THE DETERMINATION OF IMPURITY CONCENTRATIONS

IN SILICON

by

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ABSTRACT

Due to the small concentration of impurities normally present in semiconductors these impurity concentrations cannot be measured by ordinary chemical analysis. Electrical methods are the common way by which semiconductor impurity concentrations are measured.

The specific problem investigated was to determine the concentration N_d of donors and the concentration N_a of acceptors at various points in a crystal of silicon.

A description of the crystal structure and the energy band scheme of silicon is given. The density of states in the conduction and valence bands is calculated. The population of the conduction and valence bands by electrons and holes as a function of impurity concentration and temperature is derived.

A method is given from which the values of N_d and N_a may be found from Hall constant measurements at liquid nitrogen and room temperatures.

The experimental apparatus used includes a magnet, cryostat, sample holder, and Hall measuring circuit.

The results obtained from the measurements are in

agreement with those expected from the available knowledge
of the method of crystal growth.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

ACKNOWLEDGEMENTS

CHAPTER I

BASIC THEORY

1. INTRODUCTION

Silicon is one of the more common semiconductors being studied at the present time. The semiconducting properties of silicon are determined by its electron configuration and its crystal structure. The outer or valence shell of the silicon atom contains four electrons. In the silicon crystal these four electrons combine with those of other atoms to form covalent bonds which bind the atoms into the crystal structure. A two dimensional schematic drawing of the silicon crystal structure is shown in figure 1. Each pair of lines represents a covalent bond between atoms. In reality the four neighbouring silicon atoms are at the four corners of a regular tetrahedron with respect to any atom taken as a centre. In the remaining discussions on the properties of semiconductors it shall be assumed that the crystals being dealt with are single crystals, that is they retain their periodic structure throughout the crystal.

The solution of the Schrödinger wave equation in a periodic structure with its corresponding periodicity of potential gives a series of allowed energy bands within
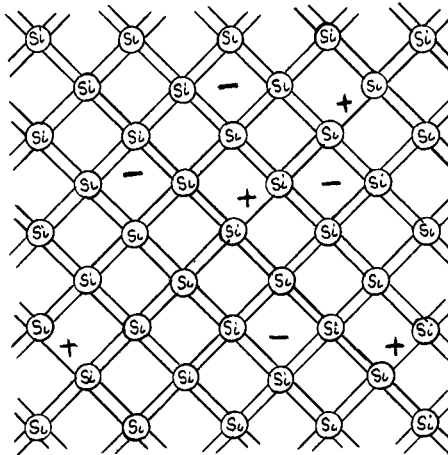
(a)   PURE   SILICON   WITH   ELECTRONS   AND HOLES
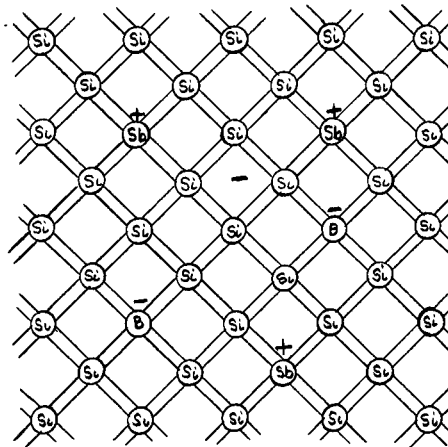
(b) SILICON   DOPED   WITH   ANTIMONY   AND BORON

FIGURE   I

which the energy of the electrons of the crystal must lie. These bands may or may not be separated by a forbidden energy gap, that is a band of energies which an electron cannot possess. The solutions will be of the form $E_\beta(\overline{K})$, where $\overline{K}$ is the wave vector of the electron and β refers to the particular energy band. $\overline{K}$ is restricted to the first Brillouin zone of the reciprocal lattice space to prevent discussing physically equivalent solutions for different values of $\overline{K}$. In a semiconductor the energy bands of greatest interest are the valence and conduction bands. The valence band is the highest energy band which is populated with electrons when they are in their lowest total energy configuration, that is at $T = 0°K$. In a semiconductor the valence band is completely filled under these circumstances. The band next highest in energy to the valence band is known as the conduction band. The forbidden energy gap between the valence and conduction bands in semiconductors is of the order of 1 eV. An electron with an energy in the valence band is equivalent to one which is bound in a covalent band with an electron of a neighbouring atom.

When an energy band is completely filled all the allowed energy states in the band are occupied. The electrons are then unable to acquire an energy in the band different from that which they possess. There can then be no net flow of charge and therefore no electric current. If, however, a

valence band electron acquires enough energy to be excited into the conduction band then only a small change in energy is required for it to move from one state to another within the conduction band. Energy states are available to which it can move. The electron can then move under the influence of an applied electric field, contributing to electrical conduction. This is equivalent to a valence electron breaking its covalent bond and becoming free to move throughout the crystal. Due to the periodic potential in which they exist, the electrons do not move as if they have the free electron mass m_o, but rather as if they have an effective mass m^*_{eij} which is a tensor quantity. At the bottom of the conduction band the effective mass is given by

$$\frac{1}{m^*_{eij}} = \frac{1}{h^2} \frac{\partial^2 E}{\partial K_i \partial K_j} \bigg|_{\overline{K}_o} \tag{1}$$

where $\overline{K}_o$ is the wave vector corresponding to the conduction band minimum.

At the same time as an electron is excited into the conduction band a vacancy occurs in the valence band. This leaves an unoccupied energy state into which an electron with an energy not much different from the empty state may easily move. As the electrons move to fill the vacancy the net effect is that of a positive charge of the same magnitude as the electronic charge moving throughout the crystal.

This can be seen by considering a crystal structure with one
of the valence electrons removed to the conduction band.
Then associated with the vacancy so produced will be a net
positive charge of magnitude q (q is equal to the magnitude
of the electron charge) due to the nucleus of the atom.
Since it only involves a small change in energy an electron
from a neighbouring covalent bond may move into that vacancy.
This can be seen to be equivalent to a positive charge q
moving with the vacancy. This apparent particle with posi-
tive charge is known as a hole. Similarly to the case of the
electron, the hole behaves as if it has a positive effective
mass. The value of the effective mass at the top of a non-
degenerate valence band is

$$\frac{1}{m^*_{pij}} = -\frac{1}{h^2}\frac{\partial^2 E}{\partial K_i \partial K_j}\Bigg|_{\overline{K}_o} \tag{2}$$

where $\overline{K}_o$ is at the valence band maximum.

When a semiconductor behaves as if no impurities are
present it is said to show intrinsic behaviour.

Consider a perfect crystal of silicon. Then replace
one of the silicon atoms by a group V atom such as antimony,
which has five electrons in its valence shell. Four of
these electrons will form covalent bands with the adjacent
silicon atoms. The remaining electron will be weakly bound
to the antimony atom. In the energy band scheme this is

equivalent to the extra electron being in an energy state
slightly below that of the conduction band. A small amount
of thermal energy will excite the electron into the conduc-
tion band. Such an impurity is called a donor impurity. It
is called a shallow donor because the donor energy level lies
very close to the bottom of the conduction band.

The effect of a low concentration of impurities in a
semiconductor may be quite marked. Since the donor electrons
require only a small amount of energy to be excited into the
conduction band compared with that required to excite the
valence electrons, it is reasonable to assume that a much
larger percentage of the donor electrons will be excited than
will be valence electrons. Therefore at appropriate tempera-
tures, a small concentration of donors could produce as many
as, or more conduction band electrons than the valence band.
Since the conductivity is dependent on the concentration of
carriers, the addition of a relatively few donor impurities
may cause great changes in the electrical conductivity.

Similarly a group III atom such as boron may replace a
silicon atom. The three valence electrons will form bonds
with three of the adjacent atoms. There is then produced an
energy level slightly above the top of the valence band into
which an electron may be thermally excited. This will create
a hole in the valence band. Such an impurity is known as an
acceptor impurity. If an electron moves from a donor to an

acceptor, then the impurity is said to be ionized. The pres-
ence of a relatively few acceptors will have a similar effect
to that of the donors.

Semiconductors to which impurities have been added are
said to be doped. When the electrical properties are domina-
ted by the presence of impurities the semiconductor is said
to show extrinsic behaviour.

Semiconductors may contain both donors and acceptors,
and, in general, one is interested in the behaviour of semi-
conductors as a function of the concentration of donors N_d
and the concentration of acceptors N_a. First one must find
the values of N_d and N_a by some means. The problem of this
thesis is to find N_d and N_a at various points within a crystal
of silicon. In order to do this the energy band scheme of
silicon and the effect of impurities on certain properties
must be known. These will be discussed in the rest of this
chapter. In chapter II the method of analysis will be out-
lined, and in chapter III the experimental details and results
will be discussed.

2.   THE ENERGY BAND SCHEME OF SILICON[1]

The structure of the energy bands of silicon has been
determined by cyclotron resonance and other methods.
Figure 2 shows the valence and conduction bands of silicon.
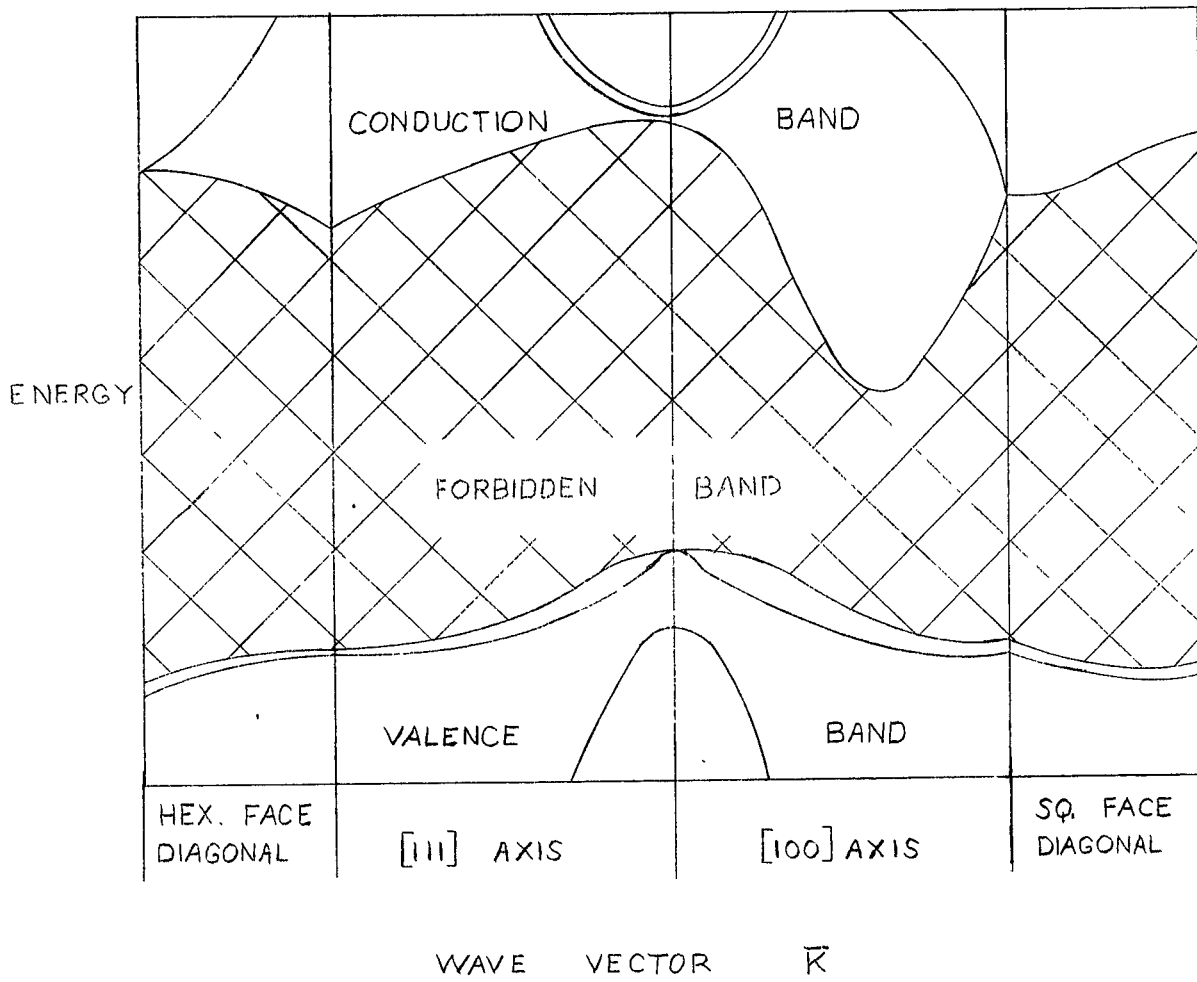
FIGURE 2   THE ENERGY BANDS OF SILICON

