22(c) low res.</td>
</tr>
<tr>
<td>6</td>
<td>X</td>
<td>23(a) typical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23(b) low res.</td>
</tr>
<tr>
<td>25</td>
<td>X</td>
<td>27 n-type Ge</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sb</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>30</td>
<td>X</td>
<td>30 typical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40 typical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44 low res.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46 almost typical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>47 typical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 n-type Ge</td>
</tr>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td>54 p-type Ge</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 typical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>101(a) typical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>101(b) typical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>102 typical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>103 low res.n-type</td>
</tr>
<tr>
<td></td>
<td></td>
<td>104 low res.n-type</td>
</tr>
</tbody>
</table>

Table 3. Partial Summary of Experiments on Small Crystals.

(Crystal number and description) (Boron unless otherwise specified)
low resistivity (low res.) on the basis of their resistivity or resistance versus temperature behavior. Crystals displaying characteristics practically identical to that of crystal No. 46 are described as typical. Those showing slight deviations from this behavior in the neighborhood of room temperature are described as almost typical. Those described as low resistivity displayed behavior differing markedly from that of crystal No. 46 until subjected to temperatures above about 200 °C. Crystals are described as n-type or p-type on the basis of results of Hall and thermoelectric experiments.

The total number of crystals tested in each type of experiment is tabulated in the second column from the left in Table 3. Only experiments from which usable quantitative data was obtained are indicated in the table. For example, the qualitative observations of thermoelectric effects on over 250 crystals are not included in the tabulation. Unsuccessful attempts to measure Hall effects in twenty-one boron crystals also are not tabulated. Indications of Hall voltages were observed with crystals No. 16, 20, 31, 36, 37 and 46, but quantitative Hall effect data was obtained only on boron crystals No. 23(b), 40 and 104, as indicated in the table.

The first six types of experiments listed in the table will be discussed under the heading of resistivity.
Immediately following the presentation of data resulting from each of the types of experiments, the results of any calculations based on this data will be presented and discussed. Some tentative explanations, comparisons with the work of others and proposals for additional work will be incorporated in the discussions.

Similar patterns will be followed in the presentation of the results of studies of Hall, thermoelectric and other effects.

B. Resistivity

1. Voltage current characteristics

   a. Results. Studies of voltage current characteristics were made on eighteen crystals. Of these the most complete study was made on crystal No. 45. Figure 27 shows most of the results of this study. In Figure 27 the total voltage $V_x$ applied across the ends of the crystal is plotted as a function of crystal current $I_x$. This method of plotting the data was chosen in preference to the more common procedure of plotting the current as a function of voltage in order that the curves appear as single valued functions. Data obtained at room temperature ($T_a=298 \, ^\circ\text{K}$) is not included in Figure 27 in order to avoid crowding near the ordinate axis. It should be noted that in this and later figures an abbreviation for the word crystal
Figure 27. Voltage Current Characteristics

Similar curves were obtained at lower and higher temperatures. All of the curves were almost the same shape when appropriate changes of scale were made.

Note: In this and later figures Xtal stands for crystal, $5.30 \times 10^5$ is equivalent to $5.30 \times 10^2$. 
(Xtal) and an abbreviated form for indicating powers of 10 are used. All of the curves in Figure 27 and the room temperature curve omitted from the figure had essentially the same form. When appropriate changes in the scale of the axes were made, the curves could be almost superimposed. The resistance of the crystal at each of the indicated ambient temperatures was assumed to be equal to the slope of the curves at zero current. However, the resistances indicated in the figure were computed by another method which will be described. It is interesting to note that at each ambient temperature as the crystal current was increased a certain peak voltage was attained. At this point the slope of the curve, or the dynamic resistance \( \frac{dV}{dI} \), was equal to zero. At higher values of crystal current the dynamic resistance became negative. This phenomenon has been previously observed by Weintraub, Lyle, Bruce and Hickling, and Shinn (Refs. 10, 11, 12, 13).

b. **Explanation.** A probable explanation for the voltage current behavior of boron as portrayed in Figure 27 is based upon the following assumptions:

1. **Resistance** \( R \) varies exponentially with the reciprocal of the true absolute temperature \( T \) of the crystal (not ambient temperature \( T_a \)).

2. The temperature of the crystal above ambient temperature is proportional to the power \( W \) expended within the crystal.
Assumption No. 1 is based on the usual expression for the resistance of a semiconductor (or thermistor). Assumption No. 2 is based on Newton's law of cooling. An analysis based on these assumptions appears in Figure 28. The quantity \( (T_a + \alpha W) \) is taken as the true temperature of the crystal. Equation (2) of Figure 28 is an expansion of Equation (1). This expansion is approximated in Equation (3). Appropriate additional notation is introduced in the figure.

The solution given in Equation (4) of Figure 28 is the equation of a straight line where the quantity \( L/W \) is considered as a function of \( W \). The true resistance \( R_a \) at the ambient temperature \( T_a \) was found by substitution of trial values of \( R_a \) until a straight line plot of the data was obtained. From the intercept \( A \) and the slope \(-B\), as defined in the figure, values for the dissipation factor \( \alpha \) and the activation energy were obtained from Equations (5) and (6).

Figure 28 also shows the results of plotting the data of Figure 27 according to this scheme. It is interesting to observe that this procedure converts the curves of Figure 27 into almost straight lines. The lines labeled (a), (b), (c), (d) and (e) in Figure 28 correspond to the curves similarly labeled in Figure 27. In addition Figure 28 incorporates a table which gives values for \( R_a \), \( \alpha \) and \( \epsilon \) resulting from each of the straight lines.
EVALUATION OF AMBIENT TEMPERATURE RESISTANCE
OF A THERMISTOR AND ESTIMATION OF ITS
TEMPERATURE POWER COEFFICIENT AND ACTIVATION ENERGY

ASSUME

\[ R = R_\infty \exp \left( \frac{-\epsilon}{k[T_0 + \alpha W]} \right) \]  

(1)

WHERE

\[ T_0 = \text{AMBIENT TEMPERATURE} ; \quad W = \text{POWER INTO XTAL} \]

\[ \alpha = \text{TEMPERATURE RISE PER UNIT POWER INPUT} \]

THEN

\[ \frac{\ln R}{W} = \ln R_\infty + \frac{\epsilon}{kT_0} \left( 1 - \frac{\alpha W}{T_0} + \left[ \frac{\alpha W}{T_0} \right]^2 \right) \]  

(2)

\[ \frac{\ln(R_\infty/R)}{W} = \frac{-\epsilon \alpha^2}{kT_0^2} W \]  

(3)

OR

\[ \frac{L}{W} = A - BW \]  

(4)

WHERE

\[ R_a = R_\infty \exp \left( \frac{-\epsilon}{kT_0} \right) ; \quad L = \log \left( \frac{R_\infty}{R} \right) \]

\[ A = \frac{\epsilon \alpha^2/2.3kT_0^2}{W} \]; \quad B = \frac{\epsilon \alpha^2/2.3kT_0^3}{W} \]

WHENCE

\[ \alpha = \frac{T_0 B}{A} \]

\[ \epsilon = 2.3kT_0 \frac{A}{B} \]  

(5) (6)

BORON XTAL \#45

<table>
<thead>
<tr>
<th>CURVE</th>
<th>(T_0) (°K)</th>
<th>(R_a) (Ω)</th>
<th>(\alpha) (deg/mm)</th>
<th>(\epsilon) (eV)</th>
</tr>
</thead>
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<tr>
<td>(a)</td>
<td>396</td>
<td>4.33×10³</td>
<td>3.1</td>
<td>0.4</td>
</tr>
<tr>
<td>(b)</td>
<td>454</td>
<td>1.30×10³</td>
<td>3.2</td>
<td>0.4</td>
</tr>
<tr>
<td>(c)</td>
<td>484</td>
<td>5.30×10³</td>
<td>2.7</td>
<td>0.5</td>
</tr>
<tr>
<td>(d)</td>
<td>559</td>
<td>4.54×10³</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>(e)</td>
<td>655</td>
<td>6.34×10³</td>
<td>1.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 28. Evaluation of Ambient Temperature Resistance

The curves of Figure 27 became straight lines when subjected to the above analysis. This method of obtaining true values of resistance at given ambient temperatures was used whenever accurate values were sought.
The following observations, however, indicate that the assumptions and approximations upon which this analysis was based are not strictly valid.

1. Data near the ordinate axis rarely fitted the straight line. (The ordinates of points in this neighborhood were very sensitive to slight variations in $R_a$.)

