

MEASUREMENTS OF ELECTRICAL CONDUCTIVITY OF FILAMENTS
OF GRAY TIN AND GRAY TIN ALLOYS

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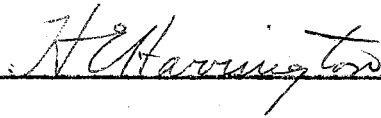
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PREFACE

Gray tin, the diamond structure phase of tin stable below the ice-point, has previously been found to be a semiconductor similar to the other Group IV elements, carbon (in the form of diamond), silicon, and germanium. Various research has been conducted on its electrical and magnetic properties since this discovery. However, additional investigation is needed to clarify the nature of, and reasons for, its semiconducting behavior.

The purpose of the present study is to contribute to the existing knowledge of the electrical conductivity and intrinsic activation energy of gray tin and its alloys.

Some difficulties have been encountered in the present study. First, no perfect method of temperature control is available. Second, gray tin samples are too brittle. Third, uniform distribution of impurity atoms in the alloys is uncertain.

Great indebtedness is acknowledged to Dr. E. E. Kohnke for suggesting the problem and guiding the experimental work. Also deep appreciation is expressed to Professor C. F. Harris for the loan of experimental equipment; to Dr. H. E. Harrington and other members of the Physics Department staff for their encouragement and suggestions; to the Physics Department of Oklahoma Agricultural and Mechanical College for granting an assistantship as financial aid to the study; and to Messrs. J. E. Tope and T. Young for corrections and suggestions concerning the manuscript.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. SURVEY OF PREVIOUS WORK	4
III. EXPERIMENTAL PROCEDURE	7
Preparation of Filaments of Gray Tin and Gray Tin Alloys	7
Apparatus and Procedure	10
a. Description of Apparatus	10
b. Mounting the Sample	12
c. Method of Measurement	12
IV. THEORETICAL BACKGROUND	15
Macroscopic Treatment	15
Statistical Treatment	16
Mobility Theory	19
V. PRESENTATION OF DATA AND DISCUSSION	22
General Observations	22
Individual Discussion	30
Conclusions	33
BIBLIOGRAPHY	35

LIST OF TABLES

Table	Page
1. Types of Pure Tin	9
2. Types of Tin Alloys	9
3. Variation of Conductivity and Apparent Activation Energy with Impurity Contents	29

LIST OF FIGURES

Figure .	Page
1. Diagram of Sample Holder and Dewar Flask	11
2. Circuit Diagram	13
3. Electrical Conductivity of JMC Pure Tin Versus Temperature	23
4. Electrical Conductivity of Sb-Sn Alloys II and III Versus Temperature	24
5. Electrical Conductivity of Ga-Sn Alloys I and II Versus Temperature	25
6. Electrical Conductivity of Ga-Sn Alloys III A and III B Versus Temperature	26
7. Electrical Conductivity of Pb-Sn Alloy III Versus Temperature	27

INTRODUCTION

Since Busch (1) and his co-workers reported in 1950 the semi-conducting behavior of gray tin, interest in this material has been increasing. Various groups in Russia, England and the United States have undertaken measurements of its Hall effect, magnetoresistance, conductivity, magnetic susceptibility and thermoelectric power.

Ordinary tin is a metal and displays the normal metallic lustre. It is classified as one of the Group IV elements. In the temperature vicinity of -30°C , a transformation from its metallic phase to another phase may occur under proper conditions and the so-called "gray tin" is the result. Such a transformation not only changes its color but also alters its metallic properties to those of a semiconductor. By addition of different proper impurities, the electrical conductivity of gray tin may be made either n-type or p-type in character. Undoped material always has proven to exhibit excess electron, i.e., n-type conductivity.

Because of the difficulties in preparation of gray tin samples, particularly because of the large volume change accompanying the white-to-gray transition, only specimens of powder form and rods of compressed powder were used respectively by Busch (2) and Kendall (3) in their measurements until in 1953 Ewald (4) devised an improved method of sample preparation. Using the Ewald method, gray tin filaments were obtained. After that, extensive investigations were systematically made by Ewald and Kohnke on the electrical conductivity, magnetoresistance (5)

and Hall effect (6) in these filaments.

Although the measurements on electric and magnetic properties in gray tin by use of filamentary samples resulted in systematic data, recheck of some previous work by improved techniques and the employing of some other elements as new impurities still appeared to be worth undertaking. First of all, in all previous measurements requiring a determination of the potential drop across the sample, potential probes were connected to the two conducting strips to which the sample was soldered. The problems of mounting the sample and construction of equipment were much simplified by this indirect connection. However, true potentiometric measurements are necessary to evaluate the exact potential drop across the sample. Secondly, earlier research work on the electrical conductivity of gray tin samples doped with some p-type impurities like Al, In and Zn indicated special difficulties both in handling due to brittleness and breakage and in interpretation of results due to possible segregation of impurities (5). Additional work with a different p-type impurity was considered desirable to check whether this was truly a characteristic effect of p-type impurities upon gray tin. Thirdly, pure filaments were found to be stabilized by the addition of germanium which prevented the gray-to-white transformation at the normal temperature (7). Since germanium is among the Group IV elements and hence a neutral impurity, investigation of the effects of other neutral elements should give more information about stabilization effects.

To satisfy the first purpose, measurements were made on samples of pure and antimony (Sb)-doped gray tin. By use of a special Ga-In solder, potential probes were successfully connected directly to the sample allowing true potentiometric measurements. The measured electrical conductivity as well as the determined apparent activation energy for both

pure gray tin and samples doped with 2.59×10^{18} Sb atoms per cc are found in good agreement with previous results.

For the second purpose, gallium (Ga)-doped samples were used. The results tend to verify earlier indications of the troubles caused by such p-type impurities as Al, In and Zn.

In the measurements made for the third purpose, lead (Pb) was chosen as the neutral impurity since it is also a Group IV element. The ability of lead to prevent the white-to-gray transformation has been noted in samples containing 1.53×10^{18} or more Pb atoms per cc. On the other hand, samples doped with 1.39×10^{17} Pb atoms per cc did transform to gray tin and seemed to exhibit improved mechanical strength which facilitated handling. However, so far no tendency for preventing the reverse gray-to-white transformation has been found in the study with lead-tin alloys.

All the present experiments were done in the relatively high temperature range from about 210°K to 273°K because of the special interest in the intrinsic range of the electrical conductivity. In Chapter V, detailed discussions are given concerning measurement results.

It is believed that more quantitative analysis and interpretation of the effects of different impurities will be made in the near future. Some suggestions for future investigations are offered in the last chapter.

CHAPTER II

SURVEY OF PREVIOUS WORK

It has been only seven years since gray tin became a subject of semiconductor study. In 1950 Busch, Wieland and Zoller (1) at the Physical Institute of the Eidgenössische Technische Hochschule of Zurich discovered that gray tin was a semiconductor similar to the other Group IV elements, carbon (in the form of diamond), silicon and germanium. Using pure and doped gray tin in powder form, Busch's (8) group from 1950 to 1953 made measurements of its Hall coefficient, magnetoresistance coefficient, temperature dependence of conductivity, and magnetic susceptibility. Although their measurements determined the relative conductivity as a function of temperature, the absolute values of conductivity and the quantitative determination of the Hall coefficient were still left uncertain since it was impossible to calculate absolute values of the current density in the powder. As for magnetoresistance measurements, it was felt possible to obtain satisfactory data because current density values were unnecessary.

Certainly a review of Busch's work indicates the main credit must go to him for prompting a renewed interest in gray tin. His pioneer experiments showed that gray tin was a semiconductor, had a relatively small forbidden energy gap, and could be made to exhibit both electronic and hole conductivity by proper alloying with impurities.

Samples in powder form were also used by Blum and Goryunova (9)

in Russia. The values of absolute conductivity which they obtained were lower by two orders of magnitude than the approximate values found by Busch.

In an effort to obtain better working samples than the powders of Busch, Kendall (10) at the Imperial College of Science and Technology in London tried electrolytic deposition at reduced temperatures and evaporation onto a cold substrate. Though unsuccessful in these attempts, he was able by using pressures of 10 tons/in² at temperatures of -125°C to prepare densely-packed, cylindrical compressed powder rods approximately 1/4 inch in diameter and 1/2 inch long. His data with this type of samples showed a lower forbidden energy gap and a higher specific conductivity than Busch and later Ewald and Kohnke (5) obtained, indicating perhaps that some of the powder transformed back to the white phase under internal pressures during the measurement process.