(a) Conduction Band of Silicon

The minima of the energy in the conduction band of silicon occur along the 100 axes in the first Brillouin zone. Evidence[2,3] indicates that the minima occur about 3/4 of the way along these axes towards the zone boundary. This gives rise to six equivalent minima in the conduction band. The surfaces of constant energy are prolate ellipsoids of revolution. This is known as the non-degenerate many valley model. It is called non-degenerate because each of the six valleys is non-degenerate. The surfaces of constant energy near the conduction band minima are then given by

$$E(\overline{K}) = E_c + \frac{h^2}{8\pi^2}\left(\frac{K_\ell^2}{m_{e\ell}^*} + \frac{K_{t1}^2 + K_{t2}^2}{m_{et}^*} \right) \qquad (3)$$

E_c is the conduction band minimum energy and K_ℓ, K_{t_1}, K_{t_2} are the longitudinal and transverse components of $\overline{K} - \overline{K}_o$, where $\overline{K}_o$ corresponds to minimum energy. The calculation of effective mass by Lax[4] from cyclotron resonance data gives longitudinal and transverse components at the band minimum of

$$\frac{m_{e\ell}^*}{m_o} = 0.98$$

$$\frac{m_{et}^*}{m_o} = 0.19$$

(b) Valence Band of Silicon

The valence band of silicon is much more complicated than the conduction band. Three of the four valence bands in silicon have their maxima at the centre of the first Brillouin zone, that is at $\overline{K} = 0$. Two of them are degenerate at their maximum energy E_v, while the maximum of the third one is slightly depressed with respect to the other two. The surfaces of constant energy of the two uppermost bands are warped spheres given by

$$E(K) = E_v - \frac{h^2}{8\pi^2 m_o}\left(AK^2 \pm (B^2 K^4 + C^2 [K_x^2 K_y^2 + K_y^2 K_z^2 + K_z^2 K_x^2])^{1/2} \right) \quad (4)$$

The constants determined by Lax[4] from cyclotron resonance data are

$$A = 4.1 \qquad B = 1.4 \qquad C = 3.7$$

K_x, K_y, K_z are the coordinates of the wave vector $\overline{K}$. The plus sign gives the surface of lower energy and the minus sign the surface of higher energy.

In many cases in the interests of mathematical simplicity the warping of the spheres is neglected and they are approximated by spheres of the same average curvature. The spherical energy surfaces are given by

$$E(\overline{K}) = E_v - \frac{h^2}{8\pi^2 m_o}\left(A \pm \left[B^2 + \frac{C^2}{6}\right]^{1/2} \right) K^2 \quad (5)$$

There are two observed energy gaps in silicon, the thermal energy gap and the optical energy gap. The difference arises from the fact that the minima of the conduction band and the maximum of the valence band do not lie at the same point in the reciprocal lattice space. The thermal gap represents the energy difference between the conduction band minima and the valence band maximu. The optical energy gap represents the minimum energy gap between energies having the same wave vector $\overline{K}$, because in the optical transition there is no mechanism for the electron to acquire a change in momentum and consequently in the value of $\overline{K}$. The thermal energy gap at 0°K is 1.153 eV and at 300°K is 1.106 eV.[5]

3. Density of States

The density of allowed states of holes or electrons in the valence or conduction bands respectively is controlled by the allowed values of $\overline{K}$.

At the band edge of a non-degenerate energy surface $\nabla_{\overline{K}} E = 0$. $E(\overline{K})$ can then be expanded in a Taylor series about $\overline{K}_O$, the extremum point. Then

$$E(\overline{K}) = E_O + 1/2 \frac{\partial^2 E}{\partial K_i \partial K_j} \overline{K}_i \cdot \overline{K}_j$$

$$= E_O \pm 1/8 \frac{h^2}{\pi^2 m_{ij}^*} \overline{K}_i \cdot \overline{K}_j \qquad (6)$$

E_O is the energy at the band edge. The plus sign is used for the conduction band and the minus sign for the valence band. In the case of the valence band of silicon the assumption is made that one can calculate the density of states separately for each of the bands defined by equation (4) and then add the results to obtain the total density of states in the valence band. Since m_{ij}^* is a symmetric tensor a suitable choice of axes may be made so that all non-diagonal elements are zero. Then

$$E(\overline{K}) = E_O \pm \frac{h^2}{8\pi^2} \left(\frac{K_a^2}{m_a^*} + \frac{K_b^2}{m_b^*} + \frac{K_c^2}{m_c^*} \right) \tag{7}$$

The density of modes in a given energy range is equal to the number of lattice points in the first Brillouin zone corresponding to that energy range. This is multiplied by two to allow for the spin degeneracy. The density of states is then given by

$$Z(E) = 4\pi \left(\frac{2}{h^2} \right)^{3/2} (m_a^* \, m_b^* \, m_d^*)^{1/2} (E-E_O)^{1/2}$$

$$= 4\pi \left(\frac{2m_d^*}{h^2} \right)^{3/2} (E-E_O)^{1/2} \tag{8}$$

where m_d^* is called the density of states effective mass.

The two valence bands of silicon lead to two types of holes, the light and heavy holes as they are called, cor-

responding to the small and large effective masses derived from the spherical constant energy surface approximation of equation (5).

The density of states mass for the heavy holes defines the density of states for heavy holes by

$$Z_h(E) = 4\pi \left(\frac{2m^*_{d_h}}{h^2}\right)^{3/2} (E_v - E)^{1/2} \tag{9}$$

There is a similar equation for the light holes.

$$Z_\ell(E) = 4\pi \left(\frac{2m^*_{d_\ell}}{h^2}\right)^{3/2} (E_v - E)^{1/2} \tag{10}$$

From their calculations using equation (5) Lax and Mavroides[6] quote

$$\frac{m^*_{d_\ell}}{m_o} = 0.14$$

$$\frac{m^*_{d_h}}{m_o} = 0.53$$

For the conduction band the density of states effective mass becomes

$$\frac{m^*_{d_e}}{m_o} = \frac{\left(m^*_\ell \, m^{*2}_t\right)^{1/3}}{m_o} = 0.33 \tag{11}$$

The six equivalent valleys make the conduction band density

of states six times that derived for a single minimum giving

$$Z_e(E) = 6 \ (4\pi) \ \left(\frac{2m_{d_e}^*}{h^2}\right)^{3/2} (E-E_c)^{1/2} \qquad (12)$$

Note that in some of the literature the factor 6 is included
in the $m_{d_e}^{*}{}^{3/2}$ term, thus multiplying our value of $m_{d_e}^*$ by
$6^{2/3}$.

4. IMPURITIES IN SILICON

The presence of a donor or acceptor impurity in silicon

causes the splitting off of a localized state in the forbidden

energy gap. The following discussion shall be confined to

shallow impurities only. A shallow impurity is one in which

the split off state is only a small fraction of the forbidden

energy gap from the valence band or from the conduction band.

All the common trivalent and pentavalent impurities with the

exception of indium fall into this classification. An

estimation of the energy of the split off state can be made

by assuming a hydrogen like orbit about the impurity atom, but

using an effective m^* instead of the electronic mass and using

an electric potential modified by the dielectric constant of

silicon. The calculation gives an order of magnitude value

of the acceptor and donor energies. It predicts the same

energy for all impurities with the same valence electron

configuration, but this is not found to be so experimentally.
One reason for the difference in impurity energies is that
in the portion of an orbit near the impurity centre the ion
core will not be shielded by the surrounding silicon atoms,
and so the approximation to the potential is not valid in
this region. Excited states have been observed in donor and
acceptor doped silicon, as would be expected from the hydrogen
like model.

Consider now an acceptor impurity, say boron, in silicon.
At low impurity concentrations, that is below 10^{16} atoms per cc
the thermal ionization energy has been found to be

$$E_a - E_v = 0.046 \text{ eV}^7$$

where E_a is the energy of the acceptor ground state. As the
impurity concentration increases the acceptor levels broaden
into a band, and at concentrations in excess of 10^{19} atoms
per cc the acceptor band merges with the valence band.

The double degeneracy of the valence band maximum also
causes a double degeneracy of the acceptor energy level.
The addition of the double spin degeneracy causes altogether
a four fold degeneracy of the acceptor levels. Only one
electron may occupy a given shallow acceptor level at any
one time, however, as its presence prevents any others from
occupying the same state. The degeneracy of the acceptor

level will have an effect on the statistics of occupation as will be seen later.

As with the acceptor impurities, the donor impurity ground state energy levels are degenerate. There are six 1s states for the six conduction band minima. One of these states is depressed with an energy E_d and the other five are degenerate at about 0.010 eV above the depressed state. In addition each state has the two fold degeneracy due to the two allowed spin values for the electron. The ground state ionization level for antimony in silicon is $E_c - E_d = 0.039$ eV.[8]

5. <u>STATISTICS</u>

There exists a probability that at any given time an energy state is occupied by an electron. If an energy state can hold any number of electrons then the system is said to obey classical Boltzmann statistics. In this case the probability of a state with energy E being occupied is proportional to exp $\frac{-E}{KT}$. If, on the other hand, the energy state E is such that only one electron may have the energy E at any one time then the probability of finding an electron in this energy state is equal to
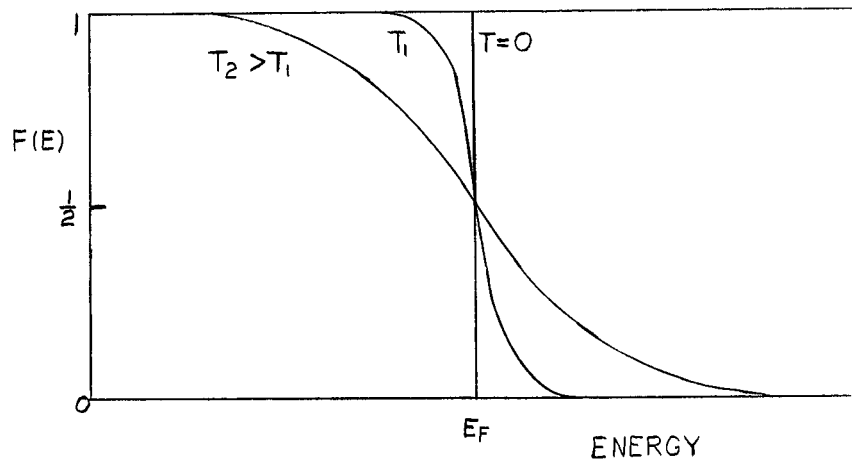
$$F(E) = \frac{1}{1 + \exp\dfrac{E-E_f}{KT}} \tag{13}$$

E_f is known as the Fermi energy and the function F(E) is the Fermi function. Systems which obey this relation are said to obey Fermi-Dirac statistics. It is noted that if

$$E - E_f \gg KT \qquad (14)$$

then the factor 1 may be neglected in equation (13) and the Fermi-Dirac statistics become identical with the classical Boltzmann statistics. The Fermi energy in equation (13) may be thought of as the energy at which the probability of occupancy is exactly 1/2. The Fermi energy is not a constant but may be a function of temperature as well as the system. In certain cases a series of energy states may be occupied by an electron, but only one of the series of energy states can be occupied at any one time. For example, a donor electron may be in its ground state or one of its excited states in silicon. The probability of any one of the states being occupied is then given by[9]

$$F = \frac{1}{1 + \dfrac{1}{\sum_i g_i \exp \dfrac{E_f - E_i}{KT}}} \qquad (15)$$

where E_i are the possible energy states and g_i the corresponding degeneracies.