2. Values of $\varepsilon$ were about 25 per cent less than those obtained by the usual plots of log $R$ versus $1/T$.

3. The value of $\alpha$ was obviously not constant.

Similar analyses were carried out for all of the crystals used for room temperature resistivity measurements. The deviations from a straight line were somewhat larger in the case of the one germanium crystal than they were for the boron crystals. Deviations in both cases may be the result of neglecting rectification effects. However, the results indicate that there is some validity in the assumption that the voltage current characteristics of crystalline boron are due to joule heating in a thermister. This explains, at least in part, the previously mentioned negative dynamic resistance reported by Weintraub, Lyle, Bruce and Hickling, and Shinn.

**c. Future work.** When the voltage current characteristics of boron were being investigated in the neighborhood of the peak voltage, regular oscillations of the voltage and current were occasionally observed. It should
be interesting to investigate this phenomenon more fully and to make an oscillographic study of voltage current characteristics as a function of frequency. If a series resistance and an alternating current were employed in a manner similar to that described by Shinn (Ref. 13), and if the peak current was somewhat above that corresponding to the peak voltage for a given crystal, it is believed that the following phenomena could be observed.

1. At sufficiently low frequencies the oscilloscope trace should appear similar to the curves of Figure 27. (The trace of course also would extend into the third quadrant.) In this case the crystal temperature would be following the power input.

2. At higher frequencies thermal lag would be expected to cause the return trace to exhibit hysteresis giving rise to the "gas discharge effect" mentioned by Bruce and Hickling, and Shinn.

3. At still higher frequencies where the thermal lag exceeded the period and the temperature was almost constant, a straight line trace through the origin without hysteresis would be expected. The slope of this line should be a function of the applied a-c voltage and as the voltage was varied the ends of the line should fall on a curve having the same form as the trace obtained at low frequencies.
2. Room temperature resistivity

   a. Results. Table 4 presents data on the dimensions and resistances of crystals that were used for direct determinations of resistivity by methods previously described. In addition this table includes data on crystals that were used in Hall effect measurements and some other information that will be discussed later. In the first two rows of Table 4 the eleven crystals on which this information is presented are identified by number and material. The one antimony crystal and the largest of the four germanium crystals which were mounted for study are included.

   The next four rows of Table 4 present dimensional data on these crystals. For purposes of this table dimensions originally measured in microscope reticule divisions were converted to microns. Only the thickness of antimony crystal No. 26, was measured and no dimensional data was taken on boron crystal No. 103. The remaining crystals for which width data are given were essentially rectangular in cross section while the cross sections of crystals No. 45, 46 and 47 were approximately circular. Data on width w, diameter or thickness d, and the segment length l_{2U} were used in direct measurements of resistivity on crystals No. 30, 44, 45, 46, 47 and 50. Data on the total length l_{15} were not used in any of the computations and are presented only as a matter of interest.
<table>
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<tr>
<th>Crystal number</th>
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<td>Sb</td>
<td>B</td>
<td>B</td>
<td>B</td>
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<tr>
<td>Width w parallel to mount. (micron)</td>
<td>110</td>
<td>91</td>
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<td>81</td>
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<tr>
<td>Diameter d or thickness perpendicular to mount. (micron)</td>
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<td>Segment length (micron)</td>
<td>124</td>
<td>121</td>
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<tr>
<td>Total length (micron)</td>
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<td>170</td>
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<td>150</td>
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<td>Segment resistance (ohm)</td>
<td>( R_{24} )</td>
<td>3.0 ( \times 10^8 )</td>
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<tr>
<td>Total resistance (ohm)</td>
<td>( R_{15} )</td>
<td>5.5 ( \times 10^5 )</td>
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<td>Geometric factor (cm)</td>
<td>( G_{24} )</td>
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<td>7.4 ( \times 10^{-3} )</td>
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<td>Geometric factor (cm) (direct method)</td>
<td>( G_{15} )</td>
<td>5.4 ( \times 10^{-4} )</td>
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<td>Geometric factor (cm) (indirect method)</td>
<td>( G'_15 )</td>
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<td>( 1.7 )</td>
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<td>( 1.7 )</td>
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### Summary and Activation Energies

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|       | 1.4 | 1.5 | 1.6 | 1.6 | 1.7 | 1.6 |

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</table>
Of course the largest single crystals of boron were chosen for study. Of these, crystal No. 47 was the longest.

The next group of data in Table 4 includes segment resistance $R_{24}$ (not including contact resistances) and total resistance $R_{15}$ (including contact resistances). Values of the segment resistance $R_{24}$ were used in computing the values of resistivity $\rho$ given in the third row from the bottom of the table.

b. Discussion. The values for resistivity $\rho$ were computed with the aid of Equations (37), (38) and (39). From these equations a geometric factor $G_{24}$ may be defined such that

$$G_{24} = \rho / R_{24} = \rho / l_{24}.$$  \hspace{1cm} (46)

Values for this geometric factor are given in Table 4. If this factor and the segment resistance of a given crystal are known, the resistivity of the crystal may be computed directly.

Another geometric factor $G_{15}$ may be defined such

$$G_{15} = \rho / R_{15}.$$  \hspace{1cm} (47)

This geometric factor depends on the irregular geometry of the ends of a given crystal and the contact resistances between the ends and the current electrodes. Values for this factor are also given in Table 4. This factor and the factor $G_{15}$ will be discussed in more detail later.
The resistance $R_{24}$ of the regular segments of the crystals used for direct measurements of resistivity were evaluated by analyses of voltage current characteristics as previously described. The standard errors of the resistance measurements were estimated at about ± 1 per cent but the standard errors of the measurements of physical dimensions were about ± 10 per cent. On the basis of these estimates the standard errors of the values for resistivity $\rho$ given in the table are about ± 20 per cent.

On the basis of resistivity and resistance versus temperature studies to be described, crystals No. 30 and 46 were chosen as being most nearly typical of the boron crystals used in this study. For this reason the value, $(1.7 \pm 0.3) \times 10^6$ ohm cm, was taken to be the most nearly representative value for the room temperature resistivity of these boron crystals.

Crystals No. 30, 44, 45, 46 and 47 were provided with two probes on the same side of the crystal as shown in Figure 18. A method for evaluating the room temperature resistivity of crystals not so equipped will be described later.

3. Resistance and resistivity versus temperature

a. Results. Figure 29 includes a tabulation of resistance data on crystal No. 47 as a function of temperature. The first experiment, No. 110, on this crystal was
Resistance $R_{24}$ as measured between the potential probes is here compared with resistance $R_{15}$ which includes contact resistances. Both were measured as functions of temperature and plotted in the conventional manner. Higher temperatures are to the left. Where the abscissa $1000/T = 1$, $T = 1000\ K = 727\ \degree C$. Where $1000/T = 2$, $T = 500\ K = 227\ \degree C$. The points at the right ends of the curves are at room temperature, $25\ \degree C$. 

**Figure 29. Resistance versus Reciprocal Temperature**
conducted at room temperature and resistances were evaluated from an analysis of the voltage current characteristics of this crystal. From Equation (46) the geometric factor $G_{24}$ for this crystal is

$$G_{24} = \varphi \frac{d^2}{4} l_{24} = \frac{R}{4} \left( \frac{114}{171} \text{ micron} \right)^2 = 0.006 \text{ cm}.$$  

This value is given in Table 4. Within the limits of experimental error this geometric factor should remain constant with changes of temperature. Therefore, with changes in temperature, resistivity $\varphi$ should remain directly proportional to the segment resistance $R_{24}$.

Figure 29 shows how the segment resistance $R_{24}$ (not including contact resistances) and the total resistance $R_{15}$ (including contact resistances) varied with temperature for crystal No. 47. The base ten logarithm of the numerical values of resistance in ohms is plotted as a function of reciprocal absolute temperature. High temperatures are to the left. The abscissa 1 corresponds to an absolute temperature of 1000 °K, 2 to 500 °K, and the abscissas of the points at the right ends of the curves correspond to room temperature, 298 °K.

Similar but not quite as extensive data was obtained on crystals No. 30 and 46. Alterations in the crystal mounts made similar experiments on crystals No. 44 and 45 impossible.
All of the data on crystal No. 47 at temperatures above 25 °C were obtained after potting the crystal in cement. Three experiments which extended the range of measurement to successively higher temperatures were performed. After each experiment the crystal was cooled to room temperature. The procedures used in taking measurements on this crystal have been previously described.

b. Discussion. In all cases where such experiments were performed it was observed that the resistivity, which is proportional to $R_{24}$, was also, within the limits of experimental error, directly proportional to $R_{15}$ throughout the temperature range of measurement. In Figure 29 this is illustrated by the fact that the curves for $R_{15}$ and $R_{24}$ plotted on a logarithmic scale are almost parallel. That is, the evidence presented in Figure 29 indicates that the geometric factor $G_{15}$ as defined by Equation 47 is also constant with changes in temperature. This implies that if the factor $G_{15}$ can be determined at some temperature, this factor can then be used for determining resistivity from the total resistance $R_{15}$ at other temperatures.

