

THE HALL EFFECT IN
SEMICONDUCTING DIAMOND

By

THOMAS YOUNG

Bachelor of Science

Boston College

Newton, Mass.

1954

Submitted to the faculty of the Graduate School of
Oklahoma State University of Agriculture and Applied Sciences
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
August 1958

NOV 7 1958

THE HALL EFFECT IN SEMICONDUCTING DIAMOND

Thesis Approved:

William J. Lewis

Thesis Advisor

H. E. Harrington

Robert McEachern

Dean of the Graduate School

410389

This research was supported by the
United States Air Force Office of
Scientific Research of the Air
Research and Development
Command under contract
No. AF 18(603) 40

ACKNOWLEDGEMENTS

The author would like to extend his sincere gratitude to the individuals whose cooperation helped make this investigation a success. He is particularly grateful to Dr. W. J. Leivo for his kind and thoughtful help throughout the course of this study. In addition, he wishes to thank Dr. H. E. Harrington, Dr. E. E. Kohnke, and C. C. Johnson, J. W. Northrip, and J. Wayland for their interest and helpful suggestions. Special mention is also due Mr. R. C. Robertson for making the Hall mount. And to my wife Clare, for her constant help and encouragement, I express my deepest thanks.

The author is also indebted to the RESEARCH FOUNDATION for their clerical help in the investigation and to the SPECIAL SERVICES SECTION of the library for obtaining much of the literature.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
Scope of Research	1
Historical Development of Hall Effect	2
Survey of Literature	4
II. THEORETICAL DISCUSSION OF HALL EFFECT	9
Particle View.	9
Wave Formulation of Hall Effect	13
Corrections to Hall Effect Equations	19
III. RESULTS.	22
Sample Description	22
Method of Measuring Resistivity	22
Hall Measurement Apparatus	23
Resistivity Results.	27
Hall Effect Results	29
IV. CONCLUSIONS.	32
Discussion of Results	32
Suggestions for Future Studies	36
BIBLIOGRAPHY.	38
APPENDIX A	40

LIST OF TABLES

Table	Page
1. Resistivity of Sample	29

LIST OF FIGURES

Figure	
1. Geometry of Hall Effect	9
2. Condition for Hall Equilibrium	10
3. Hall Angle Explained Geometrically	15
4. Cutaway Drawing of Container for Hall Mount	24
5. Hall Mount	26
6. Magnet Calibration Curve	28
7. Plot of Hall Constant Versus the Inverse Absolute Temperature	31
8. Experimental and Theoretical Plots of Carrier Density Versus Inverse Absolute Temperature	34

CHAPTER I

A. Scope of Research

This thesis, although an independent study of the Hall Effect, is a continuation of a research project which has been concerned with many other properties of semiconducting diamonds. Previous and concurrent studies have been concerned with rectification ^(1,2), surface state investigations ^(1,2), optical transmission and absorption ^(3,4), photoconductivity ^(5,6,7), photovoltaic effect ^(8,6), and measurements of lifetimes ⁽⁸⁾. In addition, several other effects such as electroluminescence, fluorescence, and phosphorescence have been noted but not completely investigated.

As has been stated, this thesis is primarily concerned with the Hall Effect in semiconducting diamonds. Although several other investigators have measured the Hall Constant in Type IIb diamonds, this is the first sample whose resistivity was as high as 10^5 ohm cm on which the Hall Effect has been reported. Previous investigations were made on samples whose resistivities were below 500 ohm cm. The relatively high resistivity of our sample made some adjustments in the technique of measurements necessary, particularly in the area of contact phenomena. Our sample is also unusual in another respect. There is a distinct difference in resistivity in opposite ends of the crystal. This difference will be discussed more fully later. This difference prevents us from regarding our sample as homogeneous throughout.

B. Historical Development of the Hall Effect.

In 1879, Edwin Herbert Hall, published an article entitled "On a New Action of the Magnet on Electric Currents". In it he described

how, while reading Maxwell's Electricity and Magnetism, he was attracted by one of Maxwell's statements to the effect that the force on a current carrying element due to an external magnetic field was exerted on the conductor rather than on the current. This struck Hall as being contrary to experience, since the force is proportional to the current rather than to any of the physical properties of the conductor. He discussed this seeming discrepancy with professor Rowland, under whom he was studying at John Hopkins University at the time. Rowland concurred with his pupil and suggested that if the force was exerted on the current rather than on the conductor, then one of two effects would possibly be present. If the current was assumed to be particle like in nature, then the forcing of the current to one side of the conductor by the magnetic field would cause an increase in the resistance of the wire. Or, if the nature of the current was that of an incompressible fluid, then there should be a displacement of the equipotential lines due to the tendency of the current to be displaced by the magnetic field.

After unsuccessfully attempting to observe a change in resistance due to an external field, Hall devised the following experiment to test the second hypothesis.

A piece of gold leaf was mounted on a glass plate and connected in series with an external electric circuit. Two probes connected to a galvanometer, were positioned on the gold leaf until no current flowed through the galvanometer. The sample was then placed between the poles of an electromagnet. On the 25th of October, 1879, Hall observed a displacement of the equipotential lines, which effect still bears his

name.

Hall conducted further experiments on this new "Electromotive force" as he called it, in several other metals. In silver, nickel, tin, copper, platinum, aluminum, and magnesium, the equipotential lines were all rotated in the same direction as in gold. However, he discovered that in iron, cobalt, zinc, and antimony, the direction of rotation was reversed. Bismuth⁽⁹⁾ presents an interesting case in that the sign of the Hall coefficient is different when the crystal axes are rotated to 90 degrees.

For many years, no satisfactory explanation of the anomalous Hall effect, the name given to the unexpected sign of the group of iron, zinc, cobalt, etc., could be given. It was observed that the monovalent elements all had a minus sign, signifying electrical conduction, but the divalent elements exhibited the anomalous effect, which should be associated with conduction by positive carriers. It was not until the band theory of solids was advanced that a satisfactory explanation of the anomalous Hall effect was formulated.

In 1909, K. Baedeker⁽¹⁰⁾ reported the results of his investigation in calcium iodide. This was the first known investigation of the Hall effect in semiconductors. Baedeker investigated two samples, which were of different resistivities. From his investigations, he concluded that the Hall coefficient was directly proportional to the resistivity and inversely proportional to the concentration of electrons⁽¹¹⁾. Later he reported that the Hall constant was independent of the magnetic field strength.

Although much work was done on metals in the period preceding the 1940's, and most recently on the rare earth elements, the most rewarding field for investigation of the Hall effect is in semiconductors. The

Hall effect in conjunction with measurements of resistivity has constituted the most basic electrical measurement for semiconducting materials.

C. Survey of Literature

Diamonds have for centuries been treasured by man because of their startling beauty when cut as gem stones. The first known mining of diamonds was carried out in India. However, since the discovery of the rich diamond fields of South Africa approximately 92% of the world's supply of diamonds, both of gem and industrial quality have come from the dark continent.

Physical investigation of diamonds has been hampered by several factors such as their extreme hardness and their relative scarcity.

It is only relatively recently that two types of diamonds have been distinguished, Type I and Type II. These two types differ in four qualities.

Type I diamonds have an absorption band at 8 microns in the infrared which is absent in Type II. Type II diamonds are usually of a more mosaic character on their surface. Type I diamonds cut off in the ultraviolet at 3000 Angstroms where as Type II diamonds transmit at wavelengths as low as 2240 Angstroms.

Recently⁽¹²⁾, the cutoff distinguishing criterion has come into question. F. A. Raal and J. F. H. Custers were able to obtain diamonds which had been flaked into steps of thickness down to approximately .04 mm. Transmission through the various thicknesses seemed to indicate that for thinner sections, the transmission cutoff approached that of the Type II diamonds. This the author postulated to be proof that Type II is purer or has less imperfections than Type I. However, if

the absorption coefficient rather than percentage absorption is plotted, the distinction in cutoff remains.

This is in agreement with the two comprehensive spectrographic analyses of diamonds. In 1942, F. G. Chesley⁽¹³⁾ ran spectrographic checks on thirty-three samples for Al, Si, Ca, Mg, Cu, Ba, Fe, Sr, Na, Ag, Ti, Cr, and Pb. Unfortunately for future work, he did not distinguish between Type I and Type II diamonds. However, two of his specimens were of much higher purity than the other thirty-one. This is approximately the expected occurrence of Type II in a random selection of diamonds. In 1957, F. A. Raal⁽¹⁴⁾ also conducted a spectrographic analysis on 25 samples. His analyses were for the same elements as Chesley's, and in addition, he was able to identify Ni content. Before his testing, he ran transmission data so as to be able to distinguish between Type I and Type II diamonds by means of their optical cutoff. He further distinguished between Type IIa and Type IIb diamonds by means of electrical measurements.