–18–

(a) $F(E) = \dfrac{1}{1 + \exp \frac{E-E_F}{KT}}$
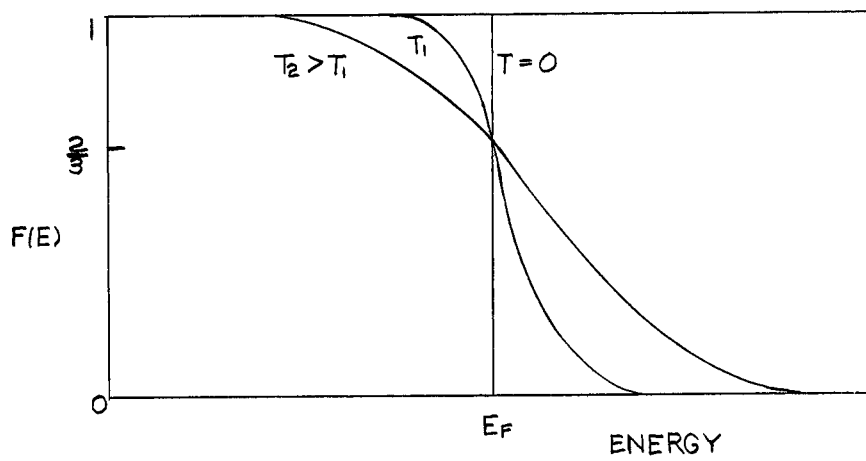
(b) $F(E) = \dfrac{1}{1 + \frac{1}{2} \exp \frac{E-E_F}{KT}}$

FIGURE 3   THE FERMI FUNCTION

6. OCCUPANCY OF STATES

The probability of finding dn electrons within an energy range between E and E + dE is proportional to the density of states in this energy range times the probability of finding one of these states occupied. This is clearly

$$dn = Z(E) \ F(E) \ dE \tag{16}$$

For the conduction band this is

$$dn = 6(4\pi) \left(\frac{2m_{de}^*}{h^2}\right)^{3/2} \frac{(E-E_c)^{1/2}dE}{1+\exp\frac{E-E_f}{KT}} \tag{17}$$

To calculate the concentration n of electrons in the conduction band one should integrate

$$n = \int_{E_c}^{E_{top}} Z(E) \ F(E) \ dE \tag{18}$$

If $E-E_f \gg KT$ then the term 1 in the denominator may be neglected. Also, as F(E) is a rapidly decreasing function of E, the limit of integration may be changed from E_{top} to ∞. Then

$$n = 6(2)\left(\frac{2\pi m_{de}^* KT}{h^2}\right)^{3/2} \exp\frac{(E_f - E_c)}{KT}$$

$$= 6 \ N_c \ \exp\frac{(E_f-E_c)}{KT} \tag{19}$$

where

$$N_c = 2 \left(\frac{2\pi m_{de}^* KT}{h^2} \right)^{3/2} \tag{20}$$

N_c is known as the effective density of states in the conduction band.

To calculate the density of holes p in the valence band the fact that $1 - F(E)$ is the probability of a state being unoccupied is used. Then for the heavy holes

$$p_h = \int_{E_{bot.}}^{E_v} 4\pi \left(\frac{2m_{dh}^*}{h^2} \right)^{3/2} \frac{(E_v-E)^{1/2}}{1+\exp\frac{(E_f-E)}{KT}} \, dE \tag{21}$$

Making similar assumptions to those used in the conduction band case leads to the expression for p_h

$$p_h = 2 \left(\frac{2\pi m_{dh}^* KT}{h^2} \right)^{3/2} \exp \frac{(E_v-E_f)}{KT} \tag{22}$$

There is a similar expression for the density of light holes, p_ℓ

$$p_\ell = 2 \left(\frac{2\pi m_d^* KT}{h^2} \right)^{3/2} \exp \frac{(E_v-E_f)}{KT} \tag{23}$$

Since

$$p = p_\ell + p_h \tag{24}$$

it is seen that we can write the density of states effective
mass for holes as

$$m_{d_p}^{*\,3/2} = m_{d_h}^{*\,3/2} + m_{d_\ell}^{*\,3/2} \tag{25}$$

and using N_v as the valence band effective density of states

$$N_v = 2 \left(\frac{2\pi m_{d_p}^{*}\,KT}{h^2}\right)^{3/2} \tag{26}$$

gives the value of p

$$p = N_v \exp \frac{(E_v - E_f)}{KT} \tag{27}$$

Multiplying equation (19) and (27) gives

$$np = n_i^2 = 6\,N_v\,N_c \exp \frac{(E_v - E_c)}{KT} \tag{28}$$

n_i is the concentration of electrons or holes when n is equal
to p, that is when the silicon shows intrinsic behaviour. It
is seen that the product np is a constant at a constant tem-
perature, and is dependent only on the form of the energy
band scheme and is independent of the impurity concentration.

Now let us look at a semiconductor with a concentration
of N_d shallow donors and N_a shallow acceptors. The condition
for electrical neutrality is that the sum of the positive

charges must equal the sum of the negative charges. Setting

p = concentration of holes in the valence band

p_a = concentration of holes bound to acceptors

N_d = concentration of donors

n = concentration of electrons in the conduction band

n_d = concentration of electrons bound to donors

N_a = concentration of acceptors

then

$$p + p_a + N_d = n + n_d + N_a \qquad (29)$$

Assume that $N_d > N_a$. Then at sufficiently low temperatures that n_i of equation (28) is much less than $N_d - N_a$ the acceptors will be almost completely ionized by the donors. The concentration of holes will also be very small. Equation (29) becomes

$$N_d = n + n_d + N_a \qquad (30)$$

Now

$$n_d = FN_d \qquad (31)$$

Combining (30) and (31)

$$F = \frac{N_d - N_a - n}{N_d} \qquad (32)$$

For donor impurities in silicon the excited states all lie

very close to the conduction band and so can be neglected in equation (15). The 1s states are all doubly degenerate due to the electron spin. Δ is taken as difference in energy between the depressed 1s state and the remaining five. Equation (15) becomes

$$F = \frac{1}{1 + \frac{1}{2} \dfrac{\exp \frac{E_d - E_f}{KT}}{1 + 5 \exp \frac{-\Delta}{KT}}} \tag{33}$$

then

$$\frac{N_d - N_a - n}{N_d} = \frac{1}{1 + \frac{1}{2} \dfrac{\exp \frac{E_d - E_f}{KT}}{1 + 5 \exp \frac{-\Delta}{KT}}} \tag{34}$$

Solving for E_f

$$E_f = E_d + KT \, \ell n \frac{N_d - N_a - n}{2 \left(1 + 5 \exp \frac{-\Delta}{KT}\right)(N_a + n)} \tag{35}$$

Substituting the value of E_f into equation (19)

$$n = 6 \, N_c \exp \frac{E_d + KT \, \ell n \left[\frac{1}{2} \dfrac{N_d - N_a - n}{\left(1 + 5 \exp \frac{-\Delta}{KT}\right)(N_a + n)}\right] - E_c}{KT}$$

$$= \frac{6}{2} \, N_c \frac{(N_d - N_a - n)}{\left(1 + 5 \exp \frac{-\Delta}{Kt}\right)(N_a + n)} \exp \frac{E_d - E_c}{KT} \tag{36}$$

or

$$\frac{n(n+N_a)}{(N_d-N_a-n)} \simeq \frac{3 \ N_C \ \exp{\dfrac{E_d-E_c}{KT}}}{1+5 \ \exp{\dfrac{-\triangle}{KT}}} \tag{37}$$

When $N_a > N_d$ similar calculations can be made to determine the concentration of holes in the valence band. In silicon the probability of an acceptor containing a hole is

$$1 - F = \frac{1}{1+4 \ \exp{\dfrac{(E_f-E_a)}{KT}}} \tag{38}$$

with the factor 4 coming from the degeneracies due to the valence band structure and spin. The concentration of holes then is given by

$$\frac{p(p+N_d)}{(N_a-N_d-p)} = \frac{N_v}{4} \ e^{\frac{E_v-E_a}{KT}} \tag{39}$$

Let us consider the behaviour of equation (37) at various temperatures. At very low temperatures when n is very small compared with $N_d - N_a$ and N_a equation (32) becomes

$$n = \left(\frac{N_d-N_a}{N_a}\right)\frac{3N_C \ \exp{\dfrac{E_d-E_c}{KT}}}{1+5 \ \exp{\dfrac{-\triangle}{KT}}} \tag{40}$$

This will be known as the low temperature region. As T
increases n increases and eventually

$$n = N_d - N_a \qquad\qquad (41)$$

p is still small as it is governed by the relation in equation
(24). This is known as the exhaustion range, that is, all the
donors and acceptors are ionized. At higher temperatures yet
the exponential term in equation (24) will be so increased as
to allow p to become significant with respect to n. There
can be no more contribution to n from the donors so additions
to n are mostly from the valence band, with the corresponding
addition of a hole in the valence band. This is known as the
intrinsic region as the specimen behaves more like an intrinsic
one. A typical plot of $\ell n\ n$ vs $\frac{1}{T}$ is shown in figure 4.
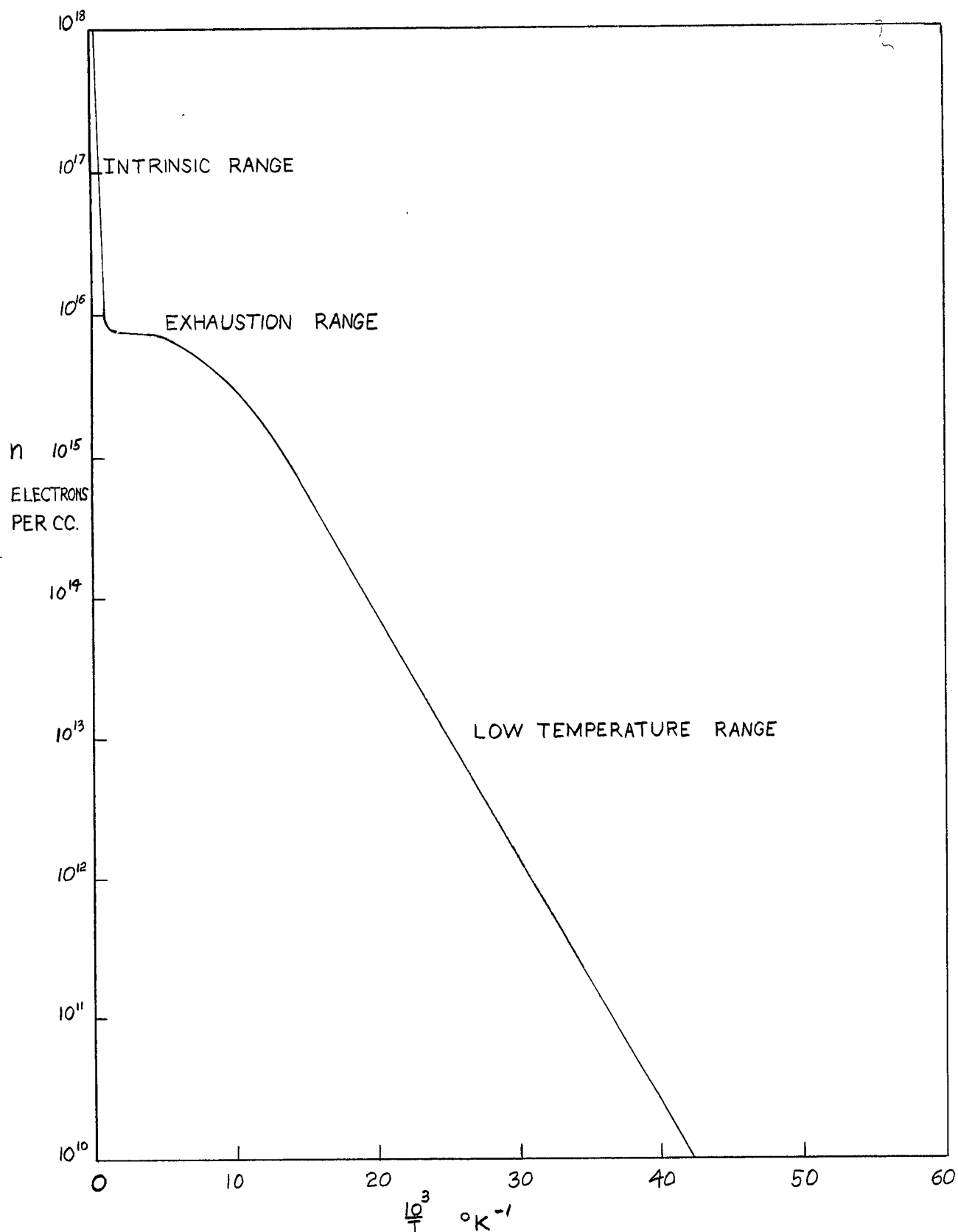p type material behaves in a similar way.

