SOME INVESTIGATIONS ON ELECTRICAL AND OTHER PROPERTIES OF THIN FILMS

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SOME INVESTIGATIONS ON ELECTRICAL AND OTHER PROPERTIES OF THIN FILMS

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CHAPTER - I

GENERAL INTRODUCTION

A. Thin films, their nature, structures and properties

During the last two decades, great technological feats have been achieved in missiles and rockets as a result of intensive space research, miniaturizations and development in electronic devices for power supply, rectifications, amplifications, detection systems, storing of light energy and release on demand, refrigeration and the like. The above have been possible because of the development of new materials known as semiconductors. Intensive researches are going on throughout the world to seek for better and better materials with special and desirable properties. As a result, interest in 'thin film physics' has greatly been stimulated.

Due to the increasing usefulness of the metals, semiconductors and dielectrics in the form of thin films, which can be prepared with great ease by vacuum evaporation technique, they are being used in many branches of physics, electronic and chemistry. Particularly, thin films are used in highly reflecting mirror coatings, protective layers, antireflection, beam-splitters; reflection and transmission type interference filters with narrow and wide band widths, polarisers, radiation detectors; coating for image forming devices, light intensifiers and solar energy converters; surface films for controlling the temperature of satellites,

passive and active electronic film components, thin film circuits and superconducting film devices.

These films can be prepared by various methods, such as cathodic sputtering, chemical deposition, vapour deposition and anodic oxidation etc. under controlled and reproducible conditions. The electrical, optical and mechanical properties of the vacuum deposited films are generally dependent upon the evaporation conditions and the purity of the samples. The quality of the deposits, their appearance and physical properties are also strongly affected by the presence of gas molecule in large amount. Further the structural, electrical, optical and mechanical properties of thin films may differ considerably from the bulk materials. The structure of evaporated films can be amorphous, polycrystalline or single crystal in nature, depending on the conditions of the evaporation, substrate temperature etc. The films can be compact and hard or porous and soft. Controlling the deposition conditions, such as rate of evaporation, substrate temperature etc. new orientation of the deposits possibly with different electrical properties can be induced without much difficulty. It is also likely that semi-conducting properties such as resistivity, thermoelectric power, nature of the carriers, etc. can be changed with the change of evaporation conditions. It has been shown by a number of workers viz. Pashley (1959), Matthews (1959), Phillips (1960) that a high density of lattice defects viz. dislocations, stacking faults, voids, microtwins, are normally present in films prepared

by vacuum evaporation technique. Their presence accounts not only for the difference in intensity of diffraction patterns by X-rays and electrons but also for the electrical behaviour. Dislocation density in thin films, which determines, like impurity effects, the activation energy can be changed at will in thin films, thus considerably modifying the semiconducting properties of the materials. By studying the thin film properties one can get fundamental information about the bulk material which may not be accessible by any other method (Mayer, 1959).

The physical properties of the material in disordered state can be studied with great ease when the material is in the form of thin film since films can be produced in such state and they have a high specific surface area. Dislocations and other imperfections in films can be easily studied by electron microscopy. The elastic and plastic behaviour of metals can be studied easily in the form of thin films.

Thin film technique has become an important tool in the solid state research especially in the field of semiconductors, magnetics and superconductivity. Before going in detail through the physical properties of the semiconducting films, it is worthwhile to state here that a thin film, mathematically, is regarded as a plane-parallel layer, which is extended infinitely, the thickness varied from zero to a value which is comparable with the wave length of light and characterised by refractive index and absorption coefficient. In reality, films are not so simple but consist of features characteristics of the growth process.

It will be seen from the thin film work that the sensitivity of the semiconducting layers towards chemical as well as physical imperfection allows a good control of the condensed layers which was not possible to achieve with other materials. It is also to be noted that the surface properties are generally quite different from the bulk properties. Microstructure of the film is generally related to the special techniques of preparation available for thin films alone that cannot be economically applied to the preparation of the bulk materials. The properties exhibited in bulk can be changed with great ease by studying the material in the form of thin film state. Even many metals behave as semiconductors only when they are in thin film state (Mayer, 1959).

In order to understand the "physics of thin films" it is essential to know the mechanism of conduction, theory of thermoelectric power and other semiconducting parameters for bulk material and their applicability to thin film. Considerable work has been carried out on the bulk materials but very little on the thin films, especially on their electrical and thermoelectrical properties. It was thought to carry out the investigation on electrical as well as thermoelectrical properties of the materials in the form of thin films. The study has thrown some new light on the conduction mechanism, thermoelectrical and other properties in thin films.

B. Theory of conductivity

It is well known that the physical properties of the materials are structure sensitive, particularly these are more so in case of semiconductors. To understand their behaviour clearly we have to understand also the mechanism of conduction in metals in the first stage and then its application to semiconductors as well as insulators.

The simple theory of mechanism of conduction both for the electrical and thermal was postulated first by Drude (1900) and developed later by Lorentz (1904-5) is known as the free electron theory of metals. The main assumption was that electrons in case of metals are free and they can move throughout the metal lattice without much hindrance similar to the movement of gas molecules in a closed space. Metal may be considered to consist of positive ions forming the lattice and the valence electrons regarded as electron gas. These electrons do not belong to any particular metal ions and can move unimpeded in the metal ion lattice. The movement of electrons in this case is guided by the Boltzmann distribution law of the classical mechanics. The effect of mutual repulsion between electrons as well as the interaction of negatively charged electrons by potential field in metal lattice is, however, neglected in free electron theory of gas. This simple theory broadly explains the general physical behaviour of metals, but

fails in some cases, as for instant, for the specific heat of metals. With the advent of quantum mechanics, Sommerfeld (1928) first applied the quantum mechanical concepts to the motion of electrons in solids.

In his theory he assumed that the electrons were quite free and did not make frequent collisions with the atoms of the solid. They could move in a field free space, the field of force due to atomic cores and other electrons being smoothed out except at the boundary of the solid. According to quantum mechanics, though the free electrons in solid are indistinguishable, the state of each electron i.e. energy level is determined by quantum numbers such as x, y, z and also spin quantum numbers that last having two values, positive as well as negative for each state. It is well known that metal contains about 10^{23} atoms per unit volume, and in the case of monovalent metals, the number of free electrons available is 10^{23} cm^{-3} and the allowed energy levels for the valence electrons of metal lie very close together.

According to Fermi-Dirac statistics, as applied by Sommerfeld, the probability of occupation of a particular quantum state by electron is given the relation

$$P_e(E) = \frac{1}{\exp.\left[(E-E_f)/kT + 1 \right]} \qquad \ldots\ldots \quad (1)$$

where E is the energy associated. With a particular level and

E_f - so called Fermi energy. In deriving the above formula, he also took into account the Pauli's exclusion principle. It is to be noted that the above expression is valid only when each quantum state is non-degenerate. In case of the degenerate levels of degree 'g' the above expression becomes,

$$P_e(E) = g \times \exp.\left\{ (E-E_f)/kT + 1 \right\}^{-1} \qquad \ldots\ldots \quad (2)$$

or the equation (1) can be written as

$$P_e(E) = f\left\{ (E-E_f)/kT \right\}$$

where $f(x) = 1/(e^x + 1)$

where $f(x)$ is called the Fermi distribution function, and the expression (2) reduces to

$$P_e(E) = g \times f\left\{ (E-E_f)/kT \right\} \qquad \ldots\ldots \quad (3)$$

It can be seen that when x is large and positive, the value of $f(x)$ will be very small. This suggests that the probability of occupation of a level is small when $(E-E_f) \gg kT$. On the other hand if x is large and negative $f(x) \simeq 1$ which indicates that the level is almost occupied if $E-E_f \ll kT$. It can be also seen that if $x = 0$ then $f(x) = \frac{1}{2}$ in such case, the probability is reduced to $\frac{1}{2}$. From the above discussion, it can be seen that in any case all levels having energy much greater than E_f, are more likely to be empty whilst, having energy much smaller than E_f, are more likely to be occupied. The energy level corresponding to E_f is called the Fermi level.

The actual distribution of electrons among the available sites at any temperature is given by so called Fermi-Dirac distribution law.

$$n(E)dE = 2N_c(E)P_e(E)dE \qquad \ldots\ldots \quad (4)$$

where $n(E)dE$ is the number of electrons in the conduction band with energies between E and $E+dE$; and $N_c(E)dE$ is the number of allowed levels per unit volume in the conduction band in the energy interval E and $E+dE$. Here the factor 2 is taken in order to take into account of the spin degeneracy of each level. Finally the formulae obtained for conductivity and carrier concentration per unit volume are as follow :

$$\sigma = \frac{ne^2}{m\bar{v}} \cdot l \qquad \ldots\ldots \quad (5)$$

$$n = \frac{8\pi}{3} \left\{ \frac{m\bar{v}}{h} \right\}^3 \qquad \ldots\ldots \quad (6)$$

where $-e$ is the charge of the electron, m is the mass of the electron, h is the Planck's constant and v is the velocity of electron at surface of the Fermi distribution.

As a result of the Sommerfeld theory, the small contribution in specific heat from the electrons was also explained. However the ideas on conduction of electricity in metals remained the same as before. Sommerfeld theory could not, however, distinguish between metals and insulators. Later on the smoothed out potential is replaced by a periodic potential by taking into account the interaction between the electrons

and atomic cores which are situated at the lattice points of the crystal. The important feature of such an potential is that it has the same periodicity as that of lattice and the motion of electron in such a potential was discussed by Bloch (1928) by means of quantum mechanics.

The solutions of the wave function for such a periodic field are of the form,

$$\psi = U_k(\gamma) e^{ik.\gamma} \quad \ldots\ldots \quad (7)$$

where $U_k(\gamma)$ has the periodicity of the lattice. On free electron model all values of the energies were allowed but in periodic potential there are forbidden ranges of energies where solutions representing an electron moving through the lattice do not exist at all. This means that electrons can occupy only certain energy levels and other energy levels are forbidden for occupation. The another consequence of above theory known as band theory is the introduction of the concept of the effective mass of electron while moving in a periodic potential field and is given by the relation,

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \cdot \frac{\partial^2 E}{\partial K^2} \quad \ldots\ldots \quad (8)$$

where m^* is the effective mass of charge carrier, E is the kinetic energy, K is the wave vector and $\hbar$ is the $h/2\pi$. It is to be noted here that m^* - effective mass of charge carrier is a function of direction in anisotropic bodies and is then expressed

by a tensor, the acceleration and force may not even be in the same direction. One more important point to be noted in Sommerfeld theory that the allowed energy levels for the valence electrons of a crystal lie very close together and their values extend from nearly the bottom of the potential trough in which the electrons move to indefinitely high values. For other electrons the energy levels are assumed to be undisturbed and are just atomic energy levels. These energy levels form a sort of band and can be regarded as a continuum for many purposes. Taking into account the formation of different bands due to the periodic potential field, we can explain the conduction phenomena in different metals as well as insulators.

Wilson in 1931 put forward the 'zone' theory and explained the conductivity of divalent metals like Ca, which should behave as an insulator.

According to zone theory, an array of monovalent atoms should always show metallic conduction as long as there is some overlap between wave functions of the atoms, because such an array is described in terms of wave functions which fill a zone completely.

Let us consider a linear monatomic metal lattice containing 'N' atoms. If each atom has two valence electrons, there will be a '2N' electrons completely filling the 'N' energy

levels since according to Pauli's principle, each energy level can allocate two electrons having opposite spin. If there is an appreciable energy discontinuity separating bands, there will be no way for an applied electric field to accelerate the electrons as there are no vacant states of higher wave number K into which the electrons may be accelerated. It will behave as an insulator.

If there is only one valence electron per atom, the corresponding number of electrons will be 'N' and there will be 'N' quantum states. According to Pauli's exclusion principle, each state can accommodate two electrons having the opposite spin direction, out of 'N' states available, only ½N will be filled by 'N' electrons. In this case the band will be only half-filled and the specimen will be conductor. Alkali metals like Na, K etc. are good examples of this whereas alkaline metals such as Ca, Mg etc. should behave as non-conductor as envisaged in the first case. But they are not so. From the three dimensional periodic model, however, it can be shown that there will be overlap of two allowed zones and hence electrons can move from one zone to another even in case of two valence electron metals like calcium and will behave as a conductor but a poor one. It has been found that the concept of band theory is suitable not only for metallic crystals but also for semiconductors, insulators and ionic crystals.

In a crystal electrons can occupy s, p, d.....states. The inner electrons are more tightly bound to the nuclei whereas the valence electrons or the outermost electrons are so to say loosely bound to the nuclei. In fact, in metallic sodium 3s electrons do not localize to any particular atom in a crystal. The inner electrons tightly bound to the nuclei do not, however, play any important role in conduction phenomena and hence they are normally not considered. So is the case with semiconductors and insulators. In non-metals the broad bands that lie above the inner electron bands can be divided into groups namely valence bands whose available states are occupied by valence electrons and the conduction band whose available states can be occupied by electrons thus contributing the electrical conductivity. These two bands are, however, separated by a forbidden band of energies as stated before in non-metals.

At absolute zero temperature the available states in valence band are completely filled whilst those in conduction band completely empty in case of non-metals particularly. With the rise of temperature transition between state in the highest filled band and the lowest empty conduction band are possible, the band gap or forbidden band however, determine the amount of energy for transition from higher to lower state.

Semiconductors

These form a class of materials whose conductivities are in between metals and insulators. It is possible, however,

that in extreme cases the conductivity of such material can be as high as a poor metal conductor or as low as that of an insulator. Generally their conductivity lies between 10^{-2} to 10^{6} ohm^{-1} cm^{-1}. The main properties of this class of materials can be denoted as, they have negative temperature coefficient of resistance, high thermoelectric power, both positive as well as negative, rectifying effects or at least non-ohmic behaviour sensitivity to light either producing a photovoltage or change of resistance. These behaviour could be explained easily from the band theory of solids as applied to the semiconductors.

At the absolute zero temperature, the conduction band in case of a pure semiconductor is completely empty which is separated from the filled band (valence band) by the forbidden energy gap ΔE_g. As the temperature is raised slowly, the electrons are thermally excited from the valence to the conduction band provided the thermal energy is greater than the forbidden energy gap. In such case the electrons now occupying the conduction band as well as the vacant lattice sites left behind thus creating a hole in the valence band, will both contribute to the electrical conductivity of the material when an appropriate field is applied. With the rise of temperature, the number of electron-hole pairs is also increased. For such a situation the number of conduction electrons in conduction band or holes in the valence band is given by

$$n_i \simeq n \simeq p = A \cdot \exp(-\Delta E/2kT) \qquad \ldots\ldots \qquad (9)$$

where n or n is the number of electrons or holes respectively, ΔE is the width of the forbidden band, k is the Boltzmann's constant and T is the absolute temperature in ^{o}K. The factor 'A' may be regarded as constant to the first approximation. Thus we can see that the value of n or p is predominently determined by the exponential factor. The hole created in the valence band however moves in the opposite direction to that of electron in the conduction band, would move when an electric field is applied. Thus in case of ideal pure semiconductor, the electrical conduction consists of motions of electrons in conduction band and of positive holes in a valence band.

If we substitute the value of 'A' in terms of effective mass, the above equation will take the form

$$n_i = 2\left\{\frac{2\pi kT}{h^2}\right\}^{3/2} \times \left\{m_e . m_h\right\}^{3/4} \times \exp.\left\{-\Delta E/2kT\right\} \qquad \ldots\ldots \quad (10)$$

where m_e and m_h are the effective mass of electron and hole respectively. It is to be noted here that the effective mass of electron will not be identical with that of hole since they arise from different bands. If we replace $(e\lambda/m\bar{v})$ in the conductivity relation obtained by Sommerfeld, by the letter 'μ known as mobility, then the expression for conductivity will take the form, $\sigma = ne\mu$ when there is only one type of charge carriers is present. In case of both the type of carriers the

above expression will be

$$\sigma = ne\mu_e + pe\mu_h \qquad ..... \qquad (11)$$

If we assume that the variation with temperature of the mobility of electrons and holes in an electric field is small compared with the variation in the exponential factor in the equation

$$n_i = 2 \left\{ \frac{2\pi kT}{h^2} \right\}^{3/2} x \left\{ m_e \cdot m_h \right\}^{3/4} x \ \exp.\left\{ - \Delta E/2kT \right\}$$

$$..... \qquad (12)$$

Then the expression for conductivity σ becomes

$$\sigma = \sigma o \cdot \exp.(- \Delta E/2kT) \qquad ..... \qquad (13)$$

as is simply proportional to the number of carriers. The temperature range in which the carrier concentration is given by the relation

$$n_i = A \cdot \exp.(- \Delta E/2kT)$$

is termed as intrinsic. When the crystal is free from any type of defects, this range would be from absolute zero to the melting point. It is also possible to observe electrical conductivity where formation of electron-hole pair is not imperative. In an ideal crystal each atom is surrounded by other atoms in a perfect periodic lattice such the electrical neutrality is maintained everywhere. But real crystals contain many defects such as incorporation of foreign atoms, existence

of vacancies, atoms at interstitial sites etc. Because of these defects, the conducting behaviour of materials changes considerably. This fact was first recognized by Gudden (1930, 1934). Such defects known as impurity centers, may introduce new energy levels within the forbidden band and serve as the sources of electrons for the conduction band (donor levels) or holes for the valence band (acceptor levels). When the concentration is high enough, the impurity levels form a band, as the interaction between them may be sufficiently strong enough to form an energy band.