His spectrographic analysis showed that Type I diamonds were relatively more impure than Type II. The main impurities present in the Type II diamonds were Si, Mg, and Al, with Al predominant in most cases. However, in further subdividing Type II diamonds into Types IIa and Type IIb, there was little significant difference in the amount or types of impurities.

The further subdivision of Type II into Type IIa and Type IIb was first suggested by J. F. H. Custers⁽¹⁵⁾ on the basis of their electrical resistivity. Normally diamonds, both Type I and Type II, have resistivities in the range 10^{12} to 10^{16} ohm-cm. However, Custers discovered certain Type II diamonds had resistivities as low as 25 ohm-cm.⁽¹⁶⁾ Custers also

made the observation that all the blue diamonds which he had investigated were Type IIb. In our own experience, we have also found this to be true.

Since Custers first announced his discovery of the two types of diamonds, many others have investigated their electrical and optical properties. In this thesis we will be primarily interested in their electrical properties.

Leivo and Smoluchowski⁽¹⁷⁾ reported resistivity measurements on a sample which yielded an activation energy of 0.35 electron volts. They were the first to identify Type IIb diamond as a temperature dependent semiconductor.

James J. Brophy⁽¹⁸⁾ investigated the Hall effect, electrical conductivity and point contact rectification of one specimen. The Hall effect was measured by means of an alternating current method. The sample was found to be p-type over the temperature range of 26° Centigrade to -40° Centigrade. The slope of the curve of the natural log of the Hall constant versus the inverse of the absolute temperature was found to yield an activation energy of 0.3 electron volts. Potential probe investigation of the surface showed that the entire surface was p-type but that considerable inhomogeneity was present. Because of these inhomogeneities, further resistivity measurements were deferred. Average values for the number of carriers / cm^3 , resistivity, and mobility were found. These were 7×10^{13} holes/ cm^3 , 760 ohm-cm and 100 $\text{cm}^2/\text{volt-sec}$ respectively. Because of the inhomogeneities, Brophy stated that these could be considered order of magnitude values only.

J. F. H. Custers⁽¹⁹⁾ reported on a Type IIb diamond whose resistivity he measured as a function of the absolute temperature. From the curve

obtained⁽²⁰⁾, an activation energy of 0.35 electron volts can be calculated. Custers also noted that the diamond acted as a rectifier and that current readings could not be repeated after the temperature once had been raised. This he mentioned as a so called "hysteresis" effect.

A fairly recently published article on a Type IIb specimen was by Austin and Wolfe⁽²¹⁾ who investigated resistivity and Hall effect as well as optical properties. Their investigations showed that the so called "hysteresis" was mainly a contact phenomena.

The Hall effect was measured over the temperature range of -100° Centigrade to 600° Centigrade using standard D.C. potentiometric and galvanometric circuits with a field of 2130 oersteds. The sample was found to be p-type over the temperature range with a carrier density of 1.8×10^{13} holes per cubic centimeter at room temperature. The activation energy was found to be 0.38 electron volts by resistivity and Hall data calculations. Calculation of the effective mass of the holes by assuming a model with just an acceptor level at 0.38 electron volts yielded a value of approximately $500 m_e$ where m_e is the mass of the free electron. This seemed unreasonable in the light of other semiconductors so a model containing both donor and acceptor levels was investigated. This yielded a value for the ratio of the number of donors to the ratio of the effective masses to the $3/2$'s power of $2 \times 10^{15} \text{ cm}^{-3}$. The value of the mobility was found to be $1550 \text{ cm}^2/\text{volt-sec}$.

Continuing work which he had begun with Dyer⁽²²⁾, Wedepohl⁽²³⁾ measured the D.C. Hall coefficient and the resistivity of six semiconducting diamonds over the temperature range from 200° Kelvin to 800° Kelvin. All specimens were p-type, with resistivities between 50 and 1200 ohm-cm. On one of the specimens, only enough data was taken to establish order of

magnitude values because of high contact resistance of the Hall probes. Of the five other diamonds, Hall data yielded activation energies in three cases of 0.34 electron volts and in the other two, 0.32 and 0.29 electron volts.

In the three cases where the activation energies were equal to 0.34 electron volts, the ratios of the effective mass of the holes to the mass of the free electron were 0.25. In the other two cases they were 0.62 and 0.16 respectively. The mobility values at 290°K averaged out to 1330 cm²/volt-sec with a range between 1140 and 1450 cm²/volt-sec.

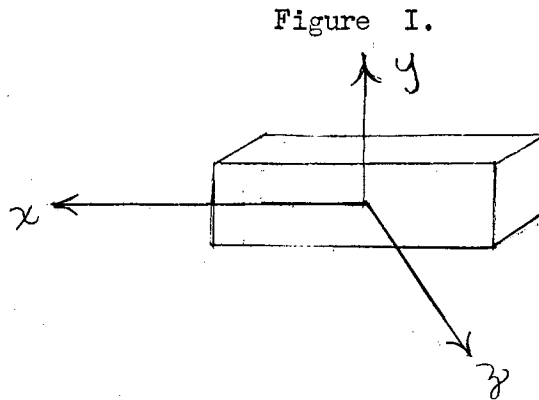
M. D. Bell and W. J. Leivo^(1,2) investigated the rectification characteristics of a Type IIb diamond and found these to be independent of the work functions of the metals involved. This they attributed to surface states. They also reported that there was an observable electroluminescence when a forward bias of 45 volts was applied. Their investigation of the photovoltaic effect showed a peak in the visible range of the spectrum at 660mμ and in the ultraviolet at 230mμ. Measurements of photoconductivity by the same group^(5,6) showed a peak at 660mμ in the visible which was the first reported photoconductivity in this range in diamond.

Chapter II

Theoretical Discussion of Hall Effect

A. Particle view

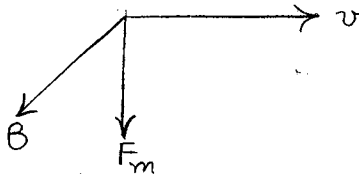
Perhaps the simplest view, albeit it is slightly misleading, of the Hall effect is from the standpoint of particles. Consider first an electron starting at the origin in Figure I.



Let the magnetic field be directed along the Z and the electric field along the X axis. From elementary electromagnetic theory, the force on a charged particle is given by

$$F_m = [v \times B] e$$

Since we have chosen an electron as our test particle, its velocity will be to the right. The vector diagram which follows shows that the electron will experience a force in the Y direction.



Thus the electron current will be in the direction of the resultant force due to the electric field and the magnetic field. In this particular case the deflection will be downward from the X axis.

This deflection of the flow lines of the current leads to a shifting of the equipotential lines in the transverse (Y) direction after equilibrium has been reached. Equilibrium will be reached when the field associated with the accumulation of electrons on the surface is large enough to cancel the force due to the magnetic field. The mathematical formulation of this statement is derived as follows:

The resultant force on the charge carrier due to the electric and magnetic fields is

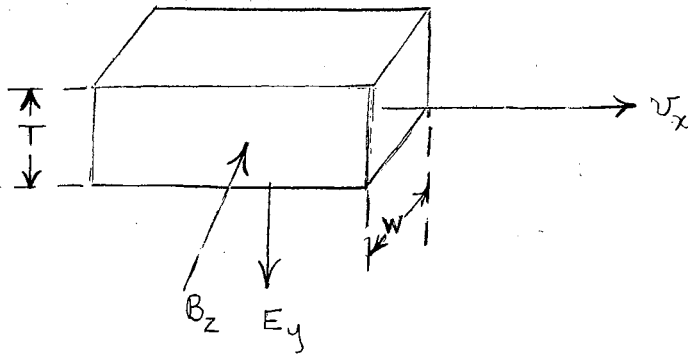
$$F = e [E + v \times B]$$

The equilibrium condition stated above is

$$F_y = 0 = e [E_y - v_x B_z]$$

for the geometry below.

Figure 2



Therefore,

$$E_y = v_x B_z$$

Now the velocity is equal to the current density divided by the number of carriers times their charge or

$$v_x = \frac{j_x}{ne}$$

where n is the number of carriers per cubic centimeter and e is their charge.

Thus the transverse component of the electric field is

$$E_y = \frac{j_x B_z}{ne}$$

The ratio of the transverse component of the electric field to the product of the longitudinal component of the current density times the magnetic field strength is defined as the Hall coefficient R_H .

$$R_H = \frac{E_y}{j_x B_z}$$

With the geometry defined as in Figure II, the current density is given by

$$j_x = \frac{I_x}{WT}$$

and the Y component of the electric field is

$$E_y = \frac{V_m}{T}$$

where I is the current in the X direction

and V_m is the measured transverse voltage. Thus

$$R_H = \frac{V_m W}{I B}$$

After changing this to practical units, we have

$$R_H = \frac{10^8 \times V \times W}{I \times B}$$

where V is in volts

W is in centimeters

I is in amperes

and B is in oersteds

In addition to this primary electromagnetic effect, there are associated thermo electric and thermo magnetic effects which enter into the problem of measuring the transverse voltage. These secondary effects (24) are the Ettingshausen effect, the Nernst effect, the Righi-Leduc effect, and for the lack of a definite name in the literature, the I R drop.