FIGURE 4 TYPICAL PLOT OF LOG n VS. $\frac{1}{T}$

CHAPTER II

ANALYSIS

1. TRANSPORT PHENOMENA

(a) Electrical Conduction

For a semiconductor having a concentration of n electrons, no holes, and a conductivity σ, an electron conductivity mobility μ_{c_e} may be defined by

$$\sigma = n\ q\mu_{c_e} \qquad (42)$$

Similarly a hole conductivity mobility μ_{c_p} may be defined. In silicon containing electrons and both light and heavy holes the conductivity is given by

$$\sigma = q(n\mu_{c_e} + p_h\,\mu_{c_h} + p_\ell\,\mu_{c_\ell}) \qquad (43)$$

Among the parameters affecting the mobility are the temperature and the ionized impurity concentration. Experimentally[10] in silicon the lattice mobility in the temperature range 150 to 400°K is found to be

$$\mu_d = A\ T^{-a} \qquad (44)$$

where a = 2.5 for electrons and 2.7 for holes. The mobility due to ionized impurity scattering is shown on theoretical grounds[11] to vary approximately as $T^{3/2}$, and to decrease with increasing ionized impurity concentration. Thus the mobility increases with temperature when ionized impurity scattering predominates and decreases with increasing temperature when lattice scattering predominates.

(b) <u>Magnetoresistance</u>

Consider an electric current I_x in a semiconductor of resistance R_o. Apply a magnetic field H_y. Then it is usually found that there is an increase in resistance   R given by

$$R = R_o \ g(H_y) \tag{45}$$

where $g(H_y)$ is some function of H_y. At low fields

$$g(H_y) = M_t \ H_y^2 \tag{46}$$

This effect is known as the transverse magnetoresistance.

(c) <u>Hall Effect</u>

When there is an electric current I_x in a specimen and a magnetic field H_y there will be produced a potential gradient E_z due to the movement of the charge in the magnetic field. This is known as the Hall effect. The Hall constant R is

defined by the equation

$$R = \frac{E_z}{I_x H_y} \qquad (47)$$

Consider the effect of n electrons all moving with a uniform velocity v_x. Then the electric current will be

$$I_x = - n v_x q \qquad (48)$$

Now apply H_y. The electrons will be under the force $-q v_x H_y$ in the z direction, causing them to be deflected. An electrostatic field will build up which in the steady state will exert a force on the electrons equal to that caused by their motion in the magnetic field. Then

$$-q \ E_z = q \ v_x H_y \qquad (49)$$

$$v_x = - \frac{1}{nq} \ I_x \qquad (50)$$

and substituting v_x in equation (49)

$$\frac{E_z}{I_x H_y} = - \frac{1}{nq} \qquad (51)$$

Thus we identify $- \frac{1}{nq}$ with R, the measured constant of proportionality

$$R = - \frac{1}{nq} \qquad (52)$$

If the carriers in the above are holes rather than electrons then

$$R = \frac{1}{pq} \qquad (53)$$

The above values of the Hall constant were derived on the assumption that the carrier velocities were uniform. However, in a semiconductor the carrier velocities are not all uniform. This leads to a Hall constant of the form

$$R = \pm \frac{r}{nq} \qquad (54)$$

where r is a numerical factor of the order of one. r is a function of the scattering mechanism, the distribution function, and the applied magnetic field. The low field limit for scattering by acoustical modes, assuming the simple band model for energies and classical statistics gives

$$r = \frac{3\pi}{8}$$

At high magnetic fields r approaches a limiting value of unity. The criterion predicted by Swanson[12] for the high field limit to be valid to within a few percent is for

$$\left(\tfrac{9\pi}{16}\right)\!\left(\mu H\right)^2 \;>\; 25 \qquad\qquad (55)$$

The values of r quoted above are general for all semiconductors. Long et al[13] found that for p type silicon there was less than 5% variation of r from weak fields up to 13,300 gauss at fixed temperatures of 54°K and 77°K. After examining their results and those of others they quote a value of

$$r = 0.80$$

at 300°K. At temperatures below 100°K the reported lack of variation of r with field indicates that r is not much different from its strong field value of unity. Their experiments were carried out with a maximum impurity concentration of 1.5×10^{15} atoms per cc. The lower mobilities associated with higher impurity concentrations might make the value of r more field dependent.

There does not seem to be much published about the high field value of r for n type silicon. However, due to the higher mobility of electrons in silicon it is to be expected that the infinite field limit will be reached sooner than in p type silicon. In view of this it has been decided to set r = 1 for n type silicon.

The Hall mobility is defined as the product

$$\mu_H = R\sigma \qquad\qquad (57)$$

and it is seen that

$$\mu_H = r\mu_c \tag{58}$$

2. OTHER EFFECTS WHICH MIGHT AFFECT HALL READINGS

In making measurements of the Hall coefficient one must
be aware of certain other effects which contribute to the
apparent Hall voltage. Appropriate steps to calculate the
additional voltages or eliminate them from readings by
experimental technique must be taken. In this section the
various effects will be discussed.

There are four such sources of error in making Hall
measurements, the Ettinghausen, Nernst, Righi-Leduc, and
magnetoresistance effects.

(a) Ettinghausen Effect

The Ettinghausen effect produces a transverse temperature
gradient when an electric current is flowing in the longitudi-
nal direction in the presence of a perpendicular magnetic
field. The Ettinghausen coefficient P is defined by

$$\frac{dT}{dy} = P \, H_z \, I_x \tag{59}$$

The effect is caused by the faster charge carriers being
deflected more in the magnetic field, and thus those with

more energy tend to move to one side of the specimen. The temperature gradient so formed creates a thermoelectric effect at the Hall probes, giving rise to an additional potential difference.

(b) <u>Nernst Effect</u>

The Nernst effect produces a transverse electric field when there is a longitudinal thermal current due to a temperature gradient in the presence of a perpendicular magnetic field. The Nernst coefficient Q is defined by

$$E_y = Q \ H_z \ \frac{dT}{dx} \qquad (60)$$

The effect is caused by the fast carriers diffusing from the higher temperature end being deflected more in the magnetic field than the slower ones diffusing from the cooler end. The transverse electric field will again be measured at the Hall probes.

(c) <u>Righi-Leduc Effect</u>

The Righi-Leduc effect produces a transverse temperature gradient when there is a longitudinal thermal current due to a longitudinal temperature gradient in the presence of a perpendicular magnetic field. The Righi-Leduc coefficient is defined by

$$\frac{dT}{dy} = SH_z \ \frac{dT}{dx} \qquad (61)$$

This effect is caused by the same process as the Nernst effect. The thermal gradient results from the concentration of fast electrons on one side of the sample. The thermal gradient thus formed produces an electric potential difference at the Hall probes, as in the Ettinghausen effect.

(d) Magnetoresistance

If the two Hall probes are not aligned directly opposite each other, then when there is an electric current there will be an IR_0 drop between the probes. When a perpendicular magnetic field is applied the drop will be $I(R_0 + \triangle R)$. This additional effect cannot be eliminated simply by subtracting the initial IR_0 drop from the final reading to obtain the Hall voltage.

The above effects which will cause errors in Hall constant measurements may be eliminated by various experimental techniques, one of which will be discussed in the chapter on experimental details.

3. METHODS OF FINDING N_a and N_d

The silicon used in most studies on the properties of semiconductors is usually of very high purity. The concentration of impurities is usually too small to be detected by ordinary chemical analysis.

Usually the methods used are electrical methods and they do not give the concentration of each individual impurity,

but rather give the concentration N_d of donor impurities and the concentration N_a of acceptor impurities, and may also differentiate between deep and shallow impurities. Generally, however, the major impurities are known qualitatively by knowing the method of crystal growth, that is by using very pure silicon and adding the desired impurities to the melt.

(a) <u>Resistivity</u>

The easiest way to measure the impurity concentration of a semiconductor is by a resistivity measurement. The conductivity σ is equal to the reciprocal of the resistivity ρ

$$\sigma = \frac{1}{\rho} \tag{62}$$

If only electrons say are present then

$$n = \frac{1}{q \mu c_e} \tag{63}$$

n must then be related to the impurity concentration. For silicon containing N_d shallow donors and N_a shallow acceptors with $N_d > N_a$ and the temperature such that the silicon sample is in the exhaustion range, the value of $N_d - N_a$ is given by

$$N_d - N_a = \frac{1}{q \mu c_e} \tag{64}$$

However, as the mobility is very dependent on temperature and ionized impurity concentration, this method has limited use when accurate results are desired.

(b) <u>Transverse Magnetoresistance Method</u>

Long, Motchenbacker, and Myers[13] have reported a method for determining both N_a and N_d by using the weak field transverse magnetoresistance. The value of $N_d - N_a$ is obtained from an exhaustion range Hall effect or resistivity measurement. A weak field transverse magnetoresistance measurement is then made at liquid nitrogen temperature. The value

$$M_t = \frac{\triangle R}{R_o H^2} \tag{65}$$

is calculated. From an empirical master curve of M_t vs. $N_{di} + N_{a_i}$ the value of $N_{di} + N_{a_i}$ is obtained. N_{di} and N_{a_i} are the ionized donor and acceptor concentrations. It is postulated that M_t is a function of $N_{d_i} + N_{a_i}$ only at constant temperature. Using the value of $N_{d_i} + N_{ai}$ found, $N_d + N_a$ is calculated from

$$N_d + N_a = N_{d_i} + N_{a_i} + \frac{1}{q}\left(\frac{1}{\mu_{300}\,\rho_{300}} - \frac{1}{\mu_{77}\,\rho_{77}}\right) \tag{66}$$

Using the values of $N_d - N_a$ and $N_d + N_a$ obtained, N_d and N_a can be calculated separately.

Again this method has the disadvantage that the

mobilities must be known. Also the empirical curve of M_t vs. $N_{d_i} + N_{a_i}$ must be obtained. To do so some other method must be used originally to obtain the data for the curve. In time, though, when master curves to cover all situations have been published this method may prove to be very satisfactory, and it has the advantage that it is relatively quick and simple to perform.

(c) Hall Effect Method

The most fundamental and still the most reliable method of obtaining impurity concentrations is by the measurement and analysis of the Hall constant as a function of temperature.

The first step upon making Hall measurements is to determine the sign of the Hall constant. From the sign of the Hall constant in the exhaustion range it is found whether N_a or N_d is greater, according to whether conduction is by holes or electrons. Assume N_a to be greater. Then over the appropriate temperature ranges the Hall constant R is measured and the calculation

$$p = \frac{r}{Rq} \qquad (67)$$

is made using the appropriate value of r. If the acceptor ionization energy is unknown a plot of $\ln \frac{p}{T^{3/2}}$ vs. $\frac{1}{T}$ can be made. In the low temperature region the slope of this plot will be equal to $\frac{E_v - E_a}{K}$. Next the value of $N_a - N_d$

may be found from the exhaustion range measurement of R. Then the value of $N_a - N_d$ may be substituted into equation (39). Hence the value of N_d may be found and then the value of N_a.

A plot of mobility vs. temperature will serve as a useful check against gross errors in the experiment, as the temperature of maximum mobility should increase with increasing ionized impurity concentration.

CHAPTER III

EXPERIMENTAL

1. EXPERIMENTAL DETAILS

The apparatus described in the following pages consists of a magnet, cryostat, thermometer, sample holder, and Hall and resistance measuring device. A block diagram of the experimental set-up is shown in figure 5.

(a) Magnet

The magnet used was a type D Newport Instruments magnet. It has two sets of pole pieces, flat and conical. The conical pole pieces give greater fields but with less homogeneity and area of field. Only the flat pole tips have been used. They are 8 in. in diameter and have a gap of 1 7/8 in. between the pole pieces. The magnet coils are water cooled. The electric current is supplied by a Newport type B power supply.

To permit more accurate current control in the magnet the original one turn current control potentiometer was replaced by a ten turn helipot of the same resistance. A General Electric IN2159 diode was placed across the input terminals of the magnet to prevent damage to the coils from the large back e.m.f. which would develop if the current

SAMPLE LEADS

THERMOMETER LEADS

DEWAR

MAGNET POWER SUPPLY

110V. A.C.

MAGNET

SAMPLE

HALL CIRCUIT

RUBICON GALV.

