

STUDIES OF SCANDIUM-GERMANIUM SYSTEMS  
and  
STUDIES OF ZINC AND SELENIUM DOPED GALLIUM ARSENIDE,

by

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B.A.Sc., University of British Columbia, 1964

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF  
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in the Department

of

PHYSICS

We accept this thesis as conforming to the  
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

December, 1965

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## II

### ABSTRACT

This investigation is concerned with a study of the properties of scandium-germanium systems, and a study of the properties of selenium and zinc doped gallium arsenide.

In part one the physical properties of scandium and germanium are used to empirically estimate the relative solubility of scandium in germanium. It was shown that scandium and germanium are miscible in the liquid phase and that scandium has a very low solid solubility in germanium.

Crystals of scandium-doped germanium were grown and analyzed using Hall constant and resistivity measurements from liquid nitrogen temperature to room temperature. The results show that the crystals grown are p-type, but that this behaviour cannot be completely attributed to scandium. However, it was shown that if scandium does not form compounds on crystal growth, it has a maximum solubility in germanium of less than one part per million.

Methods for analysing the results of experimental measurements, to determine the concentration of acceptors, donors and free carriers, and the ionization energies are given.

In part two the properties of selenium and zinc doped gallium arsenide were studied, again using resistivity and Hall measurements. Selenium and zinc were determined to be shallow donors and acceptors respectively. The concentration of the impurities present were determined and the properties of the material were discussed.

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ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. J.W. Richard for supervision of this investigation, for technical assistance and advice during the investigation, and for the very helpful discussion in the preparation of the final draft of this theses.

The author would also like to thank the National Research Council for financial assistance throughout the period of this investigation.

This work was supported by the National Research Council, under the grant number A-2204.

## PART I

### STUDIES OF SCANDIUM-GERMANIUM SYSTEMS

#### INTRODUCTION

It is desired to study the solubility of scandium in germanium and to determine the effects on the electrical properties of germanium when scandium is used as a doping impurity. For any two component system it is theoretically possible to calculate from first principles the behaviour of each component at different temperatures, pressures and crystal structures. In practice this calculation is very difficult and tedious and can be solved only after a large number of simplifying assumptions. In the final analysis it turns out that empirical relations derived from observations on a large number of two component systems will give adequate indications of the relative solubility of scandium in germanium. This is true provided the major chemical and physical properties of the components involved are known.

The properties of germanium are well known. Briefly, germanium is a semiconductor which crystallizes into the diamond lattice structure and has a forbidden energy gap of 0.785 electron volts at absolute zero temperature. Like all other semiconductors, germanium has the property that the introduction of very minute concentrations of electrically active impurities change its electrical and thermal properties drastically. The resulting properties may be determined by measuring such quantities as the Hall constant and resistivity. Thus in this manner it is possible to determine impurity concentrations in germanium of less than one part per billion.

Germanium belongs to the fourth group of the periodic table. In semiconductors of this group foreign atoms of group III and V enter this lattice substitutionally as acceptors and donors respectively. It is the relative valence between atoms of the lattice and atoms of the impurity which determines the acceptor or donor behaviour of impurities. For example, group III elements have one less valence electron than germanium and therefore are in a position to "accept" one electron to complete their tetrahedral bond with the remaining host atoms. The bound hole associated with the group III impurity in germanium has an energy slightly greater than the energy of the top of the valence band. These are known as shallow impurities. This argument can be applied to the case where scandium is an impurity in germanium. Scandium belongs to the subgroup of group III, and has a valence of three. Therefore scandium is expected to be a shallow acceptor impurity in germanium.

The properties of scandium are not well known. Even at this time there is disagreement between authors on the physical properties of scandium (see for example, values for the melting point, table I). This disagreement is due to the fact that it is extremely difficult to obtain this material in pure form and in reasonable quantities because of its high chemical activity. But it is known that scandium forms many compounds, among which there are compounds with germanium and carbon. This may prove troublesome since it is planned to study scandium-germanium systems by growing single crystals of scandium doped germanium using a carbon crucible to contain the melt. An extensive account of the properties of scandium is given below.

## 1. PROPERTIES OF SCANDIUM

### Physical Properties

Scandium occurs in nature only in the form of compounds, of which  $\text{Sc}_2\text{O}_3$  is the most abundant. These compounds do not form independent deposits but are widely dispersed throughout the earth's crust. Traces of  $\text{Sc}_2\text{O}_3$  may be found in all substances but in concentrations of less than .01% and, as such, no chief mineral source exists for the extraction of scandium. The natural occurring stable isotope of scandium is  $\text{Sc}^{45}$ . Although scandium is not classed as a rare earth element it is one of the rarest atoms which together with beryllium, cesium, niobium and others make up less than .01% of the earth's crust.

Scandium has atomic number 21, and atomic weight 44.96, it is the first element of group IIIB in the periodic table. This group also includes yttrium, lanthanum, actinium, the lanthanides and actinides. These elements are all characterized by having a full outer electron shell and a partially filled inner shell. Sc, Y, L, and Ac each have only one electron in their inner shell and therefore have similar physical and chemical properties. The ground state electronic configuration of scandium is  $1s^2 2s^2 2p^6 3s^2 3d^1 4s^2$  occupying the first four electronic shells K, L, M and N. Scandium gives up its electrons very readily and therefore is a very active element. It has an ionization energy of 7 electron volts.

Scandium metal is physically soft and possesses a silvery lustre. The solid exists in two allotropic forms  $\alpha\text{Sc}$  which is hexagonal close packed and  $\beta\text{Sc}$  which is face centre cubic. There is some doubt whether the latter allotope exists.<sup>2</sup> The properties of scandium are given in table I. Some properties of germanium are also given as they will be required in the

consideration of scandium-germanium system.

### Chemical Properties

Scandium has an oxidation state of +3, this state is very stable in aqueous solution. The divalent state  $\text{Sc}^{+2}$  has been found but it is very unstable.<sup>1</sup> Scandium shows a valence of three in all compounds formed.

Scandium is very active chemically, it forms many compounds both simple and complex, stable and unstable. Compounds of halides, sulphates, hydroxides, oxides, ammoniates, oxalates and others have been reported.<sup>1,2,3</sup> The most important compounds and some of their properties as far as this study is concerned are given below.

- $\text{Sc}_2\text{O}_3$ , Scandium Oxide, a white powder insoluble in water.<sup>1</sup>
- $\text{ScCl}_3$ , Scandium Chloride, hygroscopic white crystalline compound.<sup>1</sup>
- $\text{ScF}_3$ , Scandium Fluoride, very stable, white and crystalline.<sup>1</sup>
- $\text{ScB}_2$ , Scandium Boride.<sup>2</sup>
- $\text{Sc}_2\text{C}$ ,  $\text{Sc}_4\text{C}_3$ ,  $\text{ScC}$ , Carbides of Scandium.<sup>2,2</sup>
- $\text{ScGe}_2$ , Scandium Germicide.<sup>2</sup>

Very little is known about the carbides of scandium and  $\text{ScGe}_2$ , except that they do occur.

Scandium metal tarnishes slowly at room temperature but the corrosion rate increases rapidly with temperature. In aqueous solution the surface becomes dull and pits begin to form, in hot water scandium decomposes by the liberation of hydrogen. It is attacked appreciably by all acids strong or otherwise. No chemical polish for scandium has yet been found.

<u>PROPERTIES</u>	<u>SCANDIUM</u>			<u>GERMANIUM</u>
	1	2	Others	
Boiling Point °C	2400	3000		
Crystal Structure	hcp	hcp		diamond
	fcc	fcc?		
Density g/(cm) <sup>3</sup> @ 20°C	2.5	2.98	3.30 <sup>3</sup>	5.3
Electronegativity		1.3	2.1227 <sup>4</sup>	1.77 <sup>4</sup>
$\Delta H_f^*$ Kcal/mole			<sup>4</sup> <sup>5</sup>	
$\Delta H_s^*$ @ 25°C " "		81	80.8 <sup>4</sup>	89 <sup>4</sup>
$\Delta H_v^*$ @ B.P. " "			80 <sup>5</sup>	68 <sup>5</sup>
Melting Point °C	1200	1539	1673 <sup>5</sup>	937.6 <sup>5</sup>
Resistance ohm-cm @ 25°C		66(10 <sup>-6</sup> )		
Coeff. of Resistance /°C		.00282		
Atomic Volume cm <sup>3</sup> /g atom		15.061	15.06 <sup>4</sup>	13.64 <sup>4</sup>
Ionic Radius (Å°)			0.81 <sup>6</sup>	0.53 <sup>6</sup>
Metallic Radius "		1.645		
Neutral Atomic Radius "			1.51 <sup>5</sup>	1.22 <sup>5</sup>
Radius (coord. no. 12) "			1.641 <sup>4</sup>	1.369 <sup>4</sup>
Single Bond Radius			1.439 <sup>7</sup>	1.22 <sup>6</sup>

Table I Properties of scandium as reported by Borisenko,<sup>1</sup> Spedding and Daana<sup>2</sup> and others. Some properties of germanium are also shown.

\*  $\Delta H_f$ ,  $\Delta H_s$ , and  $\Delta H_v$  are the heats of fusion, sublimation and vaporization respectively.

## SOLUBILITY OF SCANDIUM IN GERMANIUM

### 1. EMPIRICAL CONSIDERATIONS

There are a number of ways in which the solute atom may be distributed on the lattice of the solvent. A solute atom may substitute for or fit interstitially between the host atoms or it can be associated with crystallographic defects in the solvent such as atmospheres around dislocations. The ease in which a solid solution may be formed between two components depends on a number of factors. Such factors as relative size, electronegativity and valency, free energy and liquid miscibility determine the resulting equilibrium conditions of the binary system.

#### The Hume-Rothery Rules<sup>8</sup>

Hume-Rothery formulated a number of empirical rules regarding the properties of solute and solvent and the relative solubility of the solute in the solvent.

When the relative size difference between the components is large, a strain field is set up around the solute atom. This strain field may increase only to a certain limit after which a second phase will precipitate to reduce the strain energy. A size difference of 15% produces very restricted solubility. This is the first Hume-Rothery rule.

Electronegativity is a measure of the tendency of one element to accept electrons and form bonds with another element. A large difference in electronegativity increases the probability of compound formation between the components, thus reducing the solid solubility of the solute. The second rule follows. If the electronegativity difference is more than 1.4 units the extent of solid solubility is small.

If the size and electronegativity differences are small, then it generally holds that a solvent is more capable of dissolving a solute of higher valency than one of lower valency than the solvent possesses. This can be seen by considering the relative valence electron concentration around solvent and solute atom. If the solvent has a higher valency than the solute, it has a larger electron concentration and therefore has a greater tendency of making bonds between its own atoms rather than with the solute atom. A solvent of lower valency, on the other hand, sees a higher electron concentration around the solute atom and will therefore have a tendency to bond with it.

#### Liquid Miscibility

The energy of mixing of a regular solution of two components is given by Hildebrand and Scott<sup>9</sup> as  $H_b$ .

$$H_b = \frac{1}{2}(V_1 + V_2)(d_1 - d_2)^2 \quad (1)$$

Where the subscripts 1 and 2 refer to solvent and solute respectively,  $V$  is the atomic volume,  $d$  is the solubility parameter and is defined as:

$$d = (\Delta H/V)^{\frac{1}{2}} \quad (2)$$

$\Delta H$  is either the heat of sublimation or vaporization given at 25°C.

Usually the heat of vaporization  $\Delta H_v$  is given at the boiling point of the substance, in this case the solubility parameter is approximately given by:

$$d \approx (\Delta H_v - RT)^{\frac{1}{2}} / (V_{liq})^{\frac{1}{2}} \quad (3)$$

$V_{liq}$  is the atomic liquid volume which differs less than 5% from the atomic solid volume,  $R$  is the gas constant and  $T$  is the absolute temperature.



Separation of liquid phases can be expected when the energy of mixing  $H_b$  is larger than the thermal energy  $2RT$ . This is Hildebrand's criterion for liquid immiscibility.

Mott<sup>10</sup> further took into consideration the electronegativity difference between the components. He argued that the energy of mixing is decreased by the tendency of bonds to occur and miscibility of the components is less likely. Mott defined the number of bonds  $k$  that will occur as

$$k = \frac{H_b - 2RT}{23060 (\Delta E_n)^2} \quad (4)$$

$\Delta E_n$  is the difference in electronegativity between 1 and 2. If  $\Delta E_n$  is expressed in electron volts then the denominator of (4) represents the energy in calories of forming a bond. If  $k$  is less than 2 complete miscibility occurs, for  $k$  between two and six miscibility occurs depending on size factor and when  $k$  is greater than six the liquid phases are completely immiscible. The Mott criterion has been found much more successful than the Hildebrand criterion for predicting liquid miscibility.

From the above considerations a number of predictions may be made about scandium-germanium system. Where germanium is the solvent and scandium the solute.

Since scandium is about 20% larger than germanium it is more likely to substitute for germanium atoms on the germanium lattice rather than fill an interstitial position. The electronegativity difference between germanium and scandium is 0.5 units. According to the Hume-Rothery criterion, these conditions imply a very low solubility of scandium in germanium.