The Ettingshausen effect states that a permanently maintained temperature gradient will appear if an electric current is subjected to a magnetic field perpendicular to its direction of flow. This temperature gradient is

calculated from the relationship

$$\Delta T = \frac{a}{b} PIH$$

where a is the width of the specimen

b is its thickness

I is the current

H is the magnetic field strength

and P is the Etingshausen coefficient.

The Nernst effect is the name associated with the potential gradient which appears in the Y direction if a thermal current flows in the X direction and a magnetic field is applied in the Z direction. The Nernst effect is governed by the equation

$$E_n = Q \frac{W H}{k}$$

where W is the thermal current density (defined as the product of the temperature gradient and the thermal conductivity)

E_n is the Nernst potential gradient

k is the coefficient of thermal conductivity

and Q is the Nernst coefficient.

The Righi-Leduc effect produces a temperature gradient in the Y direction when a thermal current flows in the X direction and a magnetic field is in the Z direction. This is governed by the relationship

$$T = S \frac{W H a}{k}$$

where T is the temperature difference between edges of the sample

and S is the Righi-Leduc coefficient.

The fourth associated effect occurs because of the possibility of a

voltage drop between the Hall probes before the magnetic field is imposed on the specimen.

From an analysis of the preceding relationships, it can be seen that the measured transverse voltage is in reality the sum of several terms.

Thus,

$$V_{m1} = V_H + V_E + V_N + V_{RL} + V_{LR}$$

where the subscripts are self explanatory. Of these five terms, the Hall voltage and the Ettingshausen voltage are dependent on both the current and the magnetic field strength. The Nernst and Righi-Leduc voltages depend on the magnetic field only, and the IR drop on the current only. Thus if both the current and magnetic field are reversed, then the expression becomes

$$V_{m2} = V_H + V_E - V_N - V_{RL} - V_{LR}$$

Therefore,

$$V_H + V_E = \frac{V_{m1} + V_{m2}}{2}$$

The relative magnitude of the Ettingshausen voltage will be discussed later.

B. Wave Formulation of Hall Effect

From an analysis of the expression for the Hall coefficient

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

where N is the density of carriers it can be seen that the Hall effect will be negative for conduction by negative particles. But as we have seen, several elements such as beryllium, zinc and cadmium show a positive Hall coefficient which would seem to indicate conduction by positive particles. This dilemma was not solved satisfactorily until the band theory of solids was introduced.

With the advent of quantum mechanics, the electron came to be regarded

as having the characteristics of both a particle and a wave. In this formalism, the current density j is given by

$$j = Ne v_k$$

where N and e have the same meaning as before and v_k is the average velocity of the conducting particles as a function of the wave vector k .

It may be shown ⁽²⁶⁾ that the velocity of a conducting particle is given by the expression

$$v_k = \frac{1}{\hbar} \nabla_k E(k) \quad (\text{Eq. 1})$$

where \hbar is Planck's constant divided by 2π , and $E(k)$ is the energy of the electron as a function of k .

The validity of this expression for a free electron moving in the X direction can be easily verified. The energy in such a case is

$$E(k) = \frac{\hbar^2 k_x^2}{2m}$$

Therefore

$$v_x = \frac{1}{\hbar} \frac{\partial}{\partial k_x} \left[\frac{\hbar^2 k_x^2}{2m} \right] = \frac{\hbar}{m} k_x$$

or,

$$v_x = \frac{P_x}{m}$$

where P_x is the electron's momentum in the X direction and m is its mass.

Now let the particle be accelerated by an electric field F .

Then

$$e F \cdot v_k = \frac{d E(k)}{dt}$$

Now from our equation (1)

$$\frac{dv_k}{dt} = \frac{1}{\hbar} \nabla_k [e F \cdot v_k]$$

and substituting for v_k from Eq. 1

$$\frac{dv_k}{dt} = \frac{1}{\hbar^2} e F \cdot \left[\nabla_k^2 E(k) \right]$$

From analogy with Newton's second law of motion, the term

$$\frac{\hbar^2}{\nabla_{\mathbf{k}}^2 E(\mathbf{k})} = m^*$$

is known as the effective mass.

The term $\nabla_{\mathbf{k}}^2 E(\mathbf{k})$ is evidently the curvature of $E(\mathbf{k})$ in \mathbf{k} space.

It has been shown by Bloch⁽²⁵⁾ that the motion of electrons in an ideal periodic three dimensional potential is modified from the usual parabolic $E(\mathbf{k})$ versus \mathbf{k} curve. With the banding occurring as the solid is formed, the curvature at the top of the bands becomes negative. Thus the acceleration of a particle at the top of a band will be in the opposite direction to the applied force.

This concept is usually replaced by that of positive holes which act as positively charged particles when conduction takes place near the top of the band.

There are several other Hall effect formulas which we wish to derive here. The Hall angle Θ is defined as $= \frac{\mu_H H}{c}$ in absolute esu and emu units⁽²⁶⁾, where μ_H is the Hall mobility.

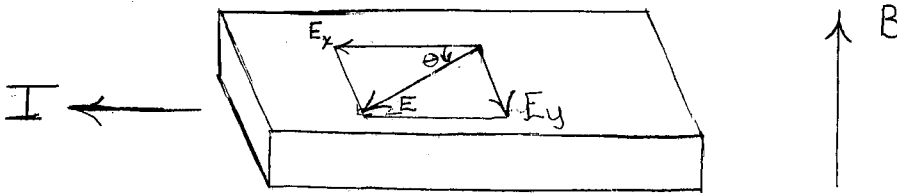


FIGURE 3

The above figure represents the Hall angle geometrically. It is seen that the $\tan \theta = \frac{E_y}{E_x}$, or for small angles, $\theta E_x = E_y$. Also the current density $j_x = \frac{E_x}{\rho}$. Therefore, $\theta j_x \rho = E_y$ or $\mu_H \rho = \frac{E_y c}{j_x H}$. But $\frac{E_y c}{j_x H}$ is the definition of the Hall constant R_H . Therefore $R_H = \mu_H \rho$ in mks units.

This gives us a measure of the number of carriers. It also enables us

to calculate the mobility if we know the resistivity of the sample. However, there are several other parameters of semiconductors which are of interest and which can be determined indirectly from the Hall effect data. These are the densities of acceptor and/or donor levels and the effective mass of the carriers. To derive expressions for these properties we must use Fermi-Dirac statistics.

The number and location of the quantum states in a solid can be shown to be essentially independent of the temperature. However, the population of these states does vary with the temperature. The function which helps us to describe this relationship is known as the Fermi-Dirac function which is defined as follows:

The value of the Fermi-Dirac function is the probability that under thermal equilibrium a quantum state of energy E is occupied by an electron (26).

Two properties of this definition should be noted. One of these is that the Fermi function is only defined for equilibrium conditions. The second condition is that it is a probability statement. A further definition is also needed—that of the Fermi level. The Fermi level is defined as the energy level for which the Fermi function has a value of $\frac{1}{2}$ and is denoted by E_F .

The Fermi function is expressed by the equation:

$$f = \frac{1}{1 + \exp \frac{E - E_F}{kT}}$$

If E is larger than E_F by several times kT , then $f \cong e^{-\frac{E - E_F}{kT}}$ which is the same distribution of electrons which is given by Maxwell-Boltzmann statistics.

If f is the probability that a state is occupied by an electron,

the probability that it is empty or in other words, occupied by a hole, is given by $f_p = 1 - f = \frac{1}{1 + \exp((E_F - E)/kT)}$

Let us now derive an expression for the density of holes in the valence band per unit volume in the crystal. This can be found from the product of the Fermi function for holes times the density of states in the valence band or $p = \int_{E_v}^{-\infty} N(E) \cdot f_p dE$ where $N(E)$ is the distribution of energy states; and E_v is the value of the energy at the top of the valence band.