The width of impurity bands is generally narrower than the other bands due to the main crystal because the number of atoms of the host crystal is higher than the number of impurity atoms. On the other hand, when the concentration of impurities is low, the impurity levels are narrow and electrons are localized at the impurity centers. The conductivity due to impurities can be illustrated in case of 'Ge' where each atom tetrahedrally surrounded by another forming a covalent bond and if however an impurity like 'Sb' or 'As' of group V corporated which takes up the one of the site of 'Ge' atom in crystal.

The four of the five valence bound electrons can be shared with the four germanium atom leaving one extra electron which is very lightly bound to the 'Sb' atom. The binding energy is so small that at room temperature practically all antimony atoms in Ge lose the extra electron, which is available

for the conduction in the empty band. The Sb atom is then said to be ionized. However, at a very low temperatures the electron is bound to the Sb atom. In band picture, we can say that at a low temperature this new level is occupied and at normal temperatures, it is empty. Thus there will be one electron in conduction band corresponding with the each empty level. Such an impurity is called a donor impurity and this sort of conduction caused by donation of electrons from the donor impurities is called n-type conduction. On the other hand, if germanium (Ge) atom is replaced by III group element such as In, the lattice around it will have a deficiency of one valence electron. A very small amount of energy is required to take an electron from one of the Ge==Ge bonds to put into one of the In==Ge bonds. At normal temperatures the In atom will have an extra electron i.e. it will be In^- and we shall have a free positive hole. In terms of band picture, it can be stated that at very low temperatures the impurity level may be regarded as an empty electron level, just above the valence band, capable of accepting an electron. At normal temperatures the excited electrons from the valence band will occupy the above empty levels, such levels are called acceptor levels. The conductivity arising from such sort of mechanism is termed as p-type conductivity.

It is to be noted here that the donor levels lie just below the bottom of the conduction band and the acceptor just

above the top of the valence band. In such cases the carrier concentration is given by n, where

$$n = N_c \cdot \exp.(+E_f/kT) \quad \ldots\ldots \quad (14)$$

provided the electrons in the conduction band are non-degenerate, and the concentration of holes in the valence band is given by p,

$$p = N \cdot \exp\left\{-(\Delta E + E_f)/kT\right\} \quad \ldots\ldots \quad (15)$$

According to law of mass action, $n \cdot p = k(T)$ where $k(T)$ is of the form $\{F(T)\}^2 \exp\left\{-\Delta E/kT\right\}$ and $F(T)$ is a slowly varying function of T.

When the donor levels N_d is much greater than the intrinsic electrons, in such a case the number of electrons in the conduction band does not vary appreciably with temperature and the semiconductor is called an n-type extrinsic semiconductor and the position of the Fermi level is given by $E_f = kT\ \ln(N_d/N_c)$.

It is interesting to note here that the band theory is worked out for a periodic array of atoms whereas the impurity atoms in semiconductors will be arranged in a random manner. However, the effect of melting on the resistance of the metal suggests that the results obtained from any theory for the effective number of free electrons in a periodic lattice ought also to be true for a disordered lattice, the only effect of the disorder being to add a residual resistance. However, Verwey et al. (1948) have shown from their study on Nickel oxide that the Wilson classification is insufficient. In 1949 Mott

has suggested that in case of the above class of materials, the description of the electronic configuration in terms of Bloch wave functions was not correct, and reported that one has to use the London-Heitler wave functions in order to describe the electronic configuration. The zone theory. however, does not predict any discontinuous change in the number of free electrons, or any discontinuous volume change. Since most of our work is concerned with the structure and physical properties of thin films, it is pertinent to enquire whether the theory of conduction for metals and semiconductors are also applicable in thin films or not.

General conclusions about the conduction either from Lorentz theory or band theory are similar though they differ in details. The important factor controlling the conductivity in metals, is the mean free path of free electrons determined by the mean velocity and the time of relaxation given by

$$\lambda = v\tau \qquad ..... \qquad (16)$$

[In all the derivation the lattice of metal extends infinitely in three dimensions but in case of films one direction (Z) is very much restricted compared to the other directions. Fuchs (1938) gave a rigorous analysis of the mechanism of electrical conduction in thin ideal metallic films having spherical Fermi surface and suggested that the fraction 'p' of electrons incident on the boundary surface are specularly reflected. The overall

conductivity in case of thin film as treated by Sondheimer (1952) is given by relation,

$$\frac{\sigma_0}{\sigma} = \frac{\phi(K)}{K} \quad \ldots\ldots \quad (17)$$

where K is the thickness/mean free path, σ_0 is the conductivity of the bulk metal, σ is the conductivity of the film metal and

$$\frac{1}{\phi(K)} = \frac{1}{K} - \frac{3}{8K^2} + \frac{3}{2K^2} \int_1^{\infty} \left\{ \frac{1}{t^3} - \frac{1}{t^5} \right\} e^{-kT}.dt \quad \ldots\ldots \quad (18)$$

The alternative expression derived from the repeated integration is

$$\frac{1}{\phi(K)} = \frac{1}{K} - \frac{3}{4} \left\{ 1 - \frac{1}{12} K^2 \right\} E_1(-K) - \frac{3}{8K^2} (1-e^{-K}) - \left\{ \frac{5}{8K} + \frac{1}{16} - \frac{K}{16} \right\} e^{-K}$$

$$\ldots\ldots \quad (19)$$

Therefore the formula for resistivities will take the form,

$$\frac{\rho}{\rho_0} = \frac{1}{1 - \frac{3K}{4} \left\{ 1 - \frac{K^2}{12} \right\} E_1(-K) - \left\{ \frac{3}{8K} (1-e^{-K}) \right\} - \left\{ \frac{5}{8} + \frac{K}{16} - \frac{K^2}{16} \right\} e^{-K}}$$

$$\ldots\ldots \quad (20)$$

where $-E_1(u) = \int_u^{\infty} \frac{e^{-t}}{t}\, dt.$

Therefore the approximate formula for thinner films i.e. $d < \lambda$.

$$\frac{\rho}{\rho_0} = \frac{4}{3\frac{d}{\lambda}\left\{\ln\frac{1}{d} + 0.4228\right\}} \qquad \ldots\ldots \quad (21)$$

and for thicker films

$$\frac{\rho}{\rho_0} = \frac{1}{d}\left\{d + \frac{3}{8}\lambda\right\} \quad \text{when} \quad d \gg \lambda \qquad \ldots\ldots \quad (22)$$

In deriving the above formula Sondheimer assumed that the scattering at the surface was entirely diffuse. If a fraction 'p' of electrons is scattered elastically at the surface then the expression for the conductivity in thin films become,

$$\frac{\sigma_0}{\sigma} = 1 + \frac{3}{8K}(1 - p) \qquad \text{when} \quad K \gg 1 \qquad \ldots\ldots \quad (23)$$

$$\frac{\sigma_0}{\sigma} = \frac{4}{3}\left(\frac{1-p}{1+p}\right)\frac{1}{K\log(1/K)} \quad \text{when} \quad K \ll 1 \qquad \ldots\ldots \quad (24)$$

From Fuchs' calculations it can be seen that if $p = 1$ (all electrons specularly reflected) the effective conductivity was independent of thickness of the film, whilst if $p < 1$ then the conductivity fell with decreasing thickness, particularly when this was less than the electron mean free path. Ham and Mattis (1960) and Price (1960) extended the theory. Price used his vector mean free path method by considering the general ellipsoidal energy surfaces for the cases $p = 1$ and $p = 0$.

Friedman and Koening (1960) from their measurements on thin specimens of bismuth reported that the boundary scattering was indeed completely speculor. Aubrey, James and Parrott (1964) reported from their study on wedge-shaped samples of bismuth that the actual relative magnitude of the conductivity in the thin limit and in the bulk was very different from the theoretical predictions. Recently Parrott (1965) gave the theory of size effect for a conductor having ellipsoidal energy surfaces based on the method of Ham and Mattis (1960), in which he assumed that 'p' is constant but is regarded as a function of the component of electron velocity normal to the surface.

From the expression derived by Sondheimer and latter used by Mayer (1959), it is possible in the present investigation to calculate the mean free path of the hypothetical model. In the above theory, it is implicit that the film is continuous in two dimensions even when the 'z' direction was nearly zero. But in reality no films are continuous unless they are of considerable thickness.

It is well known that in the initial stage of the growth of film in vacuo, the deposited film involves the formation of discrete nuclei and later on islands which on continuous deposition with increase of thickness grow in size and finally a continuous film is formed. Neugebauer and Webb (1962) pointed out that the properties of such films would also be controlled by the size and distance between the islands. According to

Neugebauer (1962), the conduction mechanism in this discontinuous film consists of (a) thermally activated charge carrier creation process involving the removal of electron from initially neutral island leaving it positively charged, (b) the drifting of these free charge down field by electron tunneling through the gaps between the islands. It follows from the model that the log σ will be proportional to the reciprocal of absolute temperature. The smaller the size of the island, the greater will be the activation energy and larger the distance between island the lower the tunneling probability and thus lower the conductivity. This theory takes into account the size effect and the distance between the islands in determining the film properties. It is a well known experimental fact that the temperature of the substrate has a great effect on the size as well as on the gaps between the islands. Another factor to consider is the film thickness. With increase of the film thickness normally the island size increases and consequently the distance between them decreases. Other factors affecting these two parameters are the material as well as the nature of the substrate. According to Neugebauer and Webb (1962) the conductivity of the island structure film is given by

$$\sigma = \frac{A\sqrt{2m\phi}}{h^2 d} \exp.\left\{\frac{-4\pi d}{h}\sqrt{2m\phi}\right\} B \exp.\left\{\frac{-e^2/\epsilon\, r}{kT}\right\} \ldots \qquad (25)$$

where A and B are constant, ϕ is the potential barrier between islands, e is the electronic charge, m is the electronic mass,

ϵ is the dielectric constant of the substrate, h is the plank constant, d is the distance between islands, γ is the average radius of an island and k is the Boltzmann constant.

In the case of real film with which we are dealing, the film thickness varies from 1,000 to 50,000 Å. In these films even though the island theory may not truly valid but one has to consider morphological feature of the film. It is well known that in most of the films the surface topography is far from being smooth, but full of ups and downs.

C. Thermoelectric power (α)

Another important transport property is the thermoelectric power (α), namely the creation of potential difference between two points when there is a temperature gradient between them. The above effect is known as Seebeck effect (Seebeck, 1822). The reverse effect known as Peltier effect consists of absorption or evolution of heat at the junction when the current is passed through the sample. These two effects are, however, related by the equation

$$\alpha = \pi / T \qquad \ldots\ldots \qquad (26)$$

where α is the Seebeck coefficient, π is the Peltier coefficient, T is the absolute temperature in ^{o}K. The thermoelectric power can also be approximately expressed by the semi-qualitative relation

$$e = C_v / N = k \qquad \ldots\ldots \qquad (27)$$

where C_v is the specific heat of the system of charge carriers, N is the number of charge carriers taking part in conduction mechanism, e is the charge of free carriers and k is the Boltzmann constant.

$$\therefore \qquad \alpha = k/e \qquad \ldots\ldots \quad (28)$$

Thus from the above equation it can be seen that the natural unit of thermoelectric power is k/e or volts/degree centigrade, and also that it is a local transport property similar to the electrical or thermal conductivity. The process of generation of thermoelectric power (α) can be visualised in a semiconductor in the following way. Let us consider a piece of material as a long box containing electrons. Because of thermal gradient, the concentration and velocities of the electrons at the hot end will be higher than at the cold end resulting in a greater diffusion of electrons along the thermal gradient than in the reverse direction. This diffusion flux of negative charge from hot end to the cold end will set up an potential difference between the two ends. Due to this electric field further diffusion of electrons will be increasingly retarded until the reverse flux of electrons, due to the creation of potential difference equalise with the electron flux caused by the diffusion. At this dynamical electron equilibrium condition the potential difference per unit gradient of temperature namely (α) will remain constant. Thus the thermoelectric power (α) is a function of both the number of charge carriers as well as the

mobility of electrons. In case of mixed semiconductors, the simultaneous diffusion of electrons and holes from hot to cold end is caused not only bu difference in carrier velocities but also by concentration gradient. It has already been mentioned that for metals the concentration of free charge carriers (10^{23} cm^{-3}) is practically not affected by temperature. In a semiconductor, on the other hand, temperature has a pronounced effect on the concentration of charge carriers, energy of each carrier, as well as on the contact potential of the semiconductors with respect to the electrode material and hence the chemical potential. Thus taking into account the above different parameters controlling the thermoelectric power, the expression for the total thermoelectric power for a material having only one type of charge carriers, will be $\alpha = \alpha_D + \alpha_n + \alpha_\phi$ where the respective terms on the right hand side means the contributions due to the variation of diffusion coefficient, concentration gradient and contact potential respectively with temperature. The total thermoelectric power (α) in case of mixed non-degenerate semiconductor is given by the expression,

$$\alpha_{n,p} = -k/e \left\{ \frac{n\mu_e\left[(5/2 - s) + n(N_c/n)\right] - p\mu_h\left[(5/2 - s') + n(N_v/p)\right]}{n\mu_e \quad p\mu_h} \right\} \quad \text{------ (29)}$$

and for mixed type of complete degenerate semiconductor

$$\alpha'_{n,p} = -\pi^2 k/e \left\{ \frac{n\mu_e\left\{\frac{1}{2} - \frac{1}{3}s\right\}(kT/E_f) - p\mu_h\left\{\frac{1}{2} - \frac{1}{3}s'\right\}(kT/E'_f)}{n\mu_e + p\mu_h} \right\} \quad \text{----- (30)}$$

where the symbols have their usual meaning.

In deriving the above expression it is assumed that the effective masses m_e and m_h are scaler quantities and the time of relaxation is a function of energy i.e. $\tau_e = aE^{-s}$ for electrons and for holes $\tau_h = a'E^{-s'}$ where the value of s and s' greatly depends upon the scattering mechanism. It is to be noted here that the relation $\tau_e = aE^{-s}$ or $\tau_h = a'E^{-s'}$ will not hold good when both ionized impurity or lattice scattering are present. In such case the time of relaxation can be expressed in the form $\tau_e = aE^{-\frac{1}{2}} \cdot \{1 + CE^{-2}\}$ where 'a' and 'C' are constants and the formula for thermoelectric power will be modified accordingly for a mixed type of complete degenerate and non-degenerate semiconductor. Ioffe (1957) has given the values of the term, $A = (5/2 - s)$ for the different type of scattering centers.

For atomic lattices. $l \propto E^0$; $\mu \propto 1/T^{3/2}$; $A = 2.0$

For ionic lattices at $kT \ll h\nu_0$; $A = 2.5$

For ionic lattices at $kT \gg h\nu_0$; $A = 3.0$

For scattering by vibrations of constant frequency

$l \propto E^{-1}$; $\mu \propto 1/T^{5/2}$; $A = 1.0$

or $l \propto E^{-3/2}$; $\mu \propto 1/T^3$ $A = 0.5$

For scattering on impurity ions,

$l \propto E^2$; $\mu \propto T^{3/2}$ $A = 4.0$

Thus it can be seen that the value of the term (5/2 - s) depends on the electron scattering mechanism and in particular on the value of $\frac{1}{l} \cdot \frac{dl}{dE}$. It is to be noted here that the above foregoing formulae are based on the assumption that in the presence of temperature gradient each small portion of the material was in equilibrium state. He discussed theoretically

Gurevich (1946) showed that this is not true. He discussed theoretically the effect on thermomagnetic effects in metals of a departure of the phonon distribution from its equilibrium state. It is well known that in quantum physics the thermal vibrations of the lattice are described by many of quasi-particles known as phonons, moving with the velocity of sound. However, phonons which have no charge and which contribute to the thermal conduction but not to the electrical conduction, may contribute to the thermoelectric power because of the phonon-electron interaction whereby electrons may drag phonons with them and vice versa. The greater is the phonon drag the stronger the interaction between phonons and carriers and the longer the relaxation time required for motion of long wave length phonons to become random again. Phonon drag effect as far as the thermoelectric power is concerned is important at the low temperatures for most of the materials.