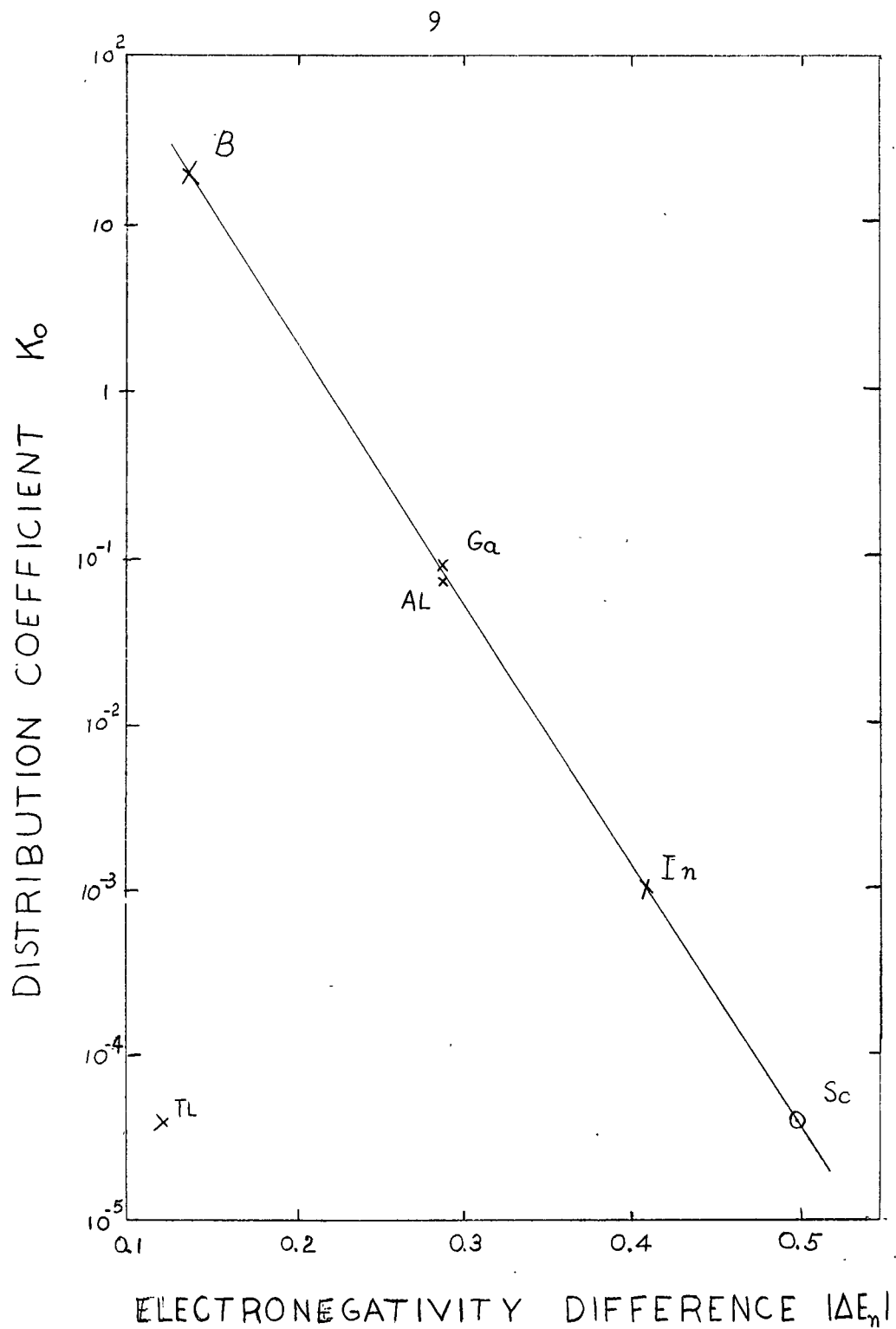


Figure 1. Correlation between distribution coefficient of group III elements in germanium and the absolute value of the electronegativity difference between these elements and germanium

The Mott number was calculated for a liquid solution of scandium in germanium. Using the heats of sublimation and equations (2) and (4),  $k$  was found to be  $-0.66$ . As a further check  $k$  was calculated at the melting point of germanium ( $936^{\circ}\text{C}$ ), this time using the heats of vaporization and equation (3) and (4) which gave a value of  $-1$  for  $k$ . Therefore scandium and germanium are miscible in the liquid state according to the Mott criterion.

## 2. CRYSTAL GROWTH

### Prediction of the Distribution Coefficient

The amount of solute or impurity which can be incorporated into a crystal upon normal freezing from a melt is characterized by a distribution coefficient  $K$ . For a binary system  $K$  is defined as the ratio of the atomic fraction of the impurity in the solid  $X_s$ , to the atomic fraction of the impurity in the liquid  $X_L$ .

$$K = \frac{X_s}{X_L} \quad (5)$$

For restricted solubility  $K$  is always less than one.  $K$  has been found to depend on the temperature below the melting point of the solvent, the rate of diffusion of the solute atom at the solid liquid interface and on the rate of crystal growth. A distribution coefficient  $K_0$  is defined as the value of  $K$  at the melting point of the solvent. And  $K_m$  is defined to be the maximum solid solubility of solute in the solvent.

Correlation between the distribution coefficient and various solute and solvent properties have been made. Trumbore<sup>11</sup> finds that correlations of the distribution coefficient with solute properties is a desirable

parameter for comparing relative tendencies of impurities to enter germanium.

Figure 1 shows the relationship between  $K_o$  and atomic radius. Figure 2 gives the variation of the absolute value of the electronegativity difference with atomic radius. And figure 3 shows the relationship between  $K_m$  and atomic radius. The data for these curves is taken from table II.

### GROUP III

Element	Atomic Radius Ao <sup>5</sup>	$K_o$	$K_m/cm^3$ ( $10^{-19}$ )	$ \Delta E_n $
B	0.7	17		0.14
Al	1.43	0.073	.42	0.29
Sc	1.51			0.50
Ga	1.33	0.087	50	0.29
In	1.45	0.001	0.4	0.41
Tl	1.90	$4(10^{-5})$		0.13

### GROUP V

Element	$K_o$
N	
P	0.08
V	$<3(10^{-7})$
As	0.02
Sb	0.003
Bi	$4.5(10^{-5})$

Table II Data used for predicting the distribution coefficient for scandium in germanium. The values  $K_o$  and  $K_m$  are taken from Trumbore.<sup>11</sup>

There is a similarity between group III and corresponding group V elements and their distribution coefficients. From table II it is found that  $K_o$  for group III differs at the most by a factor of three from  $K_o$  of the group V's. This would put distribution coefficient of scandium between  $10^{-6}$  and  $10^{-7}$  if  $K_o$  for vanadium has been determined correctly as  $3(10^{-7})$ .

Trumbore correlates values of  $K_o$  and tetrahedral radii of the elements. The radius\* of scandium is the same as that of indium but scandium has a

\*The single bond radius was used as the tetrahedral radius for scandium, the variation between the two is very small.<sup>6</sup>

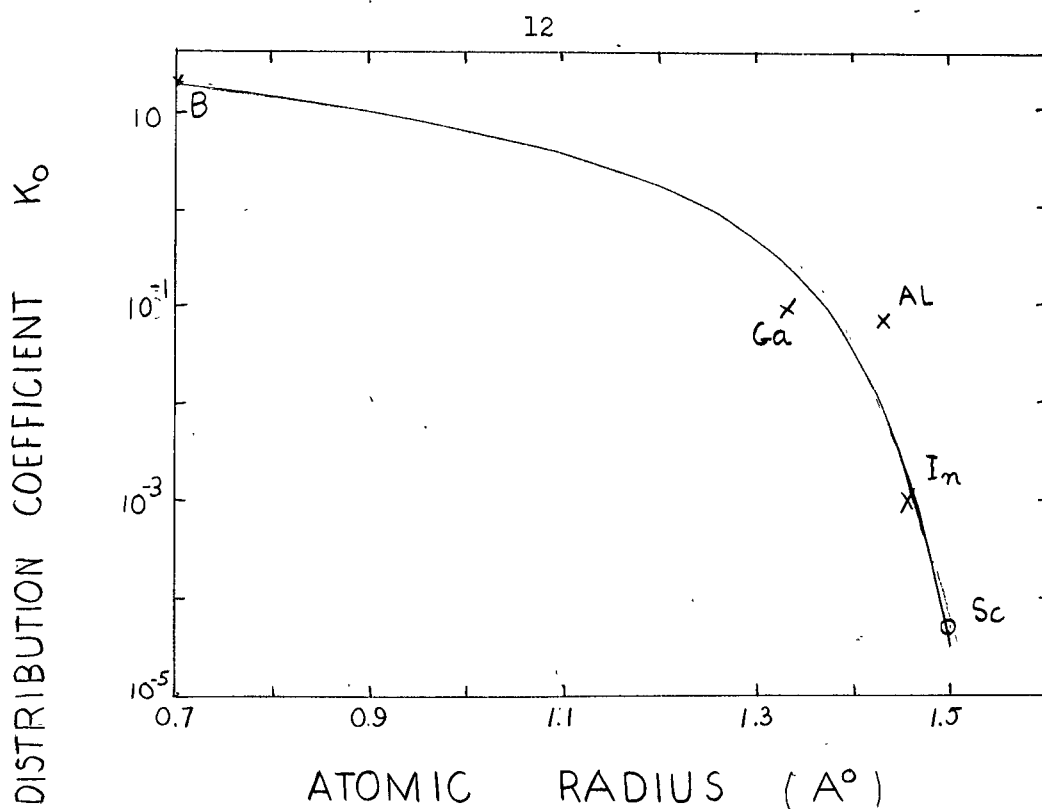


Figure 2. Correlation of distribution coefficient with atomic radius for group III elements in germanium.

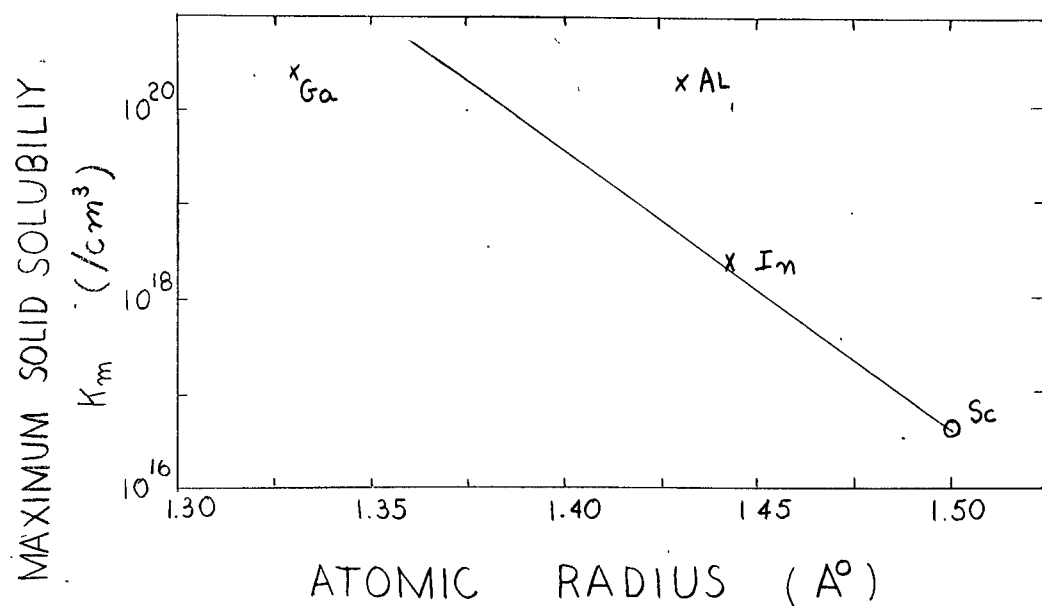


Figure 3. Correlation of maximum solid solubility with atomic radius for group III elements in germanium.

higher electronegativity difference. Therefore an upper limit of  $K_0 = 0.001$ , which is the value for indium can be set.<sup>11</sup>

Figures 1 and 2 predict a distribution coefficient of  $10^{-5}$ , which is the mean of the two limiting values  $10^{-3}$  and  $10^{-7}$  determined above. Therefore  $K_0$  for scandium in germanium will be taken as  $10^{-5}$ .

The maximum solid solubility as determined from figure 3 is  $10^{16}/\text{cm}^3$ . That is, the predicted maximum concentration of scandium which can be incorporated into germanium is  $10^{16}/\text{cm}^3$ .

#### The Purity of Scandium

To study the behaviour of scandium it was required that a number of single crystals of scandium doped germanium be grown. The impurities present in the scandium must be taken into consideration since they limit the ultimate amount of dopant to be used. And if the distribution coefficient of the impurity is very large compared to that of scandium, the impurity may have the dominant effect in germanium.

Scandium metal was obtained in ingot form from Koch Light laboratories and was 99.9% pure. Spectrographic analysis showed twelve impurities present, in concentrations ranging from 200 to 10 parts per million. Of these, only aluminium, need be considered because it has a large distribution coefficient of 0.073. Aluminium is present in the scandium metal used in 20 parts per million. Thus for any amount of scandium metal used to dope germanium, about  $1.5(10^{-6})$  of this amount will be aluminium. This implies that the distribution coefficient must not be smaller than  $10^{-5}$  as was predicted or the effects of scandium in germanium will be masked by the effects of aluminium.