110 V. A.C.

12 VOLT BATTERY

-40-
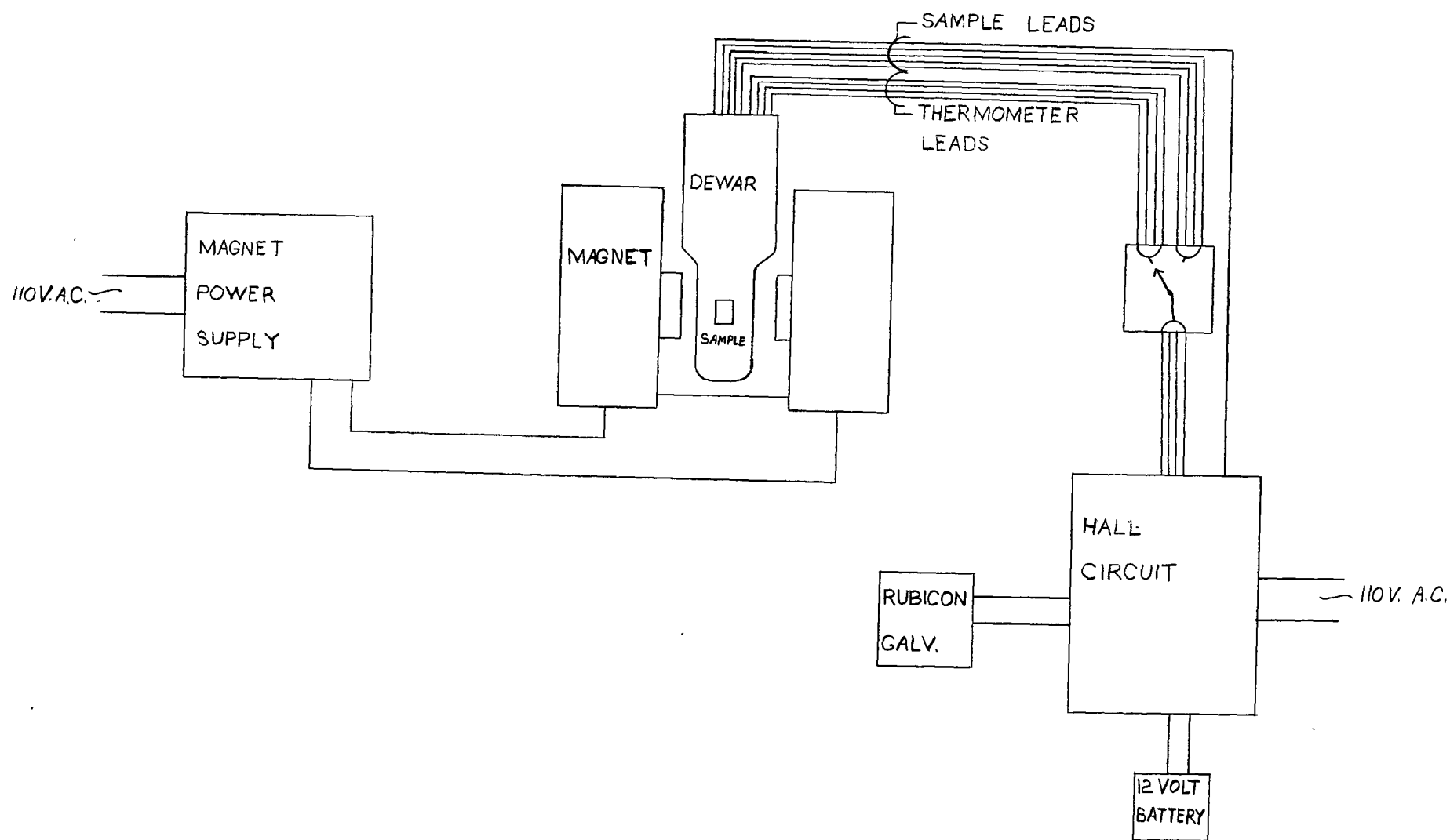
FIGURE 5   EXPERIMENTAL   ARRANGEMENT

leads failed.

The magnet was calibrated in the ranges used by nuclear magnetic resonance methods. A maximum field of 10,690 gauss was obtained.

(b) Cryostat

The cryostat used was a double walled glass dewar which fitted between the pole pieces. The specimen to be measured was placed inside the dewar at the end of a lucite rod. The dewar was filled with nitrogen to a height sufficient to cover the sample and sample holder completely. Readings were taken at liquid nitrogen temperature. The nitrogen was allowed to boil off, permitting the sample to gradually warm up. Readings were taken at various temperatures up to and above room temperature. Temperatures above room temperature were obtained by blowing hot air into the dewar with a hair dryer.

The system used was not entirely satisfactory as once the nitrogen level was below that of the sample holder, the sample warmed up at a rate such that during the time taken to make one measurement there was enough change in the temperature of the sample to cause significant errors. Constant temperature readings were made at liquid nitrogen and room temperatures, however. A metal cryostat of a type designed by the National Research Council and modified to fit within the magnet is under construction at the time of writing. It

will allow a slower rise of temperature of the sample and thus permit readings to be taken at essentially constant temperature. Also it will permit the taking of measurements down to liquid helium temperature.

(c) Sample Holder

The sample holder design is shown in figure 6. The sample rests on a half cylinder copper bar. A 0.001 cm layer of mylar is placed between the bar and the sample to provide electrical insulation and good thermal contact. The sample and mylar are held on with high vacuum grease so that the system may be used in an evacuated cryostat. The copper bar was machined to fit inside a 1/2 in. copper tube. Contact to the gold lead wires of the samples is made by means of copper strips which run from the top to the bottom of a hollowed lucite block. Leads are taken from top side terminal screws to the measuring apparatus. Adjusting screws are provided to ensure good contact between the copper strip and the sample leads. The lucite block is held in position by two screws which fit into the copper bar. The sample holder was designed as described in order to place as little stress as possible on the gold lead wires and contacts because they are quite delicate.
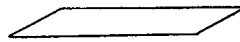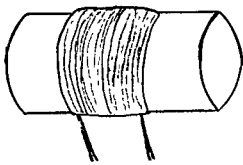
(d) Temperature Measurement

The temperature measuring device used is a copper resistance thermometer. This was chosen because of the
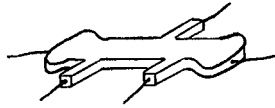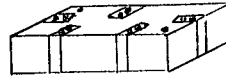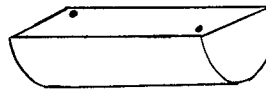
SAMPLE

MYLAR
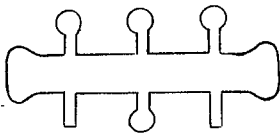
COPPER RESISTANCE
THERMOMETER
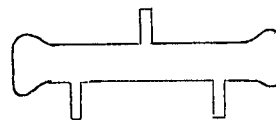
(a) SAMPLE HOLDER

(b)

(c)

FIGURE 6   SAMPLE HOLDER AND SAMPLE SHAPES

relative simplicity of manufacture and because of the suitability of the copper resistance thermometer over the range for which it was desired, i.e. 20°K to 300°K. The thermometer was constructed from No. 40 B&S copper wire from Canada Wire and Cable. The wire was bifilar wound onto the 1/2 in. copper tube of the sample holder with sufficient windings to give a room temperature resistance of approximately 100 ohms. Four copper wire leads, two to each end of the coil, were attached so that the resistance of the coil alone could be measured, and not that of the leads, which would have a different temperature from that of the coil.

The calibration of the thermometer was made by an ice-point reading. This combined with the calibration curve published by Dauphinee and Preston-Thomas[14] enabled temperature to be measured quickly to an estimate accuracy of better than 0.5°K. The resistance of the copper coil is read with the Hall measuring apparatus.

(e) Circuit for Hall Effect and Resistance Measurements

A Hall effect and resistance measurement circuit described by Dauphinee and Mooser[15] has been built. This is a square wave AC circuit using a DC magnetic field and is designed to eliminate the unwanted Ettinhausen, Nernst, Righi-Leduc, and magnetoresistance effects, and at the same time to provide quick and easy readings of Hall effect and resistance.

The actual circuit built is shown in figure 7. The chopper used is a type C-112 double low thermal chopper from Tinsley Instruments. The resistances R_7 to R_{11} are General Radio decade resistances in steps of 10,000 ohms to 1 Ohm with 0.15% precision. The resistances R_2 to R_5 are wound from several feet of appropriate wire to give the desired resistance. The 0.1 ohm to 10 ohm ranges were checked with standard resistances and found to have a precision of 0.5%. The potentiometer P_2 is a ten turn Beckman helipot of 25 ohms nominal resistance and 0.5% linearity precision. P_3 to P_6 are ten turn Beckman helipots of 5,000, 50,000, 450,000 and 1,000,000 ohms, which act as the dummy potential divider as explained by Dauphinee and Mooser. Capacitors C_1, C_2, C_3 are from Film Capacitors Ltd. They are polystyrene for low dielectric absorption.

The apparatus has a built in -50 0 50 amp ammeter as a null indicator. For most work a more sensitive instrument is needed, the choice being a Rubian galvanometer of 0.0054 μ amps per mm. sensitivity.