Finally, it is to be noted that in case of non-homogeneous materials the thermoelectric power in general is given by the expression,

$$= \frac{\Delta E}{\Delta T} = \sum_{i} \left\{ \frac{\Delta E}{\Delta T} \right\}_{i} \cdot \left\{ \frac{\Delta T_{i}}{\Delta T} \right\} \quad \ldots\ldots \quad (31)$$

where ΔE is the observed thermal e.m.f. due to the temperature difference ΔT, and the summation is taken over the 'i' parts in which the material is divided.

Another important parameter in connection with the thermoelectric power is the figure of merit 'Z' which determines the efficiency of the thermoelement used in the thermoelectric generators. This parameter (Z) is given by relation,

$$Z = \alpha^2 \sigma / K \qquad ..... \qquad (32)$$

where α is the thermoelectric power of the material, σ is the conductivity of the material and K is the thermal conductivity of the material.

D. Hall coefficient

In determining the transport phenomena in semiconductors, the parameter viz. Hall coefficient from which the mobility and carrier concentration can be found out, has to be studied.

It is well known that when an electric field is applied along the length of the sample and the magnetic field perpendicular to it, then the potential is developed along the direction which is perpendicular both to the magnetic and electric field. This transverse electric field is given by the relation,

$$V_z = \frac{R_H \cdot I_x \cdot H_y}{d} \times 10^{-8} \qquad ..... \qquad (33)$$

where V_z is the transverse electric field developed, I_x is the current passed through the sample in Amps., H_y is the magnetic field in Oersted, d is the thickness of the sample in cms. and R_H is the Hall coefficient. The Hall coefficient R_H is defined

as the magnitude of this transverse electric field per unit current density, per unit magnetic field. The Hall coefficient for one type of carriers is given by the relation,

$$R_H = \pm \gamma/ne \quad \ldots\ldots \quad (34)$$

where the minus and plus signs indicate the conduction by electrons and holes respectively, and the value of 'γ' lies between one and two, depending upon the degeneracy of the material. The practical units for R_H are cm^3/Coulomb. When both types of charge carriers viz. electrons and holes are present, the Hall coefficient is given by

$$R_H = -\gamma/e \cdot \{ nb^2 - p \} / \{ nb + p \}^2 \quad \ldots\ldots \quad (35)$$

where $b = \frac{\mu_e}{\mu_h}$, the ratio of the electron mobility to the hole mobility. In the intrinsic region, where $n = p = n_i$ equation (35) becomes

$$R_H = -\frac{\gamma}{n_i e} \times (b-1)/(b+1) \quad \ldots\ldots \quad (36)$$

This equation indicates that R_{H_i} will be negative or positive according to whether the electron mobility is greater or less than the hole mobility. Knowing the conductivity and R_H, the Hall mobility (μ_H) can be calculated from the relation $\mu_H = R_H \sigma_i$ where μ_H is Hall mobility, R_H is Hall coefficient and σ_i is conductivity.

For semiconductors, there are other parameters viz. carrier concentration, mobility, mean free path, figure of merit etc., which are also of great importance to evaluate the usefulness of semiconductors at the same time to throw some light on the electron-transport process in solid state. It is of interest to point out that thin films of semiconducting materials may have different structures than those of the bulk and it is likely that they may as well considerably modify the electrical, optical and other properties also. The theories for conductivity, thermoelectric power etc., established for bulk material may be considerably changed due to the two dimensional nature of thin films.

Reviews on the researches on the physical, optical, electrical, mechanical and other properties of thin metallic films and their applications in different branches of physics, have already been made by many authors viz. Holland (1958), Neugebauer, Newkirk and Vermilyea (1959), George, Bancroft (1962), George Hass and Rudolf E. Thun (1964), George Hass (1963), Bennett (1964), and Newman (1963).

From the above literature survey it will be seen that not much work has been carried out on the resistivity, activation energy, thermoelectric power, Hall coefficient etc. of semiconducting films of lead and bismuth chalcogenides obtained by vacuum evaporation technique. With the above idea, in view, k has been carried out on the electrical properties of nducting films of selenides and tellurides of lead and

CHAPTER - II

EXPERIMENTAL TECHNIQUES

A. A device for the measurements

A new device as developed by Goswami and Jog (1964) was also used in the present study for measurement of the different semiconducting parameters. The experimental set-up (fig. 1) consisted of two brass blocks with slots of desired sizes, two microheaters attached to each block, two glass plates over one of which the deposits were formed, two flexible platinum foils (thickness = 0.02 mm.), three thermocouples, two springs and two silver wires as leads for measuring the electrical conductivity, thermoelectric power etc. At the two ends of the films over a glass substrate (4 x 0.5 cm), platinum foils were put and over them a glass plate of the same size as that of the substrate (glass) was kept. The foils were then folded round below with a 'U' turn. The two ends of the film were inserted inside the slots of two brass blocks. The film was then tightened by means of screws. In order to measure the thermoelectric power, the current was passed through the microheaters and the temperature gradient was created. With the help of chromel-alumel thermocouples, the temperature of both the ends was recorded. A third thermocouple was also attached at the center of the film. The whole set-up was put in a pyrex boat and put inside a vacuum chamber before measuring the parameters.

Experimental set-up for measuring the semiconducting properties of thin films:

1, glass substrate with deposits; 2 and 2', platinum foils; 3, glass cover; 4 and 4', brass blocks; 5 and 5', electrode leads; 6, 6' and 6", thermocouples; 7 and 7', springs; and 8 and 8' microheater leads.

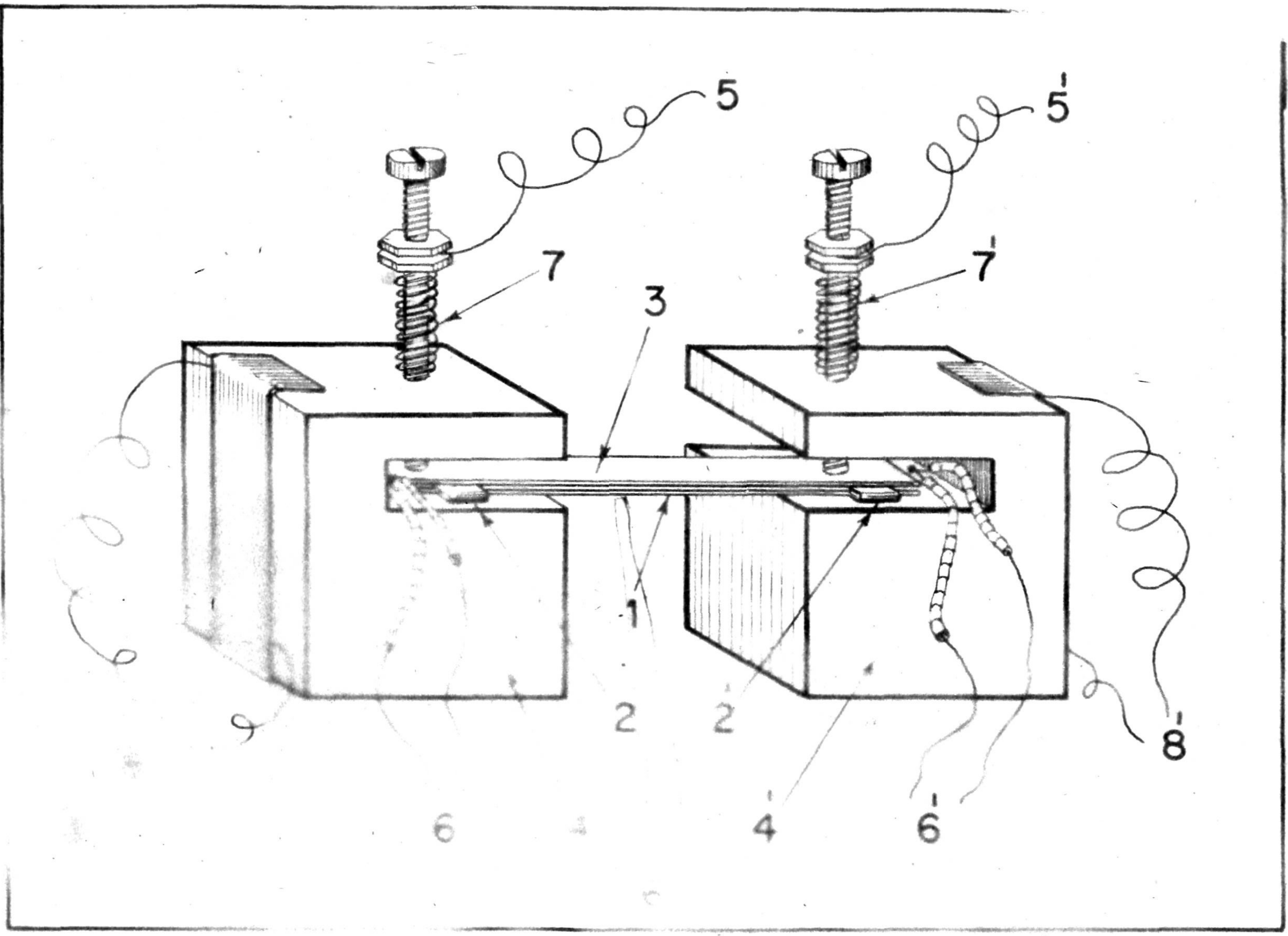


FIG-1

B. Measurement of resistivity and activation energy

Resistivity or conductivity is an important property of a semiconductor. This was measured both by A.C. and D.C. methods. For A.C. measurements especially for high resistance i.e. of the order of 50 Meg. ohm. "Universal AVO" bridge operating on 50 c/sec. For D.C. measurements "Tesla RLC" bridge was also used.

Description of the bridge

The universal AVO bridge, consisting of a bridge network is fed from a screened winding of low distributed capacity on the main transformer and it consists of an amplifier valve voltmeter having variable sensitivity. This amplifier valve voltmeter acts as a balance indicator. The bridge has standard arms of resistance for resistance measurements. We can also measure capacitance and inductance.

The Tesla Universal bridge consists of four main components. (i) the bridge proper, (ii) amplifier, (iii) A.F. oscillator, and (iv) power pack. The bridge itself consists of a series of standard resistances of two capacitance standards and of two potentiometers for loss factor compensations. A switch is provided for placing the resistors, capacitance standards and compensating potentiometers in the appropriate arms of the bridge as required for the particular measurement intended. Bridge can work at a frequency of

400 c/sec. or a D.C. voltage. For D.C. measurements, galvanometer is connected to the bridge. For A.C. measurements, a two-stage A.F. amplifier is interposed between bridge and galvanometer. This instrument provides a wide range of A.C. and D.C. measurements with loss factor compensation.

The experimental set-up as described before (A) was put in a tubular chamber provided with an external furnace heated electrically, the chamber being continuously evacuated throughout the measurements. Twelve terminals were taken out from the evacuated chamber, two for measuring the resistance across the specimen, six for thermocouples (two near the two ends of the film and the third at the middle), and four terminals (two on each side) for two microheaters to heat the specimen inside the chamber. Temperatures at the three points were measured by a Vernier potentiometer, and the resistance across the terminals by A.C. or D.C. bridge as described before. Generally temperature of the film was raised by slow heating of the external heater controlled by a variac in vacuo.

In order to have sufficient readings, the temperature was measured during the process of heating and cooling just before and after the measurement of resistance. This measurement was carried out at an interval of 2° to 5°C rise or fall of temperature. Since the specimens were in vacuo the heating was more or less uniform. This procedure took about three to four hours to complete heating and cooling cycle between room temperature and 200°C. This continuous (dynamic) method took about three to four hours to complete one cycle of heating or cooling.

We also tried to attain equilibrium temperature at each points and the resistance was measured. It was found that it would be impossible to complete the measurement of one sample even in two or three days and as there was no special advantage unless absolute values of resistance was needed this method was discontinued. The resistance of each specimen was measured for several heating and cooling cycles before taking the mean value. The resistance measurements were repeatable even after eight or ten cycles, provided maximum temperature was not beyond the temperature of the discontinuity (T_d) to be described latter on. Resistivity (ρ) was deduced from the relation,

$$R = \rho \frac{l}{b \times d} \qquad \ldots\ldots \qquad (37)$$

where R is the actual resistance measured, ρ is the resistivity, l is the length of the film used, d is the thickness of the film and b is the breadth of the film. Activation energy was calculated from the slope of the curve log R _vs_ 1/T by using the relation,

$$\Delta E = 2k \frac{\ln R_{T_2} - \ln R_{T_1}}{1/T_2 - 1/T_1} \qquad \ldots\ldots \qquad (38)$$

Thus it can be seen that instead of using resistivity or conductivity, it is possible to measure the activation energy from resistances as described in chapter No.3.

C. Measurement of thermoelectric power

The thermoelectric power given by the formula

$$\alpha = \frac{\text{P.D. between two ends}}{\text{Temperature difference between two ends}}$$ was measured

both by the integral method and differential methods. In the integral method, the temperature at the one end of the film was kept constant and that of the other end was continuously raised and the potential developed between two ends measured potentiometrically. The thermoelectric power was then calculated by the above formula. In the differential method, the temperatures of the both ends were increased by the same amount at each stage, however a definite temperature gradient between them. This was accomplished by two microheaters attached at two ends of the films with a constant temperature gradient (fig. 1). The increase in the temperature of the surrounding was carried out by the external heater. All the measurements were carried out in vacuo both during heating and cooling cycles and repeated for several times for the same sample to obtain reproducible results. Same measurements were repeated by keeping the sample in vacuo for few days or exposing it to atmosphere without changing any contact and reevacuating it.

D. Measurement of Hall coefficient, mobility and carrier concentration

The apparatus and method for the measurement of Hall effect, Hall mobility and carrier concentration are the same as used by Deokar and Goswami (1965).

The arrangement consists of electromagnets to which direct current (1-10 Amps) was fed from a stabilised power supply unit, sample holder having four pressure contacts, vernier potentiometer, sensitive galvanometer, lamp and scale arrangement, ammeter etc. The magnetic field obtained could be varied from 2,000 to 7,000 gausses with a gap between two pole pieces of 4 cms. The D.C. passed through the sample was varied from 0.1 to 5 ma. Hall probes were adjusted in such a way that the minimum voltage drop (IR) was observed. In order to avoid voltage drop (IR), Nerst effect etc., the readings for Hall voltage were taken by changing the direction of either electric or magnetic field or both together. The average reading was taken for calculating Hall coefficient. In order to avoid the Ettingshausten effect an instantaneous and small current was passed deliberately.

The Hall coefficient, Hall mobility and carrier concentration were calculated as described in chapter No.1.

E. <u>Thermoelectric test set</u>

In order to know the type of the bulk materials used in the present investigation, the thermoelectric test set which is described below was used.

The bulk material to be examined was placed on a lead plate which was connected to the one end of the microammeter and the other end of the microammeter to the platinum wire

which was attached to the warm tip of a small iron-rod. The circuit was completed by touching the warm tip of the iron-rod to the other face of the material when the material became warm in the vicinity of the point contact, due to the temperature gradient, a thermoelectric voltage developed and the current resulting from this voltage was also noticed on the microammeter. Depending upon the sign of potential at the hot or cold end the type of the material was decided. When the hot junction was positive, the conduction must predominently be due to electrons and the type of the material was 'n' type, whilst the hot junction having negative indicated the 'p' type.

F. Electron diffraction

In order to know the nature of the surface layer every sample was subjected to electron diffraction examination, both before and after the measurements to note the change of surface, if any. This was carried out by Finch type electron diffraction camera fabricated in this laboratory. It was, however, observed that in almost all cases the surface layers were either poly-crystalline or developed one degree orientation, depending upon the thickness of the films. Higher thicknesses favoured the development of one degree orientation. It was observed that due to assymetrical disposition of the source with respect to the substrates and consequent change of angle of incidence of vapour stream on the substrates often 'tilted' orientation were observed. The detailed interpretation of this type of orientation has already been given by Evans and Wilman (1952).