### Crystal Growth

The Czockralski crystal pulling technique was employed to grow single crystals of scandium doped germanium. In this method the molten germanium and its dopant are held in a crucible whose temperature is accurately controlled. A monocrystal seed of germanium, attached so that it can be lifted and rotated simultaneously, is dipped into the melt and is used as a growth nucleus. The resulting monocrystal is slowly "pulled" out of the melt. The Czockralski apparatus was available in our laboratory and has been used by Syed,<sup>12</sup> and others to successfully grow doped and intrinsic germanium monocrystals.

The charge preparation for crystal growth is very important since it insures the purity of the final product. Germanium was prepared as outlined by Syed.<sup>12</sup> Scandium, because of its high chemical activity and physical softness posed a number of problems. Minute pieces of scandium were cut off the ingot using a pair of side cutters, cleaned in a weak warm solution of nitric acid. All other conventional methods of cutting this material failed. These pieces were then cleaned.

Chemical cleaning of scandium was attempted using a number of acid and basic solutions as outlined by Spedding and Daana,<sup>2</sup> and by Holmes.<sup>13</sup> None of these yielded a clean metallic surface, most of them formed some compound with scandium which either remained as a surface layer or flaked off. Mechanical cleaning was then attempted. Sand blasting or grinding, could not be used without appreciable contamination since sand and the grinding compound would lodge in the surface of the soft scandium. Finally the surface of the scandium was meticulously scraped using a chemically cleaned razor blade.

After a thorough preparation, the germanium was put into the crucible and the scandium was placed on top of a large piece of germanium so that it could be easily observed. A normal charge for crystal growth consists of about a 100 grams of germanium and 10 milligrams of scandium. The temperature of the crucible was increased and the behaviour of the dopant was observed. When the germanium began to melt the scandium would become a creamy white colour and seemed to slowly spread over the surface of the liquid to form a very thin layer which solidified. This sheet would either attach itself to the crucible wall or float in the centre of the melt. Raising the temperature to the limit of the furnace ( $1,200^{\circ}\text{C}$ ), would not melt this layer, but did cause it to break away from the crucible wall. The presence of this solid layer made crystal growing much more difficult.

When the germanium was completely molten the monocrystal seed, of known orientation was pushed down until it broke through the thin solid layer. The temperature was adjusted to a little below the melting point of germanium and the crystal was slowly pulled.<sup>12</sup> The advancing crystal broke tiny pieces off the thin solid layer. These minute pieces were incorporated into the sides of the crystal by the freezing germanium. At other times the complete crust would solidify to the seed and the crystal could not be grown. After the crystal was fully grown it was allowed to cool slowly. Five out of six crystals attempted were grown successfully.

As crystallization occurs under equilibrium conditions the solute atoms are rejected from the liquid solid interface. This process is characterized by the distribution or segregation coefficient  $K$  which has already been discussed. The composition of the solid forming at any one time is given by  $X_s = KX_L$ . As crystal growth continues the rejection of solute atoms by the



solid enriches the melt. Which in the final analysis, causes an increase in solute concentration along the axis of growth of the crystal.

The crystal geometry was controlled by either regulating the heat input to the melt or the withdrawal rate of the crystal. A decrease in temperature caused an increase in diameter of the crystal, a decrease in pull rate caused an increase in diameter also. When the heat input was regulated such that the diameter was held uniform at a certain pull rate then the crystal grew at this rate. A steady state had then been achieved between rate of growth and heat input.

Resistivity measurements along the growth axis using a four point probe showed that the increase in solute concentration was almost linear with length, until close to the end of the crystal where the concentration increased exponentially. The ends of the crystal were not used for experimental measurements.

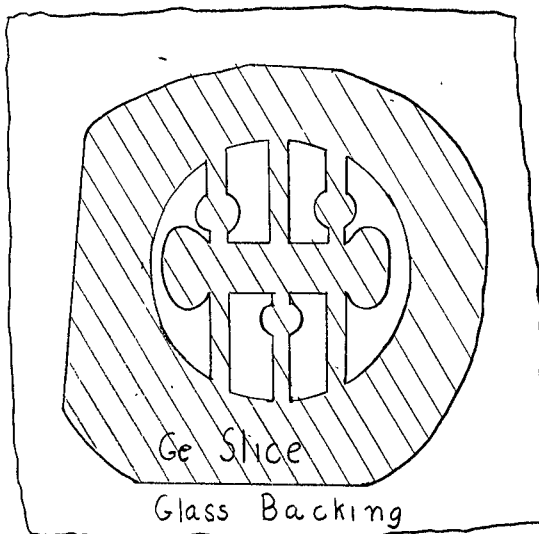
EXPERIMENTAL

## 1. SAMPLE PREPARATION

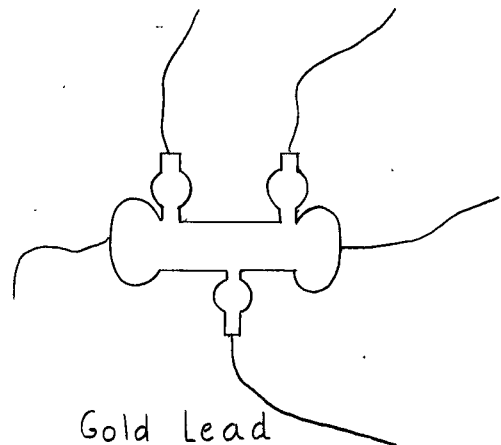
A number of slices approximately 0.050 inches thick were cut from the crystal perpendicular to and at different positions along the axis of growth. A diamond wheel or a reciprocating tungsten wire saw, using #600 carborundum mixed with grease as a cutting compound, were used to cut the slices. The slices were then polished up by lapping each face on a glass surface with #600 corborundum. They were then washed and put in boiling 3% hydrogen peroxides solution for five minutes. Each slice was inspected for flaws such as twinning and large grains. A uniform reflection across the face of the slice and the characteristic form of four flattened sides of a germanium crystal grown along the [100] direction was taken as ample evidence of monocrystallinity.

Using a four point probe the resistivity was measured at a number of points on each slice and was found to vary from 1 to 3% depending on which end of the crystal the slice was taken. This variation was considered negligible since the variation in resistivity over the small size Hall sample would be less than 1%. As many as four samples could be made from one slice. Each slice was then mounted on a fairly substantial glass plate, about 1 1/2 inches square and 1/8 inch thick, using Eastman 9-10 adhesive. Care was taken that no air pockets remained between the slice and the plate. The mounted slice was allowed to cure for about three hours at room temperature. After which a Hall sample was cut using a stainless steel dye driven by a Raytheon Ultrasonic oscillator. A mixture of water and #600 corborundum powder was used as a cutting compound. A weighted lever arrangement

brought the mounted slice against the dye and exerted a small pressure on it, which caused the dye to cut the slice. A gauge calibrated in .001 inches was provided to determine when the dye has passed through the slice. The average time taken to cut through a germanium slice 0.040 inches thick was about fifteen minutes. Unwanted arms were removed by using a small sand blaster. The Hall specimen was removed from the glass plate by heating to about  $100^{\circ}\text{C}$ , in order to break the adhesive bond. The Hall sample was carefully polished to remove the adhesive and then degreased in boiling 3% hydrogen peroxide.



(a)



(b)

Figure 4. (a) Shows a Hall sample cut by the ultrasonic grinder into a mounted germanium slice.  
 (b) Shows the finished Hall specimen (about three times full size).

### Contacts

All electrical contacts required for Hall effect measurements are made to the germanium sample using the gold alloy technique. The alloying is carried out in a stainless steel furnace equipped with a glass cover. The Hall specimen is clamped into position in a small nichrome heater using a pair of self locking tweezers. The temperature of the heater is fully controllable and the heater is small enough so that only the area to which the contact is to be made is heated. A hole in the glass cover directly above the heater allows a gold wire of 0.005 inches in diameter to be lowered with the aid of commercial micro-manipulators until the end of the wire touches the contact area. A 12X binocular microscope is used to observe the contact area and aids in guiding the gold wire to the correct position. A total of five contacts are required for each Hall specimen.

The Hall specimens are prepared by alloying gold into the specimen after gold plating or by alloying gold in directly. The achievement of a proper ohmic contact depends crucially on this preparation. The contact area must not become contaminated in any way during the whole operation.

For gold plating, the contact area of the specimen is cleaned with a warm dilute solution of 10% KOH, and then rinsed in deionized water. The contact area of the specimen is then immersed into a gold cyanide solution.<sup>14</sup> Electroplating is carried out using the solution as the electrolyte, a gold wire as the anode and the specimen as the cathode. A current of 2 ma per (mm)<sup>2</sup> of contact area is passed until this area turns to a well defined gold colour. The sample is again rinsed in deionized water and alloying is carried out immediately. The procedure is repeated for all contacts.

In the second method of preparation, the entire specimen is etched in

medium CP4 solution<sup>13</sup> and then rinsed with deionized water. All five contacts are then alloyed on. A variation in this method is the following. After the two end contacts have been alloyed, a small piece of germanium is broken off the side arms. Alloying of the last three contacts is then carried out on a fresh germanium surface. The only drawback here is that germanium samples break very easily.

In the actual alloying the temperature of the heater is raised until the contact area reaches the gold germanium eutectic temperature, judged by eye. At this point the gold plated layer suddenly changes from gold to a silvery colour with a metallic lustre. Then the gold wire is lowered into the eutectic layer. A small amount of the gold is allowed to melt to form a pool of gold for mechanical strength. The contact is allowed to cool slowly in order to minimize all strains. In the case where the contacts are alloyed on directly, the gold wire is worked over the contact area at the eutectic temperature to produce a small pool of gold. The gold wire is then immersed into the pool of gold and the sample is allowed to cool slowly. The result is that gold electrical leads have been alloyed to the sample (figure 4).

#### Contact Testing

The current carrying contacts are checked for ohmicity by measuring the D.C. forward and reverse voltage-current characteristics. Agreement between forward and reverse characteristics at room and liquid nitrogen temperatures is indicative of good ohmic current contacts. The currents used in these measurements are well in excess of those used in the measurements of Hall coefficient and resistivity.

After the current contacts have been determined to be ohmic, the side

arm contacts are checked by measuring the forward and reverse resistance between the side arm and the ends. A variation of less than 1% between the resistances will not influence the experimental results. The Hall and resistivity measurements are actually independent of side arm contact resistance, since no current is passed through them.

It was found that the contacts produced by directly alloying gold into the germanium were satisfactory. Consequently this technique of making electrical contacts to the specimen was used throughout the experiment.

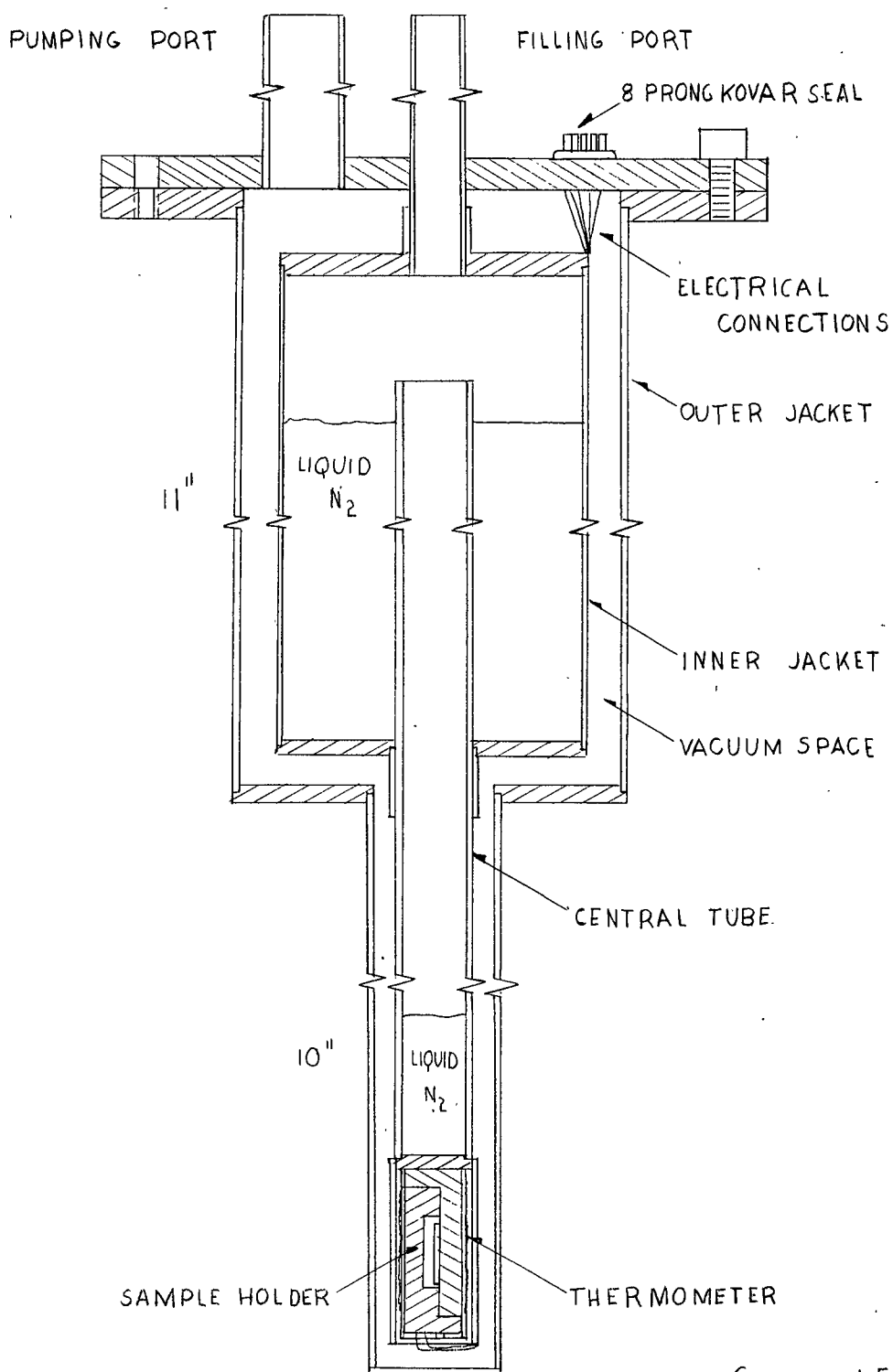
## 2. MEASUREMENTS

### Apparatus

The Hall effect circuit was built in this laboratory by D.J. Jones<sup>15</sup> and has been used to measure the Hall effect in impurity-doped silicon. The circuit provides for the measurement of the Hall constant and the sample resistivity as well as the resistance of a copper thermometer. A rubicon galvanometer of 0.0054 microamps per millimeter sensitivity is used as a null indicator.