This conclusion might appear to be obvious but it should be recognized that the contact resistance between the current electrodes and the boron crystal might conceivably vary in a way to make the conclusion untrue.
However, on the basis of the evidence presented here it was assumed that data on the variation of total resistance $R_{15}$ with temperature could be normalized and presented as resistivity data with the aid of a geometric normalizing factor $G_{15}$ as defined.

4. Normalizing resistance data

a. Discussion. Equation (47) may be rewritten in the form

$$\log/ = \log G_{15} + \log R_{15}.$$  

The amount of vertical shift required to convert data on the total resistance $R_{15}$ when plotted on a logarithmic scale, into resistivity data is therefore equal to $\log G_{15}$. It should also be noted that since conductivity $\sigma$ is the reciprocal of resistivity $\rho$

$$\log \sigma = -\log \rho.$$  

Therefore on a logarithmic plot where resistivity is positive upward, conductivity is positive downward.

In the theoretical considerations of the conductivity of semiconductors it was pointed out that the behavior of conductivity (or resistivity) as a function of temperature might depend upon the presence of impurities. However, for each crystal of a given material the conductivity behavior above some temperature should be intrinsic to the material
and independent of the presence of impurities. Therefore when resistance data for different boron crystals is plotted as in Figure 29, the slopes for all of these curves should be almost the same in the intrinsic range and their resistivities in this range should be approximately equal.

The total resistance of 28 boron crystals was studied as a function of temperature. Measurements were extended to temperatures above 600 °K in the case of 13 of these crystals. When the logarithm of total resistance was plotted as a function of reciprocal absolute temperature as in Figure 29 the majority of the curves had almost the same form and could be superimposed by shifting the plots vertically with respect to one another. The slope of the curves for a few crystals was less than that of the majority in the lower temperature ranges. However, in the upper temperature ranges the slopes of all the curves were almost identical. It was, therefore, assumed that the slope in the upper temperature range corresponded to the intrinsic behavior of crystalline boron and that deviations from this slope at lower temperatures were indicative of the presence of impurities.

Crystal No. 46 was one of three crystals for which resistivity versus temperature data was obtained similar to that previously presented for crystal No. 47. Additional data on the total resistance of this crystal as a function
of temperature was obtained at higher and lower temperatures. With the aid of a directly determined geometric factor $G_{15}$ it was possible to normalize the data on total resistance so that they might be presented as resistivity data. The resistivity versus temperature behavior of this crystal was typical of the majority of the crystals studied. This crystal was chosen as a reference crystal for the indirect evaluation of resistivity of other crystals.

b. Results. The top curve in Figure 30 is a plot of resistivity data on crystal No. 46 versus reciprocal absolute temperature. The method of plotting in Figure 30 is similar to that used in Figure 29, except that the logarithm of the numerical value of resistivity $\rho$ in ohm cm is plotted instead of $\log R$ as in Figure 29. High temperatures are still to the left and the abscissa 1 corresponds to 1000 °K while 5 corresponds to 200 °K.

The values for resistivity of crystal No. 46 in the central portion of the top curve between 25 °C and 150 °C were obtained directly from measurements of the segment resistance $R_{24}$ and a geometric factor $G_{24}$ calculated from the segment dimensions. Data for this portion of the curve were obtained while both raising and lowering the temperature. Only every eighth point thus obtained was plotted in order to avoid excessive density of points in this portion of the curve. The points plotted are
Between the temperatures 200 °K and 1000 °K the resistivity of typical crystal No. 46 decreased by a factor of almost 10^10. Crystals No. 45 and 18 were unusual in behavior. Crystals No. 22 and 23 (originally typical) were altered by the indicated heat treatments. The resistivity curve for exceptional crystal No. 103 is much like that of No. 104 in Figure 32. The thermoelectric power of crystal No. 103, shown in Figure 33, was zero at 265 °C which corresponds to point (2) above.
representative and illustrate the extent of the deviations from the smooth curve.

At temperatures below 25 °C and above 150 °C, data on the total resistance $R_{15}$ were normalized with the aid of a directly determined geometric factor $G_{15}$. The low temperature data were obtained while the crystal was slowly cooled and the high temperature data were obtained while the crystal was slowly heated. All points obtained in these ranges were plotted. It is of interest to observe that the resistivity of this crystal decreased by a factor of almost $10^{10}$ while the temperature was increased from about 200 °K to 1000 °K.

Similar plots of resistivity versus temperature for crystals No. 30 and 47 are not included in Figure 30. With the exception of slight deviations in the neighborhood of room temperature in the case of crystal No. 47, the plots for these crystals were almost identical to, but not as complete as, the plot for crystal No. 46. Directly determined geometric factors $G_{15}$ are given in Table 4. Geometric normalizing factors $G_{15}'$ were determined graphically (indirectly) by measuring the amount of vertical shift required to fit the plots of total resistance versus reciprocal temperature data on these crystals to the resistivity versus reciprocal temperature plot for crystal No. 46 in the highest temperature range of measurement.
The geometric factor $G_{15}'$ thus obtained for crystal No. 30 was equal to the geometric factor $G_{15}$ obtained by direct methods. In the case of crystal No. 47 the two geometric factors differed by less than 10 per cent.

Resistivity data on crystal No. 45 obtained by direct methods are plotted in Figure 30. This crystal displayed larger deviations from typical behavior in the neighborhood of room temperature. The geometric factors $G_{15}$ and $G_{15}'$ obtained by direct and indirect methods respectively, are given in Table 4 and agree within 5 per cent. This agreement is well within the limits of experimental error.

All of the other resistivity data plotted in Figure 30 were determined by indirect graphical methods. The data plotted were specifically chosen to illustrate deviations from typical behavior. Resistivities in these cases were determined by first plotting total resistance versus reciprocal temperature data on a scale identical to that used for plotting resistivity versus reciprocal temperature for crystal No. 46. The curves were then shifted vertically so that a fit was obtained in the upper or intrinsic range of temperatures where the slopes of the curves were almost identical. The amount of shift required to thus obtain a fit was then equal to the corresponding value of $\log G_{15}$. Values for the geometric factor $G_{15}'$ thus obtained by indirect graphical methods are given for
several crystals in Table 4. These factors were used in computing the values for resistivity \( \rho' \) (indirect method) also given in the table.

Since the geometric factors \( G_{15} \) and \( G'_{15} \) depend on the irregular geometry of the ends of a given crystal and the contact resistances between the ends and the current electrodes, no consistency between the values of these factors for different crystals should be expected. However, with exceptions, there appears to be an increasing trend in the values of these factors from crystal No. 30 through No. 104. This increasing trend is probably the result of improvements in methods of mounting used for these crystals which were assigned the higher numbers. The relatively large value of \( G'_{15} \) in the case of crystal No. 23(b) is probably the result of forming between the crystal and its current electrodes. (The word forming is here used in the sense previously discussed.)

The standard errors in the values of the indirectly determined resistivity \( \rho' \) given in Table 4 are estimated at about ± 40 per cent. This estimate is based on the standard error of the values of resistivity of crystal No. 46 plotted in Figure 30 and on the errors introduced by the graphical fitting procedure. The slopes of the curves varied only slightly in the intrinsic range but placement of the superimposed curves was very sensitive to slight
variations in slope. It is of course possible that there are other sources of error inherent to this indirect method of determining resistivity which have not been considered here and which may make the above estimate of error somewhat optimistic.

5. Activation energies

a. Results. Activation energies were computed from resistance or resistivity versus reciprocal temperature data in a manner similar to that previously illustrated in example No. 2. The activation energy $\varepsilon$ as defined by Equation (31) was computed from the slopes of the resistance and resistivity curves. Some values for $\varepsilon$ are given in Figure 30. Values for the energy gap $E_g$ (equal to $2\varepsilon$ in the intrinsic range) are given in the bottom row of Table 4. On the basis of these and other calculations of the value of $E_g$, the value of $1.55 \pm 0.5$ electron volts is taken to be the most representative value of the intrinsic energy gap for the crystalline boron used in this study.

b. Discussion. Lagrenaudie (Ref. 7) recently reported the intrinsic energy gap of crystalline boron to be 1.2 ev. This calculation was based upon data published by Weintraub (Ref. 9) in 1909. Weintraub used a constant current when making resistance measurements. At the lower ambient temperatures the crystal would have a higher
resistance and this constant current would produce a greater power dissipation in the crystal. This would result in a greater rise in the true temperature above the ambient temperature and hence in a decrease in the computed resistance. If these data were plotted in a manner similar to that of Figures 29 and 30 the slope of the resulting curve would be expected to be somewhat less than that of the curves obtained by the methods described here.

Lagrenaudie (Ref. 8) has more recently reported the intrinsic energy gap for polycrystalline boron to be 1.28 ev.