In 1953, Ewald (4) reported success in preparing filamentary samples of gray tin. The tin wires prepared by the Ewald method were free of cracks and other gross imperfections, mechanically strong, and readily obtained with dimensions of approximately 0.1 mm diameter and several centimeters length. Such samples have proved to be suitable for measurements of electrical conductivity, its change in a magnetic field, the Hall effect, and the thermoelectric power (5).

Since that time extensive measurements with filaments of gray tin and gray tin alloys have been made by Kohnke (5) and Goland (11).

Kohnke's (5) investigation at Northwestern University in 1955 on the electrical conductivity, magnetoresistance, and Hall effect in gray tin filaments not only substantiated the important features of Busch's findings but also contributed a great deal to the evaluation of absolute values of conductivity as well as the quantitative determination of the

Hall coefficient.

With the help of Hall effect and electrical conductivity data in 1956, Goland (11) at Northwestern University was able to make a satisfactory analysis of his measurement data on the thermoelectric power of gray tin filaments.

CHAPTER III

EXPERIMENTAL PROCEDURE

Preparation of Filaments of Gray Tin and Gray Tin Alloys

To prepare gray tin filaments two kinds of pure tin were used. One was supplied by the Vulcan Detinning Company; and the other, which is known to be of a high degree of purity, was provided by Johnson, Matthey & Company, Ltd. For convenience of reference, the former material will hereafter be labelled VDC Pure Tin and the latter JMC Pure Tin.

The analysis of JMC Pure Tin by Johnson Matthey & Company indicated the presence of the following impurities given in percent by weight:

Iron	0.001 %
Copper	0.0003%
Mercury	- - -
Bismuth	0.0001%
Sodium	- - -
Lead	0.0002% or less
Calcium	- - -
Magnesium	- - -

For the experimental work done, VDC Pure Tin was used only in pure form for comparison of electrical conductivity with JMC Pure Tin while JMC Pure Tin was used both for the pure sample and for all alloys.

The Ewald (14) method for preparation of fine filaments of gray tin and its alloys was employed and may be briefly described as follows;

The first step is to prepare filaments of metallic tin by a modification of the Taylor technique (12). A small pellet of pure tin is

placed in one end of a piece of 10-mm pyrex glass tubing, the other end of which has been sealed and drawn into a thin capillary of approximately 0.5-mm inner diameter. The tube is mounted vertically, attached to a rough vacuum pumping system, and the tin heated in vacuo with a flame until it melts and flows into the upper part of the capillary section. The tube is then sealed off and segments of wire approximately 10 cm in length obtained by heating a short section of the filled capillary and drawing it down to an inner diameter of about 0.1 mm.

The glass coating on the wire is dissolved in a hydrofluoric acid bath. Then the wires are given an additional one to two minute etch in concentrated sulfuric acid and rinsed with distilled water.

The white tin filaments thus prepared are cut into 2-cm lengths, buried in gray tin powder, and placed in a refrigerator where they are transformed into gray tin filaments at a temperature of approximately -30°C . The time necessary for complete transformation is of the order of one day for the "pure" wires. However, occasionally individual wires in a batch of samples do not transform under the normal conditions for a period of many days. If they are pressed at the end with gray tin powder and returned to the refrigerator, transformation usually takes place within several hours.

"Doped" samples are prepared in the same manner from alloys of the desired composition which are made from master alloys.

The time taken for complete transformation of tin alloys varies depending upon impurity. For instance, it has been impossible to transform the lead-tin (Pb-Sn) alloys which contain 1.53×10^{18} or more lead atoms per cc over a period of more than two months in the refrigerator.

Because of the tendency of the wires to curl upon transformation and their brittleness, a relatively large number of each kind of sample

was prepared and transformed so that one could be more selective in his choice of those to be measured. Selection was done with the aid of a binocular microscope with special care being taken to choose only samples which were quite straight, relatively free of pits and scratches, as uniform in cross-section as possible and free of cracks.

The various kind of samples used in the experiments are listed in the tables below.

TABLE 1

Types of Pure Tin

Laboratory Name	Mfg
VDC Pure Tin	Vulcan Detinning Company
JMC Pure Tin	Johnson, Matthey & Co. Ltd

TABLE 2

Types of Tin Alloys

Base	Impurity	Lab. Name	Impurity atoms per cc
JMC	Gallium	Ga-Sn Alloy I	4.98×10^{19}
		Ga-Sn Alloy II	4.53×10^{18}
		Ga-Sn Alloy III	4.12×10^{17}
JMC	Antimony	Sb-Sn Alloy I	2.85×10^{19}
		Sb-Sn Alloy II	2.59×10^{18}
		Sb-Sn Alloy III	2.36×10^{17}
JMC	Lead	Pb-Sn Alloy I	1.68×10^{19} *
		Pb-Sn Alloy II	1.53×10^{18} *
		Pb-Sn Alloy III	1.39×10^{17}

*No transformation has been noticed for these alloys

Apparatus and Procedure

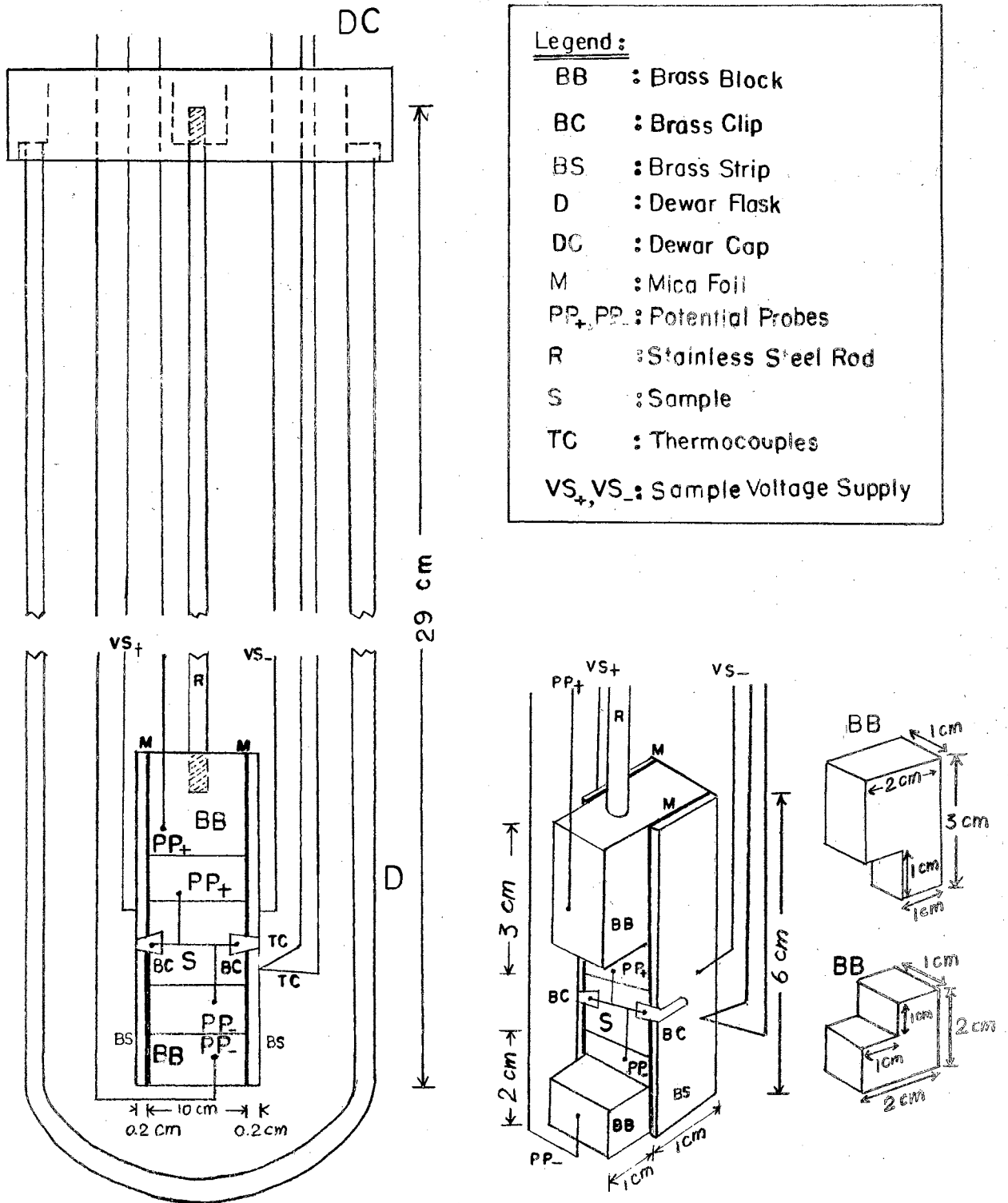
a. Description of Apparatus

The apparatus was designed to permit measurement of the electrical conductivity of filamentary samples as a function of temperature in the temperature range of 210°K to 273°K. The most important part of the apparatus, the sample holder, (see Figure I) was constructed to be suspended from a brass dewar-cap (DC) by means of a 25 cm long stainless steel rod (R) into a standard one-liter dewar flask (D). The holder basically consisted of two flexible clips of brass shim stock (BC), 0.0127 cm thick, which were soldered to brass strips (BS) 6 cm long placed parallel to each other and separated by two brass blocks (BB) each 1 cm wide. The strips were electrically insulated from the block with sheet mica (M) and connected mechanically to them by countersunk, insulated screws.