It can be shown⁽²⁶⁾ that $N(E)$ is given by

$$N(E) = \frac{4\pi}{h^3} (2m^*)^{3/2} [E - E_v]^{1/2}$$

Therefore

$$p = \frac{4\pi (2m^*)^{3/2}}{h^3} \int_{E_v}^{-\infty} [E - E_v]^{1/2} e^{-\frac{E_F - E}{kT}} dE$$

Making the substitution $E_1 = E - E_v$, Then

$$p = \frac{4\pi (2m^*)^{3/2}}{h^3} e^{-\frac{E_F}{kT}} \int_{E - E_1}^{-\infty} E_1^{1/2} e^{\frac{E_1 + E_v}{kT}} dE_1$$

or

$$p = \frac{4\pi (2m^*)^{3/2}}{h^3} e^{\frac{E_F - E_v}{kT}} \int_0^{\infty} E_1^{1/2} e^{-\frac{E_1}{kT}} dE_1$$

and after evaluation of the integral,

$$p = 2 \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} e^{-\frac{E_F - E_v}{kT}}$$

Now let us consider the case of a semiconductor with an acceptor level at E_a and a donor level at E_d . The condition of electrical neutrality demands that the total number of positive charges must equal the total number of negative charges or

$$n + n_d + N_a = p + p_a + N_d$$

where n is the number of free electrons per unit volume

n_d is the number of excess electrons trapped in donor sites per unit volume.

N_a is the number of acceptor levels per unit volume

p is the number of free holes per unit volume

P_a is the number of excess holes trapped in acceptor levels per unit volume

and N_d is the number of donor sites per unit volume.

Let us consider the case where n and n_d are negligible compared with the number of free holes. Then our equation for electrical neutrality becomes $p_a = N_a - N_d - p$

An alternate expression for the number of excess holes in acceptor levels is given by the density of acceptor levels times the probability that they are occupied or $p_a = f N_a$ where $f = \frac{1}{1 + e^{\frac{E_F - E_a}{kT}}}$ since in this case $E = E_a$.

This equation allows us to obtain an expression for the difference $E_F - E_a$ which is given by $E_F - E_a = kT \ln \frac{1 - f}{f}$

From the previous equation it can readily be seen that $f = \frac{N_a - N_d - p}{N_a}$

Substituting this value for the Fermi function into our expression for the Fermi level and simplifying, $E_F = E_a + kT \ln \left[\frac{N_d + p}{N_a - N_d - p} \right]$.

But we have seen that $p = \left(\frac{2 \eta^* mkT}{h^2} \right)^{3/2} e^{-\left(\frac{E_F - E_v}{kT} \right)}$

Substituting our value for the Fermi level into the expression for the density of holes, we obtain the expression

$$p = \left(\frac{N_a - N_d - p}{N_d + p} \right) \left(\frac{2 \eta^* mkT}{h^2} \right)^{3/2} e^{-\left[\frac{E_a - E_v}{kT} \right]}$$

The difference $E_a - E_v$ is denoted by ϵ and is defined as the activation energy or the amount of energy needed to release a hole from an acceptor level for conduction in the valence band.

Therefore,

$$p = \left(\frac{N_a - N_d - p}{N_d + p} \right) \left(\frac{2 \pi m^* k T}{h^2} \right)^{3/2} e^{-\left(\frac{\epsilon}{kT} \right)}$$

At low temperatures, N_a and $N_d \gg p$ the above equation then reduces to

$$(T)^{-3/2} p = \left(\frac{N_a - N_d}{N_d} \right) \left(\frac{2 \pi m^* k}{h^2} \right)^{3/2} e^{-\left(\frac{\epsilon}{kT} \right)}$$

We have seen previously that

$$p = \frac{1}{R_H e}$$

The above equation thus becomes

$$\frac{1}{R_H T^{3/2}} = K e^{-\frac{\epsilon}{kT}}$$

where

$$K = \frac{N_a - N_d}{N_d} \left(\frac{2 \pi m^* k}{h^2} \right)^{3/2}$$

Taking the natural logarithm of both sides of the preceding equation,

$$\ln R_H T^{3/2} = \ln K + \frac{\epsilon}{k} \left(\frac{1}{T} \right)$$

Thus a plot of the natural logarithm of the product of the Hall constant and the absolute temperature to the 3/2's power versus the inverse absolute temperature yields as a slope at low temperatures the value $\frac{\epsilon}{k}$.

The number of carriers per unit volume as a function of temperature can be determined from the relationship $p = \frac{1}{R_H e}$. From the expression

$$p = \frac{N_a - N_d - p}{N_d + p} \left(\frac{2 \pi m^* k T}{h^2} \right)^{3/2} e^{-\left(\frac{\epsilon}{kT} \right)}$$

we find the values of the densities of acceptor and donor levels and also the effective mass.

C. Corrections to Hall Effect Equations

It will be noted that the expression for the number of free holes per unit volume which we used above lacked a factor of two which is often found

because of the possibility of spin in both directions by a hole. But let us examine this more carefully. Consider a donor level which can trap one electron. The probability that the j th energy level is occupied is given by (27)

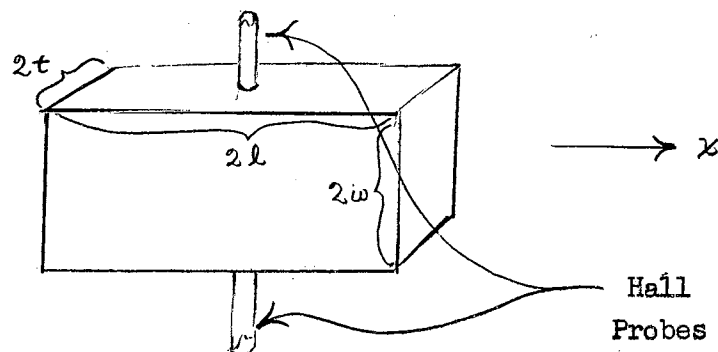
$$f_j = g_j e^{(E_f - E_j)/kT} / \left(1 + \sum_j g_j e^{(E_f - E_j)/kT} \right)$$

where g is the degeneracy of the level. The total probability that the donor atom has a bound electron is given by $f = \sum_j f_j$

$$f = \left[\frac{1 + e^{(E_d - E_f)/kT}}{g_D} \right]^{-1}$$

The factor g_D is usually taken to be 2 (27). This cancels the factor of two which is present in the allowed energy state.

There is one further correction which must be considered. This is due to the finiteness of the sample and the resulting edge effects. Consider the following experimental model.



Because of the Hall field, the edges of the sample become charged, producing an electrostatic field which can be found from E (the Hall field) and the boundary conditions. The quantity measured experimentally is the transverse potential-difference. $V_m = - \int_{-w}^w E_y dy$ as a result of the electrostatic field where V_m is the voltage measured.

Since the electrostatic field E has as its source the charge distribution on the surface the two conditions which must be satisfied are

$\nabla \times \mathbf{E} = 0$ and $\nabla^2 \mathbf{E} = 0$ in the interior of the sample. 2.

The Y component of the electrostatic field must satisfy $\nabla_y^2 E_y(x, y) = 0$ for the boundary conditions.

$$E_y(\pm 1, y) = 0$$

$$E_y(x, \pm w) = 0$$

Where the Hall probes make contact at $x = 0$, $y = \pm w$ and electrodes which have high conductivity compared to the sample make contact at $x = \pm 1$.

The solution of 2 satisfying these conditions is given by

$$E_y = \frac{4E}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k}{2k+1} \left\{ \frac{\cosh \frac{2k+1}{2} \pi \frac{y}{1} \cos \frac{2k+1}{2} \pi \frac{x}{1}}{\cos \frac{2k+1}{2} \pi \frac{w}{1}} \right\}$$

The Hall voltage V_H is given by $V_H = 2wE = \frac{R_H BI}{2t}$

$$\text{where } E = R_H \mathbf{j} \times \mathbf{B}$$

Then

$$\frac{V_m}{V_H} = \frac{8}{\pi^2} \frac{1}{w} \sum_{k=0}^{\infty} \left\{ \frac{(-1)^k \tanh \frac{2}{2k+1} \pi \frac{w}{1}}{(2k+1)^2} \right\} \cos \frac{2k+1}{2} \pi \frac{w}{1}$$

Thus from a plot of $\frac{V_m}{V_H}$ versus $\frac{w}{l}$, the relationship between V_m and V_H for any particular crystal dimensions can be found. In our case the Hall voltage is $\frac{V_m}{V_H}$ if the sample is assumed to be 6.5mm long and is equal to $\frac{V_m}{V_H} \cdot \frac{.98}{.7}$ if it considered to be 4.5mm long.

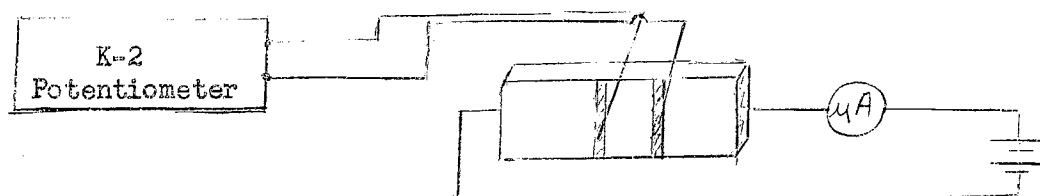
CHAPTER III

1. Sample Description

The one sample investigated was a regular parallelepiped measuring 6.5 x 3.51 x 2.25mm. The sample could be visually divided into two portions, a blue end and a white end. The blue end has a light blue coloration which is easily visible under normal illumination. Visually, its length has been estimated to be approximately 2 mm.