G. Preparation of substrates and films

In the present investigation, the films were prepared by vacuum evaporation technique. The Metrovac coating unit was used for the preparation of films. The ultimate vacuum obtained with this unit was $\simeq 10^{-4}$ mm. Hg. In order to avoid the formation of the new compounds due to the reaction of the filament material and the compound under investigation, the semiconducting material was heated indirectly by keeping it in a microconical silica basket surrounded by a helical coil of tungsten. The above filament, in the form of helical coil was heated with high current supplied from a low voltage transformer (30 volts, 60 Amps.) and the current was controlled by means of variac. Before putting the sample in the silica basket, the coil was flushed several times to remove the surface impurities. The micro silica basket, with the material under investigation, was then inserted into the helical coil. In order to avoid the surface impurities arising from the material itself, the first evaporation was made for few minutes under vacuum, without putting any substrates. Then the deposition was made on cleaned glass substrates put with the faces downward towards the source. The distance of the source from the substrates was 8 to 10 cms. depending upon the experiments. The source geometry was such that either the substrates were symmetrically disposed at equal distances or that these were at varying distances from source. In the former case,

the source was kept at position centrally below substrates and in the latter case the source was kept below but shifted to one side. In each set of evaporation 10-15 specimens were made of different thicknesses under the same conditions of evaporation. The temperature of the substrates at the time of deposition was recorded with the help of the thermocouple attached to the substrates. In order to have the deposition at higher temperature arrangement for heating the substrate in situ was also made.

The substrates used in the present investigation were generally glass plates. The glass substrates were obtained by cutting microscope slides to 0.5 x 4 cm size. They were cleaned with a mixture of chromic acid and sulphuric acid, then washed in distilled water. The plates were dried with filter papers and finally with degreased tissue papers. The substrates were always handled by tweezers to avoid grease contamination. Before weighing, the glass plates were heated in an oven at $\sim$ 85°C, for two hours, then were cooled to room temperature and weighed and these were then placed in position for deposition.

Thickness of the deposits was measured from the difference in weight before and after deposition and also from the knowledge of surface area covered and the density of the materials assuming however that the film density was the same as the bulk density.

CHAPTER - III

STUDIES ON LEAD SULPHIDE, LEAD SELENIDE AND LEAD TELLURIDE FILMS

A. Introduction

The early work on these materials particularly on PbS, which occurs in natural form as galena has been carried on for a very long time. In fact PbS is one of the first materials to be recognised as a semiconductor. Braun (1874) detected the rectifying action in lead sulphide. Its electrical properties were established by Eisenmann (1940) and Hintenberger (1942). They showed that these materials could exist either n-type or p-type and could be changed from one type to the another by suitable treatment. An excellent review on semiconductors has been given by Lark-Horowitz (1954). Smith (1951, 1953, 1955), Moss (1955) and Scanlon (1956) published review articles on lead chalcogenides. They discussed the chemical, physical, electrical as well as photo-electrical properties in detail. It is well known that in case of these compounds, the two types of forces are present i.e. electrostatic forces between charges illustrated by the polar bond in ionic crystals and other covalent bond and the type of the crystal is generally determined from the dominant force. Pauling (1945) reported that the dipole moments of the free molecules can be calculated from the electronegativity of the ions. The calculation based on the above basis Scanlon (1955) found that PbS, PbSe and PbTe

molecules were about 20%, 18% and 12% ionic respectively. He also noted on the same basis that the NaCl molecule was 50% ionic. But from X-ray study, NaCl crystals are considered to be 100% ionic. We may conclude that PbS, PbSe and PbTe crystals are more ionic than in their individual molecules but not as ionic as NaCl crystal.

The experimental values obtained for densities of PbS, PbSe and PbTe are 7.5, 8.10 and 8.16 gms/cm^3 respectively (Handbook of Chemistry and Physics - 1955, 1956). However, Brebrick (1956) found 7.597, 8.25 and 8.273 gms/cm^3 for PbS, PbSe and PbTe respectively from his X-ray study, and the direct measured values are 7.59 0.01 (PbS), 8.23 0.04 (PbSe) and 8.21 gms/cm^3 (PbTe). Parkinson and Quarrington (1954) found Debye temperature for PbS, PbSe and PbTe as lying in the ranges 149°- 230°K, 137°-168°K and 117°-139°K respectively. In 1927, Mellor, reported that these compounds are generally present as minerals galena (PbS), Clausthalite (PbSe) and allatite (PbTe). Many workers have studied crystals of galena. Lawson (1951-1952) applied the Bridgman-Stockbarger technique for growing the single crystals of PbS, PbSe and PbTe. In 1954, Pizzarello also grown the crystals by sublimation from the vapour phase. Particularly the lead sulphide, lead selenide and lead telluride films used in infra-red detectors are generally obtained by chemical deposition, vacuum evaporation and anodic sputtering techniques.

It can be concluded from thermoelectric power measurements that PbS, PbSe and PbTe can be either n-type or p-type.

Stefan (1865) was the first to report that PbS can be either n-type or p-type. It is well known that the carriers in both elemental and polar crystals in the impurity temperature range may be due to the presence of foreign impurities of a different valence but in case of lead chalcogenides the n-type or p-type region can also occur due to the presence of stoichiometric deviation. Bauer (1940) showed that heating PbSe crystals under steady pressure of Se changed n-type crystals to p-type and back to n-type when heated in vacuo. Many investigators have studied the thermoelectric power of PbS, PbSe and PbTe. Putley (1954), at room temperature, reported $\alpha = 445\ \mu V/^{\circ}C$ for $S_{32}B$ lead telluride sample and PbSe, $S_{12}A$ and S_{1213}. He noticed the maximum values for α in the above two samples of PbSe to be 360 and 330 $\mu V/^{\circ}C$ at $650^{\circ}K$ and $475^{\circ}K$ respectively and these samples showed inversion at 825° and $800^{\circ}K$. Ioffe (1957) found that α varied from 50 to 250 $\mu V/^{\circ}C$ (PbTe) over the temperature range 100°-$300^{\circ}K$. Avafa et al. (1956) reported very high values of α for PbS crystals. Finlayson and Greig (1959) also observed a very high value of α (600-700 $\mu V/^{\circ}C$) in PbS. Smirnov et al. (1961) reported $\alpha = 420\ \mu V/^{\circ}C$ at about $400^{\circ}K$ for PbSe. Berlaga et al. (1963) measured $= 112\ \mu V/^{\circ}C$ for p-type polycrystalline layers. Johnson (1964) observed the $\alpha = 445\ \mu V/^{\circ}C$ for PbTe single crystals.

Moss (1947), Moss and Chasmer (1948), from their photoconductivity measurements determined the optical energy gap

varying from 0.25 to 0.4 eV for PbS and PbSe. Gibson (1950) reported the values to be 1.4, 1.05 and 0.9 eV respectively for PbS, PbSe and PbTe from the absorption measurements on thin films and for thin single crystals 0.42, 0.26 and 0.31 eV which according to him corresponded to the photoconductive limits and this was also supported by the work of Clark and Cashman (1952) on the transmission measurements on PbS, PbSe and PbTe. By using reflection technique Avery (1951, 1953) made measurements of the absorption coefficient and optical dielectric constant. In 1954, he showed that the forbidden energy gap would be 0.42, 0.25 and 0.31 eV for PbS, PbSe and PbTe respectively and further showed the constant absorption followed by further large increase at energies above about 1.0, 0.8 and 0.6 eV for PbS, PbSe and PbTe accordingly. Moss (1955) on the other hand gave the evidence that the values for photoconductive limits were 0.40 (PbS), 0.25 (PbSe) and 0.31 eV (PbTe). Chasmer and Putley (1951) from their Hall coefficient measurements on polycrystalline samples of PbTe reported ΔE_g = 0.62 eV. Putley and Arthur (1951) reported from their measurements on natural galena that for PbS, ΔE_g = 1.17 eV. Putley (1952) from his Hall coefficient study on synthetic crystals of PbS and PbTe reported ΔE_g = 1.17 and 0.62 eV respectively and from resistivity measurements, ΔE_g = 1.05, 0.46 and 0.64 eV for PbS, PbSe and PbTe respectively. Scanlon (1953) from his Hall coefficient study on galena up to the temperature not exceeding 600°K concluded ΔE_g = 0.37 eV. However Scanlon (1958) from

the absorption study on very thin crystals determined the optical energy gap = 0.41 eV and thermal energy gap = 0.37 eV for PbS. In case of PbSe and PbTe. ΔE_{g_o} = 0.29 eV, $\Delta E_{g_{The.}}$ = 0.26 eV and ΔE_{g_o} = 0.32 eV and $\Delta E_{g_{Th}}$ = 0.29 eV respectively. Uptill now only two papers have been published on the investigation on the band structure of lead salts. Bell et al. (1953), by using cellular method determined that in the 110 direction in k-space, the minimum separations between the valence and conduction bands were 1.3 (vertical) and 0.3 eV (non-vertical); Dimmock and Wright (1964) determined the band structure of PbS, PbSe and PbTe. They considered all the six bands and the form of the disposition relations; E(K) determined by using their symmetry and $\underline{k} \cdot \underline{P}$ perturbation theory. Gibson (1952) determined the rate of change for forbidden energy gap with temperature 4 x 10^{-4} eV/°K whereas Semenov and Shileika (1964) determined the temperature coefficient of ΔE_g due to the effect of thermal expansion from the pressure coefficient of ΔE_g (-9.6 0.9) x 10^6 eV cm^2/Kg equal to 3.7 x 10^{-4} eV/°K.

In determining the effective masses, the cyclotron resonance measurement is the most powerful method. But no measurements have been successful on the lead salts. Putley (1955) determined the effective masses of holes and electrons from his thermoelectric power measurements. According to him in case of PbSe, $m_e^* = m_e/m_o$ and $m_h^* = m_h/m$ were in the range 0.25 - 0.36 at room temperature and in view of Bloem et al.(1955)

in case of PbS, m_e^* and $m_h^* = 0.25$. Whereas Petritz and Scanlon (1955) estimated from mobility data that m_e^* and $m_h^* \simeq 0.33$ when they have considered only polar scattering. By taking into account both polar as well as acoustical scattering they found $m_e^* = 0.22$ and $m_h^* = 0.1$. In (1954) Smith has determined the value of $\sqrt{m_e^* . m_h^*}$ in the ranges 0.13 - 0.21, 0.19 - 0.31 and 0.16 - 0.27 for PbS, PbSe and PbTe respectively. Moss (1955) quoted from Marfarlane's and Pincherle's data the values for $\sqrt{m_e^* . m_h^*}$ of 0.34, 0.31 and 0.20 - 0.25 in case of PbS, PbSe and PbTe compounds respectively. Smirnov et al. (1961) and Johnson (1964) have shown that the effective mass of lead family compounds varies as T^a where 'a' varies from 0.4 and 0.6-0.7 respectively. Bauer (1940) from his Hall coefficient study on PbSe polycrystalline samples deduced the values for carrier concentration of $2 \times 10^{17} - 10^{19}$ cm^{-3}. Eisenmann (1940) reported that the carrier concentrations were generally greater than 10^{17} cm^{-3} and mobility in natural crystals varied from 13 to 300 cm^2/volt-sec. (p-type) and 30 to 400 cm^2/volt-sec. (n-type) though for few samples, it was 700 cm^2/volt-sec. Chasmer and Putley (1951) have measured the mobility at temperature 77.4^o and 290°K on PbTe and reported very high values of mobilities. On a similar line, many workers have estimated the values of mobility, carrier concentration and variation of mobility with temperature. Putley (1952), Petritz and Scanlon (1955) and Smith (1954) have reported from Hall coefficient study that mobility in lead chalcogenides found to vary as $T^{-5/2}$ whereas

Silverman and Levinstein (1954) estimated that mobility should vary as T^{-2} to T^{-3}. In 1957 Shogenji and Uchiyama from their Hall effect and resistivity study on p-type PbTe in the temperature range liquid air to 450°K deduced that mobility varied as $T^{-5/2}$. Recently Krishnamurthy and Sinha (1964) have theoretically deduced the mobility law $\mu \propto T^{-5/2}$ in case of lead sulphide group of semiconductors.

As a result of the discovery of the photoconductive properties of these materials in the period of 1940 to 1950 a large amount of work was carried out on these materials in the form of evaporated thin films which could be changed from n-type to p-type and vice versa by heat treatment in various atmospheres. Chasmer (1948) and Kolomiets (1948) showed independently that these layers were polycrystalline and their properties depended on the surface properties of the individual grains and also on the form of the contact between them. Many authors have discussed the properties of evaporated thin films. Particularly, photoconducting properties of PbSe films have been studied by Humphrey and Petritz (1957), Humphrey and Scanlon (1957) and Wood (1956), and lead sulphide films by Lummis and Petritz (1957) and Mahlman (1956). Lead telluride films have been studied by Silverman and Levinstein (1954) and by Levinstein (1956). The effect of oxygen on PbS films have been examined by Harada and Minden (1956) and on PbSe films by Jones (1957). They have shown that oxygen may be diffused into the material and extracted by heating in vacuo. The effect

of O_2 is to turn the n-type material to p-type. Broudy and Levenstein (1964) have discussed the high frequency behaviour of the PbTe films very low mobilities in case of thin films of PbS, PbSe and PbTe has been reported by Lavy (1953), Halvorsen (1950). Recently Schoolar and Zemel (1964) reported the mobility values for epitaxial single crystal films of PbS, which corresponded to that of bulk. Yoshimi Makino (1964) also determined that mobilities for PbTe films deposited on mica were the same as that of bulk.

The above brief review showed that even though considerable work has been carried out on the semiconducting properties of chalcogenides of lead, very little investigation has been carried out on the thin films, especially measurements on the semiconducting parameters. Since in many applications thin films of these chalcogenide are used, it was thought worthwhile to make studies on thin films. In the following a detailed study has been made on the measurements of the semiconducting parameters of thin films.

B. Experimental

Preparation of compounds

(a) Lead sulphide :- Lead nitrate was dissolved in the distilled water and then warmed. Hydrogen sulphide gas was passed through the solution continuously for about two hours, till the reaction was complete. Lead sulphide precipitate was filtered, washed first with H_2S water for several times and then

with little warm distilled water till it was free from H_2S and finally with a little alcohol. The precipitation thus obtained was dried in a vacuum desaicator and used for evaporation.

(b) Lead selenide :- Lead selenide was prepared by melting the two elements in atomic proportion (1:1) in a suitable silica tube. The lead used (Johnson Matthey and Co.) was of purity 99.99% . The selenium powder (BDH) was of purity 99%. This mixture was then melted in a silica tube, first cleaned with boiling nitric acid and then with distilled water and finally with distilled alcohol and dried. Before melting the tube closed at one end was evacuated till the vacuum was of the order of 10^{-5} mm of Hg. and then sealed. It was then heated to about 300°C in an electric furnace for two hours then the temperature was raised to 600°C and kept at this temperature for one and half hour. Finally the temperature was raised to 1000°C and heated at this temperature for six hours. After the completion of reaction of lead and selenium the temperature of the furnace was lowered to 700°C then silica tube was removed from the furnace and cooled suddenly by inserting in cold water. Lead selenide was removed from the silica tube and used for the experimental purpose, taking precaution that the outer surface was scrapped at first to minimise the adherent impurities.

(c) Preparation of lead telluride :- Lead telluride was prepared by melting the lead and tellurium in atomic proportion (1:1) in a similar way as that of lead selenide. The maximum temperature in this case was $\simeq$ 1000°C.

C. Results

Before measuring the semiconducting parameters of the films namely the resistivity (ρ), thermoelectric power (α), Hall coefficient (R_H), carrier concentration (n), mobility (μ_H), the mean free path of charge carriers (ℓ_0), temperature coefficient of resistance (TCR) etc. for different samples, a few preliminary experiments were made to see the effects of some of the variables with evaporation conditions, such as, the rate of deposition, film thickness, the stress of films as deposited on the glass substrates etc. on the resistance of the film. Since the measurements of the different parameters have to be repeatable and there should be consistancy of the results, the effects of the evaporating conditions on the film properties were minimised by appropriate methods. It is of interest to mention here that the resistance dropped asymptodically with thickness, ultimately becoming nearly constant, the limit of which depends upon the evaporation conditions as well as on the materials. For very low thicknesses the resistances of the films were enormously high, falling steeply with slight increase of thickness. This characteristic of the resistance was, however, present in almost all the cases. Even though they did not lie exactly on the same curve.

It has also been found that with the change of rate of evaporation the slope of the curve for the variation of resistance with the reciprocal of the thickness, changed considerably.