The choppers were adjusted with the aid of an electronic switch and oscilloscope to the correct phasing. Van der Pauw[16] has pointed out how errors could arise in the readings due to the effects of stray capacitance. He also explains the necessary steps to eliminate these errors. In accordance with his instructions capacitors C_4 and C_5 were added. Also
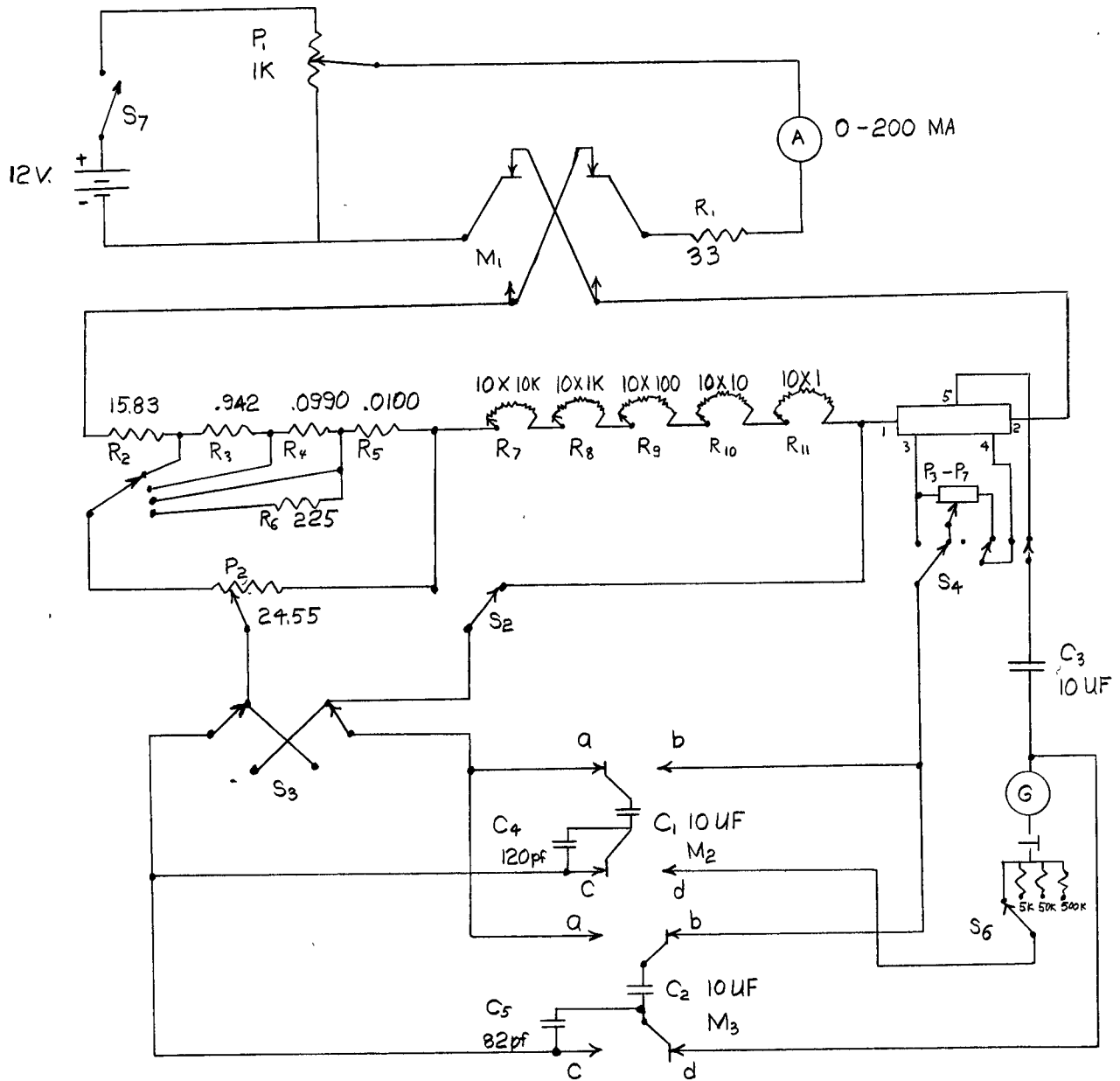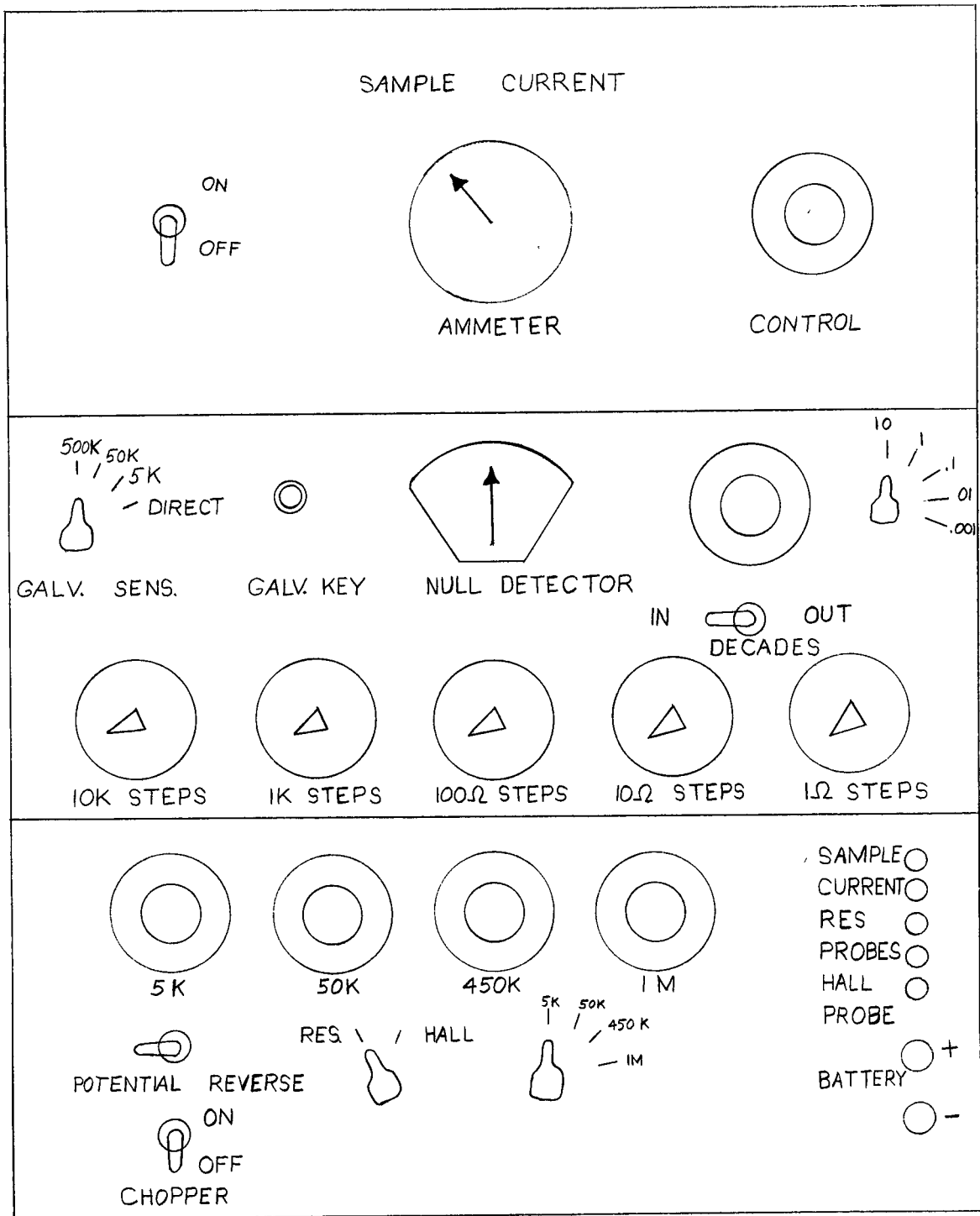
FIGURE 7   THE HALL MEASURING CIRCUIT

FIGURE 8 HALL CIRCUIT CONTROL PANEL

switches a and b were made to close before switches c and d
on choppers M_2 and M_3.

2. SAMPLES AND SAMPLE PREPARATION

The samples used in these experiments were cut from a
silicon crystal grown at Bell Labs. The crystal was grown in
the ⟨111⟩ direction. The first third of the crystal was
boron doped. Antimony was then added to the melt causing the
remainder of the crystal to be antimony doped with boron as a
minor impurity. Slices approximately 1 mm. thick were cut
perpendicular to the axis of crystal growth, using the wire
saw. They were ground flat and then bridge-shaped samples
(see figure 6b) were cut on the Raytheon ultrasonic grinder.
In order to cut the samples without shattering they were
glued to a flat piece of glass with Eastman 910 adhesive.
After the samples were cut they were heated to $200°C$ to
destroy the adhesive bond with the glass.

The samples were etched in boiling 15 percent hydrogen
peroxide for five minutes.

3. CONTACTS

The most difficult part of the sample preparation was
making the electrical contacts. Due to the oxide layer
which forms almost immediately on a fresh surface of silicon

when exposed to the atmosphere, alloying directly to an etched surface as is done with germanium is not possible. The procedure used, as suggested by Turner,[17] is as follows.

First a gold plating solution was prepared. This was accomplished by dissolving 1.05 gm. of 99.999% pure gold wire from Sigmund Cohn in 500 ml. of solution containing 7.5 gm. of KCN and 2.0 gm. of $Na_2 HPO_4 \cdot 12H_2O$, both of which were of high purity. The solution was stirred with a glass stirring rod driven by an electric motor while being kept at a temperature of 70 to 80°C. One week was required for the gold to dissolve. All glassware used in the preparation of the solution was carefully cleaned with chromic acid and then rinsed several times in deionized water. The water for the solution was also deionized.

The surface to which contact was to be made was ground with carborundum on a clean glass plate and then washed with deionized water. A clip electrode was attached to the silicon specimen and the surface to be plated was dipped into a saturated potassium hydroxide solution, which was kept at a temperature just below its boiling point. The purpose of the potassium hydroxide bath is to remove the oxide layer from the specimen. The specimens were kept in the potassium solution until it began to react strongly with the surface, as noticed by the fizzing which occurred, usually after one minute or so. The contact surface was then quickly placed in the plating solution while the potassium hydroxide was

still reacting. The plating bath was held at 80°C. A piece
of pure gold wire, the same as that used to make the plating
solution, was used as the anode. The plating was carried out
for approximately one minute with a current density of 6 ma.
per cm^2. The surface was washed in deionized water. If the
plating was successful the surface appeared a shiny gold
colour with a uniform thickness of gold plate. Difficulties
were encountered in trying to plate specimens of the shape
shown in figure 6a. The closeness of the side arm probes
allowed plating solution to be drawn up by capillary action
to the regions between the probes, and to be plated there,
causing possible shorting between probes. As a result the
samples were cut to the shape shown in figure 6b.

Gold leads were alloyed to the gold plated surfaces
using the alloy machine. The specimen was heated in an inert
nitrogen atmosphere using a nichrome wire as a heater. Pure
gold wire was used for the p type material and pure gold wire
with 0.6% antimony doping was used for the n type material.
When heated the gold plate and the silicon formed a eutectic
into which the gold wire was alloyed. The pure gold wire
flowed easily into this eutectic. The alloying to the n type
silicon was more difficult. Considerable working over of the
surface with the antimony doped wire was required before the
wire would flow into the eutectic. Once this was done, how-
ever, good contacts could be obtained.

4. EXPERIMENTAL RESULTS

Measurements were performed on three samples cut from separate slices along the axis of crystal growth. One of these was p type with boron as the major impurity. The other two were n type containing antimony as the major impurity. The current leads were checked for carrier injection. The Hall constant was measured as a function of magnetic field at liquid nitrogen and room temperatures. Measurements of the Hall constant and resistance were made at temperatures from liquid nitrogen up to room temperature, from which the concentrations of N_a and N_d were calculated.

(a) Carrier Injection

The contacts in all samples were checked for carrier injection by the measurement of the resistivity and Hall constant as a function of electric field at room temperature and liquid nitrogen temperature. In all cases it was found that there was no carrier injection for electric fields up to several times greater than those used in the experiments.

(b) Hall Constant vs. Magnetic Field

A plot of Hall constant vs. magnetic field for the three samples used is shown in figures 9 and 10. It is seen that in both the n type samples there is a significant difference between low and high fields, and that the high field value appears to be approaching a limiting value, justifying the assumption of the use of r = 1. In the p type sample there

was not much variation of Hall constant with magnetic field, in agreement with the results of Long et al.