2. Resistivity

Resistivity measurements were made on the sample using a direct current, potential probe method. The following circuit was used.



Due to the relatively high resistivity of the sample, it was necessary to make contacts by means of silver paint, Du Pont 4817. The current contacts were made by painting the whole surface at both ends. The potential probe contacts were made by painting strips on the surface. The probes were then lowered onto the painted strips. The potential difference between the strips was measured by means of a Leeds and Northrup K-2 potentiometer. The resistivity was then calculated by means of the equation $\rho = \frac{V}{I} \frac{A}{l}$, where V is the voltage between the strips, I is the current in the sample, A is the total cross sectional area, and l is the distance between the strips. This method of measuring resistivity assumes that the lines of flow are parallel and that the strips do not disturb the field. The first of the conditions is probably closely approximated by painting the ends of the diamond completely. However,

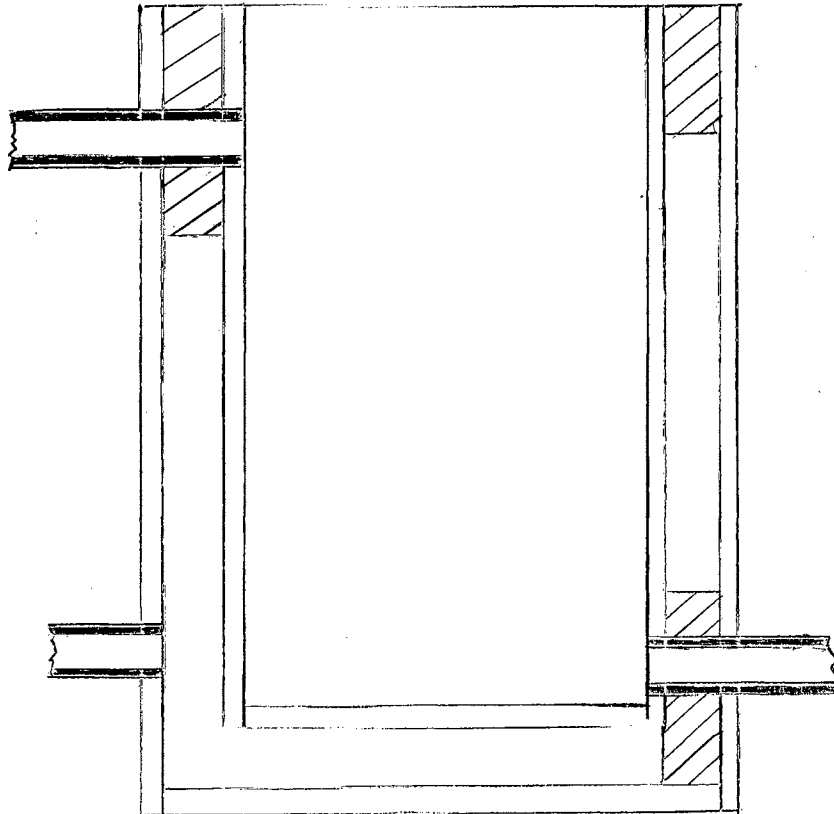
the second condition must be assumed. It was necessary to make the strips of an appreciable width in order to reduce the contact resistance.

The diamond itself could be divided into a blue and a white end on the basis of resistivity. The resistivity of the blue end was found to be much less than that of the white end. In spite of this difference in conductivity, there was no discernible rectification over the junction between the two sections. This could be due to a relatively gradual change in carrier concentration corresponding to a barrier with an appreciable width.

The resistivity along the 6.5 mm dimension in the white end was also found to be different from the resistivity of the 3.5 mm dimension. Unfortunately the surface resistance of the 2.2 mm dimensions precluded any attempt to measure its resistivity. All attempts to make contacts on the smallest dimension resulted in contact resistances which were too high for any appreciable current to deflect the galvanometer.

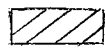
3. Hall Measurement Apparatus

The Hall sample holder consisted of two parts. The outer container (Fig. 4) was a nickel silver double walled can with provisions made for evacuating the space between the cans. The joints were silver soldered because of the temperature we wished to attain. The fillers indicated in Fig. 4 were made of insulating fire brick. These were used to insulate the inner and outer cans from each other. There was a problem involved in the use of the fire brick since it was porous in nature. There was a problem involved in evacuating the space between the inner and outer container. This was surmounted by sealing the insulating brick fillers with applications of Sauereisen cement, a cement of good insulating qualities. This enabled us to obtain a fairly good vacuum between the cans. However, this

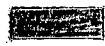


Legend:

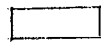
Scale 1:1



Fire brick



Copper tubing



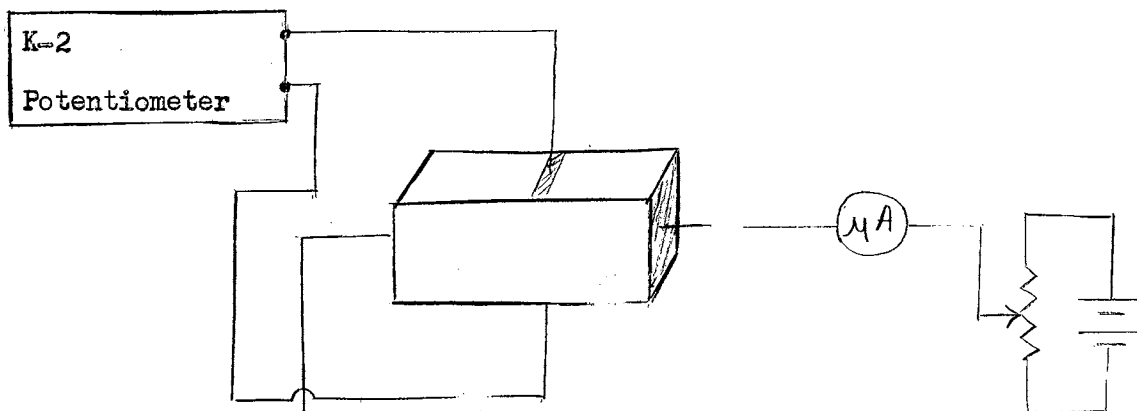
Nickel silver

Figure 4 Cutaway view of outer portion
of Hall effect apparatus

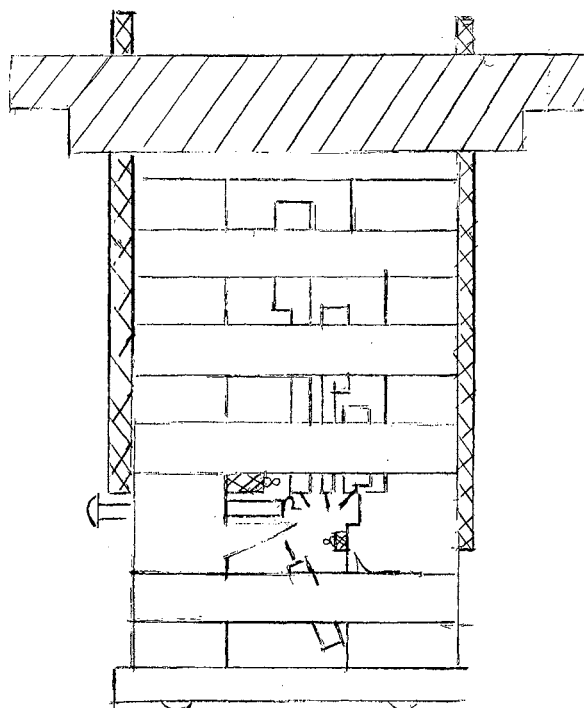
evacuation was subsequently found to be unnecessary in our temperature range. The gas inlet, exhaust, and the evacuation tubes were made of copper which was silver soldered to the inner container and entered the outer can through plugs of the insulating fire brick.

Figure 5 shows the Hall mount itself. The main body of the mount is nickel silver with the top being insulating fire brick. The cross members were insulated from the rest of the apparatus by mica washers, and the brass screws at the top and bottom insulated from the top and bottom member by glass inserts. The contacts themselves were made of constantan wire, and the thermocouples were of copper and constantan.

The following circuit was used to measure the Hall Effect.