In an internal report supplied to the present writer by L. Apker of General Electric Laboratories, Taft (Ref. 62) reported on conductivity studies of boron prepared by pyrolysis of boron hydrides and chloride. From a straight line drawn through his data ranging from 225 °K to 1000 °K Taft reported a value of 1.0 ev for the intrinsic energy gap. However, the best straight line drawn through his data in the range 700 °K to 1000 °K yields $E_g = 1.5$ ev.

To avoid the effect of impurities or defects in lowering the activation energy the slope only at the highest temperatures should be used when computing the energy gap $E_g$.

6. Impurities and heat treatment

a. Discussion. The deviations from typical behavior shown in Figure 30 may be attributed to the presence of
impurities, such as foreign atoms or crystal defects, in individual crystals. Crystals No. 45 and 18 had received no known special treatment but their deviations from typical behavior at the lower temperatures indicates the presence of some impurities in relatively small amounts. Crystal No. 22 originally exhibited typical behavior but while measurements were being made on this crystal the series resistance was accidentally shorted and the current rose momentarily to a value estimated at 0.5 amp. (The instability inherent to the voltage current characteristics of crystalline boron contributed to several similar accidents with other crystals. Crystal No. 22 was one of few to survive.) When resistance versus temperature was again measured the curve labeled 22(b) was obtained. It is believed that crystal No. 44 whose behavior paralleled that of 22(b) had suffered a similar accident in preliminary tests.

This accident led to the conclusion that heat treatment had resulted in the introduction of impurity centers capable of contributing carriers. This was verified by subjecting originally typical crystal No. 23 to a similar treatment. In this case the current overload was more carefully controlled to 0.2 amp. and left on for about 30 minutes. The resulting crystal was labeled No. 23(b) and resistivity data (normalized resistance data) on this heat
treated crystal is plotted in Figure 30. The data plotted for crystal No. 22(c) was obtained after this crystal had been heated to about 700 °C and while the crystal was being cooled to room temperature. It thus appears that defects can be introduced into a boron crystal by a heat treatment involving either a high ambient temperature or a high crystal current.

When a number of crystals were being tested qualitatively for thermoelectric effects two crystals were found which showed thermoelectric behavior differing markedly from that of the majority. These crystals were labelled Nos. 103 and 104. A plot of resistivity (normalized resistance) versus reciprocal temperature for crystal No. 103 is shown in Figure 30. A similar plot for crystal No. 104 is presented later in connection with Hall effect data in Figure 32. The results on these two crystals lead to the conclusion that some of the crystals initially contained impurities. These impurities may have been foreign atoms, possibly tantalum, or physical defects resulting from thermal treatment.

If crystal No. 46 were perfectly pure the plot of the logarithm of resistivity versus reciprocal temperature for this crystal might be expected to be almost a straight line. Deviations from straightness, however, have been observed frequently for other semiconductors when the resistivity...
and temperature were plotted in a similar manner (Ref. 27). Several possible explanations have been offered.

V. Johnson (Ref. 63) has suggested that the conditions under which the crystals are grown may give rise to a multiplicity of impurity levels not well defined in location in the forbidden energy band. The resulting conductivity might be expressed as a sum similar to Equation (13) or more simply

\[ \sigma = \sum Q_i \exp \left( -\frac{\varepsilon_i}{kT} \right), \quad (48) \]

where the coefficients \( Q_i \) include the mobilities as given in Equation (13). The resistivity data for crystal No. 46 can be fitted over the temperature range indicated with the aid of Equation (48) and only four values for \( \varepsilon_i \). These are: \( \varepsilon_1 = 0.79, 0.50, 0.34 \) and 0.25 ev.

L. Apker (Ref. 64) has offered another possible explanation in terms of ion adsorption on the surfaces of insulators and semiconductors. Dr. Apker pointed out that the number of adsorbed ions should vary inversely with temperature, that the surface charge due to the adsorbed layer could serve either to trap or contribute carriers, thus increasing or decreasing the intrinsic resistivity at the lower temperatures where the adsorbed layer was heaviest. In the case of boron it would be necessary that such an ionic layer contributed carriers thereby lowering the intrinsic resistivity at lower temperatures. Dr. Apker
also suggested an alternate possibility. At the higher temperatures the surface of the boron crystal might react reversibly with surrounding ions to form a surface layer of lower resistivity. If, at temperatures in the neighborhood of 1000 °K, a reaction took place which was no longer reversible at any temperature, this latter hypothesis might also explain the apparent permanent alteration of the conductivity characteristics of boron crystals when heated to high temperatures.

There is another possible explanation for the deviations from linearity observed in plots like that for typical crystal No. 46 in Figure 30. This explanation is based on the possibility that the mobilities of carriers or the intrinsic energy gap have greater temperature dependence than that predicted by the usual theories. Doucet and Guignard (Ref. 27) have given a semi-empirical equation which takes into account such temperature dependence. Their equation may be rewritten as follows:

$$\sigma \sim T^{-P} \exp \frac{E_0}{2k(T + C)}$$

where the parameter $P$ takes into account the temperature dependence of mobility and the parameter $C$ takes into account the temperature dependence of the intrinsic energy gap. Various theories give values of $P$ ranging from $1/4$ to $5/2$, but most experimental results demand larger
values in order to obtain an empirical fit.

The resistivity versus temperature data for crystal No. 46 can be fitted with the aid of Equation 49 when P = 9 and C = 0, or when P = 0 and C = 330 °K. Other combinations of these parameters would also fit the data.

C. Hall Effect

1. Results

a. Introduction. Table 5 presents some of the experimental data and calculated results on Hall effect for one antimony, one germanium and three boron crystals. The single probe (Evans) method previously described was used in obtaining all the data recorded in the table. With the exception of runs No. 7 through 11 the data on each run represents the average of data obtained with crystal current flowing in each of the two directions. All the runs involved reversal of the applied magnetic field.

Run No. 1 on antimony crystal No. 26 represents the average of four readings. The effective resistivity of this crystal recorded in the table was taken from a handbook (Ref. 18). The Hall voltage observed in the case of this crystal was relatively small by comparison with the Hall voltages observed in the case of boron. However, Hall voltages from this small antimony crystal were
### Table 5. Hall Effect Data

<table>
<thead>
<tr>
<th>Crystal number and material</th>
<th>Run No.</th>
<th>Magnetic field (gauss)</th>
<th>Crystal voltage (volts)</th>
<th>Crystal current (micro-amp)</th>
<th>Effective resistivity (ohm-cm)</th>
</tr>
</thead>
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<tr>
<td>26 antimony</td>
<td>1</td>
<td>7500</td>
<td>0.48</td>
<td>300000</td>
<td>$4.17 \times 10^{-6}$</td>
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<tr>
<td>50 germanium</td>
<td>2</td>
<td>8600</td>
<td>9.4</td>
<td>6850</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6900</td>
<td>9.4</td>
<td>6870</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5200</td>
<td>9.4</td>
<td>6890</td>
<td>2.2</td>
</tr>
<tr>
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<td>5</td>
<td>2600</td>
<td>9.4</td>
<td>6900</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1500</td>
<td>9.4</td>
<td>6710</td>
<td>2.2</td>
</tr>
<tr>
<td>104 boron</td>
<td>7</td>
<td>7000</td>
<td>31.2</td>
<td>375</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>7000</td>
<td>52.7</td>
<td>740</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>18000</td>
<td>52.7</td>
<td>740</td>
<td>310</td>
</tr>
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<td>12.0</td>
<td>104</td>
<td>500</td>
</tr>
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<td>-103</td>
<td>500</td>
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<td>12.2</td>
<td>107</td>
<td>490</td>
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<td>13</td>
<td>14400</td>
<td>12.2</td>
<td>107</td>
<td>490</td>
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<td></td>
<td>14</td>
<td>11200</td>
<td>12.2</td>
<td>107</td>
<td>490</td>
</tr>
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<td>15</td>
<td>5800</td>
<td>12.2</td>
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<td>490</td>
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<td>89</td>
<td>2500</td>
</tr>
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<td>18000</td>
<td>39.6</td>
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</tr>
<tr>
<td>$I_x$ (nano-amp)</td>
<td>Effective resistivity (ohm-cm)</td>
<td>$T'$ (°C)</td>
<td>$V_H$ (microvolts)</td>
<td>$R_H$ (cm$^3$/coul)</td>
<td></td>
</tr>
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<td>----------</td>
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<tr>
<td>0.0000</td>
<td>$4.17 \times 10^{-6}$</td>
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<td>$-0.028 \pm 0.002$</td>
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<td>25</td>
<td>48600</td>
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<tr>
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<td>-120 ± 40</td>
<td>-134 ± 47</td>
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<td>24</td>
<td>-100 ± 20</td>
<td>-1400 ± 120</td>
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<tr>
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<td>180</td>
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<td>+3 ± 2</td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td>80</td>
<td>229</td>
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<td>+0.4 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>89</td>
<td>2500</td>
<td>28</td>
<td>-250 ± 100</td>
<td>-2650 ± 1100</td>
<td></td>
</tr>
<tr>
<td>.0378</td>
<td>$1.7 \times 10^6$</td>
<td>25</td>
<td>+220 ± 180</td>
<td>+ (2.8 ± 2.3) X 10^5</td>
<td></td>
</tr>
</tbody>
</table>
relatively easy to measure. The standard error of the Hall voltage recorded for this crystal is based upon the deviations from the mean value for the four readings originally recorded. The computed Hall coefficient of $0.028 \pm 0.002 \text{ cm}^3/\text{coul}$ for this crystal compares favorably with the value of approximately $0.02 \text{ cm}^3/\text{coul}$ given by Sietz (Ref. 23).