The top brass block, the construction of which is shown in Fig. 1, was 3 cm long and 2 cm high. On its top it was tapped for a threaded hole used to fasten one end of the stainless rod (R). The forward position of the upper part was made to protect the mounted sample. One of the two potential probes (PP+) was soldered to the lower part.

The bottom block was shorter in length but had the same design as the top one. To this block the other potential probe (PP-) was attached.

The two connections (VS+, VS-) from the sample voltage supply were soldered to the outer sides of the two brass strips (BS). The copper constantan thermocouples (TC) used to measure sample temperature was attached to one brass strip (BS). All the leads from the sample holder can be attached to the external measuring circuit by solder joints at the dewar cap (DC).



Front View of Sample Holder
Inside Dewar Flask.

3-D Diagram of Sample
Holder

Top and Bottom
Brass Blocks

FIGURE 1. DIAGRAM OF SAMPLE HOLDER
AND DEWAR FLASK

b. Mounting the Sample

As mentioned in Sec. a, samples of gray tin and its alloys were rather brittle and hence the mounting problem proved to be a very difficult one. Extreme patience and very careful handling were necessary.

The gray tin filament was actually connected to two brass clips (BC) to minimize the effect of strains caused by the differential thermal expansion of sample and sample holder. Since the low transformation temperature of gray tin made it impossible to use common solders, the problem of connecting the sample to clips was solved by using a special low melting point solder composed of one part indium to four parts gallium which was liquid at room temperature and solid at the measurement temperatures.

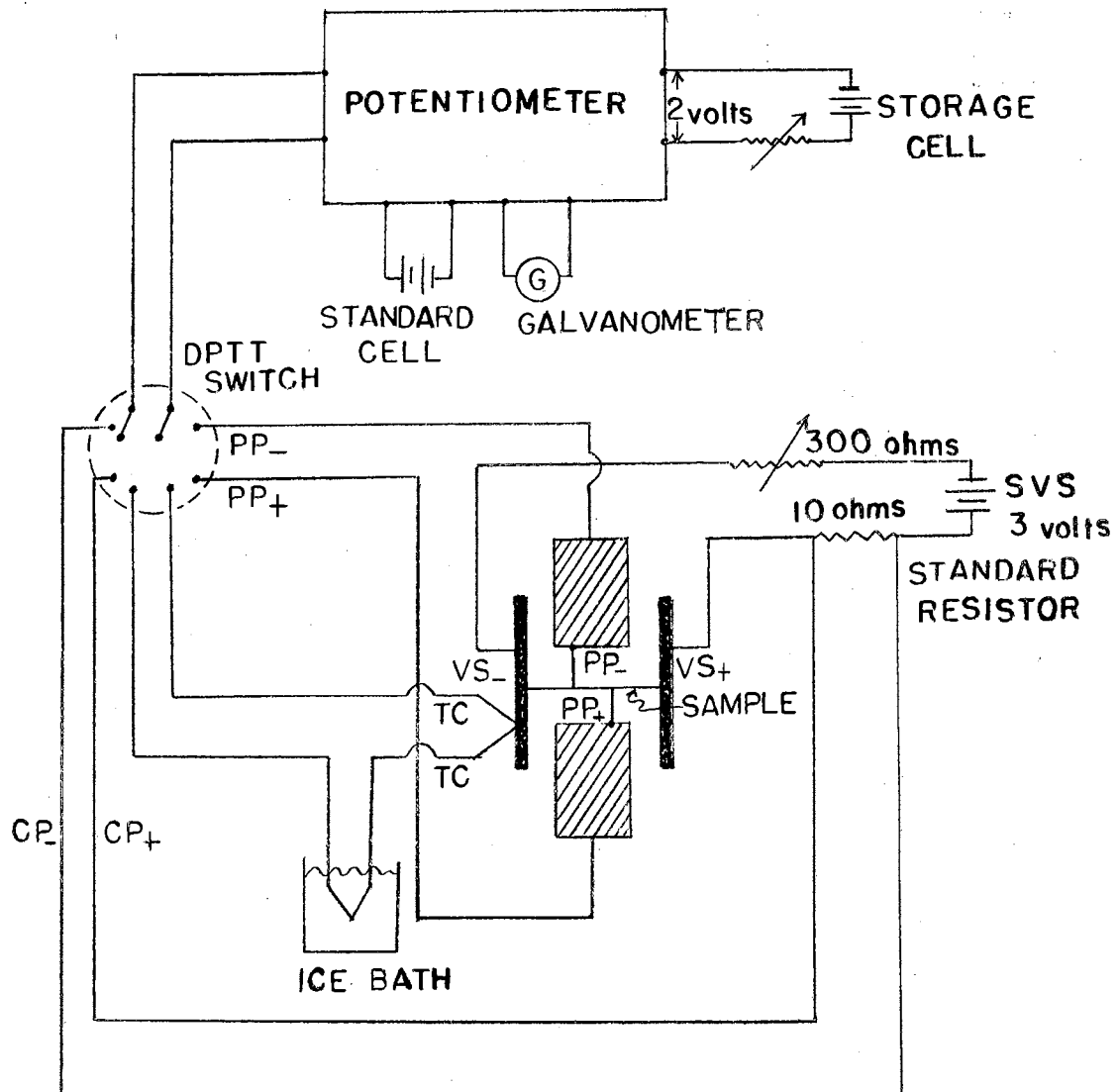
The connection of the two potential probes to the sample also was a difficult job. Extremely fine copper wire--trade name "Nyclad"--of 0.009 cm diameter was used for the probes. Direct connection to the sample was accomplished with a minute amount of the above mentioned solder.

The filaments were never kept at room temperature for more than two minutes at a time so that it was always necessary to do the mounting and connecting in several steps, cooling the filament between each step.

c. Method of Measurement.

All electrical conductivity measurements were made using a dc, constant sample current method. The main measuring instrument was a Leeds and Northrup Type K2 potentiometer with an Eppley standard cell. The sample current was furnished by a 3 volt dry cell and measured by determining the I-R drop across a 10 ohm standard resistor also supplied by Leeds and Northrup. The circuit is diagrammed in Figure 2.

The copper-constantan thermocouple emf was converted to temperature



Legend :

CP₊, CP₋ : Current Probes

DPTT SWITCH : Double Pole Triple Throw Switch

PP₊, PP₋ : Potential Probes

SVS : Sample Voltage Supply

TC : Thermocouples

VS₊, VS₋ : Sample Voltage Supply Leads

FIGURE 2 CIRCUIT DIAGRAM

using Scott's (13) calibrated table.

The measurement procedure was as follows: A sample wire (sample dimensions were of the order of 5 mm length and 0.15 mm diameter) was soldered to the sample holder clips using the special Ga-In solder. All probe leads were connected to the external circuit by conventional solder joints at the dewar cap. These connections were made rapidly with the experimental arrangement suspended in the cold atmosphere just above the measurement bath which consisted of dry ice in acetone and which was contained in the dewar flask.

Following connection, the sample on its holder was lowered into the acetone bath which had a temperature of about -60°C when measurements got started.

Approximately each half-hour after starting three emfs were measured. The first one, (E_{th}), was the thermal emf used to calculate the sample temperature, the second, (E_{RS}), employed to determine the sample current, was the potential drop across the standard resistor; and the third, (E_S), was the drop between the two potential probes soldered to the sample.

Since the sample temperature rose as the acetone warmed up, different values of these emfs were measured each time. In order to compensate for slight temperature drift during a set of measurements, the thermal emf was measured twice and averaged. At no time was the drift more than 1/10 of a degree.

To obtain absolute values of the electrical conductivity, dimensions of the sample were measured with a measuring microscope using a Gaertner eyepiece.

The experimental data are presented in graphical form in a subsequent chapter.