In figure 2, the graphs 1 and 2 are respectively for low and high rate of evaporation of PbTe. The change of slope is seen quite clearly in the two curves. It is well known that a thin film has a tendency to evaporate at much low temperature than that for bulk. In order to see the effect of temperature on the evaporation of the film (material), initially resistance measurements were carried out with increase of temperature in vacuo in all cases. The figure 3a shows the change of log R with T for PbTe film. It is seen that the resistance decreased continuously with the increase of temperature. The temperature region in which the resistance became minimum and on further increase of temperature the resistance instead of falling, increased suddenly and became infinite. This temperature region has already been termed as the temperature of discontinuity (T_d) by Goswami and Jog (1964). This effect is no doubt due to the breakdown of the film between the two electrodes. If, however, the film was heated to maximum temperature below this temperature of discontinuity, the resistance measurements were repeatable as seen from the fig. 3b, even when repeated for five or six times. A little hysteresis type of loop was observed between the heating and cooling cycles which could be avoided by better control of temperature during the measurements.

In order to remove the stress often noticed in the deposited films, the specimens were annealed at suitable temperatures well below the T_d temperature in vacuo as was found out

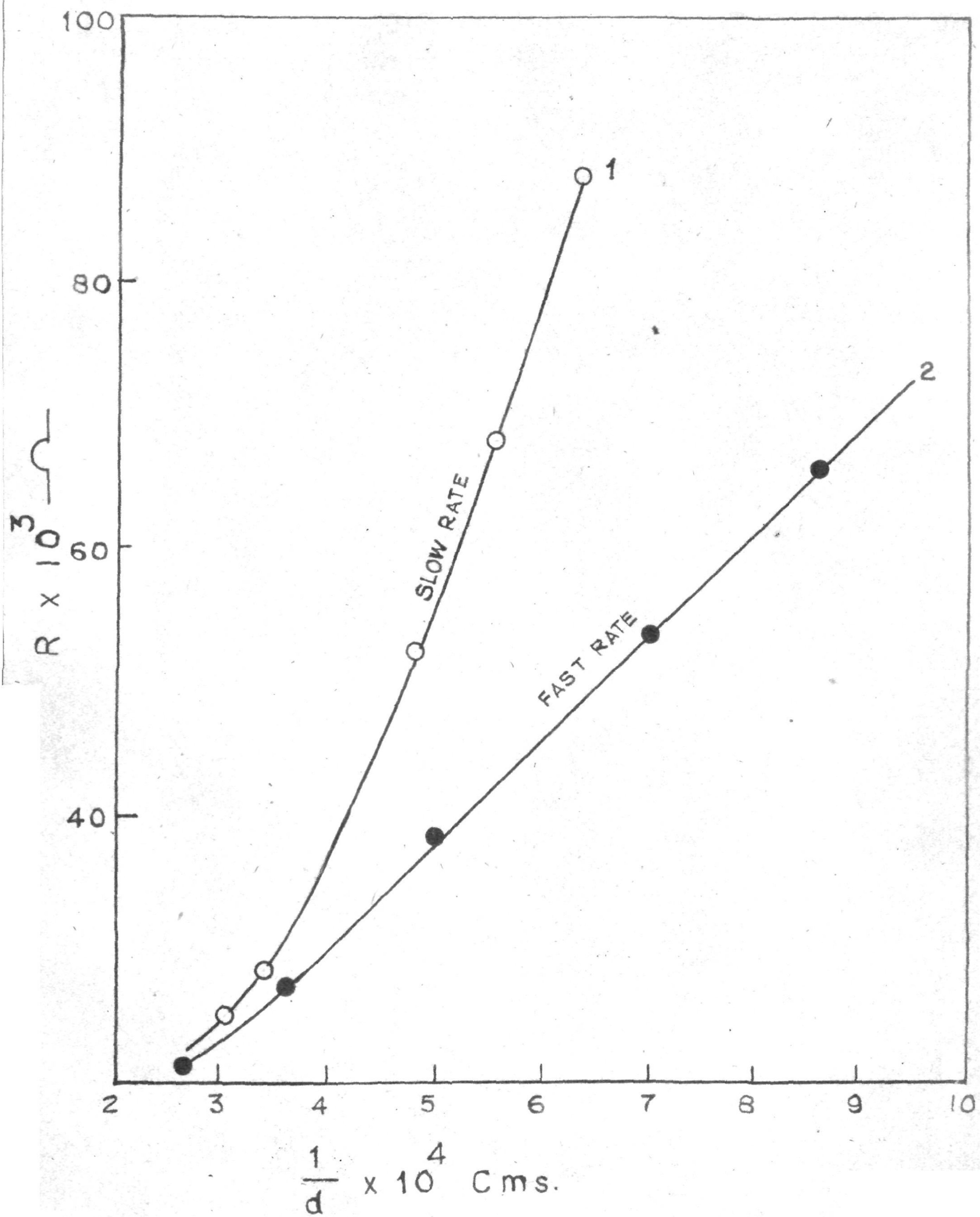


FIG-2

R in Ω

Td

Temp in °c

FIG-3a

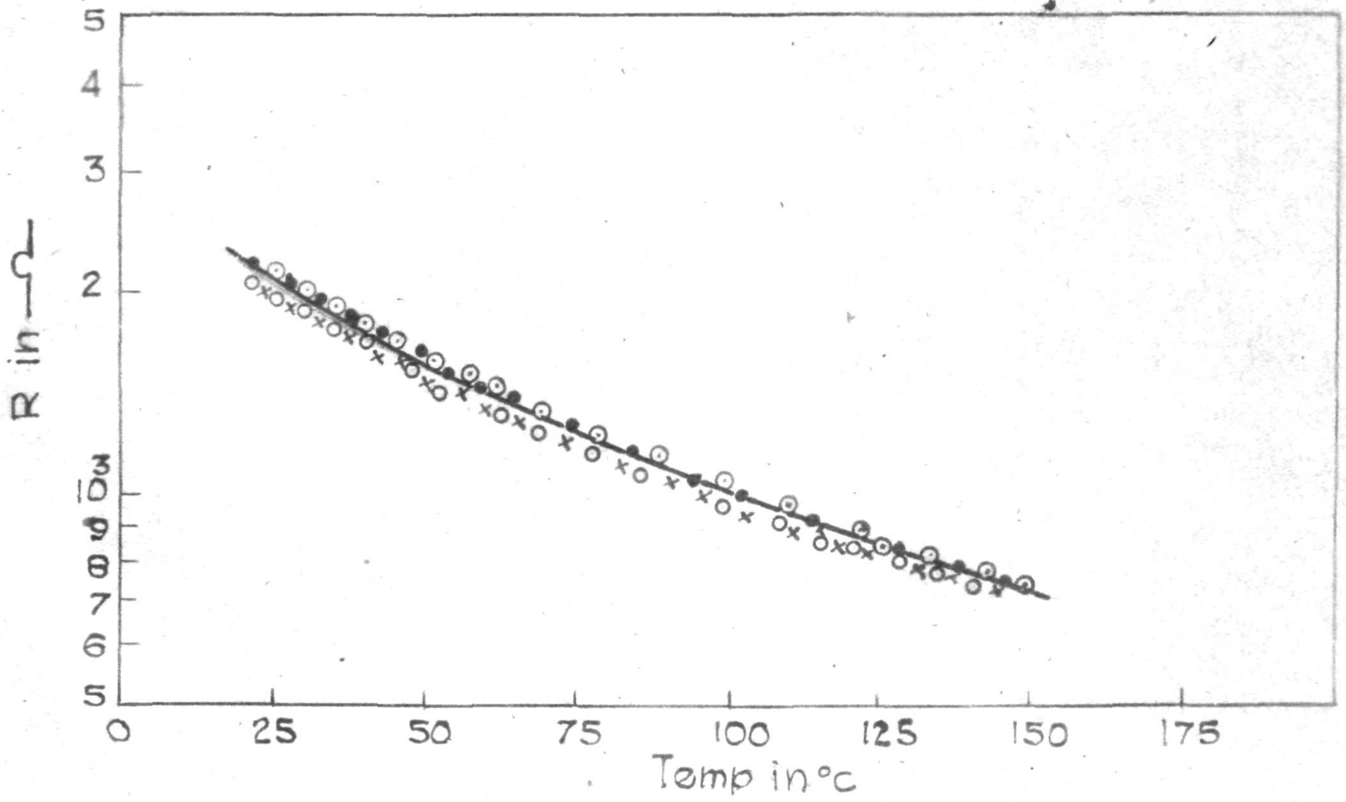


FIG-3b

before, sometimes samples became annealed simply by slowly raising the temperature and later on cooling it to room temperature also in vacuo.

(i) Resistivity and activation energy

Lead sulphide films :- The resistance for the different samples was measured with increase of temperature in vacuo and log R *vs* 1/T curves were plotted for different heating and cooling cycles. The nature of the curve for log R *vs* 1/T is shown in fig.4 for a typical film of thickness 25,000 Å. It is seen that log R at first increased with increase of temperature up to 135°C, then decreased continuously with further rise of temperature. It indicates that the conductivity was increased with the rise of temperature. On cooling resistance continued to increase closely following the heating curve up to about 135°C and continued again to rise but with a different slope with the falling of temperature, unlike the initial portion of the heating curve (A). If resistance measurements were again continued for heating followed by cooling cycles, these curves followed mostly the same path. Often the hysteresis type of loop was observed between heating and cooling curves and this could be minimised by a better control of the temperature.

It can be seen that the curve had two different slopes at two different regions viz. B and C. The region A corresponding to the temperature range 30 - 130°C in the first stage of heating; B, 135 - 300°C; and C, 30 - 135°C for subsequent heating

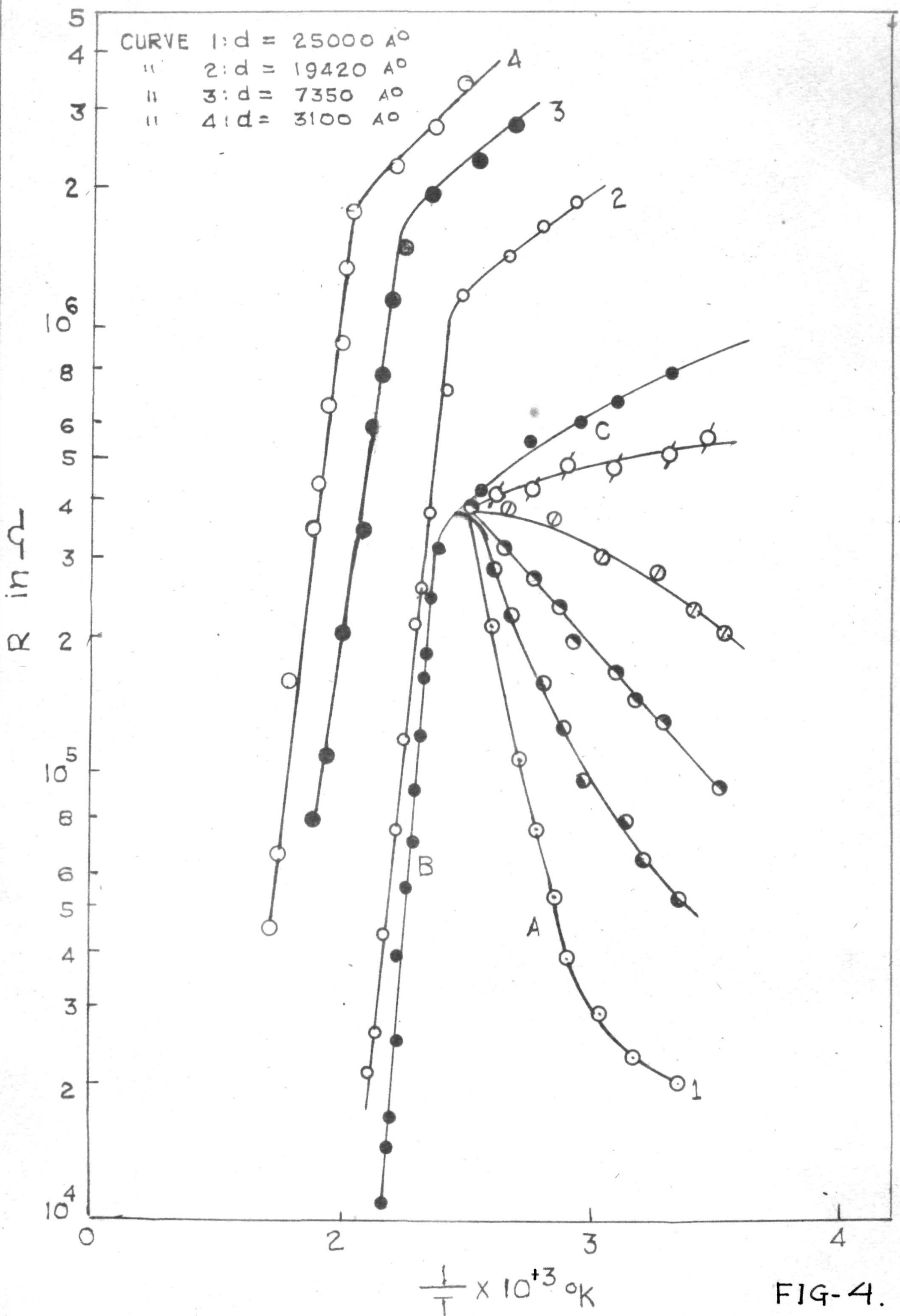


FIG-4.

and cooling cycles. It is possible to measure the activation energy (ΔE) from the linear portions of the curve, either from resistivity (ρ) or resistance (R) i.e.

$$\rho = \rho_o \exp.(\Delta E/2kT) \qquad \ldots\ldots \qquad (39)$$

$$R \cdot \frac{b \times d}{\ell} = \rho_o \exp.(\Delta E/2kT)$$

$$R = R_o \exp.(\Delta E/2kT)$$

where $R_o = \rho_o \times \frac{\ell}{b \times d}$ $\quad \therefore \quad \ln R = \ln R_o \quad E/2kT$

$$\text{Therefore} \qquad \Delta E = \frac{\ln R - \ln R_o}{1/T} \cdot 2k \qquad \ldots\ldots \qquad (40)$$

The value of (ΔE) in the region B and C are nearly about 1.45 and 0.6 eV respectively for a film of thickness 25,000 Å. The fig.4 also shows the different log R vs 1/T curves for different film thicknesses and the table No.1 shows corresponding activation energy (ΔE) values in B and C regions. It is interesting to note that curve has two distant slopes at B and C regions. The slope at lower temperature region seems to be associated with the impurities effects caused by defects or faults in the structure, whereas the higher value at B higher temperature region, no doubt, energy band gap associated with increase of electron-hole pairs for intrinsic region. Another important feature of the activation energy value is that though the thicker films had more or less same ΔE and it slowly increased by decrease of film thickness.

TABLE - 1

LEAD SULPHIDE

Film No.	Thickness Å	(ΔE) eV in B region	(ΔE) eV in C region
1.	3,100	1.684	0.650
2.	7,350	1.593	0.592
3.	19,420	1.550	0.550
4.	25,000	1.478	0.535

TABLE - 2

LEAD TELLURIDE

Film No.	Film thickness Å	Activation energy (ΔE) eV
A (slow rate of evapora--tion)	1,578	0.440
	2,085	0.435
	2,920	0.420
	3,760	0.411
	8,300	0.380
	12,000	0.370
B (high rate of evapora--tion)	8,450	0.332
	10,250	0.323
	15,700	0.225

FIG.-7.

The nature of the curve at (A) is peculiar since resistance increased with temperature instead of being lower. This did not conform with the semiconducting behaviour of the PbS films. It was found that this peculiar effect was due to the superimposition of other effects on the semiconducting layers. This was borne out by the following experiments. Heating of the films in vacuo or keeping the film under dynamical vacuum for some time, however, modified the nature of the curve as shown for the film of thickness 25,000 A° (fig.4) tending to BC portion. If, however, the films were allowed to come in contact with air for some time after cooling in vacuo, the curve again tend to follow the path A. The starting position might be anywhere between A and C depending upon the time of exposure to air. These experiments clearly indicated that adsorption of air by the films caused this so called increase in resistance with temperature.