Runs No. 2 through 6 on germanium crystal No. 50 are similar but more complete than runs made on three other germanium crystals. Crystal No. 50 was relatively large and was provided with five probes to facilitate measurements of both resistivity and Hall effect. The values for resistivity of this crystal recorded in Table 5 were obtained directly from resistance and dimensional data. Hall voltages observed in the case of this crystal were relatively large and easy to measure even when the magnetic field was reduced to 1500 gauss. Different values of magnetic field strength were used for each of the five runs on crystal No. 50 recorded in Table 5. This permitted a check on the manner in which Hall voltages obtained by the single probe method varied as a function of magnetic field. These results are plotted in Figure 31 and will be discussed in more detail later.

Crystal No. 10, to which most of Table 5 is devoted was one of two low resistivity boron crystals selected
from among over 250 boron crystals on the basis of qualitative measurements of thermoelectric effects. These qualitative measurements indicated that Crystal No. 104 was an n-type crystal. Runs No. 7 through 11 were preliminary runs on this crystal. These runs were for the purpose of detecting any measurable Hall effects in crystalline boron. With the exception of run No. 11 these runs were conducted with crystal current in one direction. The data obtained from the preliminary runs on crystal No. 104 showed that crystalline boron did have a measurable Hall effect, that this effect was a function of crystal current and magnetic field, and was independent of the direction of crystal current.

Runs 12 through 15 on crystal No. 104 were for the purpose of investigating more fully the relationship between Hall voltage and magnetic field strength. At the lower values of magnetic field strength a relatively larger quantity of data was required in order to reduce the computed standard error to an acceptable value.

Runs 16 through 23 on crystal No. 104 were for the purpose of investigating more fully the relationship between Hall voltage and crystal current. At the highest values of crystal current used the Hall voltages showed a reversal of sign.
After completing the Hall effect measurements on crystal No. 10\textsuperscript{4} a study was made of its total resistance as a function of temperature. These resistance data were normalized in the manner previously described. The geometric normalizing factor \( G_{15} \) thus obtained was used in computing the values for resistivity of crystal No. 10\textsuperscript{4} given in Table 5.

The following method was used for estimating the temperature of the crystal at various values of crystal current. It was assumed that the effective (or static) resistance \( V_x/I_x \) at a given current \( I_x \) and crystal temperature \( T' \) was equal to the extrapolated resistance \( R_a \) at an ambient temperature \( T_a = T' \). Effective resistances were computed from the crystal voltage and crystal current data given in Table 5. These values of resistance were used in conjunction with an independently obtained plot of resistance versus temperature data for obtaining the values of estimated temperature \( T' \) given in the table.

Only one run was conducted on each of the crystals No. 23(b) and 40. An exceptionally long run including 418 readings was required in the case of typical crystal No. 40. The high resistivity of this crystal made noise and drift problems especially serious in this case.

b. Hall voltage versus magnetic field. The data on runs No. 2 through 6, 8 and 9, and 12 through 15 given in Table 5
provided information for a study of the dependence of Hall voltage on magnetic field strength in n-type germanium and n-type boron. The results of this study are plotted in Figure 31. The ordinate scale to the left was used for plotting the magnitude of Hall voltages in millivolts observed in the case of germanium crystal No. 50. The ordinate scale to the right was used for plotting the magnitude of Hall voltages in microvolts observed in the case of boron crystal No. 104. The abscissa scale at the bottom of Figure 31 was used for plotting the magnetic field strength in gauss for both cases.

The slope of the straight line at (a) in Figure 31 was used for computing the Hall coefficient for germanium crystal No. 50 given in Table 5. The standard error of this coefficient given in the table is based on the deviation of the plotted points from the straight line. The standard errors of the individual points are indicated in the figure in the cases of lines (b) and (c) for boron crystal No. 104. In all three cases it is observed that the Hall voltage is directly proportional to the magnetic field strength within the indicated limits of experimental error.

c. Hall coefficient versus temperature. Hall voltages from boron crystal No. 104 were definitely not directly proportional to crystal current. It was assumed
Figure 31. Hall voltage versus Magnetic Field

Data are from Table 5. Curve (a) is for germanium, runs No. 2 through 6. Curve (b) is for boron, runs No. 8 and 9. Curve (c) is for boron, runs No. 12 through 15. Standard errors are indicated for the curves (b) and (c) on the crystalline boron. Both ordinate scales correspond to absolute values of Hall voltages.
that this was due to changes in crystal temperature with
crystal current and the data obtained from runs 16 through
23 of Table 5 were used for study of the Hall coefficient
as a function of crystal temperature. As previously de­
scribed the effective resistances of the crystal corre­
spending to the various values of crystal voltage and cur­
rent were computed and temperatures then obtained from a
plot of total resistance versus temperature which had been
independently obtained. Effective temperatures of the
crystal were estimated in this indirect manner. There is
no assurance that the temperatures thus estimated repre­
sent the true mean temperature of the crystal but these
estimated temperatures were used for plotting Hall coef­
ficient as a function of reciprocal absolute temperature
as shown in curve (b) of Figure 32.

Figure 32 shows plots of the resistivity and Hall
coefficient of crystal No. 104 as a function of reciprocal
absolute temperature. The ordinate scale to the left was
used for plotting the logarithm of the numerical value of
resistivity in ohm cm. The ordinate scale to the right
was used for plotting the logarithm of the absolute numeri­
cal value of the Hall coefficient in cm$^3$/coul. The
abscissa scale is the same as that used previously in
Figures 29 and 30. The resistivity curve (a) of Figure 32
was obtained by normalizing resistance data in the manner
Figure 32. Resistivity and Hall Coefficient

Curves (a) and (b) present the observed resistivity and Hall effect data on exceptional crystal No. 104. For curve (b) temperatures were estimated from effective resistance. Curve (c) is a hypothetical curve showing approximately the behavior to be expected from an impurity semiconductor with a resistivity curve like (a) and which changes its type in the intrinsic range. The two branches of curves (b) and (c) are of opposite sign.
described. The Hall coefficient curve (b) consists of a negative and a positive branch. The negative branch of this curve corresponds to a predominance of negative carriers while the positive branch corresponds to a predominance of positive carriers. Curve (c) is a hypothetical Hall coefficient curve which will be discussed in a following section.

2. Discussion

a. Hall voltage versus magnetic field. The elementary theory of the Hall effect previously presented predicts that Hall voltage should be directly proportional to magnetic field strength. Within the limits of experimental error the results shown in Figure 31 conform to this prediction. These results also give some confidence in the methods used in this study. There are, however, several other possible sources of error that should be considered.

b. Errors in Hall effect measurement. Errors resulting from the finite length of specimens being tested for Hall effect have been considered by Isenberg, Russell and Greene (Ref. 65). These writers considered the case of a rectangular specimen of length 1 and width w with current electrodes making uniform contact over the entire surface of the ends of the specimen. They showed that as the length to width ratio 1/w decreases the Hall voltage
to be expected also decreases. This effect is sometimes called the Isenberg effect. However, for a specimen having a length width ratio of 2.0 the decrease in expected Hall voltage is less than 10 per cent and when this ratio is 1.5 the decrease is less than 15 per cent. Others (Refs. 35 and 57) have shown that when the area of contact between the current electrodes and the specimen is small, the decrease in expected Hall voltage is less. Because of the irregular geometry at the ends of the specimens used in this study, the small area of contact at the ends, and because, in the case of this study, the results of the Isenberg effect are well within experimental error, this correction is neglected here.

Some other effects which may complicate Hall effect measurements include the Ettinghausen, Nernst and Righi-Leduc effects (Ref. 66). When direct current methods are used for Hall effect measurements all of these effects, with the exception of the Ettinghausen effect, are cancelled when an average is taken of the four measurements obtained with crystal current and magnetic field each applied in both directions. The Ettinghausen effect must be given further consideration.