CHAPTER IV

THEORETICAL BACKGROUND

Microscopic Treatment

According to Goldberg (14), a very general expression for the electric current density, \vec{J} , in a cubic semiconductor in the presence of a magnetic field \vec{H} , and an electric field \vec{E} is the following:

$$\begin{aligned} \vec{J} = & \sigma_0 \vec{E} + \alpha \vec{E} \times \vec{H} + \beta \vec{E} H^2 + \gamma \vec{H} (\vec{E} \cdot \vec{H}) + \delta M \vec{E} \\ & + \sigma_0^* \vec{\nabla} T + \alpha^* \vec{\nabla} T \times \vec{H} + \beta^* \vec{\nabla} T H^2 + \gamma^* \vec{H} (\vec{\nabla} T \cdot \vec{H}) + \delta^* M \vec{\nabla} T \end{aligned} \quad (4.1)$$

where the Greek letters indicate complicated integral forms involving the statistical distribution function, M is a diagonal tensor involving magnetic field components and $\vec{\nabla} T$ is the temperature gradient.

For the experimental work done, no magnetic fields were used and thus terms involving \vec{H} are of no interest. Furthermore, all terms involving $\vec{\nabla} T$ can be disregarded since isothermal conditions were maintained experimentally.

The result of this simplification is, as expected, the familiar expression

$$\vec{J} = \sigma_0 \vec{E} \quad (4.2)$$

Or in terms of \vec{E} , we get

$$\vec{E} = \frac{\vec{J}}{\sigma_0} \quad (4.3)$$

Maintaining $\vec{J} = (J_x, 0, 0)$, we obtain

$$E_x = \frac{1}{\sigma_0} J_x \quad (4.4)$$

Since $E_x = \frac{V}{l}$ and $J_x = \frac{I}{A}$, substitution of these two expressions into Equ. (4.4) gives

$$\frac{V}{l} = \frac{1}{\sigma_0} \frac{I}{A}$$

or

$$\sigma_0 = \frac{l I}{A V} \quad (4.5)$$

where l is the length of the sample, I the current passing through it, A the cross-sectional area and V the potential drop across the length of the sample.

The units ordinarily used in the laboratory are mixed units, i.e.,

i) centimeter, gram, second for mechanical quantities;

ii) volts, coulombs for electrical quantities.

Hence equation (4.5) gives σ_0 in $(\text{ohm cm})^{-1}$ while l in cm, I in amperes, A in cm^2 , and V in volts.

Statistical Treatment

From a different point of view, the electrical conductivity in the body of a semiconductor may also be expressed in terms of the charge carriers (15)

$$\sigma = n q \mu_n + p q \mu_p \quad (4.6)$$

where

n = density of negative carriers = electrons/ cm^3

p = density of positive carriers = holes/ cm^3

μ_n = mobility of negative carriers = $\text{cm}^2/\text{volt-sec}$

μ_p = mobility of positive carriers = $\text{cm}^2/\text{volt-sec}$

q = electronic charge = 1.60×10^{-19} coulombs

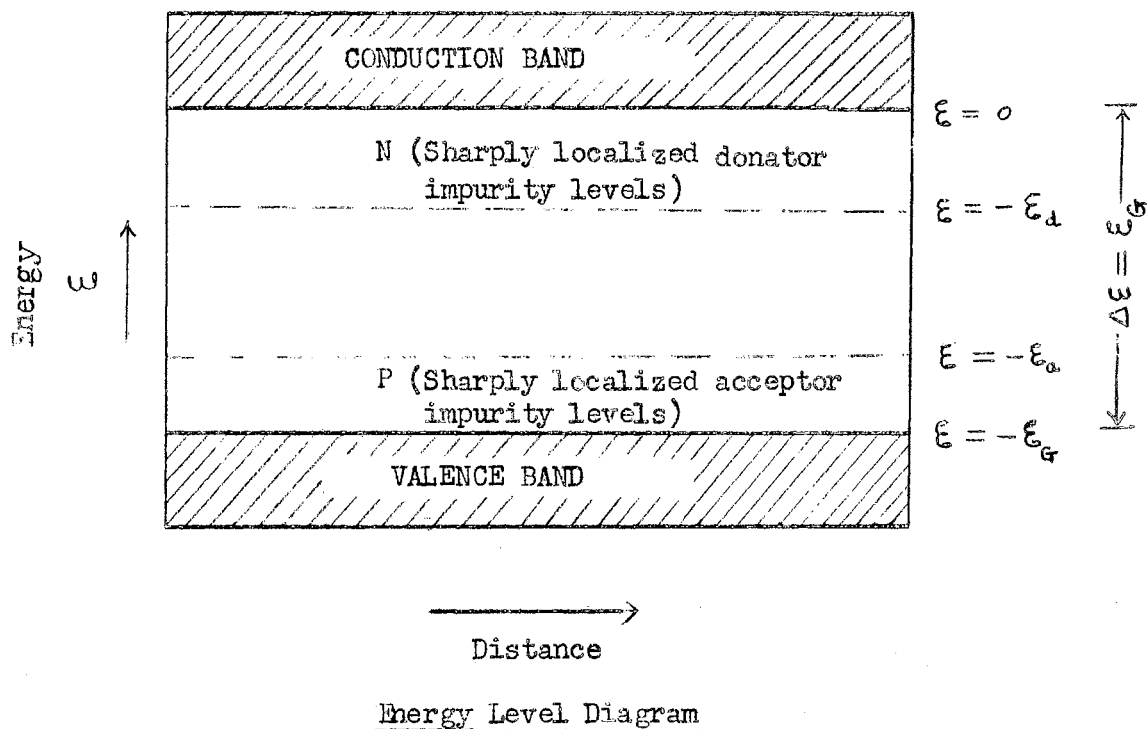
For an intrinsic sample, $n_i = p_i$ (16). Therefore its electrical

conductivity is

$$\sigma_i = q n_i \{ \mu_{n_i} + \mu_{p_i} \} \quad (4.7)$$

Where the subscript i indicates that the concerned quantities are evaluated for the intrinsic sample.

To evaluate n_i , the procedures developed from the concept of quantum states in the solid are summarized below. According to Blakemore (17), the following energy level diagram is used.



By using the Fermi-Dirac statistics for a semiconductor and making the simplifying assumption of spherical energy surfaces in momentum space to obtain the density of states, the number of electrons per unit volume in the conduction band and the number of holes per unit volume in the valence band can be obtained (18):

$$n = \int_0^{\infty} N(\epsilon) d\epsilon = 4\pi \left(2 m_e kT / h^2 \right)^{3/2} \int_0^{\infty} \frac{\eta^{1/2} d\eta}{1 + e^{\eta - \eta^*}}$$

or representing the integral by $F_{1/2}(\eta^*)$

$$n = n_0 \left(\frac{m_e}{m} \right)^{3/2} F_{1/2}(\eta^*) \quad (4.8)$$

and

$$p = n_0 \left(\frac{m_h}{m} \right)^{3/2} F_{1/2}(-\eta^* - \eta_G) \quad (4.9)$$

where

$$n_0 = 4\pi (2m kT/k^2)^{3/2} = 5.541 \times 10^{15} T^{3/2} \text{ cm}^{-3} \quad (4.10)$$

m_e = the electronic effective mass

m_h = the hole effective mass

m = the electronic mass = 8.999×10^{-28} grams

$$\eta = \epsilon/kT$$

$$\eta^* = \epsilon^*/kT \quad (\epsilon^* \text{ is called the Fermi Level})$$

$$\eta_G = \epsilon_G/kT \quad (-\epsilon_G \text{ is the energy level at the top of the valence band})$$

The function $F_{1/2}(\eta^*)$ is called "Fermi Function" and values of it have been tabulated as a function of temperature in the range:

$$-4 \leq \eta^* \leq +20$$

by McDougall and Stoner (19). When $\eta^* < -2$, the classical statistics for the mechanical distribution of Maxwell and Boltzmann is a good approximation of the Fermi-Dirac distribution function and the expression for the Fermi Function thus becomes

$$F_{1/2}(\eta^*) = \frac{1}{2} \pi^{1/2} e^{\eta^*} \quad (4.11)$$

In the intrinsic case where free carriers are produced by direct excitation of electrons from the valence band to the conduction band there are either no carriers due to impurities or relatively so few that any effect they might have may be completely disregarded. Hence, combining equations (4.8), (4.9) and (4.11), one obtains

$$n_i = n_o \left(\frac{m_e}{m} \right)^{3/2} \frac{\pi^{1/2}}{2} e^{\eta^*} = p_i = n_o \left(\frac{m_h}{m} \right)^{3/2} \frac{\pi^{1/2}}{2} e^{(-\eta^* - \eta_g)} \quad (4.12)$$

from which the Fermi level can be obtained as

$$\epsilon^* = -\frac{\epsilon_g}{2} + \frac{3kT}{4} \ln \left(\frac{m_h}{m} \right) \quad (4.13)$$