The magnetic field is provided by a water cooled electromagnet with conical pole pieces of four inch diameter and 2 1/4 inch gap. The magnet was calibrated using a fluxmeter (Rawson type 504) and a search coil. Fields up to 25,000 gauss can be obtained. The homogeneity of the field was checked and found to be satisfactory.

A metal dewar was constructed to allow measurements to be taken at temperatures between 77 and 300°K. The dewar consists of an outer jacket separated from the inner jacket by a vacuum space, (figure 5). The inner jacket contains a stainless steel tube whose lower end is sealed with a



SCALE  $\sim \frac{1}{2}$  FULL SIZE

Figure 5. Metal dewar used to vary temperature of the Hall specimen from 66°K to 300°K.

copper plate. A short copper tube attached to this plate holds the resistance thermometer as well as the sample holder. Electrical connections run from the sample and thermometer out of the copper tube up along the outside of the central tube and inner jacket to the eight prong kovar seal in the top plate. These leads provide for temperature and Hall measurements by the Hall circuit. The inner jacket can easily be removed from the outer jacket so that samples may be changed. A filling port permits the inner jacket and central tube to be filled with refrigerant. While a pumping port allows the vacuum to be maintained between the two jackets. The dewar has a long tail so that the sample holder is centred between the magnet's pole pieces when the dewar is in place.

A copper resistance thermometer is used to measure the temperature. This is simple to construct, has a linear response over the range of temperature required and recycles within a very small error. It is constructed from No. 40 B & S copper wire (Canada Wire and Cable) wound bifilar onto a copper tube. A four lead arrangement to the coil makes it possible to measure the thermometer's resistance only and not that of the leads, which may be at a different temperature. It has a room temperature resistance of 140 ohms. The thermometer is calibrated at the ice point and the remaining temperatures are established from a published table.<sup>16</sup> This thermometer allows rapid temperature reading with an error less than 0.5°K.

#### Method

Hall measurements are made using a 35cps square wave current in a constant magnetic field as described by Dauphinee and Mooser.<sup>17</sup> An alternating capacitor-resistance bridge measures the ratio of the resulting voltage to the current passing through the specimen using a nulling



procedure. A D.C. galvanometer is used as a null indicator. In this manner both resistivity and Hall measurements can be made using the same circuit.

Passing an alternating current through the sample eliminates a number of thermal effects which are present in D.C. measurements. Such effects as Ettinghausen, Nerst, Righi-Leduc as well as magnetoresistance are eliminated. Furthermore all measurements are made under equilibrium conditions and are independent of the lead potential since at balance no current should flow in them.

Hall and resistivity measurements are made at temperatures between 77 and 300°K in the following manner. The central tube and inner jacket are filled with coolant (figure 5). This cools the sample to 77°K. The liquid nitrogen in the central tube boils more rapidly than in the inner jacket and disappears in a short time, while an appreciable amount is retained in the jacket (figure 5). This prevents rapid warming of the sample holder. Steady state between the rate at which heat is conducted away from the sample holder and the radiation incident from the outside jacket is reached around 200°K. The range from 200 to 300°K is spanned when the coolant has completely boiled off and the inner jacket warms to room temperature. The highest rate of heating occurs just above 77°K and is about two degrees per minute, this rate is reduced to less than one-half of this value in the next twenty degrees. The copper thermometer can be used as a heater to increase the warm up rate between measurements. The heater supplies about 0.05 watts of power to the sample holder.

Each measurement made on the specimen takes less than fifteen seconds so that the temperature of the sample remains virtually unchanged during this time. The current carried by the sample during the measurement produces

negligible heating. Normally, about five hours are necessary to span the temperature range from liquid nitrogen to room temperature.

### Specimen Mounting

The Hall specimen is mounted on a lucite backing in the form of a half cylinder (figure 6). Spring contacts to the gold leads of the sample ensures good electrical contact as well as ease of mounting. The sample has no strains on it, since it hangs freely by its leads. Proper thermal contact with the heat sink is provided by resting the lucite half cylinder on a copper half cylinder which makes direct contact to the thermometer as well as the bottom of the central tube (figure 5). A 0.04 inch thick slice of sapphire held to the flat face of the copper with epoxy provides good thermal conduction as well as electrical insulation of the sample from the copper. Glycerine is used to keep the sample in good thermal contact with the sapphire. It has a low vapor pressure and prevents temperature gradients from occurring along the sample.

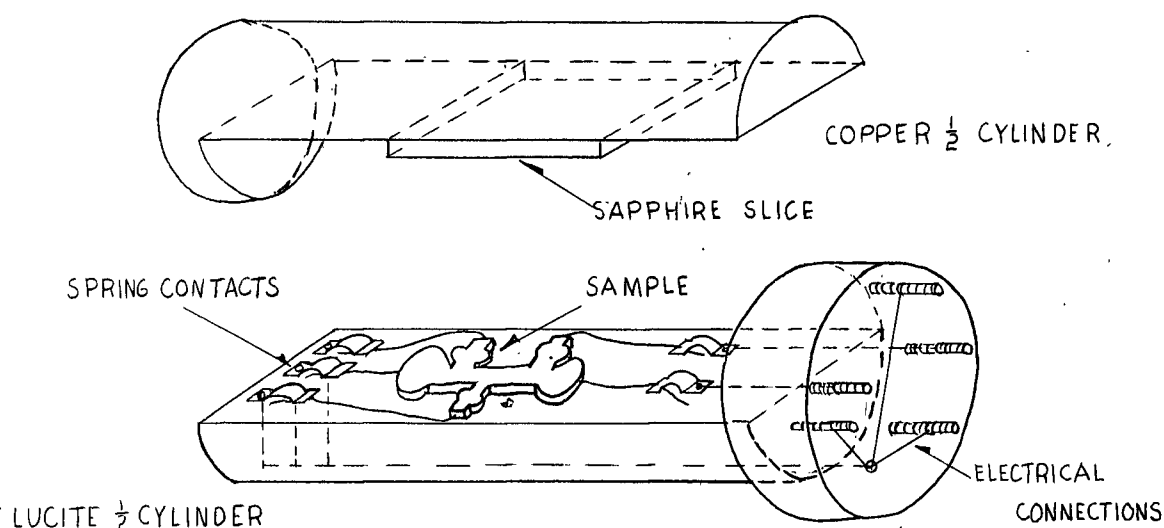


Figure 6. Diagram showing sample holder assembly. Approximately twice actual size.

## CARRIER PROPERTIES

### 1. ELECTRICAL PROPERTIES

#### Conductivity

The conductivity of a substance depends on the number of mobile charge carriers present and their ease of movement under an externally applied electric field. If ohms law is obeyed then the conductivity,  $\sigma$ , is the ratio of the current density  $\bar{J}$  to the electric field  $\bar{E}$ .

$$\sigma = \frac{\bar{J}}{\bar{E}} = nq \frac{\bar{V}}{\bar{E}} \text{ ohm cm}^{-1} \quad (6)$$

where  $n$  is the concentration of mobile charge carriers,  $\bar{V}$  is the average drift velocity of the carrier,  $q$  is the charge of the carrier in magnitude and  $u$  is the mobility.

Equation (6) may be rewritten in general for a semiconductor

$$\sigma = q(nu_n + p_l u_l + p_h u_h)$$

where  $n$  and  $p$  now are the free electron and hole concentrations respectively.  $p_l$  and  $p_h$  are light and heavy hole concentrations which add to give  $p$ .

In this experiment the resistivity, which is the inverse of the conductivity, is measured.

#### Hall Effect

A specimen carrying a current in the  $x$  direction  $I_x$ , and subjected to a magnetic field in the  $z$  direction  $H_z$ , perpendicular to  $I_x$ , experiences an electric field  $E_y$  normal to both  $I_x$  and  $H_z$ .  $E_y$  is proportional to the product of magnetic field and current density  $J_x$ . The constant of

proportionality  $R$  is known as the Hall constant.

$$E_y = R J_x H_z$$

Hall experiments measure the voltage  $V_y$  due to  $E_y$ .

$$V_y = \frac{10^{-8} R I_x H_z}{t} \quad (7)$$

where the current  $I_x$  is measured in amperes, the field  $H_z$  in gauss, and the thickness  $t$  in centimeters. The Hall constant  $R$  then has units of  $\text{cm}^3/\text{coul}$ .

For one type of carrier the Hall constant is given by

$$R = \frac{r}{q(p \text{ or } n)} \quad (8)$$

where  $q$  now represents the magnitude and sign of the electronic charge,  $r$  is the ratio of the Hall mobility to the conductivity mobility. In the high magnetic field limit  $r$  becomes 1.

In this experiment  $H_z$  is larger than 20 kilogauss and the approximation  $r = 1$  is valid. Measurements of  $R$  at different temperatures gives the carrier concentration as a function of temperature as long as conduction is due predominantly to one type of carrier.

The product  $R\sigma = u_H$ , is known as the Hall mobility. It can be seen that  $u_H/u = r = 1$  in this experiment.

## 2. ANALYSIS OF CARRIER BEHAVIOUR

Analysis of carrier behaviour in semiconductors is carried out in the

light of Fermi-Dirac statistics. The fermi-Dirac distribution function  $F(E)$  gives the probability that a state of energy  $E$  is occupied by an electron.

$$F(E) = \frac{1}{1 + \exp(E - E_f)/KT} \quad (9)$$

where  $E_f$  is the Fermi energy,  $K$  is the Boltzmann constant,  $T$  the absolute temperature.

Extrinsic semiconductors contain acceptor and donor impurities in varying concentrations. To discuss the properties of p-type germanium the following quantities are defined.

$N_a, N_d$  - concentration of acceptor and donor atoms respectively.

$N_a^-, N_d^+$  - concentration of ionized acceptor and donor atoms respectively.

$p, n$  - concentration of free holes and electrons in valence and conduction band respectively.

$E_v, E_a$  - the energy at the top of the valence band and of the acceptor level.

The concentration of ionized acceptor atoms is then given by

$$N_a^- = \frac{N_a}{1 + \frac{1}{2g} \exp(E_a - E_f)/KT} \quad (10)$$

The coefficient of  $N_a$  on the right hand side of (10) is the probability that an acceptor level is occupied by an electron. The spin factor 2 is included and  $g$  is the remaining degeneracy of the ground state acceptor level.

The number of holes in the valence band is given by

$$p = N_v \exp(E_v - E_f)/KT \quad (11)$$

where

$$N_v = 2(2\pi m^* KT/h^2)^{3/2}$$

where  $m^*$  is an average effective mass for both light and heavy holes. Equation (11) is obtained assuming parabolic band structure and Boltzmann statistics.

Charge neutrality imposes the condition

$$p + N_d^+ = n + N_a^- \quad (12)$$

The temperature variation of holes ( $p$ ) in p-type material ( $N_a > N_d$ ) can be found using the above relations. Consider only the region of partial ionization of the acceptors so that  $p < N_a$  but much larger than the intrinsic carrier concentration. And further consider that some compensation exists so that most of the donors are ionized, their electrons going into acceptor states. Then  $N_d^+$  can be approximated by  $N_d$  and equation (12) simplifies to

$$p = N_a^- - N_d \quad (13)$$

Using relations (10) and (11) equation (13) becomes

$$\frac{p^2 + pN_d}{(N_a - N_d - p)} = \frac{N_v}{2g} \exp(E_v - E_a)/KT \quad (14)$$

Two approximations may be made to (14). If  $p \ll N_d$ , this will happen at very low temperatures or fairly high donor concentrations, then (14) reduces to

$$p = \frac{N_v(N_a - N_d)}{2gN_d} \exp(E_v - E_a)/KT \quad (14a)$$

Thus a plot of the natural logarithm of  $(pT^{-3/2})$  against  $1/KT$  will be a straight line in this region, with a negative slope equal to the ionization energy of the acceptors  $(E_v - E_a)$ .