(c) <u>Determination of N_a and N_d</u>

The concentrations of N_d and N_a were calculated by the method suggested in chapter II. For the p type sample the value of p found at liquid nitrogen temperature was substituted into equation (39). The high concentration of acceptors indicated by the large exhaustion range value of N_a - N_d led to the choice of E_a - E_v equal to 0.043 eV.[7] Using equation (39), which has the degeneracy factor g=4, gave a negative value of N_d. Using g=3 gave a value of N_d of -0.075×10^{16} atoms per cc., a result which is essentially zero with respect to the value of N_a - N_d. The choice of g=2 gave N_d equal to 0.23×10^{16} atoms per cc. For their most pure samples Long et al[13] obtained the best fit to equation (39) using g=4. For their most impure sample containing 0.84×10^{15} atoms per cc the best fit was obtained using a value of g between 3 and 4. In view of the higher impurity concentrations found here it would seem that the correct value of g would be between 2 and 3. Using the limiting value of g=2 an upper bound of 0.23×10^{16} atoms per cc for N_d can be set.
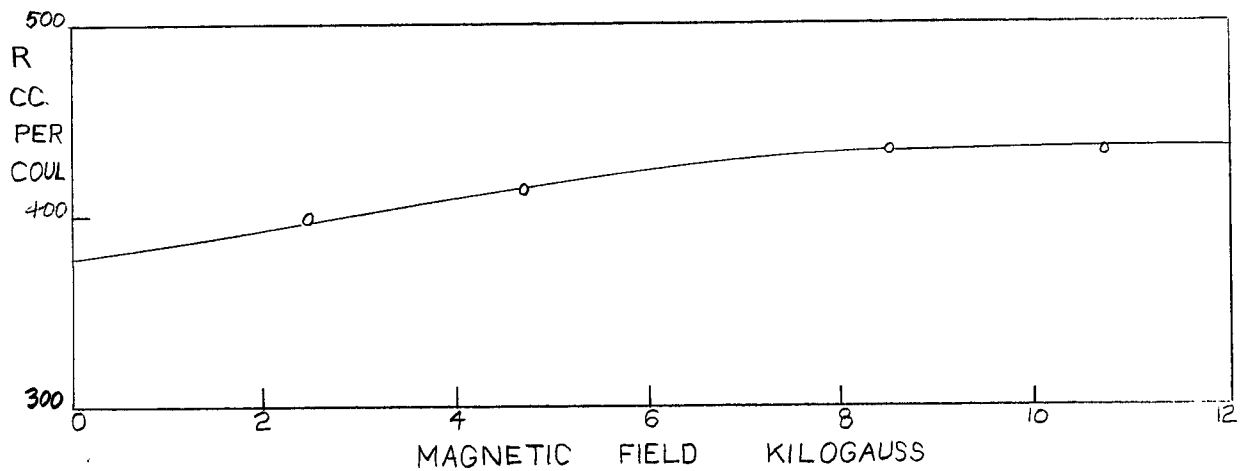
The values of N_a in the two n type samples SCV111.3 and SCV111.5 were calculated from equation (37), again using the values of n obtained at liquid nitrogen temperature. E_c - E_d was taken as 0.039 eV from the data of Morin et al.[8] The
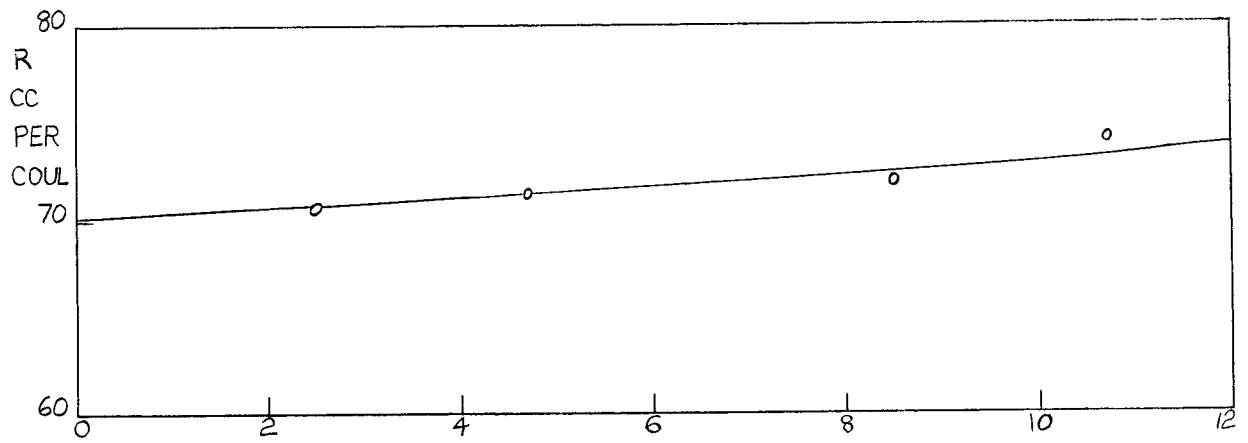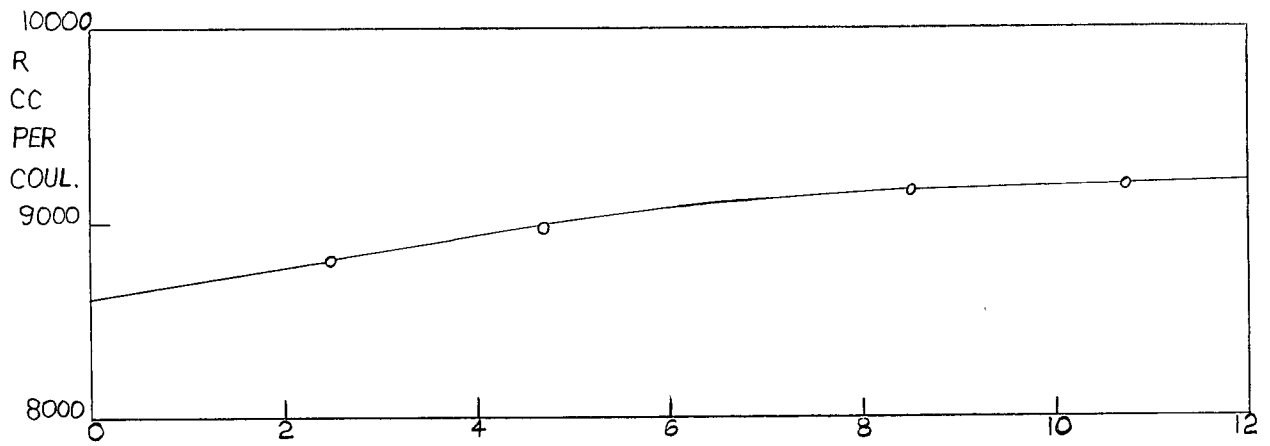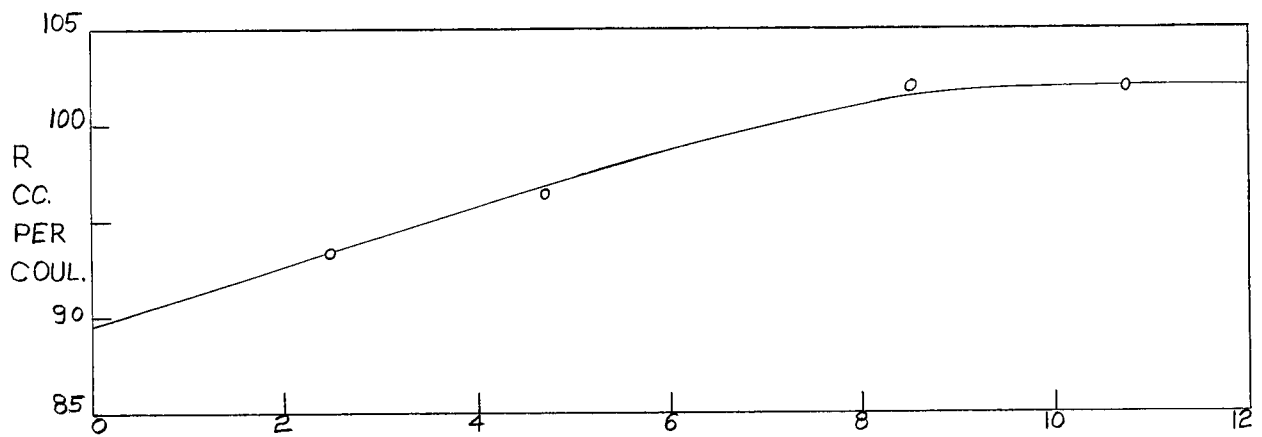
(a) SCVIII·2   T = 294°K
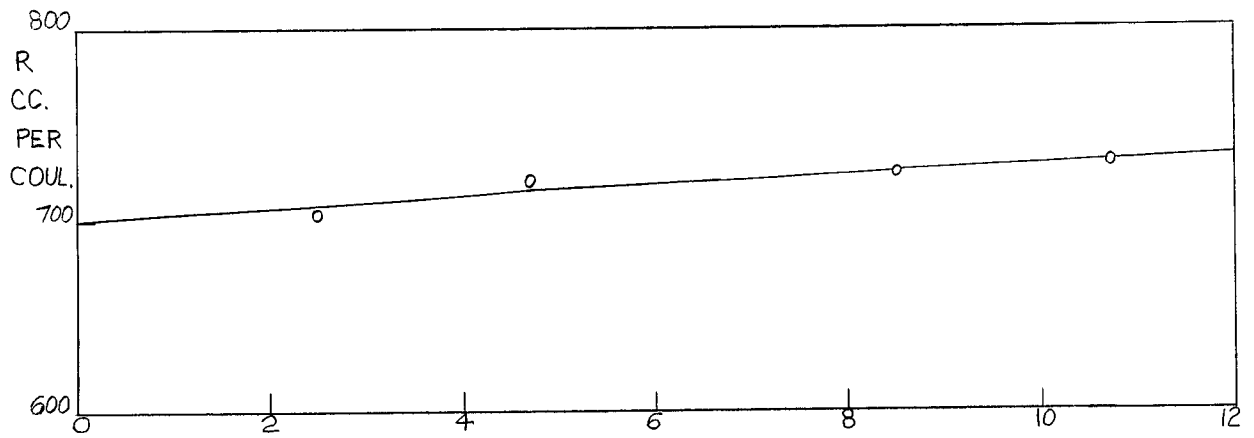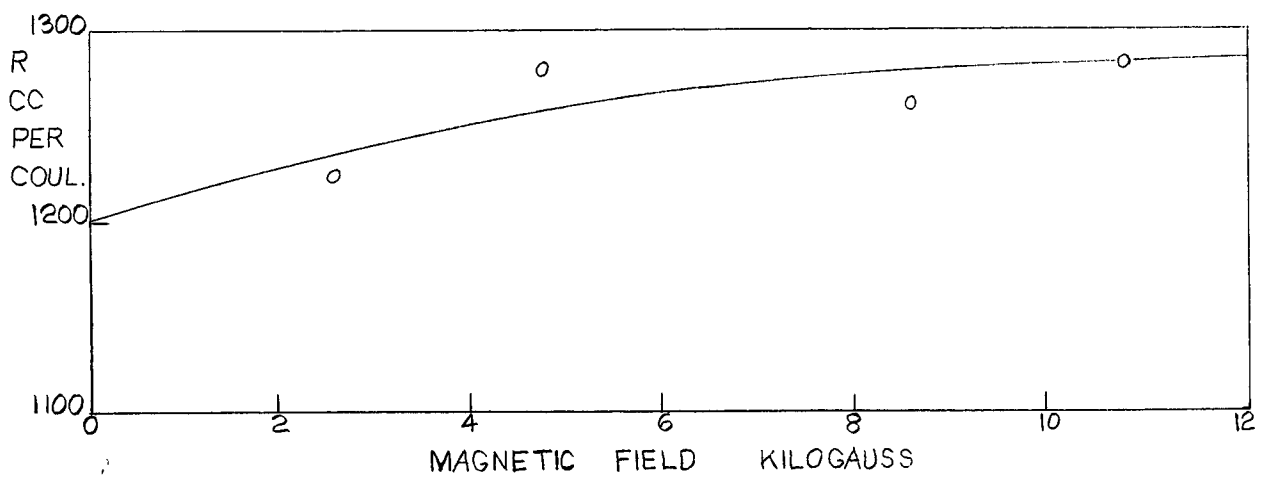
(b) SCVIII·2   T = 78°K

(c) SCVIII·3   T = 294°K

FIGURE 9   R VS. H

(a) SCVIII·3   T = 78°K

(b) SCVIII·5   T = 294°K

(c)   SCVIII·5   T = 78°K

FIGURE 10   R VS. H

value of $\triangle = 0.010$ eV was based on theoretical predictions of Kohn and Luttinger,[18] and the experimental results of Long and Myers[19] with phosphorous doped silicon. Since the value of N_a calculated from equation (37) is only a slowly varying function of $\triangle$, knowledge of the exact value of $\triangle$ is not important. The calculated values of N_a and N_d are listed in table I.

TABLE I

Sample	N_a atoms per cc	N_d atoms per cc
SCVIII.2	6.6×10^{16}	$< 0.23 \times 10^{16}$
SCVIII.3	5.4×10^{16}	6.9×10^{16}
SCVIII.5	2.6×10^{16}	8.8×10^{16}

A plot of μ_H vs. T is shown in figure 12. Note that the maxima of μ_H occur at higher temperatures with higher impurity concentrations.

The results obtained are in agreement with those expected from the knowledge of crystal growth. The first part of the crystal was boron doped only, and so only a small concentration of donors is to be expected. The boron concentration decreases along the length of the crystal because the melt becomes boron poor, due to the fact that boron is more soluble in solid than liquid silicon. On the other hand, starting

from the point where the antimony was added to the melt the antimony concentration increases along the length of crystal growth because antimony is more soluble in liquid than solid silicon. Figure 13 shows the concentrations of boron and antimony as a function of crystal length.