The galvanometer used in the potentiometer circuit was a Leeds and Northrup current sensitive galvanometer, serial number 624261. A current sensitive galvanometer was used because of the high contact resistance encountered in the Hall probes. The magnet was a Varian Associates magnet, Model 4004. The current for the magnet was furnished by a bank



Legend:

Scale 1:1

 Fire brick

 Ceramic


 Nickel Silver

Figure 5 Side View of Hall mount
showing position of thermocouples

of wet cell batteries. The magnetic field was calibrated for a fixed air gap of 1.4 inches by means of a search coil of 91 turns and a ballistic galvanometer, Leeds and Northrup serial number 405720. Figure 6 shows the relationship between the current in the magnet coil and the field intensity. Most of the Hall data were taken with a magnet current of 5.5 amps and a magnetic field intensity of 6950 oersted. Room temperature measurements of the Hall coefficient for fields varying from 1150 to 8020 oersteds indicated that the Hall coefficient over this range of magnetic field strength was essentially constant.

The diamond was heated during the Hall measurements by means of a flow of hot nitrogen. The nitrogen was heated by passing it through a copper tube which was wound with nichrome wire. A constant current of approximately 11 amperes flowed through the nichrome heating element. The temperature was varied by controlling the nitrogen flow. It was found that in the temperature range from room temperature to 527° C the temperature in the diamond's surroundings after reaching an equilibrium condition remained constant throughout the course of the measurement process. Evacuation of the outer chamber was found to be unnecessary in this temperature range.

B. Results

1. Resistivity

Resistivity measurements revealed that the sample was far from being homogeneous. Measurements were made with current flowing along the 6.5 mm dimension or lengthwise and the 3.51 mm dimension or crosswise. All attempts to measure the resistivity with current flowing across the 2.25 mm dimensions were unsuccessful because the contact resistance was so high that no measurable current flowed through

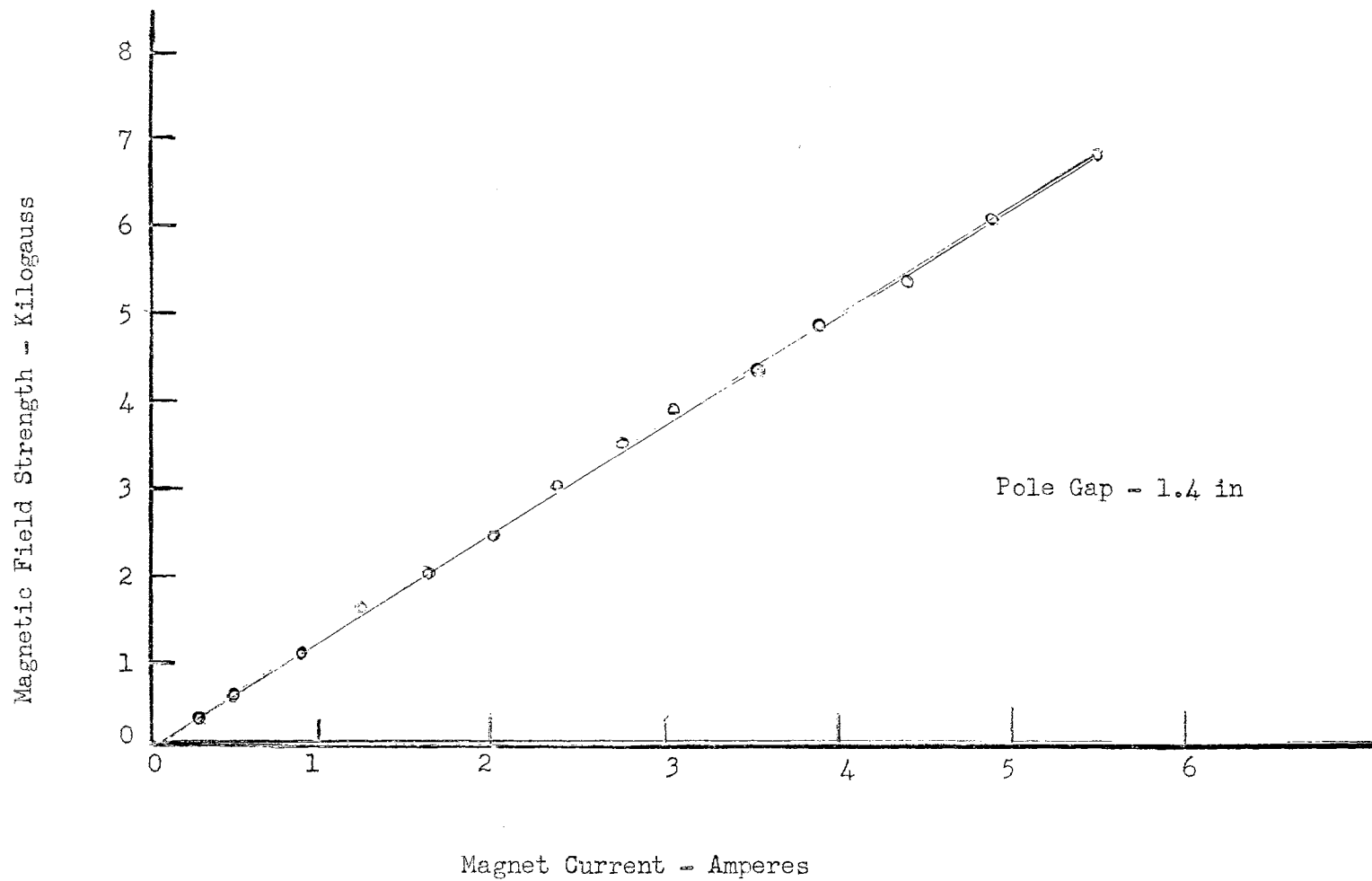


Figure 6 Calibration curve of magnet

the galvanometer circuit.

The following table summarizes the results of these measurements.

Table of Resistivities

Lengthwise		Crosswise	
section of diamond	Resistivity	section of diamond	Resistivity
blue end	62.6 ohm-cm	blue end	287 ohm-cm
white end	3.5×10^5 ohm-cm	white end	1.77×10^5 ohm-cm

Table 1

Although there were considerable differences in the resistivities for various directions, the values for the several sections were found to be self consistent within 5%. Thus the assumption that the white end is homogeneous at least in the lengthwise dimension seems to have some basis in fact. However, there is some question as to whether the measured resistivity is truly a bulk property or a surface phenomena. Johnson⁽⁶⁾ in his work on photoconductivity on the same sample has had some indication that the photoconductivity induced by visible irradiation may be due to surface effects. This may apply equally well to the resistivity measurements.

2. Hall Effect Measurements

Hall effect measurements were carried out in the temperature range from room temperature to 527° Centigrade. Throughout the entire temperature range, there was never a measurable difference between the readings of the three thermocouples. Thus there was no measureable Ettingshausen Effect and the voltage measured was essentially the Hall voltage only.

Figure 7 is a plot of the natural log of the product of the Hall coefficient and the absolute temperature to the three-halves power versus the inverse of the absolute temperature.