In a second approximation it is assumed that  $p \gg N_d$ . This may occur at moderately low temperatures of for very low donor concentration. Thus (14) becomes

$$p = (N_v N_a / 2g)^{1/2} \exp(E_v - E_a)/2KT \quad (14b)$$

In this case only half the ionization energy is involved in the exponential term.

At higher temperatures most of the acceptors are ionized so that  $N_a^-$  can be approximated by  $N_a$ , but  $p$  is still larger than  $n$ . This is known as the saturation region which occurs just before  $n$  becomes comparable to  $p$ . For this region equation (13) gives

$$p = N_a - N_d \quad (15)$$

In the temperature region where  $p > n$ , measurement of the Hall constant gives the temperature variation of the free hole concentration ( $p = 1/Rq$ ). Thus by proper fitting of the relations derived above the acceptor ionization energy, the concentration of donors and the concentration of acceptors may be determined for a p-type semiconductor.

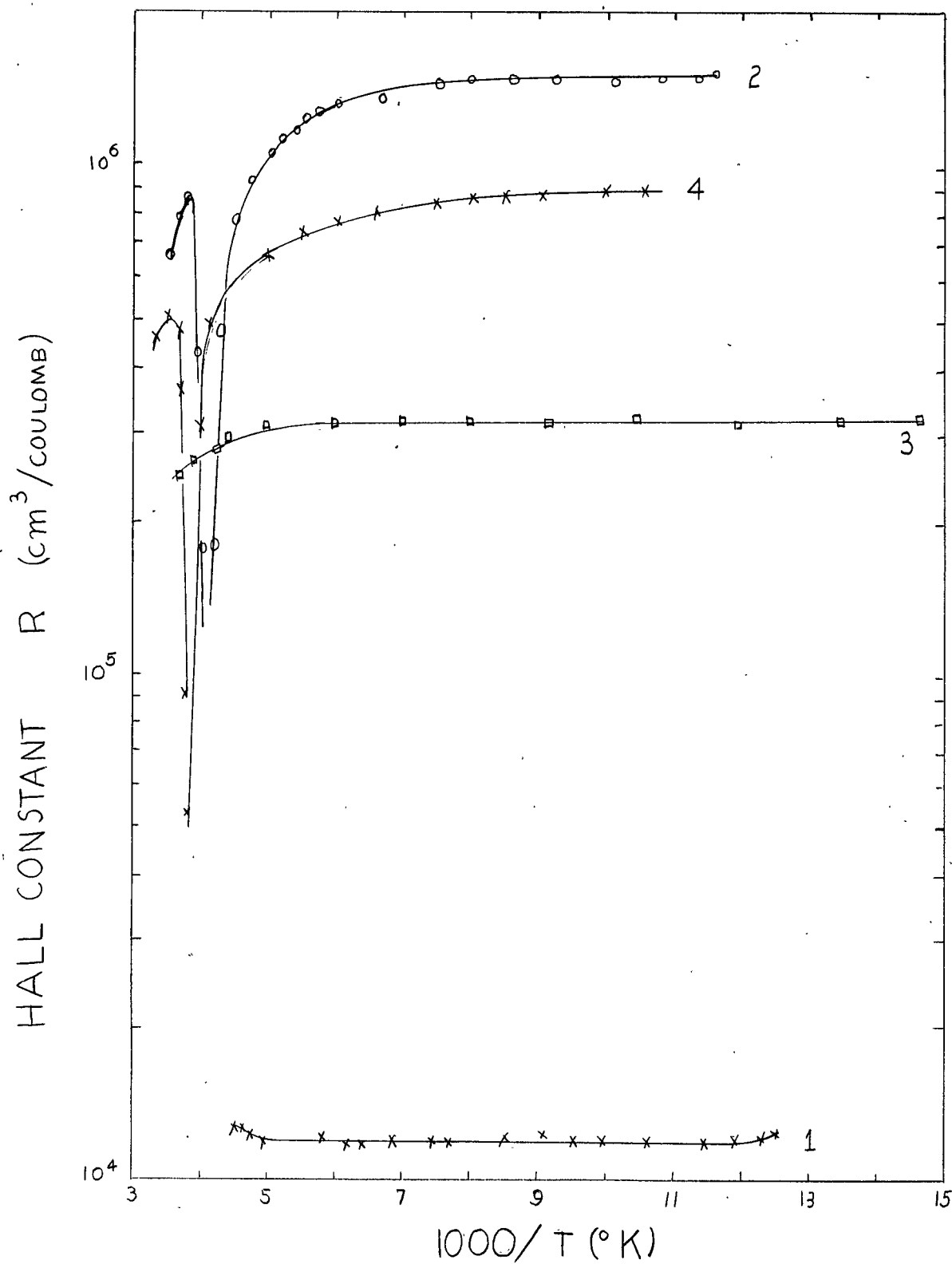


Figure 7. The inverse temperature dependence of the Hall effect for one representative sample from crystals 1, 2, 3 and 4 (for specimen 1, the Hall constant has been multiplied by 10).



## RESULTS

Hall and resistivity measurements were made from liquid nitrogen temperature to room temperature on a number of samples of scandium doped germanium from each of the four crystals grown. Table 3 presents a tabulation of experimental data and results for one representative sample from each single crystal grown. It gives the amount of scandium and germanium used, the concentration of scandium and aluminium atoms in the melt, the concentration of aluminium atoms in the crystal, the concentration of holes and their mobility. Figure 7 gives the inverse temperature variation of the Hall constant for each of these samples. And figure 8 presents the temperature of variation of resistivity for samples one and two only.

### 1. DISCUSSION OF HALL RESULTS

The curves of the Hall constant versus the reciprocal of temperature, exhibit the well known behaviour of p type germanium (figure 7). Two of these curves show the Hall coefficient going rapidly from positive to negative as the electron concentration becomes comparable to that of the holes. This point occurs for crystals two and four at 245 and 268°K respectively. Crystal 3 shows some temperature dependence close to room temperature while the Hall constant of crystal 1 is essentially temperature independent. It is found that the turning point temperature increases with increasing hole concentration, as is expected.

The Hall data obtained from various samples taken from the same crystal are in good agreement. Any deviation can be accounted for by the method of crystal growth which causes a concentration gradient along the crystal growth axis.

Crystal#	1	2	3	4
Sc mg	24.8	2.0	10.0	8.0
Ge gm	50.8	114.0	96.0	145.1
Sc in melt $(10^{-13})/\text{cm}^3$	34.50	1.24	7.35	3.90
Al in melt " "	69.00	2.48	14.70	7.80
Al in crystal " "	5.0	0.2	1.0	0.63
p 80°K " "	500	0.41	2.00	0.71
u $\text{cm}^2/\text{V sec}$ (100°K)	2,450	3,000		
u $\text{cm}^2/\text{V sec}$ (300°K)	8,500	12,500		

Table III Tabulation of experimental data and results for scandium doped germanium.

All the Hall curves are characterized by a region where the Hall constant is independent of temperature (figure 7). This indicates that in this region all of the impurities are ionized. This is the saturation region and according to equation (15) the number of holes,  $p = 1/R_H$ , gives  $N_A - N_D$  (table III). Since all the impurities are ionized before the temperature reaches 77°K, the ionization energy of the impurity must be approximately equal to the value of the thermal energy at this temperature, or about 0.01 electron volts or less.

The p-type behaviour shown by the single crystals grown can be attributed to presence of aluminium. Aluminium is known to behave as an acceptor in germanium with an ionization energy of 0.0102 electron volts. Table III gives the concentration of aluminium atoms in the crystal. This is calculated using the known distribution coefficient of aluminium in germanium (table II) and equation (5). This is the concentration of aluminium only

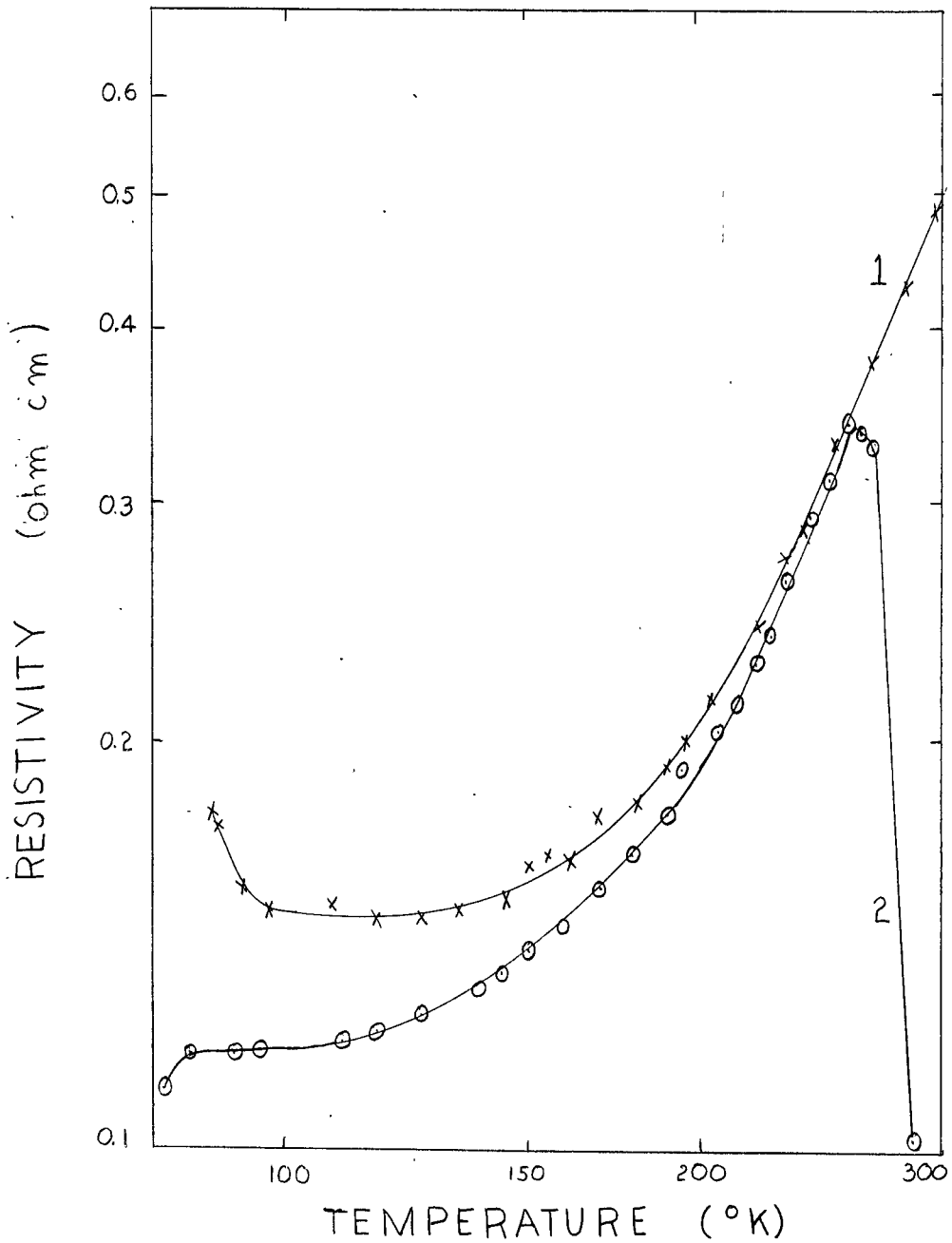


Figure 8. The temperature variation of resistivity for crystals 1 and 2 of scandium doped germanium (for sample 2 the resistivity has been multiplied by  $10^{-3}$ ).

at the beginning of crystallization and is the lowest concentration to be found in the crystal (see crystal growth). With reference to table III, it can be seen that except for crystal 1 all the holes present can be accounted for by the aluminium impurity. The large discrepancy in this crystal can be explained in the following manner. Crystal 1 was grown from a small charge of germanium mixed with a relatively large amount of scandium. Thus the grown single crystal will have a large concentration gradient of aluminium impurities. The Hall and resistivity measurements were made on samples cut from the end of the crystal with the highest impurity concentration. Consequently the aluminium impurity concentration in these samples could be two orders of magnitude greater than in samples cut from the low concentration end.

## 2. DISCUSSION OF RESISTIVITY RESULTS

Figure 8 shows the temperature variation of resistivity for samples 1 and 2. These samples represent the maximum and minimum impurity concentration respectively. The mobility data for samples 3 and 4 is not shown since there is very little difference between them and sample 2 in this respect.