Substitution of Equ. (4.13) into Equ. (4.12) gives the final expression for the number of intrinsic electrons or holes:

$$n_i = p_i = \frac{\pi^{1/2}}{2} n_o \left(\frac{m_e m_h}{m^2} \right)^{3/4} e^{-\epsilon_g/2kT} \quad (4.14)$$

Hence from equation (4.7), the conductivity for the intrinsic sample is:

$$\sigma_i = q \{ \mu_{n_i} + \mu_{p_i} \} \frac{\pi^{1/2}}{2} n_o \left(\frac{m_e m_h}{m^2} \right)^{3/4} e^{-\epsilon_g/2kT} \quad (4.15)$$

Mobility Theory

By definition the mobility of a charge carrier is the ratio of its average velocity to electric field without regard to algebraic sign (15). Thus we have

$$\mu_n = \frac{|\overline{v_n}|}{E}, \quad \mu_p = \frac{|\overline{v_p}|}{E} \quad (4.16)$$

where $\overline{v_n}$ means the average velocity of negative charge carriers and $\overline{v_p}$ that of positive charge carriers.

These mobilities can be also expressed as (15)

$$\mu_n = \frac{q\tau_n}{m_n}, \quad \mu_p = \frac{q\tau_p}{m_p} \quad (4.17)$$

by introducing the mean free time τ_n and τ_p .

In order to investigate the relationship between temperature and mobility the motion of the charge carriers through the crystal lattice has to be studied.

Three types of scattering mechanisms are usually employed to account for the carriers' motion: scattering by neutral impurities, by ionized impurities and by the acoustical vibrations of the lattice itself.

By studying the scattering of an electron by an isolated hydrogen atom, Erginsoy (20) was led to an expression for the mean free time (or relaxation time τ) of charge carriers scattered by neutral impurities which is independent of velocity.

Since the impurities in gray tin must have a low activation energy and hence a high degree of ionization, it is believed more important to attribute the effect of scattering in gray tin to ionized impurity centers. According to Conwell and Weisskopf (21) the relaxation time for this type of scattering is proportional to the cube of the charge carrier velocity. Thus through complicated calculations, Equ. (4.17) reduces to

$$\mu_n \propto \tau^{3/2}, \quad \mu_p \propto \tau^{3/2} \quad (4.18)$$

However, the above discussed types of scattering are predominant at low temperatures, while lattice scattering might be considered more important at high temperatures near the top of the measurement range especially if the impurity concentration is relatively low. According to Shockley (22), studies in scattering by thermal agitation have introduced a deformation potential formula which predicts a relaxation time which is inversely proportional to charge carrier velocity. This leads to a lattice-scattering mobility that varies as $\tau^{-3/2}$. By using two constants of proportionality B_1 and B_2 , equation (4.17) reduces to;

$$\mu_{n_i} = B_1 \tau^{-3/2}, \quad \mu_{p_i} = B_2 \tau^{-3/2} \quad (4.19)$$

where the subscript i indicated that the mobilities are evaluated in the intrinsic range.

Combining Equas (4.10), (4.15), and (4.19) one easily obtains

$$\sigma_i = q \left\{ B_1 + B_2 \right\} T^{-3/2} \frac{\pi^{1/2}}{2} \times 5.541 \times 10^{15} T^{3/2} \left(\frac{m_e m_h}{m^2} \right)^{3/4} e^{-\epsilon_g/2kT}$$

which reduces to

$$\sigma_i = A e^{-\epsilon_g/2kT} \quad (4.20)$$

where A is a constant if effective masses are independent of temperature.

Equ. (4.20) indicated that the intrinsic energy gap can be obtained directly from the slope of a $\ln \sigma$ vs $1/T$ graph if the above assumptions are valid.

CHAPTER V

PRESENTATION OF DATA AND DISCUSSION

General Observations

The results of electrical conductivity measurements on the samples of pure gray tin and samples prepared by alloying the tin with certain impurities are presented in Figures 3 to 7. The impurity concentrations for the alloys were calculated from the quantity of impurity added to the melt, the larger specific volume of gray phase being taken into account. Before individual discussion of the effects of impurity concentration, some general results can be noted.

In the first place, it can be noticed by comparison of these figures that at the high temperature end of the measurement range, the conductivity curves for the pure gray tin sample and for those with the lowest amounts of impurities give a straight line when the logarithm of conductivity is plotted against $1/T$. However, many samples of the Ga-Sn Alloy III displayed inconsistent results, a fact which will be discussed in more detail in the next section.

With a large increase in impurity concentration the linear portion of the conductivity curve disappears as noted especially for Ga-Sn Alloy I (see Figure 5).

These two behaviors are qualitatively consistent with the simple theory for intrinsic semiconductors.

The conductivity of pure gray tin, according to this theory as given in Chapter IV, would show an exponential increase with increasing