The Ettinghausen effect is essentially a difference in temperature between the two sides of the crystal which arises when a current through the crystal is perpendicular
to a magnetic field. This difference in temperature is the result of a greater carrier density and consequent greater current density at one side of the crystal and gives rise to thermoelectric effects between probes contacting the crystal. The Ettinghausen effect may be eliminated by the use of alternating current for measuring the Hall effect. In this case the frequency of the alternating current must be sufficiently high so that it is not possible for any transverse thermal gradient to be set up during each half cycle. In this manner a uniform temperature of the crystal may be maintained between Hall electrodes in contact with the specimen. Measurements obtained in this manner are sometimes described as measurements of the isothermal Hall effect while those obtained by direct current methods are described as measurements of the adiabatic Hall effect.

Recent theoretical studies have shown that the difference between the adiabatic and isothermal Hall effects should be smaller than previously predicted (Ref. 23). L. S. Stilbans (Ref. 67) pointed out that previous calculations neglected the thermal conductivity of the specimen due to lattice vibrations and concluded that the real difference between the two effects was almost negligible. V. A. Johnson and F. L. Shipley (Ref. 68) have shown that the difference between the two effects should be only a few
thousandths of one per cent in the middle temperature ranges but that the difference should be greater at high and low temperatures. However in an investigation of the adiabatic and isothermal Hall effects in single crystals of tellurium Fukuroi, Tanuma and Tobisawa (Ref. 69) found a measurable difference between the two effects at temperatures less than 230 °C and found differences as high as 50 per cent at higher temperatures. Therefore there remains some question as to the importance of the difference between the adiabatic and isothermal effects in the present investigation. It should be recognized that the measurements reported here are measurements of the adiabatic Hall effect while the calculations which follow are based on the isothermal Hall effect.

If an appreciable temperature gradient existed between the two sides of the crystal, due to Ettinghausen effect, a spurious voltage could be introduced by the thermoelectric emf between the tungsten probes and the boron crystal. In this investigation it was simply assumed that any voltages arising from the Ettinghausen effect were substantially smaller than the Hall voltage. This assumption is usually valid for other materials. However, since the thermoelectric power of crystalline boron is exceptionally high there remains some doubt as to the importance of the Ettinghausen effect in these measurements.
Because the experimental errors in the measurement of small Hall voltages from the small electrically noisy crystals used in this study were relatively large, it was assumed that all the possible sources of error discussed above might be neglected.

**c. Hall coefficient versus temperature.** If the plot of Hall coefficient as a function of reciprocal absolute temperature had had the form of the hypothetical curve (c) of Figure 32 an explanation would have been relatively simple. Curves similar to curve (c) have been observed by others (Refs. 3, 24, 35). The explanation is based on the following considerations.

Resistivity $\rho$ (or reciprocal conductivity $1/\sigma$) varies inversely as carrier density according to Equation (11). When one type of carrier predominates, the Hall coefficient also varies inversely as carrier density according to Equation (19). The resistivity is also inversely proportional to the mobility of the carriers. The carrier density is exponentially dependent upon reciprocal temperature and the temperature dependence of mobility is theoretically relatively small. Therefore in the temperature range where one carrier predominates, the curves for resistivity and Hall coefficient plotted as in Figure 32 should be almost parallel. Failure of the two curves (a) and (c) to be exactly parallel in the lower temperature range to
the right, could be attributed to a normal variation of mobility with temperature.

Both branches of curve (c) could be explained by assuming that the crystal contained n-type impurity centers which contributed electrons and that the mobility of holes exceeded that of electrons. In the impurity range to the right, where the electron density \( n_e \) greatly exceeded the hole density \( n_h \), a negative Hall coefficient would be observed. In the intrinsic range to the left, where the resistivity curve is steeper and where the two densities are approximately equal, a positive Hall coefficient would be observed owing to the greater mobility of the holes.

The definite break in resistivity curve (a) between impurity and intrinsic range occurs at a temperature between 600 °K and 700 °K. The above explanation would serve to explain a change in sign of the Hall coefficient at a temperature in this neighborhood. In this study a change in sign of the Hall coefficient was observed at an estimated temperature of about 400 °K. The curve (b) of Figure 32 was drawn through the observed data. Several possible explanations of this observed curve might be suggested.

One possible explanation of the observed results is based upon the assumption that when the estimated temperature was about 400 °K the interior of the crystal was at
a much higher temperature and the exterior surface was at some much lower temperature. Under these conditions the interior core of the crystal might have a positive Hall angle sufficiently large to cancel the effect of a negative Hall angle in the exterior shell. This would require the temperature of the core to be in the intrinsic range above 600 °K. The absolute values of the Hall coefficient and Hall angle in the intrinsic range are certainly less than one tenth of their absolute values in the lower temperature portions of the impurity range. Therefore the thickness of the core would have to be at least 10 times the combined thickness of the two opposite layers of the outer shell in order for the two Hall angles of opposite sign to cancel. The cross sectional area of the interior core would then necessarily be at least 100 times that of the outer shell and the effective resistance of the crystal would be determined by the temperature of the interior core. The effective resistance of the crystal was used as a basis for estimating the temperature of the crystal. Under these conditions the estimated temperature would be approximately that of the core instead of some temperature at least 200 °K below that of the core. Therefore this explanation of the observed results is not considered to be satisfactory.
Another possible explanation of the observed results might be based on the assumption that boron crystal No. 104, used in this study, contained both n-type and p-type impurities. A slight break in the resistivity curve (a) of Figure 32 at a point corresponding to a temperature of about 450 °K lends some credence to this hypothesis. The negative branch of the Hall coefficient curve (b) could then be attributed to the greater density of electrons in the lower temperature range while the positive branch of the curve could be attributed to a greater density of holes in the upper range. This explanation, however, presupposes the possibility of the coexistence of p-type and n-type impurities in a given crystal. This possibility is subject to question and this explanation must therefore be accepted only with reservations.

The behavior of the Hall coefficient at temperatures above room temperature is not fully explained. However, the data may be plotted as a reasonably smooth curve having a form approximately like that to be expected. This lends evidence to support the conclusion that the room temperature data may be used in computing values for the densities and mobilities of the carriers.

3. Carrier mobilities and densities
   
a. Introduction. The data used in computing values for carrier mobilities and densities was that obtained
near room temperature on crystals No. 50, 104, 23(b) and 40. Computations were performed in a manner similar to that illustrated in example No. 5. Standard errors were calculated in a manner similar to that illustrated in example No. 6.

b. Mobilities. The mobility of electrons in germanium crystal No. 50 was computed in a manner similar to example No. 4. The room temperature data on resistivity and Hall coefficient of this crystal in Table 5 was used in the calculation. The value obtained for the mobility of electrons in this sample of germanium was 2600 cm$^2$/volt sec. This compares favorably with values ranging from 2400 to 3800 cm$^2$/volt sec. obtained by others (Ref. 35). Other investigators (Ref. 24) have obtained higher values. However the above calculation provides some additional evidence in support of the methods used in this investigation for Hall effect measurement.

Example No. 5 used the room temperature data on resistivity and Hall coefficient of crystal No. 104 given in Table 5. The values used were: $\rho = 610$ ohm cm and $R_H = -400$ cm$^3$/coul. The value obtained for the electron mobility was $\mu_e = 0.6$ cm$^2$/volt sec. A similar calculation was performed using the data given in Table 5 on crystal No. 23(b). The values used were $\rho = 2500$ ohm cm and $R_H = 2650$ cm$^3$/coul. The value obtained for the
electron mobility in this boron crystal was \( \mu_e = 0.9 \text{ cm}^2/\text{volt sec} \). The standard error of this latter value for the electron mobility is higher than that in the case of crystal No. 104. A weighted mean value for the mobility of electrons in the crystalline boron used in this study is

\[
\mu_e = 0.7 \pm 0.3 \text{ cm}^2/\text{volt sec.} \quad (50)
\]

The indicated standard error for this value is based on the standard error previously discussed. If the errors in the indirect measurement of resistivity and in the measurement of Hall voltages by the methods described here are larger than those assumed, it is of course possible that the error in the value of electron mobility in crystalline boron given in Equation (50) may be larger than that indicated.