The hole mobility in germanium is known to vary as  $T^{-a}$ , where  $a$  is a constant. Equation (6) gives the relationship between conductivity (the reciprocal of resistivity) and mobility. The resistivity measurements are made in the saturation region, and therefore the number of holes are constant in this region. Thus any temperature variation of resistivity is due only to changes in mobility. The two resistivity curves are very much alike and possess a slope of 2.2 from about 160°K upwards (figure 8). Therefore

the mobility has a  $T^{-2.2}$  temperature dependence. This agrees fairly closely with the dependence  $T^{-2.3}$  for mobility obtained by Brown and Bray.<sup>18</sup>

The values of the mobility for samples 1 and 2 are shown in table III. These have been calculated from the ratio of the Hall constant to the resistivity at 100°K and 300°K respectively. For sample 2, the mobility at 300°K is obtained by extrapolation. From these figures it is immediately apparent that the variation of mobility with impurity concentration is very small. For the mobility changes by less than 50% while the impurity concentration changes by three orders of magnitude. Therefore impurity scattering is very small and is not one of the dominant scattering mechanisms in germanium.

CONCLUSIONS

The results of this experiment indicate;

- (a) From the observations of crystal growth, scandium seems to form a compound with either germanium or carbon which is solid at the melting point of germanium. This compound can be either  $\text{ScGe}_2$  or a carbide of scandium produced by interaction with the graphite crucible.
- (b) It has been shown that scandium and germanium should be miscible in the liquid phase.
- (c) The p-type behaviour shown by the single crystals grown can be attributed to the aluminium impurity present in the scandium.
- (d) If some scandium does enter germanium, it has a maximum distribution coefficient of  $10^{-6}$  and a maximum solid solubility of less than  $10^{15} / \text{cm}^3$ .
- (e) The hole mobility in germanium has a temperature dependence of  $T^{-2.2}$  between  $160^\circ\text{K}$  and room temperature.
- (f) The effect of impurity scattering in germanium on hole mobility is negligible at concentrations from  $10^{12} / \text{cm}^3$  to  $10^{16} / \text{cm}^3$ .

## PART II

### STUDY OF SELENIUM AND ZINC DOPED GALLIUM ARSENIDE

#### INTRODUCTION

Gallium arsenide (GaAs) belongs to the III - V group of semiconducting compounds which are represented by the formula  $A^{III} B^V$ . These compounds all crystallize into the zinc blende lattice structure which is really a diamond lattice with unlike atoms. In the zinc blende lattice, each A atom is tetrahedrally surrounded by four B atoms and vice versa. The bonding between A - B atoms is mostly homopolar as in germanium because each atom is still sharing on the average four valence electrons. But in addition there exists some ionic bonding due to the disparity of charge between  $A^{III}$  and  $B^V$ . It is this added ionic bonding which gives the III - V compounds a larger band gap and higher melting point than the corresponding group IV element.<sup>19</sup> Germanium is the corresponding group four element for gallium arsenide.

The band structure of GaAs was first obtained by assuming it was not much different than that of germanium since they have the same unit cell, and interatomic distance, and therefore identical brillouin zones. Experimentally and by theoretical arguments as well, it has been shown that the valence bands of the two materials are almost identical while the conduction band of gallium arsenide has its principal minima at  $\bar{K} = 0$  whereas germanium does not. The band structure for gallium arsenide is shown in figure 6.<sup>20</sup>

The subsidiary minima in the [100] direction are only 0.36 electron volts above the principal minima and therefore must be taken into account in

analyzing Hall effect and conductivity measurements above room temperature.

### Impurities in Gallium Arsenide

It is possible to extend the argument used to describe impurity behaviour in group IV semiconductors to the III - V compounds. In which case group II elements of the periodic table which substitute in the lattice for the trivalent atoms would be acceptors. And group VI atoms which replace the pentavalent atoms would be donors. It is expected that these impurities are shallow, especially in the case of donor impurities. The latter should have a very small ionization energy if only because of the small effective electron mass.

Then, for gallium arsenide, zinc would act as an acceptor while selenium would be a donor. It has already been shown that zinc is an acceptor in this material, with a low ionization energy of 0.014 electron volts.<sup>21</sup> Selenium is a donor in this material.<sup>22</sup> From the above remarks, selenium should have a very small ionization energy.

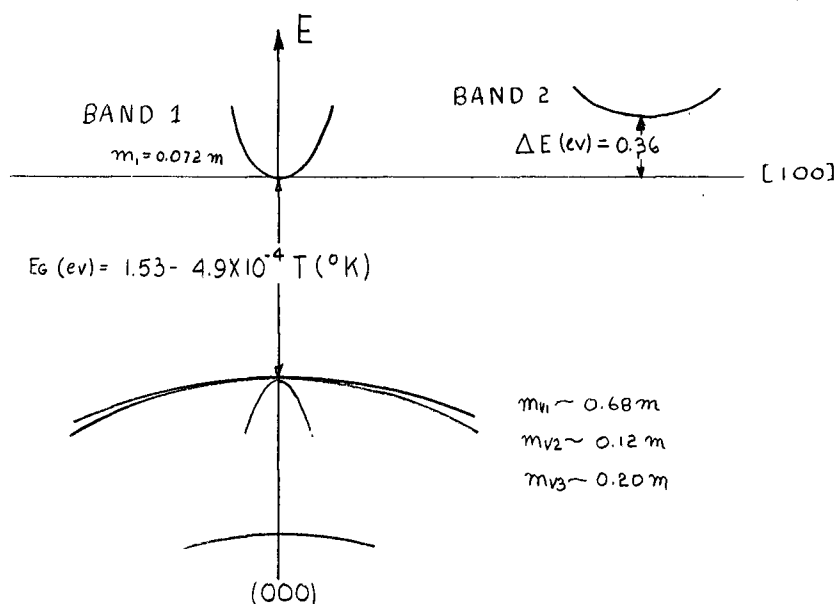


Figure 9. Band structure of gallium arsenide in the vicinity of conduction and valence band edges.<sup>20</sup>



## EXPERIMENTAL

The experimental procedure and apparatus used to study gallium arsenide is basically the same as outlined for germanium in part I. The only major differences are that the gallium arsenide crystals were not grown in this laboratory and a different technique of applying electrical contacts is used. The latter will be described below under the heading of contacts.

The gallium arsenide material was checked for monocrystallinity. It was found that the zinc doped gallium arsenide was not a single crystal but contained at least four visible grains running diagonal to the lengthwise direction of the crystal. The cross section area of the material is just large enough to cut a Hall sample which means that at least one grain boundary will cut completely across the Hall specimen perpendicular to the direction of current flow. This might interfere with the electrical measurements. The selenium doped material was found to be monocrystalline.

### Electrical Contacts

Attempts to use the gold alloy technique of applying electrical contacts to gallium arsenide Hall specimens failed. This is due to the higher eutectic temperature between gold and gallium arsenide which cannot be reached with the nichrome heater. Indium contacts were used instead.

Successful indium contacts can be made to GaAs using the following procedure. After the Hall blanks are cut they are cleaned for five minutes in boiling 3% hydrogen peroxide, the contact area is then sandblasted with a small sandblaster to roughen the surface. The specimen is then placed on a piece of glass on a hot plate. A small piece of indium is put on each contact area and the temperature is raised until the indium melts. At this temperature a tough oxide layer rapidly forms around the indium which

prevents it from flowing over the contact area. A razor blade is used to break this layer and to scrape the indium over the contact area. This is done until the indium "wets" the material. When the contact area is satisfactorily covered with indium, the end of a small length of gold wire (0.005 inch diameter) which has been tinned with indium is put on the contact area. The sample is cooled. Strong mechanical bonds are established in this manner. The indium contacts are easily fabricated and yield low resistance ohmic contacts.

The contacts are tested as outlined under contact testing of part I.

## CARRIER PROPERTIES

### Electrical Properties

The electrical properties as far as conductivity and Hall effect are concerned have already been outlined in general in Part I, but a few additions are necessary. Two types of impurity conduction are possible. The first type is by transfer of charge between impurity centres. The second is by ordinary conduction in the conduction band. For electron conduction only, the conductivity is the sum of the two contributions.

$$\sigma = q(n_1 u_1 + n_2 u_2) \quad (6')$$

where  $n_1 u_1$  and  $n_2 u_2$  refer to the conduction band and impurity conduction respectively. The Hall coefficient is then expressed as

$$R = \frac{(r_1 n_1 u_1^2 + r_2 n_2 u_2^2)}{q(n_1 u_1 + n_2 u_2)^2} \quad (8')$$

where  $r_1$  and  $r_2$  express the ratio of the Hall and drift mobilities. Varying the temperature changes  $n_1$  and  $n_2$ , with the restraint that  $n_1 + n_2$  is a constant.

Two different mechanisms exist for impurity conduction depending on the relative distance between donor centres and the overlap of their wave function.<sup>23</sup> At low impurity concentrations, conduction takes place by a phonon assisted "hopping" process. This process is dominant only at very low temperatures and need not be considered here. At high concentrations the overlap of wave functions may be large enough to initiate impurity band conduction. This type of conduction is independent of temperature at low

temperatures.<sup>23</sup> But at the relatively higher temperatures used in these experiments, it is expected that the impurity band overlaps with the conduction band. Thus effectively reducing the problem to single band conduction, in which case, the expressions for  $R$  and  $\sigma$  convert to their simple forms.

The empirical criterion for the transition to impurity band conduction is at  $\frac{R_0}{a} \leq 3$ , where  $R_0$  is the mean distance between donors, and  $a$ , the modified Bohr radius.<sup>23</sup>  $R_0$  and  $a$  are given explicitly by

$$R_0 = (3/4\pi N_d)^{1/3} \quad \text{and} \quad a = k a_h (m/m^*)$$

where  $m^*$  is the electron effective mass,  $k$  is the dielectric constant and  $a_h$  is the Bohr radius of the hydrogen atom. For gallium arsenide,  $a$  is approximately equal to 76 angstroms.

The effect of the minima occurring in band 2 on impurity conduction need not be considered since the temperatures reached are not high enough to put an appreciable number of electrons in this band.

#### Method of Analysis

If impurity band conduction can be neglected, that is for low concentrations where  $\frac{R_0}{a} > 3$ , the analysis of gallium arsenide follows a parallel pattern as described for germanium. In this case the Hall constant yields  $n$  as a function of temperature and, with the proper assumptions,  $N_d$ ,  $N_a$  and the ionization energy can be determined. If impurity band conduction cannot be neglected, the problem becomes one of determining the four unknowns,  $n_1$ ,  $n_2$ , and  $u_2$  from the two relations (6') and (8') for  $r_1$  and  $r_2$  equal to one, at low temperatures.

At higher temperatures, such as those used in this experiment, the

impurity and conduction bands overlap, effectively giving rise to one band. In which case the ionization energy of the impurity cannot be determined. The number of carriers  $n$  can then be determined from the Hall constant or from a theoretically calculated mobility versus total ionized impurity concentration curve at  $300^\circ\text{K}$  for n-type GaAs.<sup>20</sup> This curve is accurate for concentrations between  $10^{15}/\text{cm}^3$  to  $10^{18}/\text{cm}^3$ . This curve plus another experimental curve are given in figure 10.<sup>24</sup>

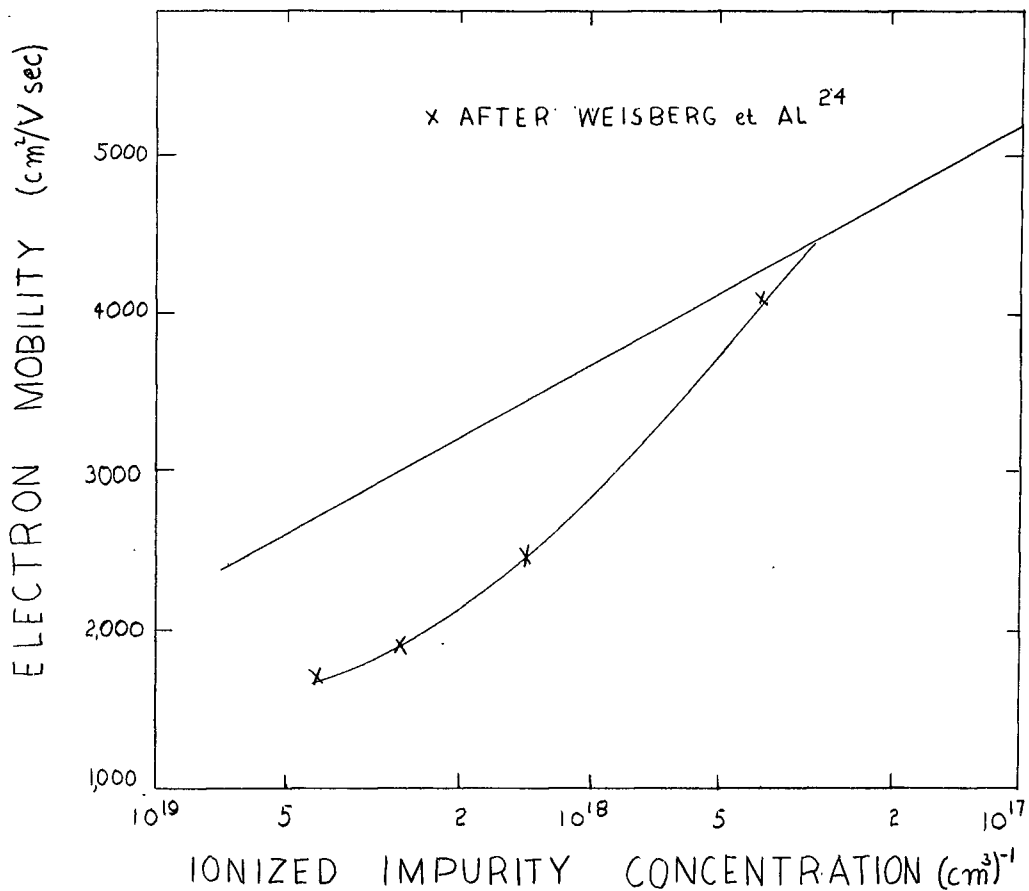


Figure 10. Calculated electron mobility as a function of ionized impurity concentration at  $300^\circ\text{K}$  for gallium arsenide. The calculated curve actually extends to concentrations of  $10^{15}/\text{cm}^3$ .<sup>20</sup>

RESULTS

## 1. SELENIUM DOPED GALLIUM ARSENIDE

Hall and resistivity measurements from 66°K to 300°K were made on two samples of selenium doped gallium arsenide. A third sample was used as a check and gave almost identical results as sample one. Table III summarizes the results of these experiments. Figure 11 gives the variation of Hall mobility with temperature. And figure 12 give the voltage current characteristics of all three samples at 77°K and 300°K respectively.