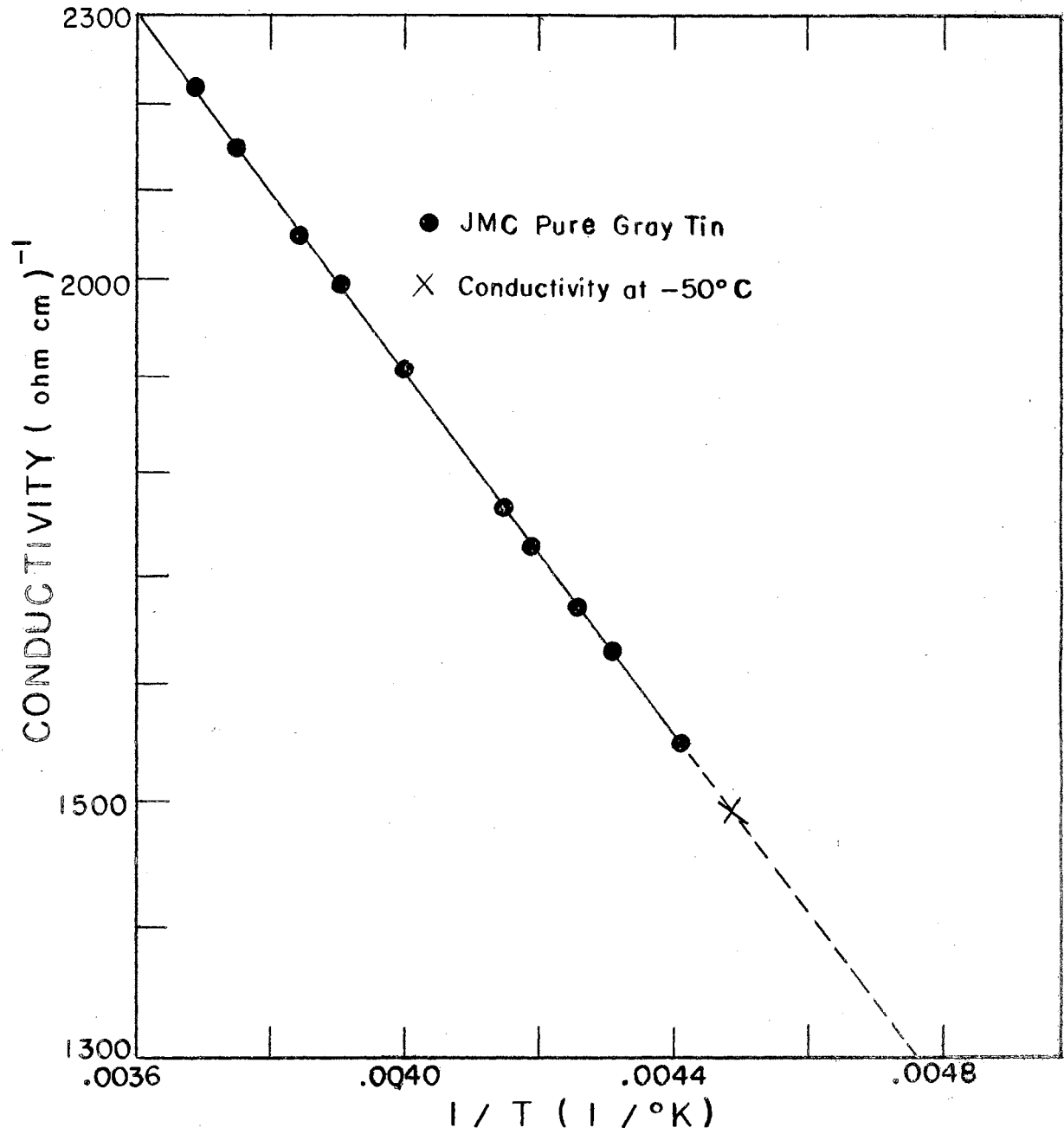


FIGURE 3 ELECTRICAL CONDUCTIVITY OF JMC PURE TIN VERSUS TEMPERATURE

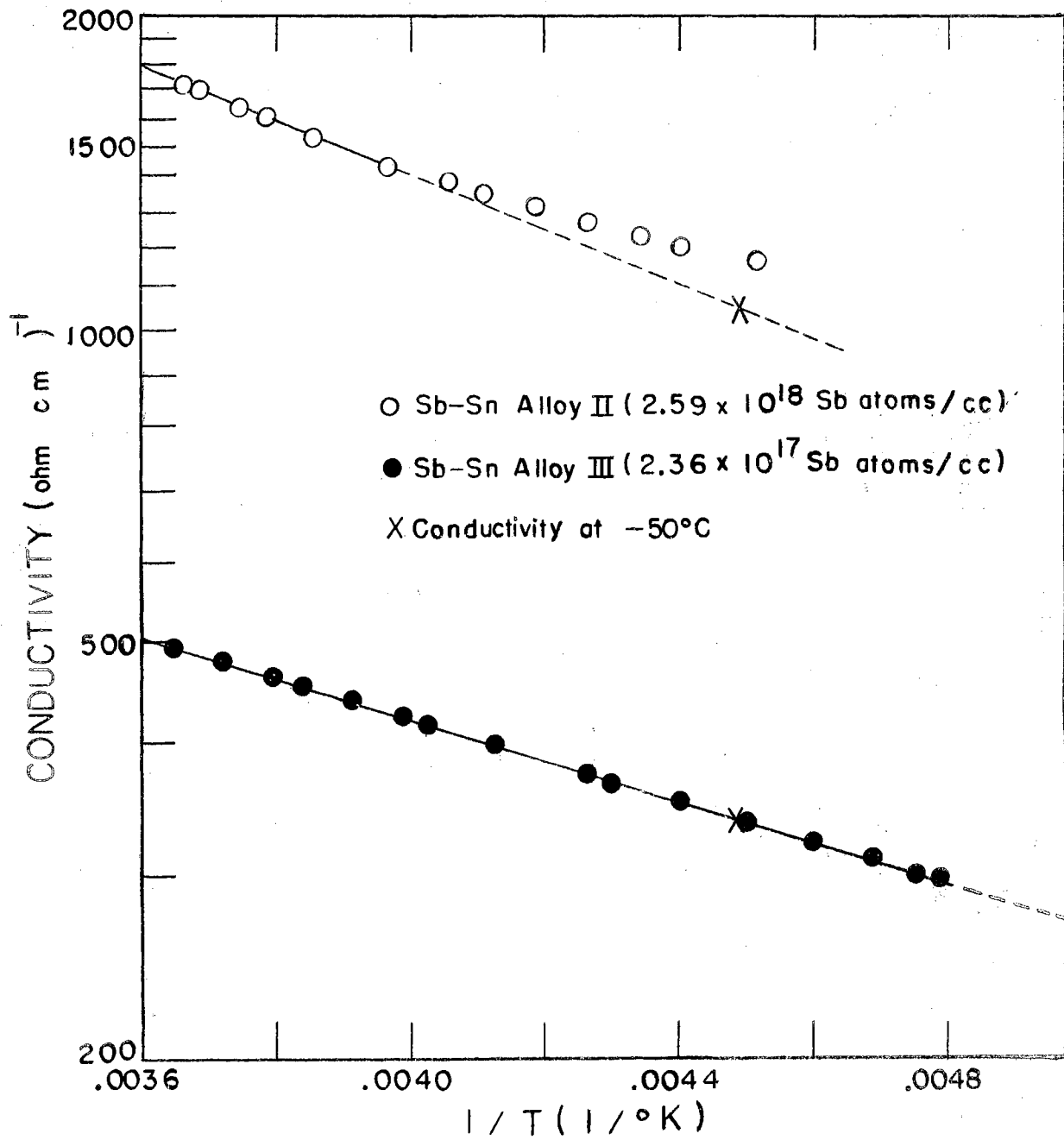


FIGURE 4 ELECTRICAL CONDUCTIVITY OF Sb-Sn ALLOYS II AND III VERSUS TEMPERATURE

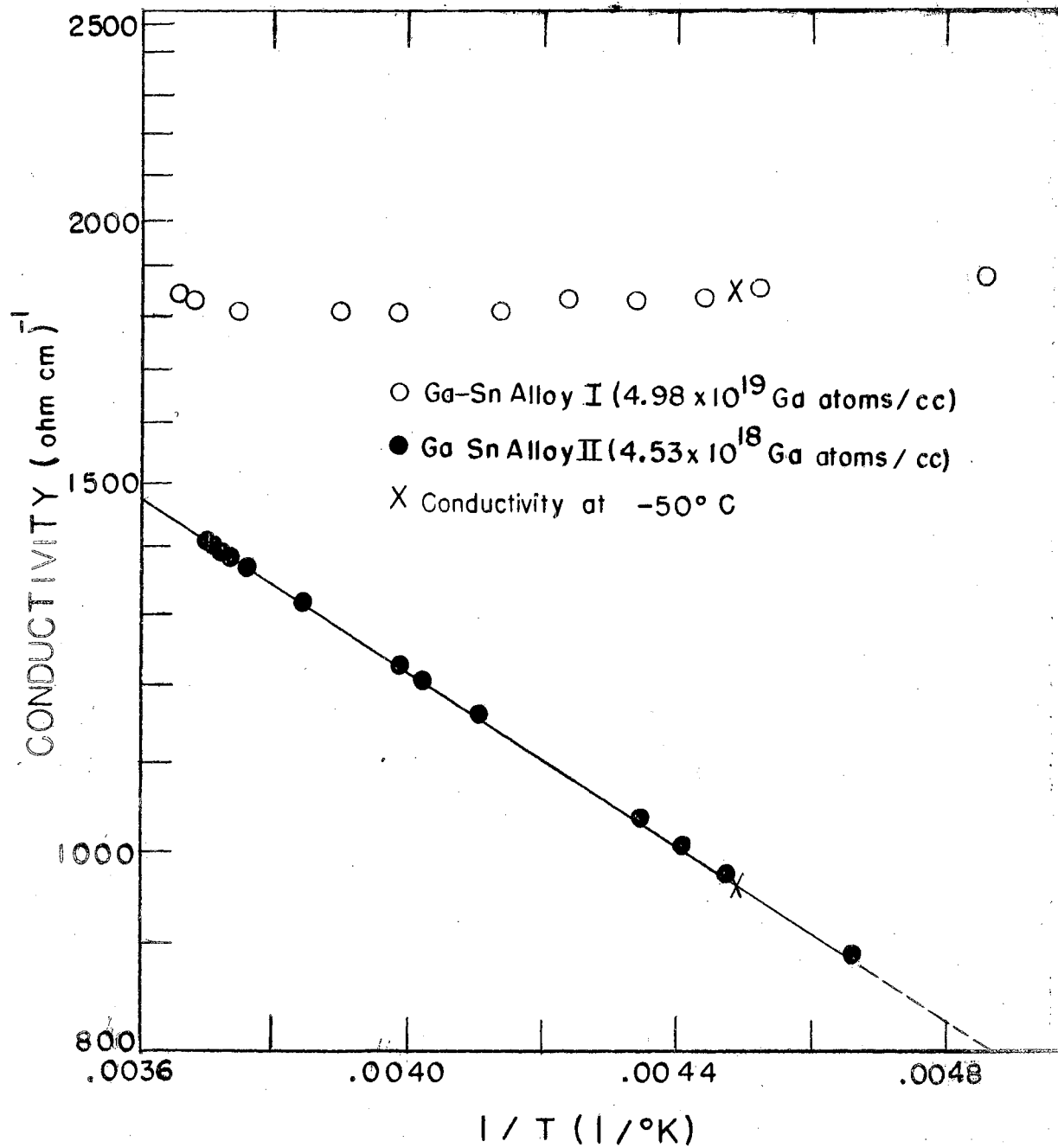


FIGURE 5 ELECTRICAL CONDUCTIVITY OF Ga-Sn ALLOYS I AND II VERSUS TEMPERATURE

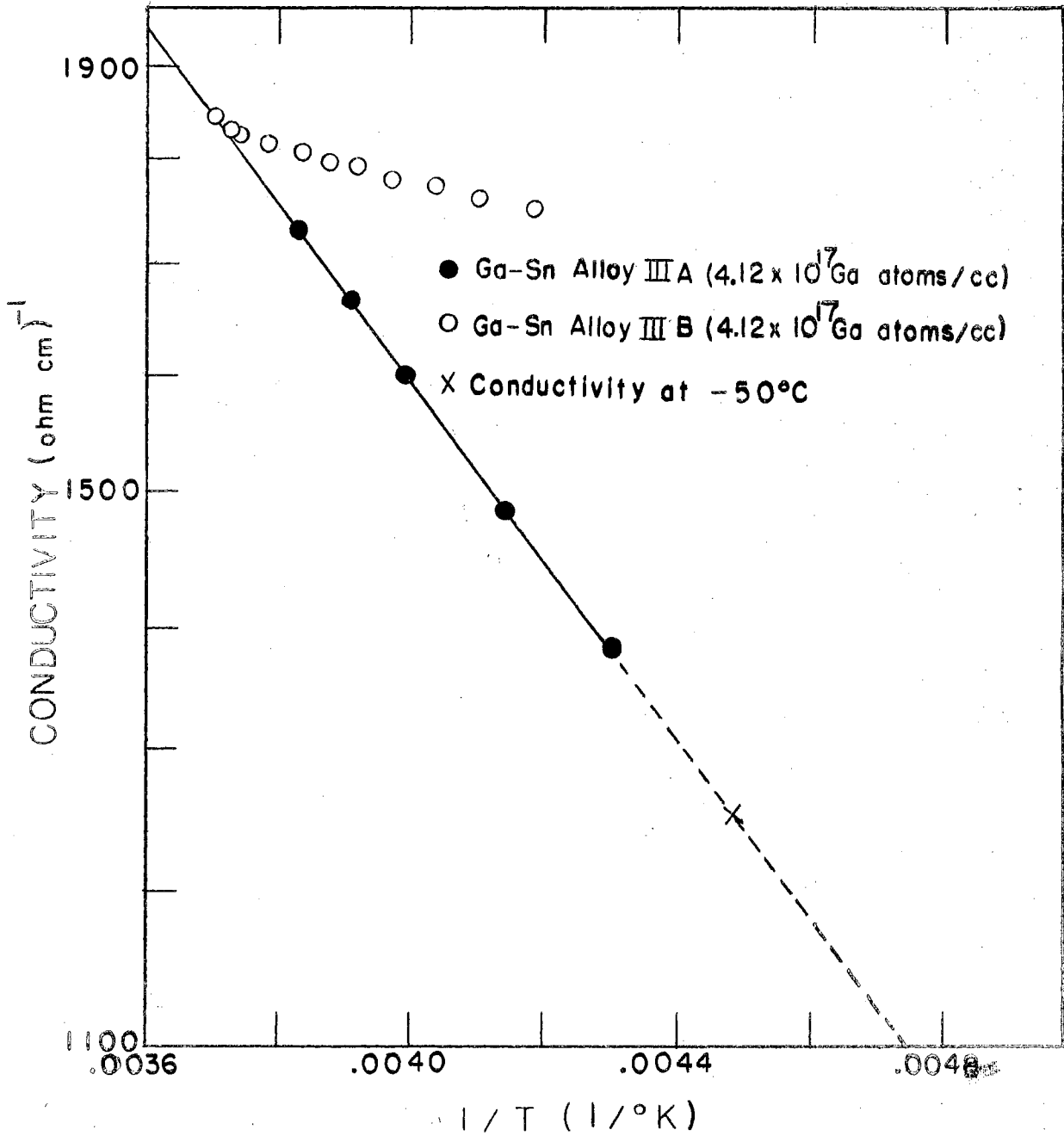


FIGURE 6 ELECTRICAL CONDUCTIVITY OF Ga-Sn ALLOYS III A AND III B VERSUS TEMPERATURE

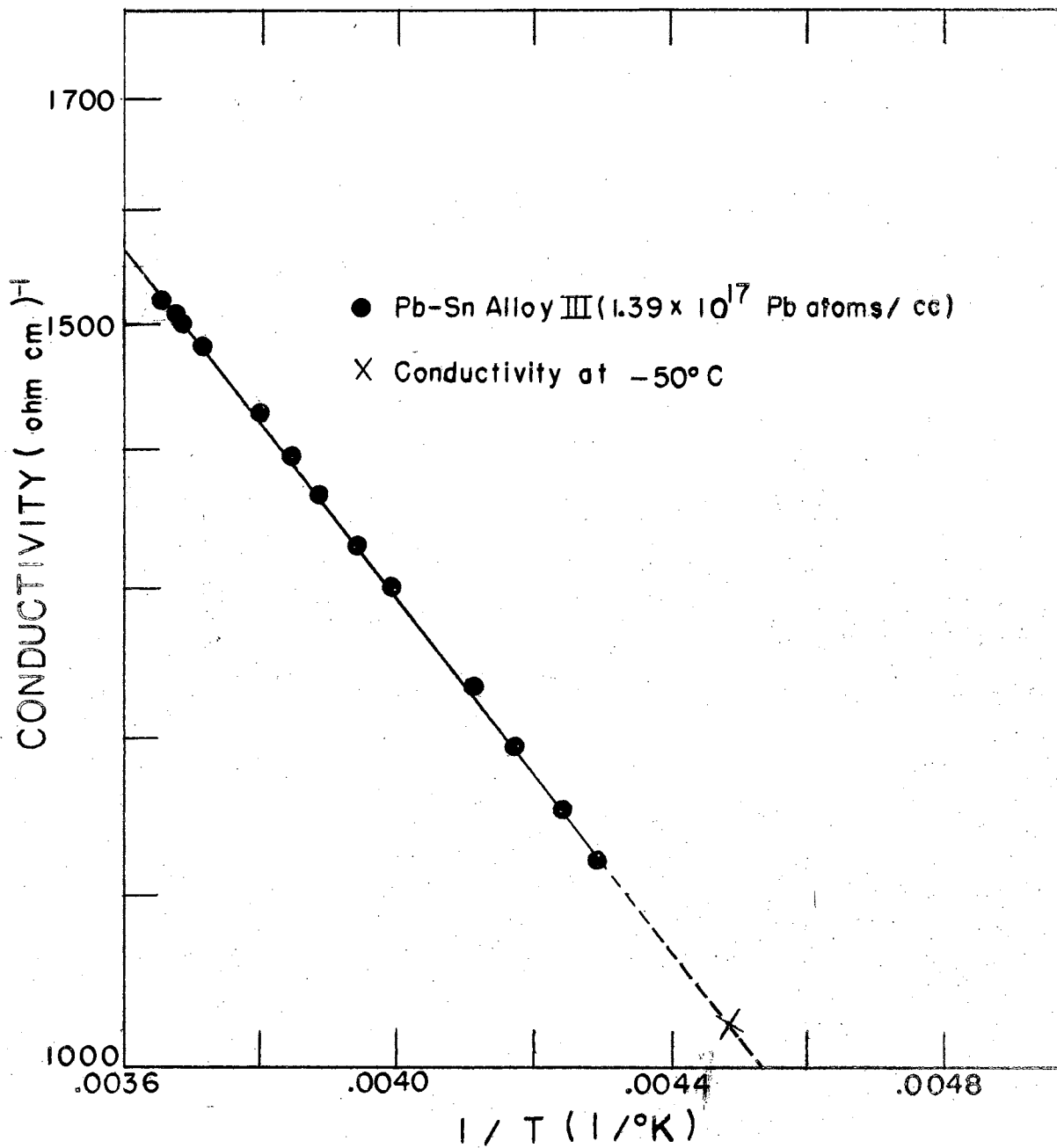


FIGURE 7 ELECTRICAL CONDUCTIVITY OF Pb-Sn ALLOY III VERSUS TEMPERATURE

temperature at the high temperature end of the measurement range. For alloys with very small impurity concentrations, the effect of the added impurities should be relatively small and noticeable mainly at lower temperatures. Higher concentrations of impurity would be expected to affect results at high temperatures, decreasing the intrinsic temperature range, and perhaps even giving the conductivity a metallic character.

Secondly, while previous measurements have indicated that the addition of impurities results (5) in an increase in the "intrinsic" activation energy, the results of the present measurements display some discrepancies in this respect. Values of activation energies determined from the slopes of the intrinsic linear portions of the conductivity curves are given in Table 3. In the case of JMC pure gray tin, the activation energy determined from several different samples is 0.088 ev which is in good agreement with the results of Busch's (2) and Ewald's (5) groups. However, the activation energies of several of the gray tin alloys containing Sb, Ga, and Pb are lower than that of the pure sample. Particularly unexpected is the decrease in the activation energy observed for Sb-Sn Alloy III. It is rather difficult to give a satisfactory explanation for this observation. One factor is the possible nonuniform distribution of impurity atoms in the alloys.