<u>Lead selenide films</u> :- Lead selenide films were annealed at about 325°C in vacuo below the T_d temperature (350°C) determined in usual way as described before. The resistance measurements were made between the temperature range -15° to 300°C. A typical graph 5, shows the variation of log R with the reciprocal of the absolute temperature. The resistance was often found to increase continuously with the rise of temperature, from room temperature to 125°- 200°C, depending upon the thickness of the film; as was observed in case of lead sulphide films during the initial heating period. With further rise of temperature, however,

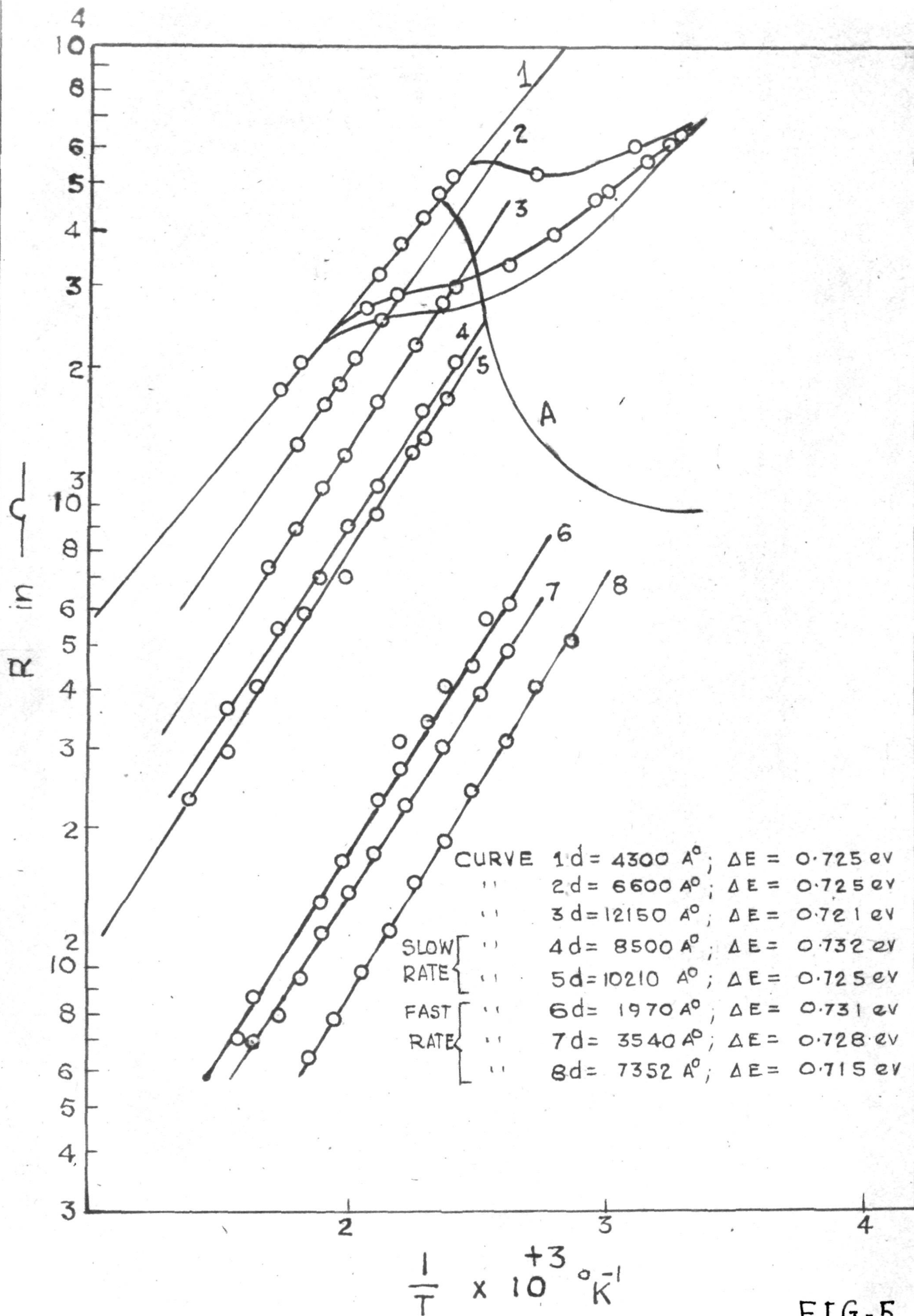


FIG-5.

the usual curves for semiconducting material lowering of resistance with increase of temperature were again observed. The cooling curve (log R <u>vs</u> 1/T), however, did not follow the previous (heating) path throughout the temperature range. A large hysteresis type loop was observed between heating and cooling cycles even when the temperature was controlled, in a temperature range 30-225°C, though at higher temperatures (≫ 250) hysteresis type loop was not appreciable. During the cooling process, the resistance was found to increase throughout the temperature range studied i.e. 325°- 30°C. On second heating without exposing the film to the atmosphere, the resistance decreased and rose a little and again decreased with further rise of temperature. Above 135°- 200°C, the curve followed the previous heating path and cooling curve followed its original path. However, it was again confirmed as in the case of PbS films that the initial portion (A) of the curve did not represent the characteristics and behaviour of the material but to some adsorption effects, namely, physical and chemical of the PbSe films and hence could be removed by heating in vacuum or keeping the films under vacuo for a longer period. The curves (log R <u>vs</u> 1/T) in the low temperature region were not exactly linear and hence the activation energy varied continuously. The fig.6 shows the variation of log R <u>vs</u> T, when the measurements were carried out after an interval of 24 hours.

The activation energies for different film thicknesses were calculated from the slope of the curves (log R <u>vs</u> 1/T) in

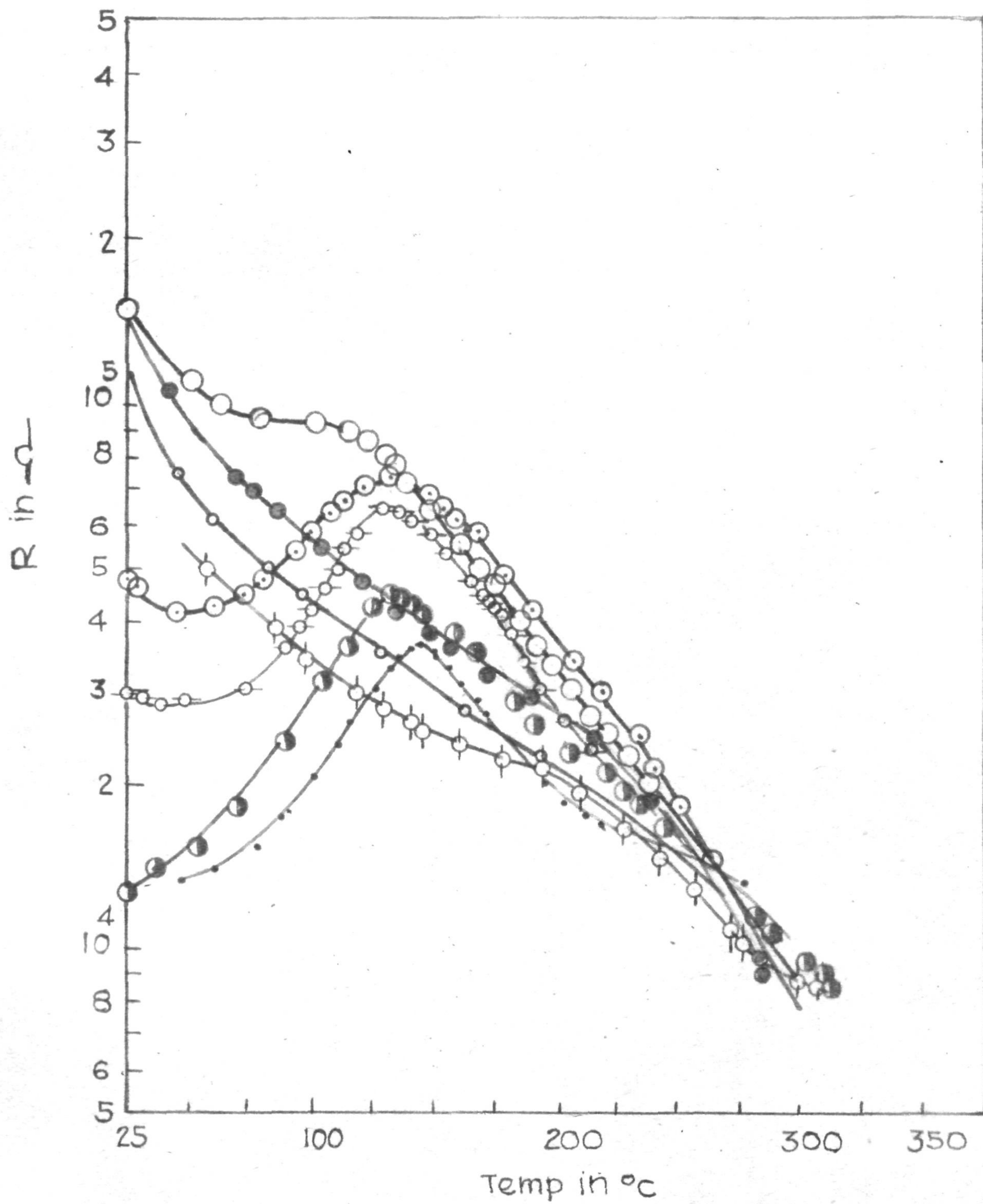


FIG-6

the fig.5, at high temperature range, where the curves were nearly linear. It was found to vary from 0.7 to 0.9 eV for the films of different thicknesses varying from 50,000 Å to 1,000 Å. It was also noticed that the activation energy increased with the decrease of the film thickness, as was observed in case of lead sulphide films.

Lead telluride films :- The temperature of discontinuity for PbTe films was found out to be about (200°C) and the annealing was carried out at temperature $\simeq$ 175°C. The resistance measurements were made from -12° to 150°C in the usual way. Typical curves (fig.7) show the variation of log R *vs* 1/T for different film thicknesses. It is of interest to see that unlike the cases for PbS and PbSe, there was no adsorption effect as could be seen from the continuous decrease of resistance with the rise of temperature throughout the temperature range studied. The activation energy calculated from the slope of these curves for different films was found to vary from 0.2 to 0.44 eV depending upon the thickness of the film as seen from the table No.2. In this case also the activation energy was found to be a little higher for lower film thicknesses.

(ii) Thermoelectric power

Lead sulphide films :- Films prepared, annealed etc. as before were subjected for the thermoelectric power measurements. This was done by creating a continuous and uniform temperature gradient along the length of the specimens with the help of the

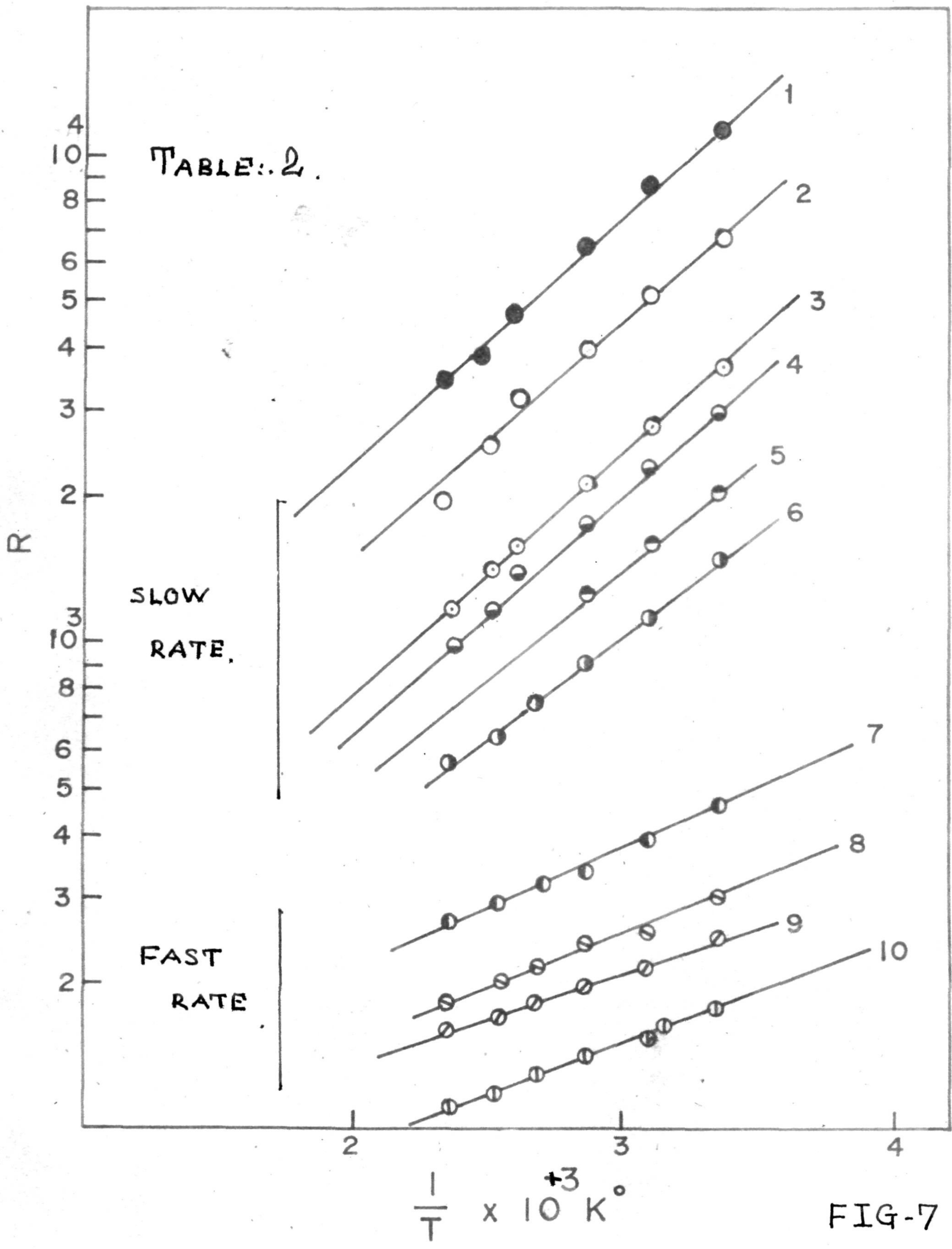


FIG-7

microheater attached to the one end of the sample holder. The temperature was noted at three points viz. at two ends as well as at the middle of the film, with the help of the chromel-alumel thermocouple to see the uniformity of the temperature gradient. The thermal e.m.f. thus created was measured potentiometrically.

Using the sign conventions as described in the previous chapter for the type of the conductivity, most of the lead sulphide films were found to be 'p' type, i.e. the conduction is mainly due to the free holes. Typical curves for thermal e.m.f. vs temperature difference between ends are shown in fig.8, which indicate that the thermal e.m.f. increased continuously with the rise of temperature difference between the two ends up to 130°- 175°C depending upon the thickness of the film. Above this temperature the thermal e.m.f. for PbS suddenly decreased and at about 130°- 200°C became zero; finally at still higher temperature thermal e.m.f. changed its sign as the terminals were interchanged. With further increase of temperature up to the maximum temperature of our experiment, the thermal e.m.f. continued with its new sign. During the cooling process the curve 1' followed a slightly different path, though similar in nature to that of the heating cycle. It is of interest to state here that the corresponding values of the thermal e.mf on the cooling curve were slightly smaller than those obtained during the heating cycle. However the samples were heated below the temperature corresponding to the maximum thermal e.m.f. the heating and cooling curves followed the same path, ~~though~~

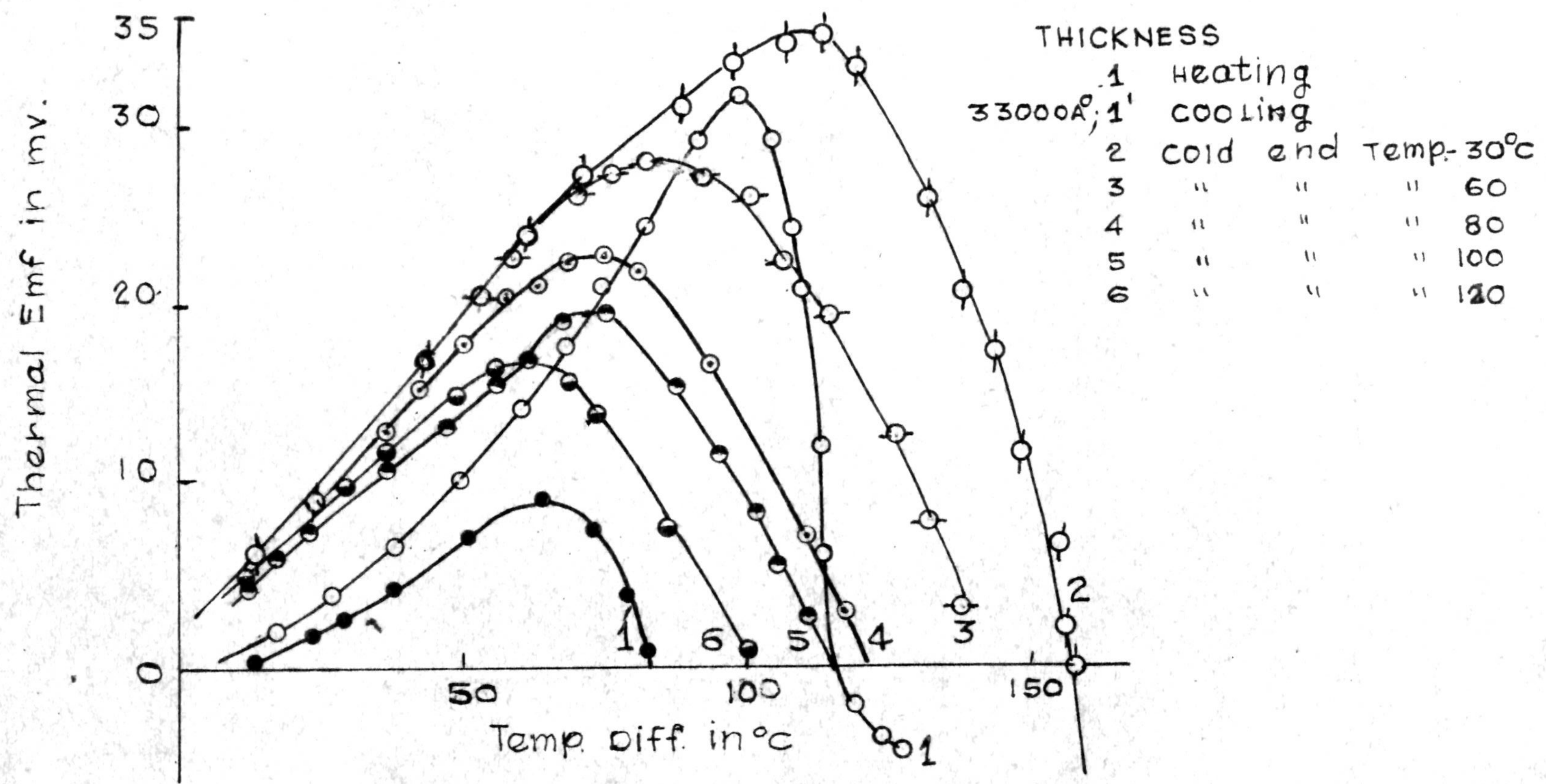


FIG-8.