Specimen	1	2
$R \text{ cm}^3/\text{coul} \quad (300^\circ\text{K})$	-34	-37
$\sigma \text{ (ohm cm)}^{-1} \quad (66 - 300^\circ\text{K})$	69	62.5
$\mu_H = R\sigma \text{ cm}^2/\text{V sec} \quad (300^\circ\text{K})$	2340	2250
$n \text{ /cm}^3 \quad (10^{-18}) \quad (300^\circ\text{K})$	1.6	1.8
$R_0 \text{ Angstroms}$	62	60
$\frac{R_0}{a}$	0.8	0.8

Table IV Results from Hall and resistivity measurements on selenium doped gallium arsenide.

The measurements on selenium doped gallium arsenide show the following (Table IV). The Hall constant is negative and small, it has a weak temperature dependence, increasing by only 10% from 66°K to 300°K. This indicates that the carriers present are electrons and therefore selenium is a donor in this material. The small change in this constant with temperature implies that most of the donors are ionized. The conductivity, on the other

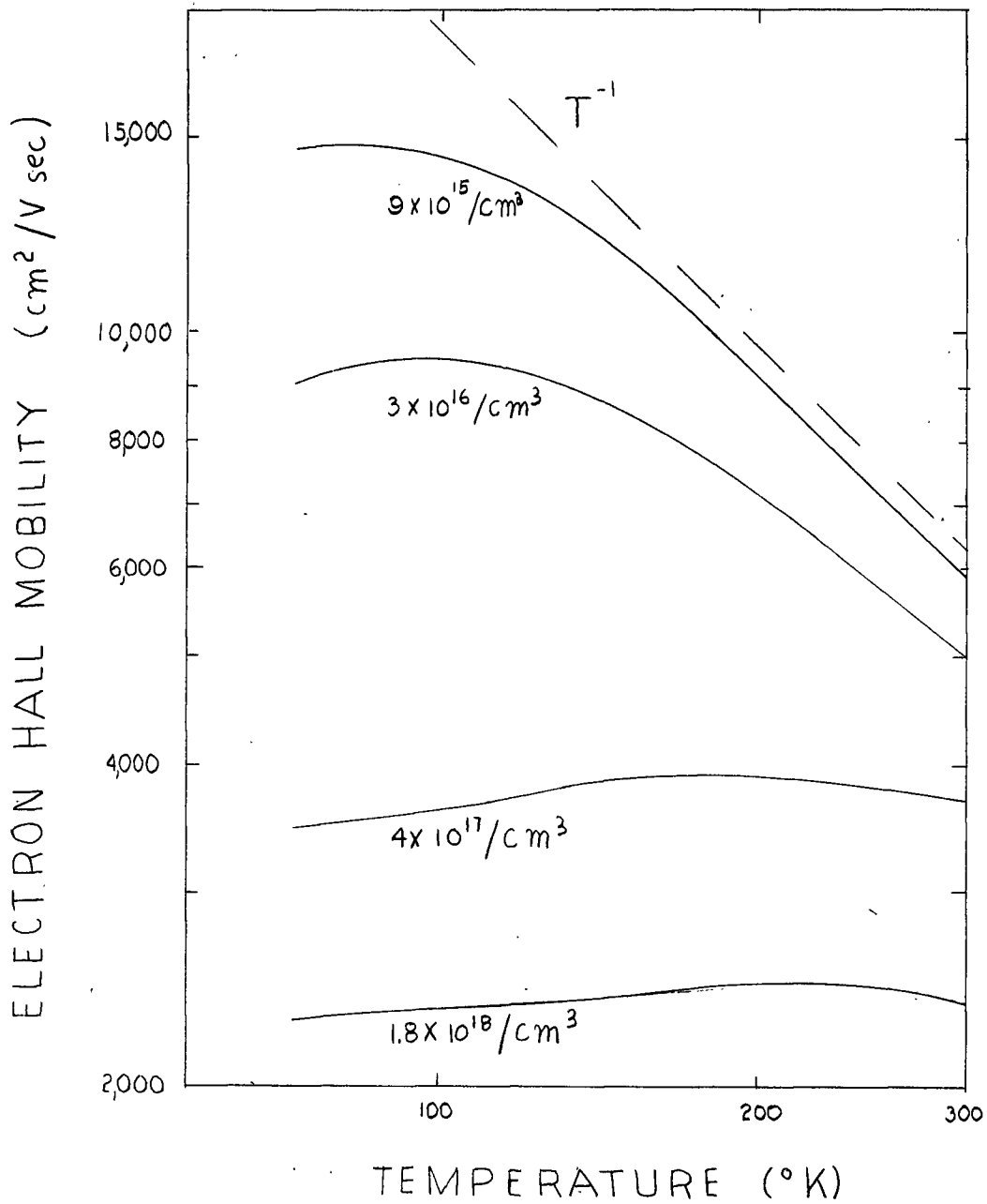


Figure 11. The temperature variation of electron Hall mobility in n-type gallium arsenide for different impurity concentrations ( $N_d$ ). The bottom curve ( $N_d = 1.8(10^{18})/\text{cm}^3$ ) is from this study, while the top three curves have been reported by others.<sup>22</sup>

hand shows no temperature dependence over the same range and is quite large. The latter indicates that very little compensation exists. Therefore the concentration of free electrons  $n$ , is approximately equal to  $N_d$  which is equal to  $N_d^+$ .

The concentration of free electrons  $n$ , may be obtained by two methods. Consider only sample 2 for brevity. First, if it is assumed that the Hall mobility and conductivity mobility are equal, then the theoretical mobility curve (figure 10) yields  $N_d^+ = n = 9(10^{18})/\text{cm}^3$ . This value is discarded since the curve is no longer accurate at this large concentration. If the experimental curve of Weisberg (figure 10) is used, the value  $n = 1.8(10^{18})$  per  $\text{cm}^3$  is obtained. In the second method,  $n$  is determined from the single band Hall constant, again assuming  $u_H = u$ , giving  $n = 1.7(10^{17})/\text{cm}^3$ . Thus two values of the electron concentration result, one of these must be rejected.

The use of a single band Hall constant is justified by the fact that the high donor concentration gives rise to impurity band conduction. This band overlaps with the conduction band, because if it did not, the Hall mobility would show a much larger temperature dependence than indicated in the experimental results (figure 11). The overlap allows these bands to be represented by a single band with mobility  $u$ . If a value for  $r = u_H/u$  equal to two is chosen, then  $n$  becomes  $3.4(10^{17})/\text{cm}^3$  and  $u$  is  $4500 \text{ cm}^2/\text{V sec}$ . This value of  $n$  is in agreement with the results which would be obtained from the theoretical mobility curve.

On the other hand,  $n = 1.8(10^{18})$ , obtained from the experimental curve puts the Hall mobility curve in the correct position with respect to those of lower concentrations (figure 11). Since the Hall mobility is directly



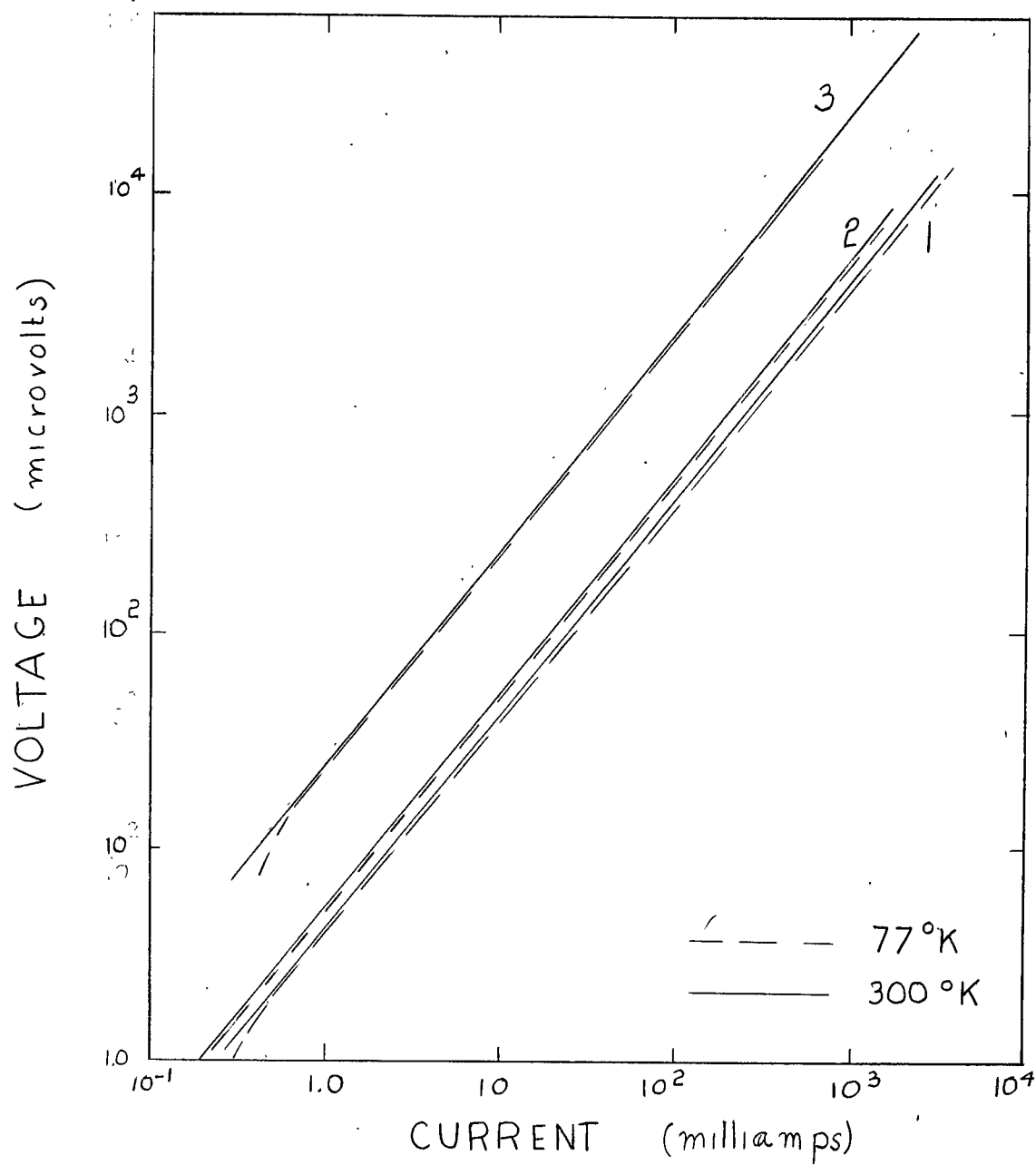


Figure 12. The voltage-current characteristics for three selenium doped gallium arsenide samples at 77°K and 300°K respectively (for sample 3, the voltage has been multiplied by ten).

calculable from these experiments, this value of  $n$  will be regarded as correct and the value computed from the Hall constant is discarded. The correct values of  $n$  for samples 1 and 2 are given in table IV.

The values of  $R_0/a$ , that is the relative overlapping of wave functions between nearest donors, are calculated using  $N_d = n$ . In both cases it is much less than the value of three, set as the upper limit for impurity band conduction. Therefore impurity band conduction is taking place.

The specimens exhibit ohmic behaviour at 77°K and 300°K for a large range of applied voltages (figure 12).

## 2. ZINC DOPED GALLIUM ARSENIDE

Hall and resistivity measurements were made on two samples of zinc - doped gallium arsenide from liquid nitrogen to room temperature. The two samples give approximately the same results. It was pointed out previously that this material was not single crystal, but consisted of at least four macroscopic single crystal grains. The boundaries of these grains cut across the Hall specimen and interfere with electrical measurements. These rectifying grain boundaries give rise to the diode like behaviour of the V-I curve at 77°K (figure 13), and the large spread of points in the Hall constant (figure 14). However, the material seems to be ohmic at room temperature.