For the sake of comparison the absolute conductivities at -50°C of different samples are listed in Table 3. Generally speaking, addition of impurity results in a decrease in absolute value of the conductivity. Ga-Sn Alloy I is an expected exception and its conductivity at -50°C is higher than that of pure gray tin. Although Ga-Sn Alloy III A exhibits higher conductivity than Ga-Sn Alloy II at the same temperature -50°C , the data obtained from samples of Ga-Sn Alloy III can hardly be considered certain because of great difficulties constantly associated with the

TABLE 3

Variation of Conductivity and Apparent Activation
Energy with Impurity Content

Type of Sample	Impurity Concentration	Apparent Activation Energy E_G (ev)	Conductivity at -50°C $(\text{ohm cm})^{-1}$
JMC Pure Tin		8.8×10^{-2}	1482
Sb-Sn Alloy II	2.59×10^{18} Sb-atoms/cc	9.6×10^{-2}	1089*
Sb-Sn Alloy III	2.36×10^{17} Sb-atoms/cc	7.8×10^{-2}	338
Ga-Sn Alloy I	4.98×10^{19} Ga-atoms/cc		1843
Ga-Sn Alloy II	4.53×10^{18} Ga-atoms/cc	8.2×10^{-2}	962
Ga-Sn Alloy III A	4.12×10^{17} Ga-atoms/cc	8.6×10^{-2}	1244*
Ga-Sn Alloy III B	4.12×10^{17} Ga-atoms/cc		
Pb-Sn Alloy III	1.39×10^{17} Pb-atoms/cc	8.2×10^{-2}	1023*

* Values extrapolated from straight line portion of conductivity curve.

measurement of individual samples. Further remarks on this kind of alloy will be included in the next section.

Individual Discussion

Through the experimental work JMC Pure Tin has proven easy to work with and consistent in the results previously obtained. The activation energies determined from several samples have the same value of 0.088 ev which is in satisfactory agreement with the results of Busch (2) and Kohnke (5). The absolute conductivity for JMC Pure Gray Tin at -50°C has been computed as $1482 (\text{ohm cm})^{-1}$.

A score of experiments with VDC Pure Tin have been tried but none has led to satisfactory results. Many of them resulted in conductivity curves of a type which indicated that sample cracks occurred during the temperature change in the measurement process. Others were unsatisfactory because a complete sample break ended measurements. Perhaps VDC Tin contains troublesome impurities but no definite assertion can be made without a careful analysis of its contents. Hence it is suggested here that further investigation be made on this kind of "pure" tin.

The measured value for absolute conductivity at -50°C of the gray tin sample doped with 2.50×10^{18} antimony atoms per cc (i.e. Sb-Sn Alloy II) is $1089 (\text{ohm cm})^{-1}$ and its activation energy is determined as 0.096 ev. Both figures are very close to the results noted by Kohnke (5) for a doped gray tin samples with 1.3×10^{18} antimony atoms per cc for which he obtained values of 0.0941 ev for the activation energy and $1018 (\text{ohm cm})^{-1}$ for the conductivity at -50°C .

Contrary to the findings on Sb-Sn Alloy II, there is a large discrepancy, particularly in the values of conductivity for Sb-Sn Alloy III in comparison with the results of Kohnke (5) on a similar sample. From present data, the alloy containing 2.36×10^{17} antimony atoms per

cc shows values as low as $338 \text{ (ohm cm)}^{-1}$ for its conductivity at -50°C and as low as 0.078 ev for its activation energy. According to Kohnke (5), the conductivity for a sample doped with 3.1×10^{17} antimony atoms per cc was found to be $1102 \text{ (ohm cm)}^{-1}$ at -50°C and the activation energy 0.0862 ev . It is possible that the lower conductivity of Sb-Sn Alloy III can be accounted for by the presence of cavities inside the sample, but this has not been confirmed as yet. However, according to a theory of degeneracy proposed for In-Sb by Burstein (23) as well as a number of experimental observations on that material by Tanenbaum and Briggs (24), an increase in the apparent energy gap might be expected to accompany an increase of impurity content. This would mean that Sb-Sn Alloy III should have a higher activation energy than JMC Pure Tin. Present results on Sb-Sn Alloy III are contrary to this expectation.

To the author's knowledge, no previous investigation work has been reported on the conductivity of filamentary gray tin samples doped with gallium atoms. Hence no comparison can be made between present findings and previous results.

In the measurement range, the conductivity of the sample containing 4.98×10^{19} gallium atoms per cc remains practically independent of temperature. This behavior suggests that the high impurity concentration yields so many impurity carriers that their effect is to overshadow normal semiconducting behavior, making the sample degenerate. Also its conductivity at -50°C was measured as high as $1843 \text{ (ohm cm)}^{-1}$ further confirming degeneracy. It should be noted that either from Ewald and Kohnke's (5) observations or from present findings for all alloys not obviously degenerate, the purest gray tin has the highest value for its conductivity.

Kohnke (5) found that samples doped with p-type impurities such as

In, Al, and Zn, were particularly difficult to handle as far as conductivity measurements were concerned. The author has had similar experiences. Gray tin sampled doped with the p-type impurity, Ga, also proved difficult to measure. For example, for Ga-Sn Alloy III, over a dozen experiments were made and all except two were halted before completion because of a sample break. Furthermore, even the results of these two relatively successful measurements still disagree widely in the shape of their conductivity curves. (see Fig. 6) For instance, Ga-Sn Alloy III A has $1244 \text{ (ohm cm)}^{-1}$ for its absolute conductivity at -50°C and 0.086 ev for its apparent activation energy, while alloy III B exhibits a behavior similar to that of Alloy I. Both alloys are supposed to have the same concentration-- 4.98×10^{10} gallium atoms per cc. Nonuniform distribution of impurity atoms throughout the alloy might provide an explanation for this discrepancy and has been proposed for similar discrepancies in Al-Sn Alloys (5). Less trouble occurred in the experiments with samples of Ga-Sn Alloy II, for which the apparent activation energy has been determined to be 0.082 ev, still slightly less than the 0.88 ev value given by the pure material. It is quite obvious that further research work on gray tin doped with p-type impurities is necessary to find out why mechanical properties of the samples are affected and conductivity measurements often give inconsistent results.

The last type of sample was prepared by alloying JMC pure tin with lead. Three Pb-Sn alloys were made with different concentrations, namely, Alloy I, containing 1.68×10^{19} lead atoms per cc; Alloy II, 1.53×10^{18} lead atoms per cc; Alloy III, 1.39×10^{17} lead atoms per cc. However, only Alloy III transformed to the gray phase.

Unfortunately only the inhibiting effect on the white-to-gray transformation has been noted so far and the possibility of a reverse effect

remains to be studied. The conductivity of Pb-Sn Alloy III at -50°C was extrapolated as $1023 (\text{ohm cm})^{-1}$ from the straight portion of its conductivity curve. The activation energy determined for this alloy is 0.082 ev , again slightly lower than that obtained for the pure sample.

Conclusions

From the foregoing discussion, some conclusions have been reached and some suggestions can be offered for future research.

Since present measurements tend to indicate that the previously observed pattern of apparent energy gap increase with increasing impurity content holds only for higher impurity concentrations, additional measurements should be done on samples containing less than 10^{17} impurity atoms per cc.

Through the present measurements it has been noticed that differences between samples show up more clearly at low temperatures. Therefore further measurements should extend to the liquid nitrogen range, i.e., down to 77°K , to verify the importance of small differences in apparent gap energy and to correlate the results on different samples supposedly having the same impurity content.

To facilitate further measurements of conductivity it is worth trying to improve the physical characteristics, such as shape, etc, of samples since most unsuccessful experiments have been due to sample cracks or complete breaks. As for p-type alloys, additional attempts to obtain even distribution of impurity atoms are suggested.

According to Ewald (7), the addition of germanium to pure tin sample will stabilize its gray phase up to $+60^{\circ}\text{C}$, while ordinary gray tin transforms back to the white phase at room temperature. There may be other materials which can prevent the gray-to-white transformation above room

temperature and make industrial applications of this material possible. Further studies on lead alloys would appear to be of immediate interest. In addition, no experiment has so far been reported on the effects of the addition of two impurities and this project is also suggested as worthy of consideration.

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