The value of N_a found in sample SCVIII.2 will be subject to experimental error and possible error in the value of r used. This should not be greater than 10% altogether. Only a value of the upper bound for N_d has been quoted for reasons explained previously. The greatest source of uncertainty in the values of N_a and N_d calculated for samples SCVIII.3 and SCVIII.5 comes from the uncertainty in the ionization energy used. An error of 0.0008 eV or 2% in the value of $E_c - E_d$ will cause an error of about 10% in the values of N_a and N_d calculated. In addition an experimental uncertainty of 5% will make the uncertainty in the calculated values about 15%.
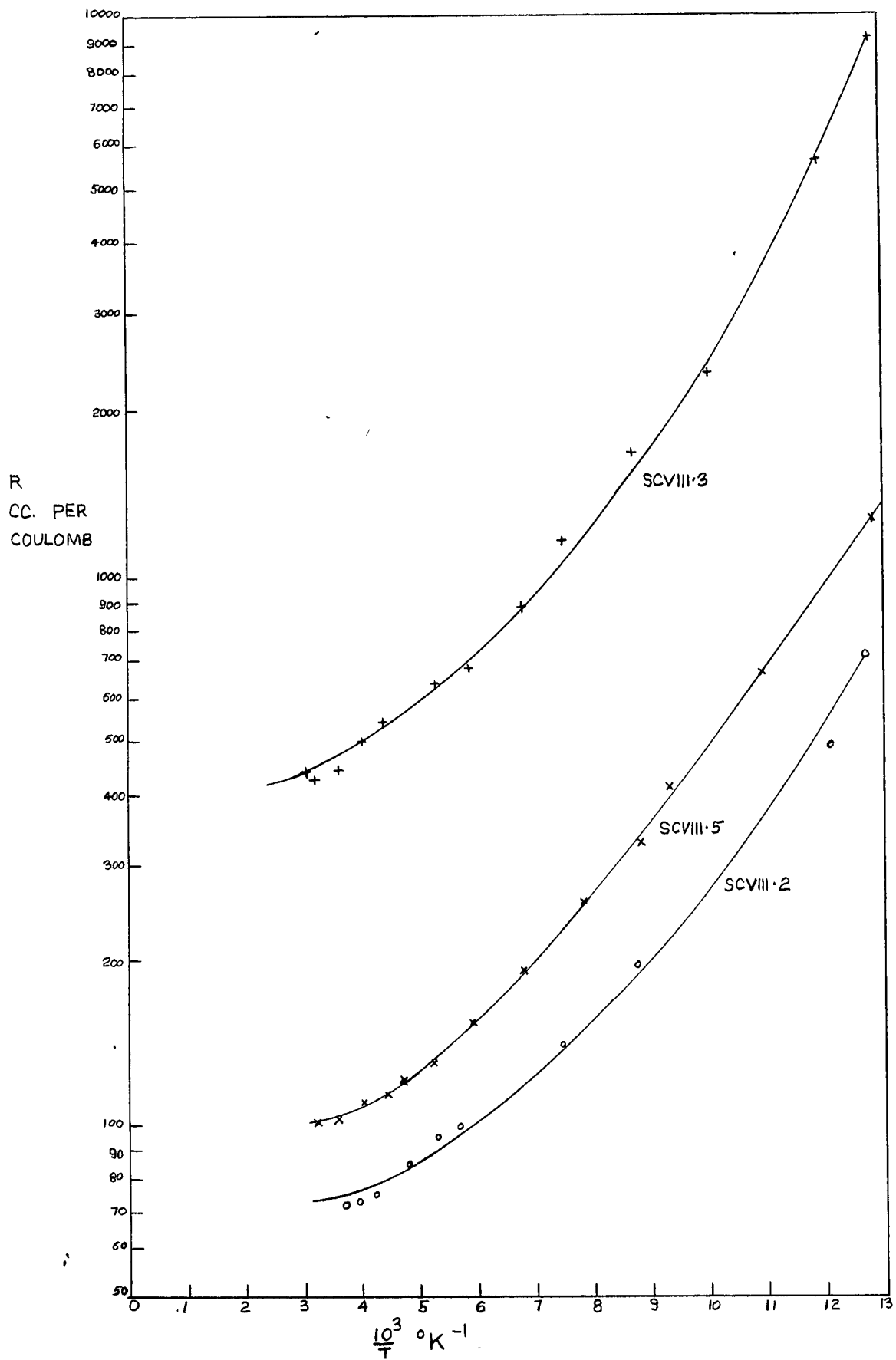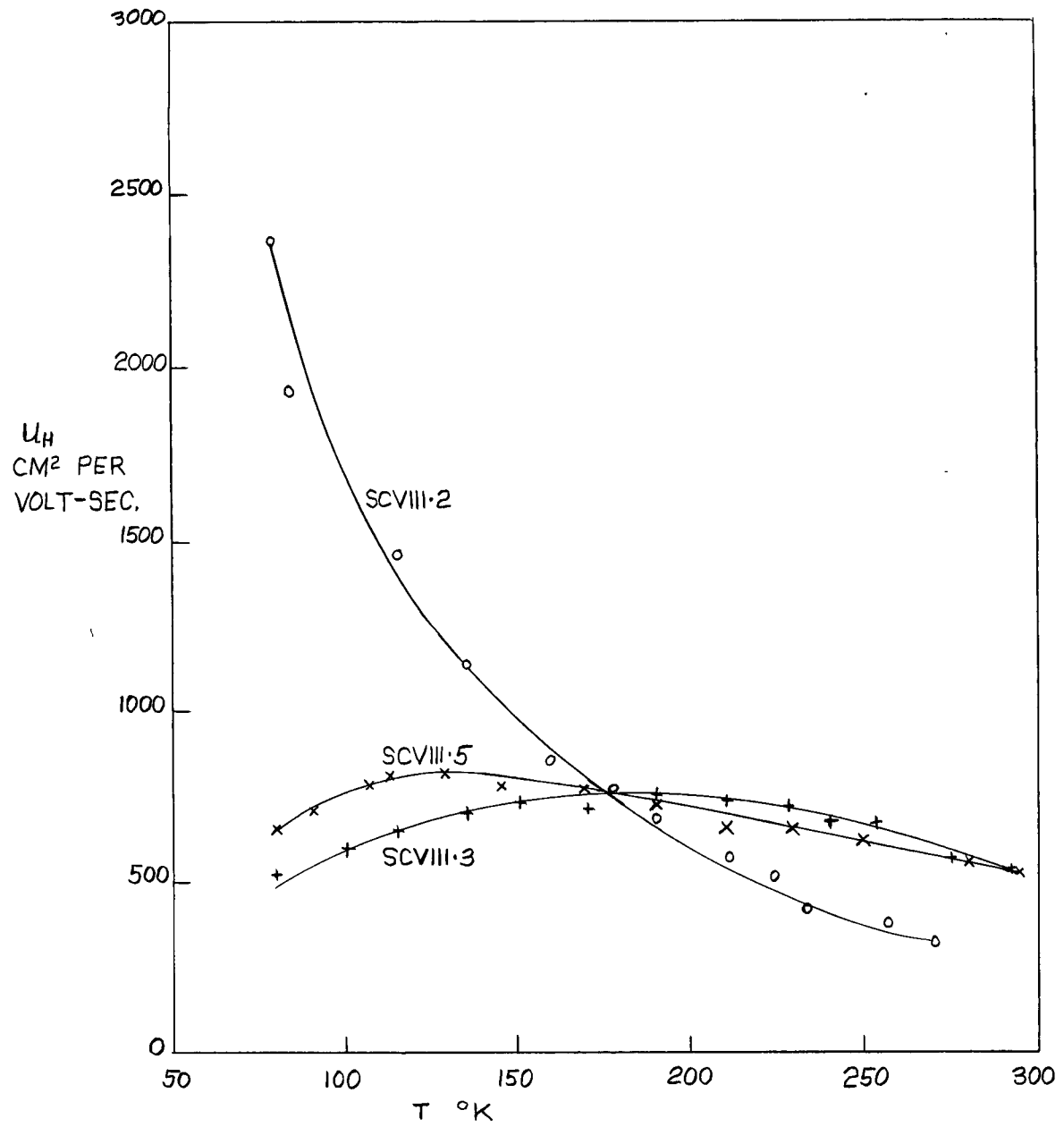
FIGURE II   LOG R VS. $\frac{1}{T}$

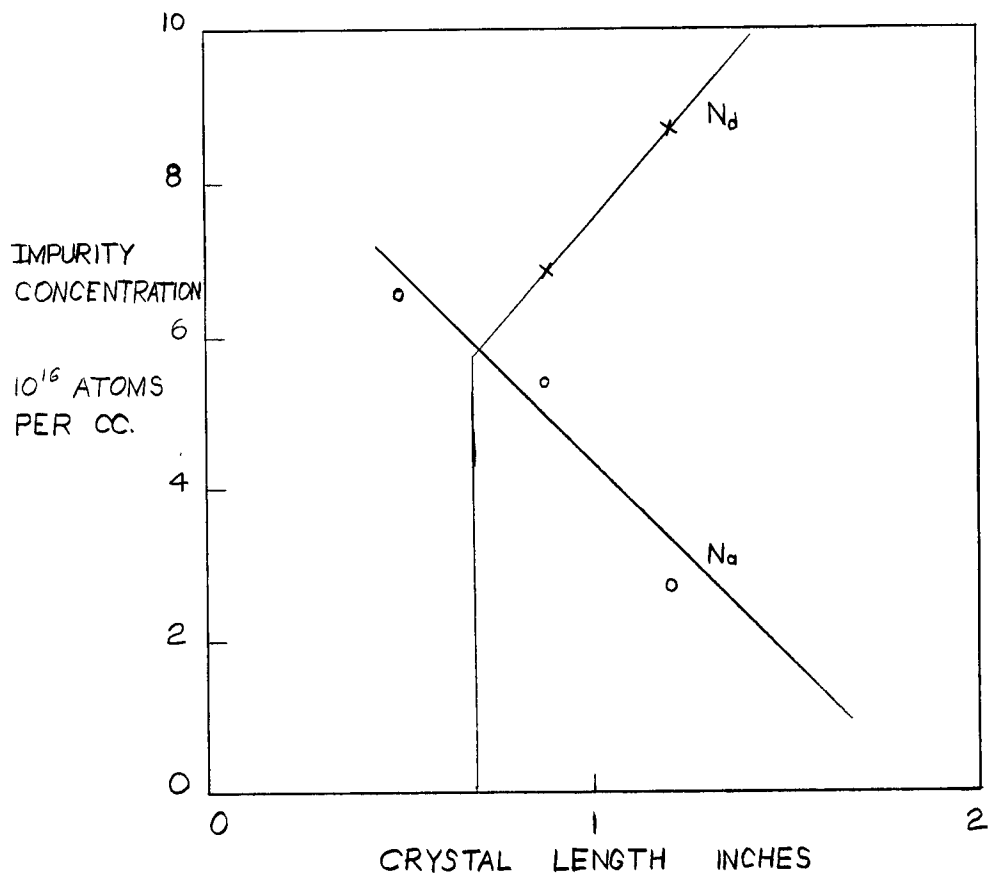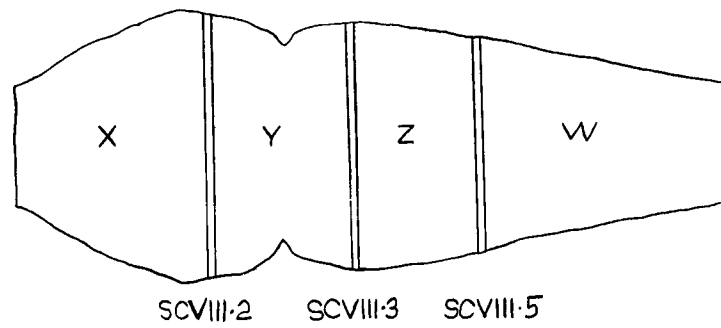FIGURE 12   HALL MOBILITY VS. TEMPERATURE

FIGURE 13 CONCENTRATION OF IMPURITIES ALONG CRYSTAL LENGTH

BIBLIOGRAPHY

1. F. Herman, Proc. IRE 43, 1703 (1955).

2. W. Kohn, Phys. Rev. 98, 1561 (1955).

3. G. G. Macfarlane and V. Roberts, Phys. Rev. 98, 1865 (1955).

4. B. Lax, Symposium on Physics of Semiconducting Materials, University of Michigan, June 7, 1955.

5. J. R. Haynes, M. Lax and W. Flood, Bull. Am. Phys. Soc. II 3, 30 (1958).

6. B. Lax and J. G. Mavroides, Phys. Rev. 100, 1650 (1955).

7. F. J. Morin and J. P. Maita, Phys. Rev. 96, 28 (1954).

8. F. J. Morin, J. P. Maita, R. G. Shulman, and N. B. Hannay, Phys. Rev. 96, 833 (1954).

9. P. T. Landsberg, Proc. Phys. Soc. B69, 1056 (1956).

10. P. P. Debye and T. Kohane, Phys. Rev. 94, 724 (1954).

11. D. Long and J. Myers, Phys. Rev. 115, 1107 (1959).

12. J. A. Swanson, Phys. Rev. 99, 1799 (1955).

13. D. Long, C. D. Motchenbacher, and J. Myers, J. App. Phys. 30, 353 (1959).

14. T. M. Dauphinee and H. Preston-Thomas, Rev. Sci. Inst. 25, 884 (1954).

15. T. M. Dauphinee and E. Mooser, Rev. Sci. Inst. 26, 660 (1955).

16. L. J. v.d. Pauw, Rev. Sci. Inst. 31, 1189 (1960).

17. D. R. Turner, J. of the Electrochemical Society 106, 786 (1959).

18. W. Kohn and J. M. Luttinger, Phys. Rev. 98, 915 (1955).

19. D. Long and J. Myers, Phys. Rev. 115, 1119 (1959).