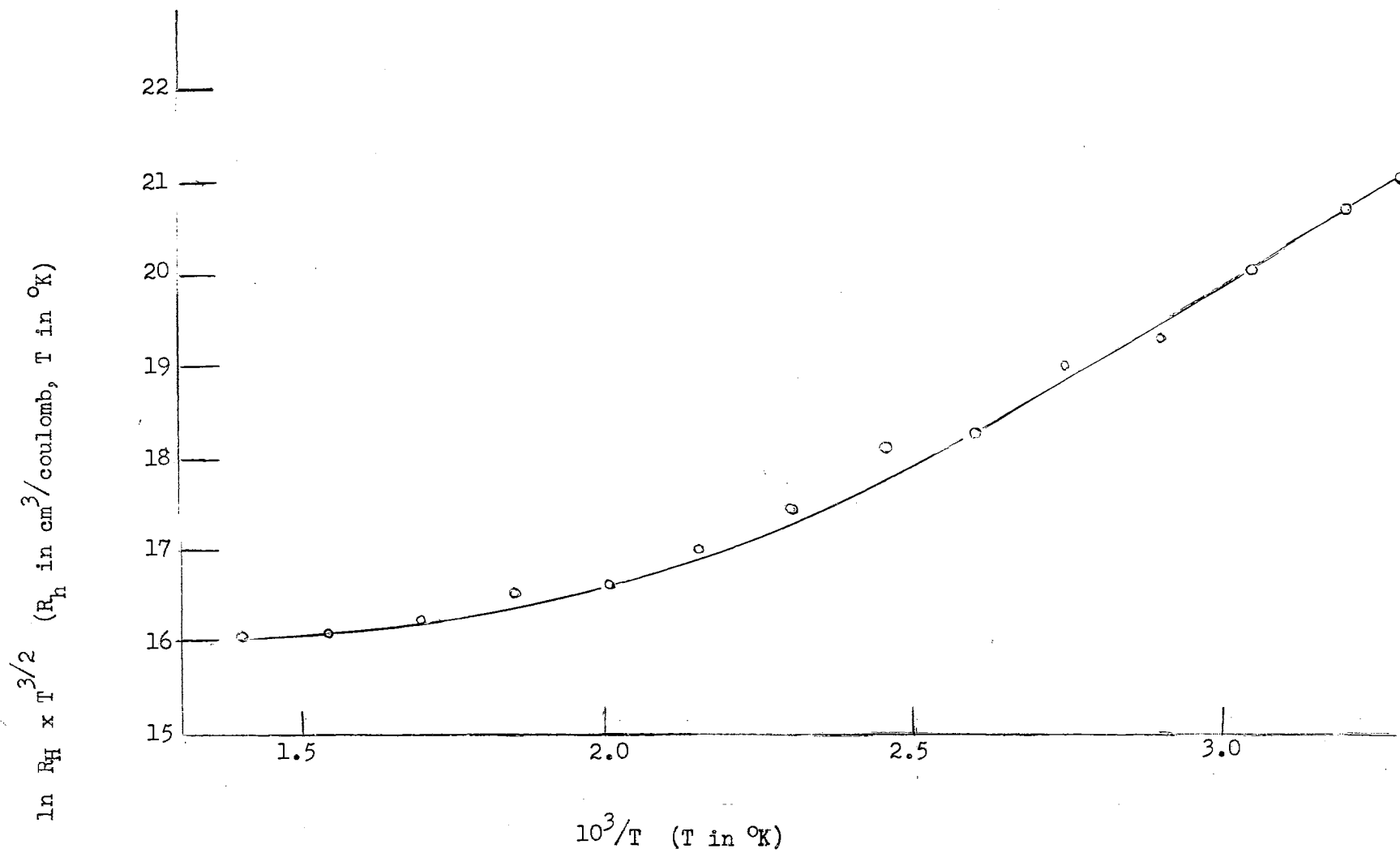


Fig. 7 Natural logarithm of Hall constant vs inverse absolute temperature.

CHAPTER IV

A. Discussion of Results

One of the most important parameters connected with impurity semiconductors is their activation energy. As was shown in Chapter II, this can be determined from the low temperature portion of the plot of the logarithm of the product of the Hall constant and the absolute temperature to the $3/2$'s power versus the inverse absolute temperature. Analysis of the straight line portion of Figure 7 shows an activation energy of 0.35 electron volts. This agrees with values reported by Brophy⁽¹⁸⁾, Austin and Wolfe⁽²¹⁾, and Wedepohl⁽²³⁾ from Hall Effect data and Leivo and Smoluchowski⁽¹⁷⁾, Custers⁽¹⁹⁾, and Austin and Wolfe⁽²¹⁾, from resistivity measurements. Stein^(3,4) obtained an absorption peak in the infrared at 0.35 electron volts using the same specimen. Concurrent studies of photoconductivity conducted by C. C., Johnson⁽⁶⁾ also on the same sample show a slight peak at 3.6μ at temperatures in the neighborhood of -114°C which corresponds to .345 electron volts. Calculation for a hydrogen-like atom in a dielectric of diamond gives an ionization potential of 0.4 electron volts. Thus it would seem that diamond is a chemically activated semiconductor.

There are several other parameters which can be determined by measurement of the Hall Effect as a function of the temperature. These values are dependent, however, on the model which is assumed. The first model which was investigated was the simplest possible one with one acceptor level and no donor levels.

Calculations of the effective mass were carried out using the relationship

$$p = N_a^{\frac{1}{2}} \left(2 \pi m^* kT / h^2 \right)^{3/4} e^{-\frac{\epsilon}{2kT}}$$

and led to a value of approximately 500 times the rest mass of the electron. Since this seemed rather improbable in the light of investigations in order semiconductors, another model was deemed necessary.

In the next model considered, there were two acceptor levels, one at 0.35 ev and the other at 2.2 ev. The latter energy level corresponds approximately to the photoconductivity peak in the visible range obtained by Bell⁽²⁾ and Johnson⁽⁶⁾. Analysis of this equation led to an effective mass for the holes of approximately 10^{-36} grams which seemed much too small.

Thus it seemed necessary to resort to a model containing both donor and acceptor levels. The simplest model of this sort contains one acceptor and one donor level with the acceptor level located at .35 ev. Unfortunately, some difficulty arose when attempting to solve this equation in closed form.

Substituting values for temperature and the corresponding density of holes in the equation

$$p = \frac{N_a - N_d - P}{N_d + p} \left(\frac{2 \pi m^* kT}{h^2} \right)^{3/2} e^{-\frac{\epsilon}{kT}} \quad \text{Eq. 3}$$

gave three equations in three unknowns, N_a , N_d , and m^* . However, when the equations were solved algebraically, one of the unknowns always had a minus value. This minus sign is inadmissible physically. It probably arose from the experimental deviation of the points from the theoretical curve. Thus a slight error in a point determined experimentally would cause the curve to fall on a theoretical curve which did not correspond to the physical situation.

Finally, the problem was solved by graphical means. Values for N_a , N_d , and m^* were substituted in Eq. 3 and the density of the carriers plotted as a function of the absolute temperature. A series of these theoretical curves were compared with the curve obtained experimentally until a good degree of agreement was reached. In Figure 8, the two

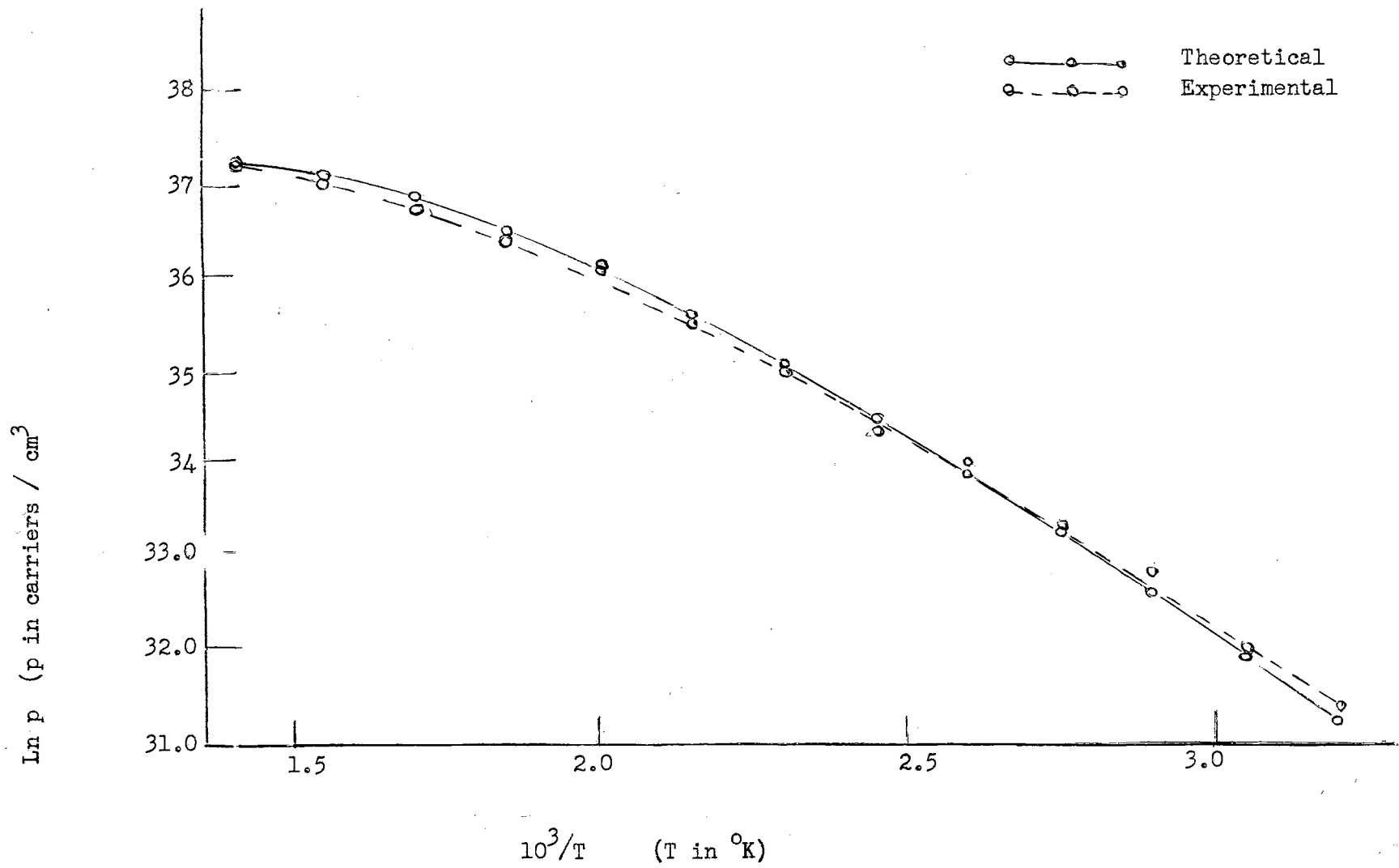


Figure 8 Experimental and Theoretical plot of $\ln p$ vs $1/T$

curves are shown. The values for the parameters for this experimental curve are

$$N_a = 3.25 \times 10^{16} / \text{cm}^3$$

$$N_d = 9.5 \times 10^{15} / \text{cm}^3$$

$$m^* = .6 m_e$$

The mobility of the majority carriers can be calculated from Hall Effect data by use of the expression

$$\mu N e = \sigma$$

Where μ is the mobility

N is the density of carriers

e is their charge

and σ is the conductivity.