The Hall and resistivity curves for this material can be approximated to within 10% by the following expressions

$$R = 100(0.31T + 64.1)^{1/3} - 30, \quad \rho = -0.002T + 0.68$$

These expressions hold for the temperatures between 100°K and 300°K. It is

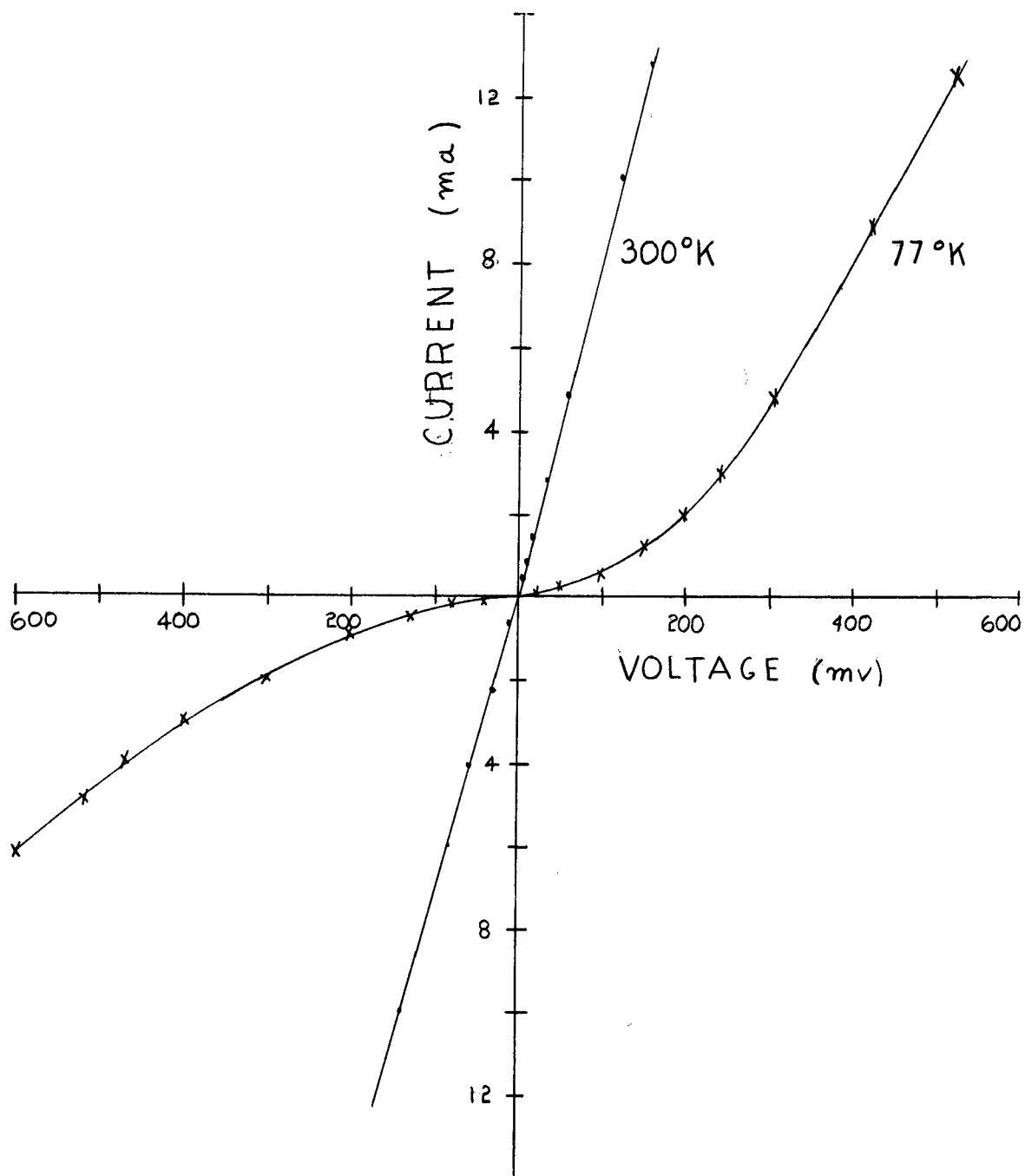


Figure 13. The current-voltage characteristics of zinc-doped gallium arsenide at 77°K and 300°K. Note the diode-like behavior at 77°K.

seen that  $R$  has a  $T^{1/3}$  temperature dependence while  $\rho$  decreases linearly with increasing temperature (figure 14).

The Hall constant for this material exhibits the same p-type behaviour shown by germanium in part I. This constant rapidly changes from positive to negative at 208°K. However, this change is not due to the intrinsic electron concentration, in the conduction band, becoming comparable to the hole concentration, since the forbidden energy gap, in this material, is much larger than that of germanium. But it is due to the large disparity between hole and electron mobilities in gallium arsenide (in germanium the two mobilities are comparable). In which case the contribution of both carriers must be taken into account and the expression for the Hall constant and conductivity become

$$R = \frac{pu_p^2 - nu_n^2}{q(pu_p + nu_n)^2} \quad \text{and} \quad \sigma = \frac{1}{\rho} = q(pu_p + nu_n) \quad (16)$$

where  $u_p$  and  $u_n$  are the hole and electron mobilities respectively. For low impurity concentration gallium arsenide and for temperatures between 100°K and 300°K,  $u_n$  varies with temperature as  $T^{-1}$  (figure 11), and  $u_p$  has a temperature dependence of  $T^{-2}$ .<sup>24</sup> Furthermore, it is known that  $u_p$  is less than  $0.1u_n$  in this temperature range. Therefore it is possible for a low donor concentration ( $n \ll p$ ) to cause the Hall constant to change sign. This occurs because the square of the mobilities are involved in the numerator of  $R$ .

The values  $u_p$ ,  $u_n$ ,  $p$  and  $n$  may be determined provided values for  $u_p$  and  $p$  can be approximately found at some temperature. A rough indication of the hole concentration is obtained from the single band Hall constant at the

lowest temperature reached in the experiment. This gives the hole concentration as  $2(10^{16})/\text{cm}^3$ . The Hall mobility suggests a value of  $550 \text{ cm}^2/\text{V sec}$  for the hole mobility at the turning point temperature. Furthermore, zinc is known to be a shallow acceptor. Therefore  $p$  should remain almost constant with temperature. Similarly the very small electron effective mass indicates that the ionization energy of any donor present in GaAs will be small. Thus  $n$  should also remain almost constant with temperature. Therefore using the known temperature dependence for the mobilities and the carrier concentrations combined with the values for  $p$  and  $u_p$ , the four unknowns may be determined over the temperature range from  $100^\circ\text{K}$  to  $300^\circ\text{K}$ .

The resistivity may be combined with the expression for the Hall constant (16) to reduce the number of unknowns from four to three. It is found that the electron concentration must increase by three orders of magnitude to keep the hole concentration and the mobilities within reasonable bounds. This result is obviously incorrect and occurs because of the wrong temperature dependence of the resistivity obtained from this experiment.

If the carrier concentrations are almost constant and the mobilities decrease with increasing temperature, then the resistivity should increase with temperature. The experimental results show the resistivity decreasing with increasing temperature. The discrepancy between expected and experimental results is due to the diode-like behaviour of this material at low temperatures. For the voltages used in this experiment, 0.1 to 0.2 volts, the slope of the  $V$ - $I$  curve at  $77^\circ\text{K}$  is much less than that of the curve at  $300^\circ\text{K}$ . The resistivity is the inverse of this slope. Therefore the high resistivity shown at low temperature is due to the rectifying effects of the grain boundaries in the Hall sample. Thus the resistivity data is not useful.

Then the unknowns must be determined only from the Hall curve. This yields the following at room temperature;  $n = 1.25(10^{14})/\text{cm}^3$ ,  $p = 2.5(10^{16})$  per  $\text{cm}^3$ ,  $u_n = 5,780 \text{ cm}^2/\text{V sec}$  and  $u_p = 270 \text{ cm}^2/\text{V sec}$ . These values lead to agreement with the measured temperature dependence of the Hall constant to within 15% at all temperatures between  $100^\circ\text{K}$  and  $300^\circ\text{K}$ , provided  $n$  and  $p$  remain constant and the mobilities have the temperature dependence stated previously.

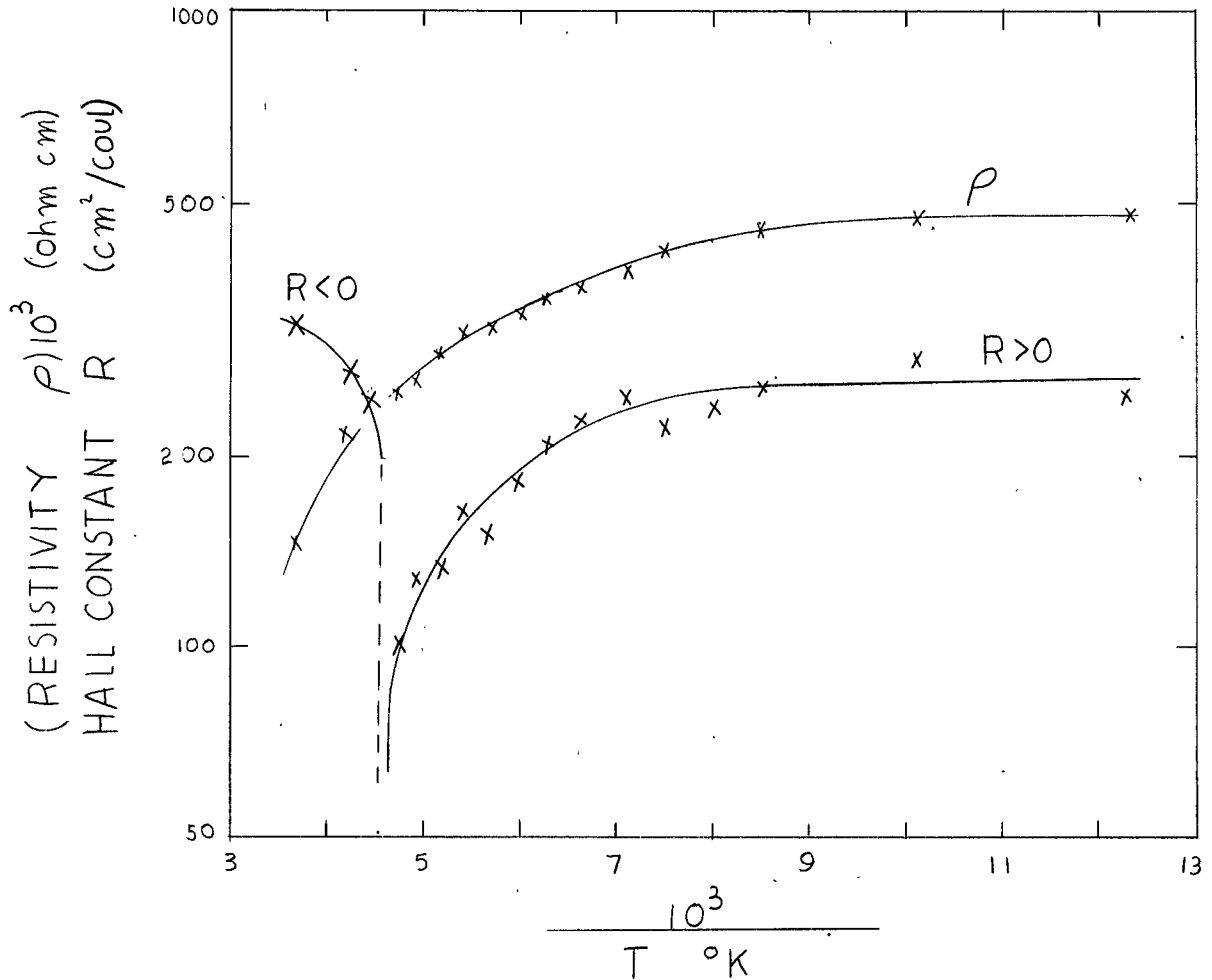


Figure 14. Inverse temperature variation of the Hall constant and the resistivity for zinc-doped gallium arsenide.

### CONCLUSIONS

(a) The results of experiments on selenium doped gallium arsenide indicate the following. Selenium is a donor atom in gallium arsenide. When it is present in high concentrations, impurity band conduction takes place.

However, it is found that at temperatures used, in these experiments, this band overlaps with the conduction band, giving rise to one band as far as electrical properties of the material are concerned. The concentration of donor atoms present is approximately equal to the concentration of free electrons. This was found to be  $1.5(10^{18})/\text{cm}^3$ . At this concentration the Hall mobility shows only a slight temperature dependence. It is found from these experiments combined with the results of others, that the mobility decreases with increasing donor concentration (figure 11). Therefore at high concentrations, ionized impurity scattering is a dominant scattering mechanism in this material. The ionization energy of selenium could not be determined from these experiments.

(b) A number of conclusions may be drawn from experiments performed on zinc doped gallium arsenide. It is found that zinc behaves as an acceptor atom in this material. The concentration of zinc atoms is approximately equal to the concentration of holes present, which is determined to be  $2.5(10^{16})/\text{cm}^3$ . It is found that even though the concentration of acceptors is much larger than that of donors, the Hall constant is forced to change sign at relatively low temperatures. This is due to the large difference between hole and electron mobilities. The presence of grain boundaries in this material did not interfere appreciably with measurements of the Hall constant, which has a temperature dependence of  $T^{1/3}$ . The ionization energy of zinc could not be determined from these experiments.

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