though a little hysteresis type loop was observed which can be minimised by a better control of the temperature. If, however, maximum temperature of the hot end was raised to the inversion temperature, the thermal e.m.fs. measured during cooling had much smaller values as plotted in fig.8. It is seen here that the cooling curve followed a different path but similar to that of heating curve as mentioned before. The hot end of the sample had to be cooled to a low temperature before any other information could be obtained. It is interesting to mention that the temperature corresponding to the maximum thermal e.m.f. shifted to the high temperature side as the thickness of the film decreased. The fig.9 shows the corresponding thermoelectric power in different temperature regions. From the above figure it can be seen that the thermoelectric power increased slowly with temperature and decreased to zero and finally became negative at higher temperatures. The change of $+\alpha$ to $-\alpha$ was often restored back after cooling the sample. The feature of change of positive thermoelectric power to negative with the rise of temperature is a peculiar one, similar to that of change of sign of α, with the change of sign of charge carriers, as reported by many workers in case of other semiconductors. Since in the present case no intentional impurities were introduced into the sample, change of sign of α was, no doubt, due to the temperature effect. Since carrier concentration is a characteristic of sample it appears that the change of sign is linked with the mobility of the carriers which is generally

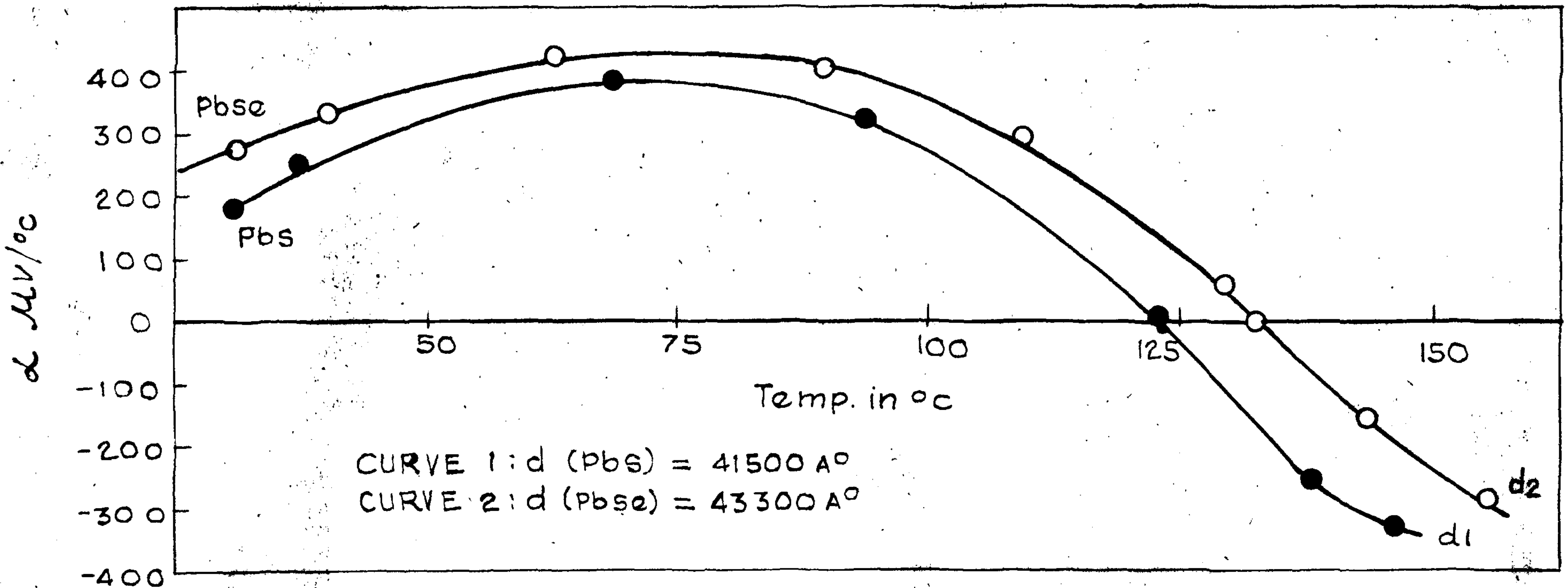


FIG-9.

affected by the temperature. The thermoelectric power became maximum at about 135°- 200°C depending upon the thickness of the film. It is interesting to mention here that the maximum value of thermoelectric power corresponded with the maximum value of the resistance as found in the initial heating process during the resistance measurements. In the present investigation, it was noticed that with the decrease of the film thickness, the maximum value of the thermoelectric power occurred at higher temperature and also the point of inversion shifted to higher temperature side.

It is also noteworthy to state here that after the inversion point, the thermoelectric power showed n-type behaviour. One important feature about the cold junction temperature was that the maximum value of the thermal e.m.f. dropped down as the cold end temperature was increased and the point of inversion shifted slightly to the lower temperature side as shown in fig.8. This observation suggested that when the difference of temperature between two ends was high, the carrier concentration gradient may occur and thereby the values of the thermal e.m.f. and the point of inversion were affected. The change of thermoelectric power with temperature in the range 30°- 150°C in which practically no hysteresis type of loop was observed between heating and cooling cycles for different film thicknesses is shown in fig.9a.

Thermoelectric power was also studied by using the differential method, in which a small constant temperature

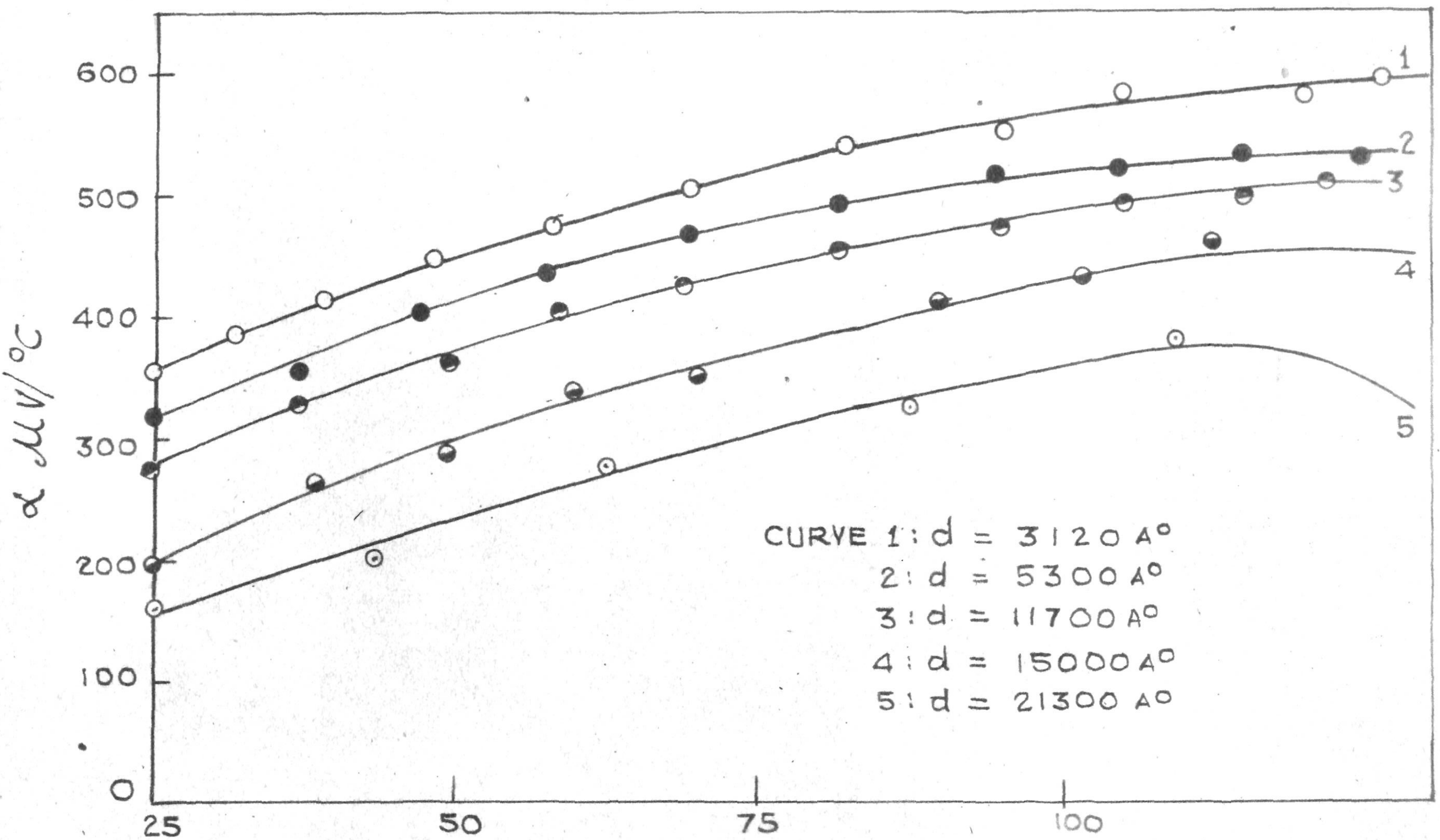


FIG-9 a.

gradient along the sample was created with the help of an outside furnace and also by using the microheaters whatever the case might be. From the typical curves for thermoelectric power with the mean temperature, it could be seen that the curves were of similar nature as discussed previously, however, the point of maximum thermoelectric power and the point of inversion were slightly shifted to low temperature side, for the same thickness of the film.

Lead selenide films :- Thermoelectric power (α) in this case is measured by both the methods namely 'Integral' and 'Differential' as discussed in case of lead sulphide films.

The measurements of thermal e.m.f. with the temperature showed that the thermal e.m.f. increased with the rise of temperature difference between the two ends, up to 135°- 175°C depending upon the thickness of the film. Above this temperature it was slowly decreasing and reached to zero value and finally on further rise of temperature, the thermal e.m.f. became negative. At a still higher temperature, thermal e.m.f. further increased with its new sign. Though the curve followed a different path on cooling the sample, the nature of it was similar to that of the heating curve. The fig.9 also shows the variation of thermoelectric power with temperature. The general behaviour of the thermoelectric power with temperature was similar to that of p-type PbS films. The fig.10 shows the measurement of thermoelectric power for films of varying thickness carried out below the temperature corresponding to the maximum

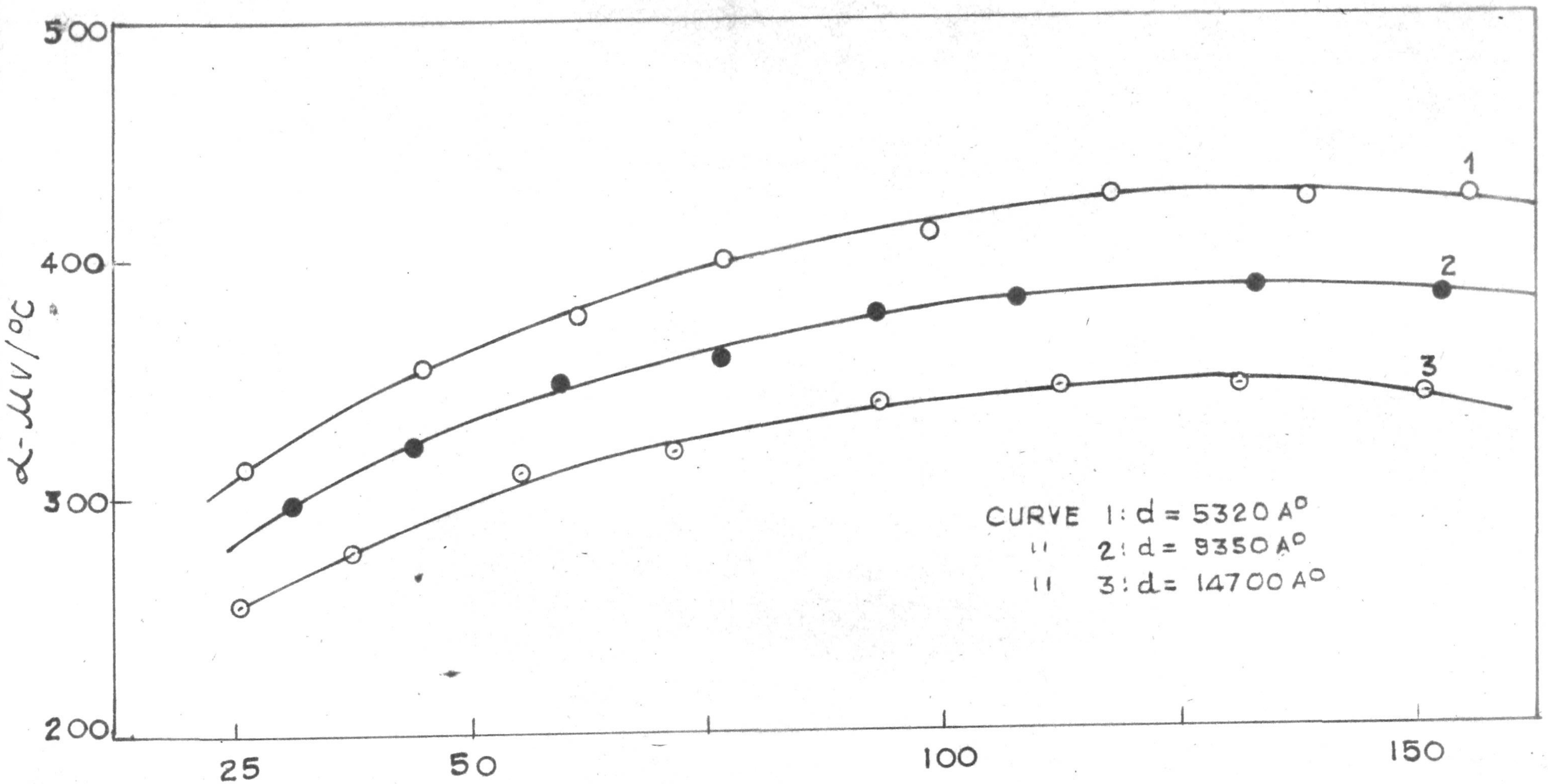


FIG-10.

thermoelectric power observed, the heating and cooling curves followed more or less the same path, though a little hysteresis type of loop was observed. This could be removed by a better control of the temperature. It can again be seen that the values of thermoelectric power were higher for the lower film thickness at the corresponding temperatures and also the point of inversion had higher values. By studying the same films by differential method, it was observed that the general behaviour of thermoelectric power with temperature was similar as discussed in the previous chapter except that the corresponding values of thermoelectric power were slightly smaller than those observed by integral method. This difference suggests that the carrier concentration gradient had a considerable effect on the thermoelectric power as due to the high temperature difference between the two ends, there might be non-equilibrium distribution of charge carriers. From simultaneous measurement of resistance and thermoelectric power it was found that the maximum value of thermoelectric power corresponded the maximum value of the resistance. It may be pointed out here that all the PbSe films were found to be of p-type only.