On the basis of Hall and thermoelectric effect measurements it was assumed that typical crystals like No. 40 were in the intrinsic range at room temperature. Table 5 therefore provides no data for computing the mobility of holes in crystalline boron. However, the Hall effect data on crystal No. 40 and thermoelectric data on other typical crystals indicated that the mobility of holes in crystalline boron exceeds that of electrons. Equation 26 and the resistivity and Hall effect data on crystal No. 40 provided means for computing the difference between the two
mobilities. The values substituted in Equation (26) were:

\[ R_h = 2.8 \times 10^5 \text{ cm}^3 /\text{coul} \]

When the standard errors of these values were considered the following value for the difference between the mobilities of holes and electrons in crystalline boron was obtained.

\[ \mu_h - \mu_e = 0.2 \pm 0.15 \text{ cm}^2 /\text{volt sec} \]  \hspace{1cm} (51)

Assuming the electrons have the same mobility in crystals No. 10 and No. 40, combination of Equation (50) and (51) gives for the mobility of holes in boron crystal No. 40 the following value.

\[ \mu_h = 0.9 \pm 0.4 \text{ cm}^2 /\text{volt sec} \]  \hspace{1cm} (52)

From Equations (50), (51) and (52) a quantity useful in other calculations may be computed. This quantity appears in Equations (25) and (29) and has the following approximate value.

\[ \frac{\mu_h - \mu_e}{\mu_h + \mu_e} = 0.12 \]  \hspace{1cm} (53)

The values or the mobility of the carriers in these samples of crystalline boron are very low by comparison with the mobilities in other substances reported by others (Ref. 5, 22, 23, 24, 31, 33, 35, 57, 70). This, of course, at least partly accounts for the difficulties in making
Hall effect measurements as observed in this and other investigations (Refs. 8, 13, 62). It is possible that the low mobilities of the carriers in crystalline boron may be attributed to its complicated structure (Refs. 16, 17). Mobilities of approximately the same order of magnitude have been reported for barium oxide and titanium oxide (Refs. 37 and 71). Lower mobilities for electronic carriers have been reported for some alkali halides and insulators (Refs. 56 and 71).

c. Densities. The density of electrons in crystal No. 104 at room temperature was computed in example No. 5. The room temperature Hall coefficient of this crystal was used in this computation. The value obtained was

\[ n_e = 1.0 \times 10^{16} \text{ electrons/cm}^3 \text{ at } 24 \, ^\circ C. \]  

(54)

An estimate of the number of impurity centers in crystal No. 104 was obtained by extrapolating the impurity portion of the resistivity curve (a) of Figure 32 to \( T = \infty \) as implied by Equation (4). The value obtained is approximately

\[ n_s = 5 \times 10^{18} \text{ impurity centers/cm}^3. \]  

(55)

It was assumed that crystal No. 40 was in the intrinsic range at room temperature. The Hall effect data on this crystal and the relation given in Equation (53) were substituted in Equation (25) to give for the density of
carriers of either type,

\[ n_c = 3 \times 10^{12} \text{ holes or electrons/cm}^3, \text{ at } 25^\circ \text{C}. \] (56)

The total carrier density was then

\[ n_t = n_h + n_e = 6 \times 10^{12} \text{ carriers/cm}^3, \text{ at } 25^\circ \text{C}. \] (57)

When the resistivity curve for crystal No. 46 was extrap-olated to \( T = \infty \) and the value for \( n_c \) given in Equation (56) was multiplied by the ratio of room temperature resistivity to the resistivity at \( T = \infty \), the following estimate of the density of sources of these carriers was obtained,

\[ n_s = 3 \times 10^{21} \text{ sources/cm}^3. \] (58)

It was assumed that each of these sources contributes one electron and one hole to the conductivity and that the mobilities of the carriers are equal. From Avogadro's number, \( 6.03 \times 10^{23} \) atoms/mol, the molecular weight of boron, 10.8 gm/mol, and the density of crystalline boron, 2.3 gm/cm\(^3\), the atomic density \( n_a \) of crystalline boron was computed to be

\[ n_a = 1.3 \times 10^{23} \text{ atoms/cm}^3. \] (59)

The ratio between \( n_a \) and \( n_s \) given by Equations (59) and (58) indicates that about one atom in 40 can contribute an electron and a hole as carriers in crystalline boron.

Because of the large experimental and computational errors involved in reaching this conclusion it cannot be stated
definitely that every atom in crystalline boron is not a potential source of carriers. However, this gives some indication that in the 50 atom unit cell of crystalline boron (Ref. 16), the two atoms which have four bonds, in contrast to the other 48 which have six bonds, may be the source of the carriers.

4. Other properties of the carriers

a. Effective masses. When the quantity \( (m_h m_e/m^2)^{3/4} \) was introduced into Equation (3) and values for the fundamental constants \( m, k \) and \( h \) were substituted into the equation the following equation was obtained:

\[
(m_h m_e/m^2)^{3/4} = \frac{n_c \cdot 9K^{3/2} \text{ cm}^3}{5 \times 10^{15} \cdot T^{3/2} \exp(-E_g/2kT) \text{ carriers}}.
\] (60)

The slope of the resistivity curve for crystal No. 46 in Figure 30 at room temperature gave \( E_g = 1.0 \) ev. When this value for \( E_g \) and the value for \( n_c \) given by Equation (56) were substituted in Equation (60), the following approximate value for the effective mass of either holes or electrons in crystalline boron was obtained,

\[ m_h = m_e = 10m. \] (61)

A similar calculation using the high temperature value \( E_g = 1.6 \) ev. but the room temperature value of \( n_c \) gave the following approximate values for the effective masses.
\[ m_h = m_e = 20000 \text{ m} \] (62)

When it was assumed that the decrease in resistance of a typical crystal, like No. 46, from room temperature to 1000 °K was due principally to an increase in the number of carriers the value \( n_c = 3 \times 10^{19} \text{ carriers/cm}^3 \), at 1000 °K was obtained. A computation for the effective masses at 1000 °K gave

\[ m_h = m_e = 1500 \text{ m} \] (63)

Because of the large experimental and computational errors involved in these calculations little confidence can be placed in any of the above values for the effective masses of the carriers. It does however appear that the effective masses of the carriers in crystalline boron are larger by at least one order of magnitude than the mass of a free electron.

b. Mean free path. Equation (7) and the above estimates of the effective masses were used for computing the mean free paths of the carriers in crystalline boron. Estimates for the mean free paths ranging from about 1.5 Å to 150 Å were obtained. These values may be compared with the minimum interatomic distance of 1.8 Å in crystalline boron. Although the estimates of the mean free path are as unreliable as those of effective mass, it appears that the mean free path of the carriers in crystalline boron is less
than in other semiconducting materials. Mean free paths in other semiconductors range from about 40 Å to more than 2000 Å (Refs. 22, 24).

D. Thermoelectric Effects

1. Results

a. Qualitative. Qualitative measurements of the thermoelectric effect were used to find the first boron crystal which showed measurable Hall effect. The observation of a large thermoelectric effect in crystalline boron was taken as evidence that a Hall effect should exist. Because the discussion of Hall effect more logically followed that of resistivity this discussion of thermoelectric effect has been postponed.

Preliminary tests on n-type and p-type germanium were performed in order to check the qualitative observations reported by others (Refs. 43, 72). When a tungsten probe was brought into contact with a sample of n-type germanium and the tungsten probe was heated slightly, the germanium crystal was observed to become negative with respect to the tungsten probe. This is characteristic of n-type behavior. As the tungsten probe was heated to higher temperatures the magnitude of the potential difference between the crystal and the probe was observed to increase in a
fairly uniform manner.

Usually when this experiment was repeated without changing the point of contact between the probe and crystal, a different phenomenon was observed. Upon repetition of the experiment when the tungsten probe was warmed slightly, the crystal became positive with respect to the tungsten probe. This is characteristic of p-type behavior. However as the probe was heated to higher temperatures, the potential difference between the crystal and the probe passed through zero and the crystal then became increasingly more negative with respect to the probe.

When p-type germanium was tested in a similar manner the effect observed was similar to this latter phenomenon. At low temperatures the potential difference between the crystal and the probe was positive as is characteristic of p-type behavior. At higher temperatures the potential difference between the crystal and the probe was negative.

Most of the boron crystals tested displayed a uniformly increasing positive potential difference between the crystal and the probe as the temperature of the probe was increased. The potential differences observed in the case of boron were approximately five times as large as those observed in the case of germanium.

Two boron crystals were found which initially exhibited a negative potential difference between the
crystal and the probe but which at higher temperatures became positive. With the exception of the direction of the potential difference and its magnitude, this behavior corresponded to that observed with p-type germanium and in the later runs on germanium originally n-type. When the total resistance of these boron crystals was measured in a very qualitative way, it was concluded that the resistivity of these crystals was much less than that of the majority.

b. Quantitative. The equipment and experimental and computational procedures employed in making quantitative measurements of thermoelectric power have been previously described. The results of representative sets of measurements are shown in Figure 33. Previous reference has been made to the physical arrangement of the crystal and thermocouples shown at (a) in Figure 33.