As shown in Chapter II, the Hall constant

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

Since the conductivity is the reciprocal of the resistivity,

$$\mu = \frac{R_H}{\rho}$$

Since our Hall constant was measured on the white end, we first used in the above calculations the value of resistivity for the white end. This yielded a value for the mobility of $0.75 \text{ cm}^2 / \text{volt-sec}$. The accepted value for mobility of holes in diamond is approximately $1500 \text{ cm}^2 / \text{volt-sec}$. If, however, a value of resistivity of 200 ohm-cm , intermediate between that of the blue end and that of the white end, is used, then the value of mobility of $1375 \text{ cm}^2 / \text{volt-sec}$ is obtained.

This seeming discrepancy could possibly be explained as follows. If the static charge which produces the Hall voltage tends to diffuse over the surface until a uniform surface charge distribution is reached, then the

measured Hall voltage would be an average value between the true Hall voltages associated with each end. If this were the case, a value for the resistivity somewhere between the values of the two portions of the diamond should be used to calculate the mobility.

If the above explanation were the correct one, then it would be possible to experimentally verify it since the Hall constant would be independent of position on the crystal. Therefore, measurements of the Hall constant were taken at the blue end and were found to agree with those taken on the white end, the agreement being within 6.4%.

B. Suggestions for Future Studies

There are several further studies which are direct measurements of quantities present in the Hall effect equations which would prove profitable. Two of these are direct measurement of the mobility and the effective mass of the majority carriers.

There is still much work to be done on the percentage of conductivity which is due to surface conditions. A plot of the Hall constant versus length along the crystal would yield interesting data as to the approximate distribution of surface charge between the distinct regions. This would afford an insight into the possible reasons for this difference in conductivity. Measurements of optical absorption by Stein⁽⁴⁾ on the blue end of our sample indicated the possibility that the white end has less impurities than the blue end. This could be confirmed by the above mentioned Hall measurements.

Type IIb diamonds exhibit an interesting electroluminescence. A similar electroluminescence can be induced in Type I diamonds by suitable electrode painting. This investigation would also be of great interest. Studies of the decay time in phosphorescence would yield some information

concerning lifetimes inclusive of trapping. Finally, from a more theoretical standpoint, there is much work to be done on transition probabilities in diamond.

BIBLIOGRAPHY

1. Bell, M. D. and W. J. Leivo. "Rectification and Photovoltaic Effect in Semiconducting Diamond." Bulletin of the American Physical Society, (April 1957), No. 4.
2. Bell, M. D. "Rectification and Photoeffects in Semiconducting Diamonds." (Unpublished Master's Thesis, Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma, August 1956.)
3. Stein, H. J. and W. J. Leivo. "Optical Absorption in Semiconducting Diamond." Bulletin of the American Physical Society, (March 1956), No. 3.
4. Stein, H. J. "Optical Properties of a Semiconducting Diamond." (Unpublished Master's Thesis, Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma, 1957.)
5. Bell, M. D. and W. J. Leivo. "Photoconductivity in Type II b Diamonds." Bulletin of the American Physical Society, (December 1956), No. 8.
6. Johnson, C. C. "Photoconductivity in Semiconducting Diamonds." (Unpublished Master's Thesis, Oklahoma State University of Agriculture and Applied Science, Stillwater, Oklahoma, May 1958.)
7. Johnson, C. C. and W. J. Leivo. "Photoconductivity in Semiconducting Diamonds." Bulletin of the American Physical Society, (March 1958), No.
8. Wayland, John. "Measurement of Carrier Lifetimes in Semiconducting Diamond." (Unpublished Master's Thesis, Oklahoma State University of Agriculture and Applied Sciences, Stillwater, Oklahoma, 1958.)
9. Campbell, L. L. Galvo and Thermomagnetic Effects, (Longman, Green and Co., New York, 1923.)
10. Baedeker, K. Ann. Physik, 29 (1909), 566.
11. Baedeker, K. Physik Z., 13 (1912), 1080.
12. Custer, J. F. H. and F. A. Raal. "Fundamental Absorption in Diamond." Nature, Vol 179 (1957), 268.
13. Chesley, F. G. "Investigation of the Minor Elements in Diamond." Amer Min., 546 (1947), 309.
14. Raal, F. A. "A Spectrographic Study of Minor Element Content of Diamond." Amer. Min., 546 (1957), 309.

15. Custers, J. F. H. "Unusual Phosphorescence of a Diamond." Physica, 18 (1952), 489.
16. Custers, J. F. H. "Type II b Diamond." Physica 20, (1954) 183.
17. Leivo, W. J. and R. Smoluchowski. "A Semiconducting Diamond." Phys. Rev., 98 (1955), 1532 (A).
18. Brophy, J. J. "Preliminary Study of the Electrical Properties of a Semiconducting Diamond." Phys. Rev., 98 (1955), 1532.
19. Custers, J. F. H. "Semiconductivity of a Type II b Diamond." Nature, Vol. 176 (1955) 173.
20. Personal Communication between J. F. H. Custers and W. J. Leivo communicated to the author by W. J. Leivo.
21. Austin, I. G. and R. Wolfe. "Electrical and Optical Properties of a Semiconducting Diamond." Phys. Rev., 99 (August 1955), 1336.
22. Dyer, H. B. and P. T. Wedepohl. "Electrical Measurements on Type IIb Diamonds." Proc. Phys. Soc., (London), B 69 (March 1956), 410.
23. Wedepohl, P. T. "Electrical and Optical Properties of Type II b Diamond." Proc. Phys. Soc., (London) B 70 (1957) 177.
24. Lindberg, O. "The Hall Effect." Proc. Inst. Radio Engrs. 40, (1952) 1414.
25. Bloch. F. Zeit fur Physik 52 (1928), 555, as cited in Kittel Introduction to Solid State Physics, (John Wiley & Sons, Inc. New York, 1953.)
26. Schockley, W. Electrons and Holes in Semiconductors. (D. Van Nostrand Company, Inc., New York 1950.)
27. Fan, H. Y. Solid State Physics, (Vol 1 Academic Press Inc. New York 1955.)

Appendix A - Discussion of Magnitude of Hall voltages.

At a magnetic field strength of approximately 6000 oersteds and a temperature of 310°K, the measured Hall voltages were equal to 235 μ volts with a current of 10 μ amperes. Since there was always some transverse IR drops present across the crystal, the actual potentiometer readings were higher. For example, with the above conditions, the Hall voltages measured were the differences divided by two of readings of 69.74 mv and 69.27 mv.

The above measurements were made with a potentiometer of the type used in the experiment. The potentiometer was calibrated with a standard cell of 1.018 v. The potentiometer was used in the following manner: The crystal was placed in a magnetic field of 6000 oersteds and a current of 10 μ amperes was passed through it. The Hall voltage was measured by the potentiometer. The potentiometer was then reversed and the same measurements were made. The difference between the two readings was divided by two to give the Hall voltage.

VITA

Thomas Young

Candidate for the Degree of

Master of Science

Thesis: THE HALL EFFECT IN SEMICONDUCTING DIAMOND

Major Field: Physics

Biographical:

Personal data: Born in Waltham, Massachusetts, July 18, 1932, the son of Jessie and Thomas Young.

Education: Received primary education in the public schools of Watertown, Mass. Graduated from St. Mary of the Assumption High School in Brookline, Mass. Received the Bachelor of Science degree from Boston College in June 1954, with a major field of Physics and a minor in Mathematics and Philosophy. Completed requirements for the Master of Science degree Oklahoma State University in August 1958.

Experience: Entered the United States Army in October 1954. Served with the 617th FAOB BN at Fort Sill, Oklahoma, as a radio repairman. Was discharged in August 1956.

Organizations: Member of Sigma Pi Sigma, American Institute of Physics, and the American Physical Society.