The graph at (b) in Figure 33 shows the results obtained on one sample of n-type germanium. The data was plotted so that the family of curves shown at (b) in the figure have for the most part a positive slope. However it should be noted that the values of thermoelectric power computed from these curves were for the most part negative. Thermoelectric powers computed from similar families of curves for both p-type and n-type germanium and for both p-type and n-type boron were plotted to obtain the curves shown at (c) through (g) in Figure 33. The standard errors
Figure 33. Thermoelectric Power

The arrangement diagramed at (a) was used and the temperature $T_1$ was varied while holding $T_2$ constant. The potential difference $V$ between the platinum electrodes in contact with the crystal was positive when the electrode at $T_1$ was positive with respect to the electrode at $T_2$. The potential difference $-V$ for the first and later runs on an originally n-type germanium crystal is plotted at (b). Thermoelectric powers $dV/dT$ derived from the curves at (b) are plotted at (c) and (d). Similarly derived curves for p-type germanium and several boron crystals are plotted at (e), (f) and (g). For boron crystal No. 103 the cross over point of curve (g) at 265 °C is indicated on the resistivity plot of Figure 30 at point (2).
of the average values of thermoelectric power obtained from curves such as those shown at (b) are indicated in the lower set of curves.

Curve (c) of Figure 33 was obtained from data from a first run on n-type germanium as shown at (b). Curve (d) was obtained from data on later runs on a germanium crystal originally n-type but which was clearly converted to p-type by the heat treatment. Curve (e) was obtained from data on p-type germanium. Curve (f) was obtained from data on four runs on boron crystals which appeared to represent the majority. Curve (g) was obtained from data on boron crystal No. 103 which in preliminary qualitative tests had behaved in a manner similar to boron crystal No. 104. Boron crystal No. 104 was later mounted and used for making the Hall effect measurements previously described. Crystal No. 103 was lost in the process of making measurements of thermoelectric effects.

2. Discussion

a. Comparison. Granville and Hogarth (Ref. 43) conducted some qualitative studies of thermoelectric effects in n-type and p-type germanium. A galvanometer was used for indicating the sign and magnitude of the Seebeck emf. This procedure is subject to question since the resistance of the galvanometer was comparable to that of the crystal
and the resistance of the crystal varied with temperature. However, results similar to those reported here were observed. A negative Seebeck emf. which increased in magnitude with an increase of probe temperature, was observed in the case of first runs on n-type germanium. A positive Seebeck emf. was observed at low temperatures in the case of p-type germanium and in the case of second runs on n-type germanium. It is concluded that the results observed in second runs on n-type germanium by these and the present writer are due to the heat treatment (Ref. 72) converting the n-type germanium to p-type germanium.

Measurements of thermoelectric effects in polycrystalline boron have been reported by Lagrenaudie and Taft (Refs. 8, 62). Both of these writers reported that boron behaves as a p-type semiconductor. No quantitative data was reported by Lagrenaudie but Taft reported values for the thermoelectric power of boron ranging from 150 microvolts/°C to 500 microvolts/°C. These values compare favorably with those obtained by the present writer.

b. Calculations. The formula given by Fukuroi, Tanuma and Tobisawa in Equation (28) in its limiting forms as given in Equations (29) and (30) was used for computing the thermoelectric power of p-type and n-type boron. Only approximate calculations were made. The quantity given in Equation (53) and the room temperature value $E_g = 2 \xi = 1.0$ ev.
were used. The values for the thermoelectric power $dV/dT$
obtained were $+200$ microvolts/°C and $-200$ microvolts/°C for p-type and n-type boron respectively.

E. Other Effects

1. Rectification

   a. Results. The results of a representative set of measurements of rectification effects on crystal No. 46 are given in Table 6. The entries in the table indicate the resistances measured between pairs of electrodes in contact with the crystal in ohms $\times 10^8$. The electrodes as labeled in Figure 6 are indicated in the top row and the left column of Table 6. The entries in the table indicate the resistances as measured when the corresponding electrode in the top row was positive and the corresponding electrode in the left column was negative.

   b. Discussion. An inspection of Table 6 reveals that electrodes B, D and E displayed a consistently high resistance when measured with respect to any of the other electrodes. Certain of the entries in the table have been underlined in order to emphasize the comparison between the values obtained when a given electrode was positive and when it was negative. For example the resistance measured between electrodes A and B when B, a consistently high
Table 6. Rectification by Poor Contacts

Crystal No. 46

Resistances between electrodes in ohms $\times 10^8$

<table>
<thead>
<tr>
<th>Negative electrode</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>4</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Table 7. Effect of Forming Contacts

Crystal No. 46, after forming

Resistances between electrodes in ohms $\times 10^8$

<table>
<thead>
<tr>
<th>Negative electrode</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>5</td>
<td>5</td>
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<td>C</td>
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<td>10</td>
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</tr>
<tr>
<td>D</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>4</td>
<td>6</td>
<td>6</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>
resistance electrode, was positive, was measured at $10 \times 10^8$ ohms, while resistance measured when A was the positive electrode, was $5 \times 10^8$ ohms. Further examination of the table shows that when the high resistance contacts B, D and E were the positive electrodes the resistances measured with respect to the lower resistance contacts A and C were consistently higher than when the high resistance contacts were the negative electrodes. In other words the direction of easiest flow (lowest resistance) was when the crystal was positive with respect to the poorest contact. This behavior is characteristic of a p-type semiconductor. Similar behavior in polycrystalline boron has been reported by Lagrenaudie (Ref. 8). This evidence helps to support the conclusion that crystalline boron is a predominately p-type semiconductor.

2. Forming

a. Results. The results of forming experiments on crystal No. 46 are given in Table 7. The results are tabulated in the same manner as those of Table 6. Since the same crystal was used, the results may be compared with those of Table 6.

b. Discussion. An inspection of Table 7 reveals that the contact resistance between electrodes B and D and the crystal was reduced by a factor of approximately 2 by the
forming operation. Other instances were observed where the contact resistance was reduced by a factor of 10 or more. Table 7 shows that the contact resistance between electrode E and the crystal was not greatly reduced by the forming operation and that this electrode still retained its ability to rectify.

3. Photoconductivity

a. Results and discussion. No reduction in the resistance of boron crystals was observed when they were exposed to x-rays. Some reduction was observed when they were exposed to ultra-violet radiation. The largest reductions in resistance occurred when the crystals were exposed to white light. Reductions in resistance ranging from 10 to 50 per cent were observed. The amount that the resistance was reduced was unaltered by the interposition of a two inch layer of water or by immersing the crystal in carbon tetrachloride. A simple calculation also showed that the observed reduction in resistance could not possibly be due to radiant heating of the crystal. In addition the intrinsic energy gap, $E_g = 1.55$ ev, corresponds to an absorption band beginning in the red part of the visible spectrum and extending into the higher energy portions of the visible spectrum. This is also consistent with the black to blue-black color of crystalline boron. The
optical properties of polycrystalline boron have been more fully investigated by Lagrenaude (Ref. 7). It is concluded that crystalline boron is photoconducting in response to some frequencies of light falling in the visible spectrum.
The boron crystals used in this study were prepared by reducing boron tribromide with hydrogen upon contact with a hot (1500 °C) tantalum filament. The largest single crystals weighed less than ten micrograms and were a few hundred microns in length. The high purity of the specimens was verified spectrographically and their crystalline nature was verified by means of Laue photographs.

Micromanipulative techniques for mounting very small crystals with several electrical contacts were developed. Microscopic single crystals of boron were mounted with as many as five spring loaded tungsten probes. Measurements were made of voltage current characteristics, resistivity, Hall and thermoelectric effects as functions of temperature. Qualitative studies were made of rectification, forming and photoconductivity.

The voltage current characteristics of crystalline boron were explained in terms of joule heating. The resistivity of crystals typical of the majority of those tested was found to be approximately 1.7 X 10^6 ohm cm at 25 °C. The resistivity of a typical crystal decreased by a factor of almost 10^10 between the temperatures of 200 °K and 1000 °K. From resistance data obtained in the temperature range between 700 °K and 1000 °K the intrinsic
energy gap $E_g$ between the filled and conduction bands was computed to be about 1.55 ev.

Hall, thermoelectric and rectification studies showed the purest specimens of crystalline boron were predominantly p-type. It was found that heat treatment could convert typical p-type boron crystals into relatively low resistivity n-type crystals. Hall effect measurements were made on one such heat treated crystal and on another low resistivity n-type crystal selected on the basis of qualitative thermoelectric measurements. From these Hall effect data the mobility of electrons in these particular crystals of boron was calculated to be about 0.7 cm$^2$/volt sec. From Hall effect data obtained on a typical crystal the mobility of holes was calculated to exceed that of electrons by about 0.2 cm$^2$/volt sec. The effective masses of the carriers were calculated to exceed ten electron masses and the mean free paths of the carriers to be between one and one hundred minimum interatomic distances.
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