Lead telluride films :- Lead telluride films prepared, annealed etc. were subjected to the thermoelectric power measurements, both by differential and integral methods. From the variation of thermal e.m.f. with the temperature of the hot end, it can be seen that thermal e.m.f. increased continuously with

the rise of temperature. Unlike lead sulphide and lead selenide the thermal e.m.f. did not decrease over the temperature range -15° to $150^{\circ}C$ even for thicker films. The figure 11 shows the variation of thermoelectric power (α) with temperature for different lead telluride films. It can be seen from the above results that α initially increased slowly and then had a tendency to be practically constant and at a still higher range of temperature it had a little decreasing tendency. It is interesting to note here that like resistivity, α had higher values for thinner films compared to that for thicker films and vice versa. It may be pointed out here that measurements of α by integral method yielded values a little higher than by the differential method. All the samples were found to be 'p' type.

(iii) Temperature coefficient of resistance (TCR)

Lead sulphide, lead selenide and lead telluride films :-
In the previous section the results on the measurements of resistivity, activation energy and thermoelectric power were shown. Another parameter of equal interest is the temperature coefficient of resistance (TCR) which is defined as the change in resistance per unit resistance per degree change in temperature i.e. $TCR = \frac{1}{R} \cdot \frac{dR}{dT}$, where R is the mean resistance at temperature $\frac{T_1 + T_2}{2}$ where $dT = T_2 - T_1$ and $dR = R_2 - R_1$ and $R = \frac{R_2 + R_1}{2}$. The resistance measurements at different temperatures for PbS, PbSe and PbTe were made in the usual way. Using the previous relation, the values of TCR at different temperatures

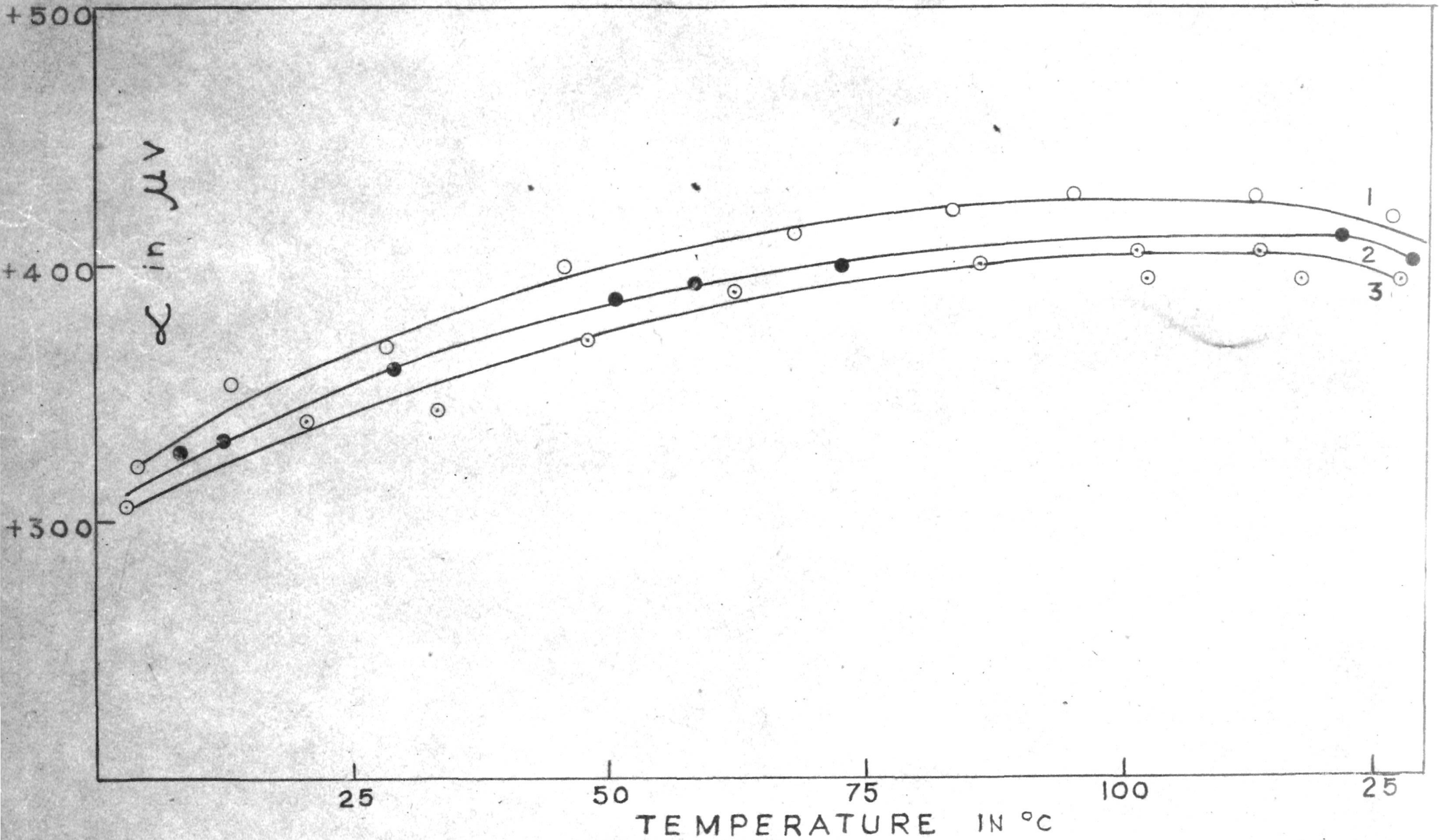


FIG-11.

were then calculated. The results are tabulated in a table No.4. The figure 12 shows the variation of TCR with temperature for PbS, PbSe and PbTe compounds plotted on a linear scale. It is interesting to note here that all the samples had a negative temperature coefficient over the temperature range studied, particularly for PbTe and PbS. In case of PbSe a positive temperature coefficient of resistance was observed below 135°-200°C depending upon the thickness of the film. It has already been pointed out in the previous section that the adsorption effects were present in thin films of PbS and PbSe and more predominent in the latter. The TCR of PbS and PbSe was measured only at high temperature region. The fig.12 shows that the negative TCR for PbS, PbSe and PbTe reaching a maximum value with the rise of temperature. With a further increase in temperature TCR attained its maximum negative value for each film and then increased slowly with rise of temperature and finally became nearly constant. The maximum and minimum values of TCR in the curves TCR vs temperature appeared to be dependent upon the rate of deposition, morphology of the deposit and conditions of deposition.

(iv) Mean free path

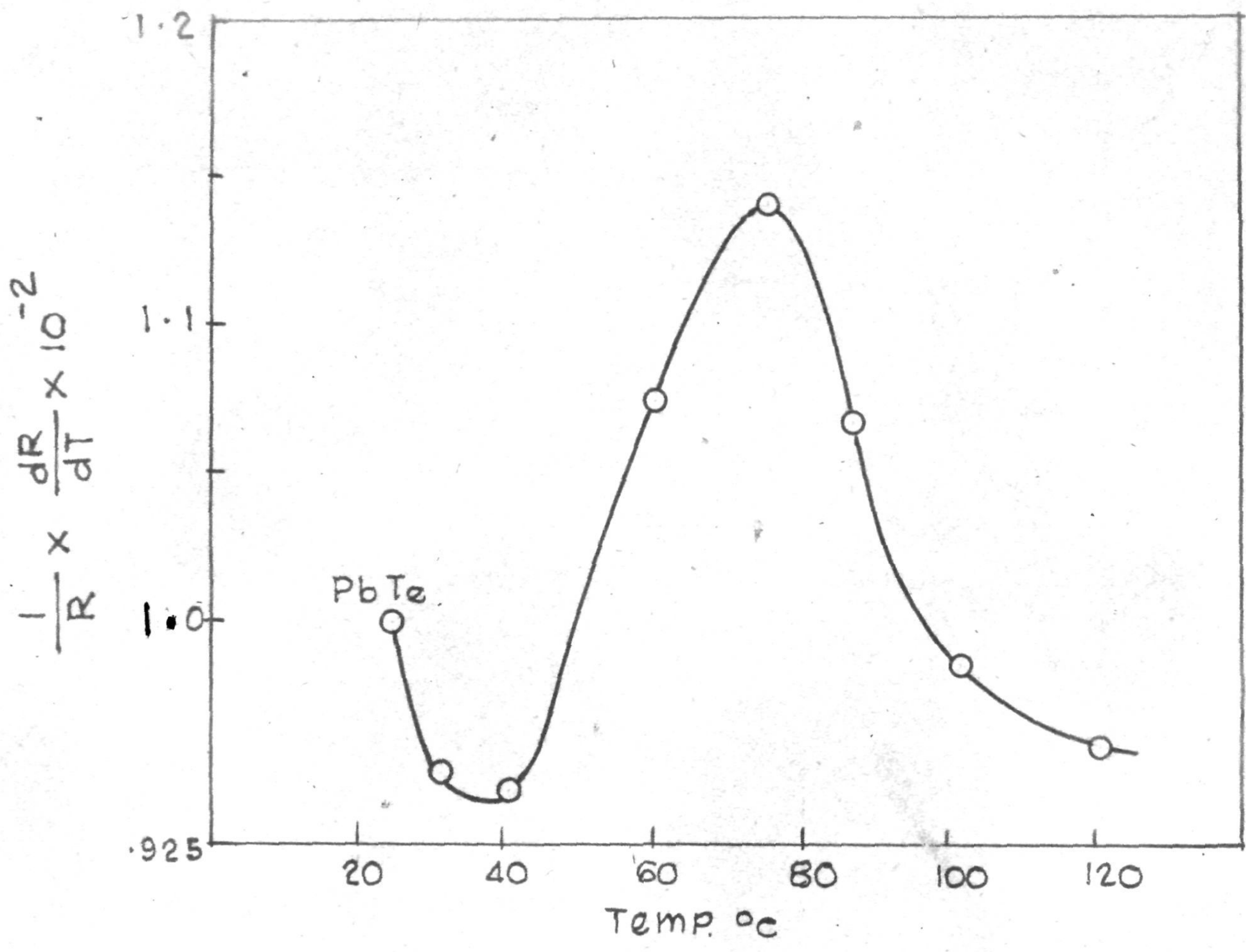
The mean free paths for PbS, PbSe and PbTe compounds were calculated from the resistivity measurements at different temperatures for the films of different thickness prepared under the same conditions of evaporation.

TABLE - 4

Lead sulphide		Lead Selenide		Lead telluride	
Temp. °C	TCR deg^{-1}	Temp. °C	TCR deg^{-1}	Temp. °C	TCR deg^{-1}
150	0.875	158	0.973	25	1.000
160	0.770	175	0.910	30	0.950
166	0.788	184	0.995	40	0.940
176	0.715	195	0.887	60	1.750
184	0.890	214	0.790	75	1.400
190	0.825	254	0.720	86	1.070
192	0.925	-	-	100	0.980
198	0.930	-	-	120	0.960
207	0.878	-	-	-	-
215	0.883	-	-	-	-
223	0.840	-	-	-	-

TABLE - 5

Lead telluride		Lead selenide	
Temp. °C	Mean free path (l_0) cm.	Temp. °C	Mean free path (l_0) cm.
25	7.245×10^{-4}	150	3.86×10^{-5}
50	6.166×10^{-4}	175	1.42×10^{-5}
75	4.901×10^{-4}	-	-
100	4.160×10^{-4}	225	1.19×10^{-5}
125	3.592×10^{-4}	250	0.74×10^{-5}



1·0
0·9
0·8
0·7
Pbse
Pbs
$\frac{1}{R} \times \frac{dR}{dT} \times 10^{-2}$
130
150
170
190
210
230
250
Temp °c

FIG-12.

It has been already shown that the mean free path could be calculated from the relation as shown in the chapter No.1.

$$\rho . d = \rho_{\infty} (d + \frac{3}{8} l_0)$$

where d is the thickness of the film, ρ is the resistivity of the film, l_0 is the mean free path of the charge carriers, ρ_{∞} is the resistivity of the bulk material having the same structure and same number of defects approximately as that of films.

The figs. 13 and 14 show the variation of ρ.d with increase of d for PbTe and PbSe. It can be seen that the product of ρ.d increased with the increase of thickness for the above three films. The curves were practically straight lines with constant slope making intercepts on the ρ.d axis. These curves hence could be represented in the form of equation $y = mx + c$ where c is the constant term. It can be seen from the above relations that the slope of the curve gave the value of ρ_{∞} and the intercept on the ρ.d axis gives the value of $\frac{3}{8} l_0 . \rho_{\infty}$. The value of mean free path at different temperatures for the lead chalcogenides was thus calculated and the results are tabulated in table No.5 for PbSe and PbTe.

It is also possible to calculate mobility (μ) from the mean free path by using an expression based on Lorentz-Sommerfeld theory,

$$\mu = \frac{e . l_0}{225 \sqrt{2 \pi m^* kT}} \text{ cm}^2/\text{volt.sec}$$

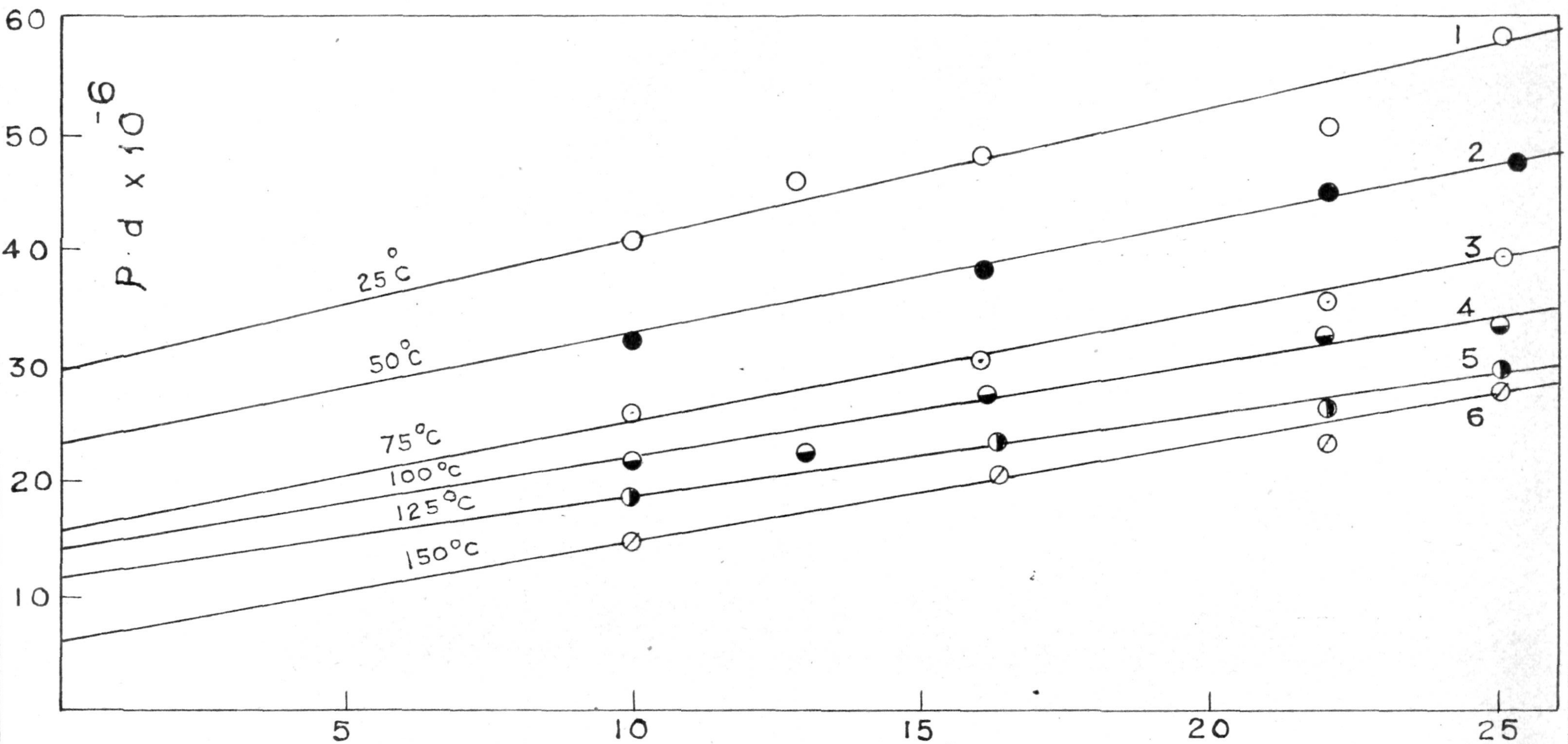


FIG -13.

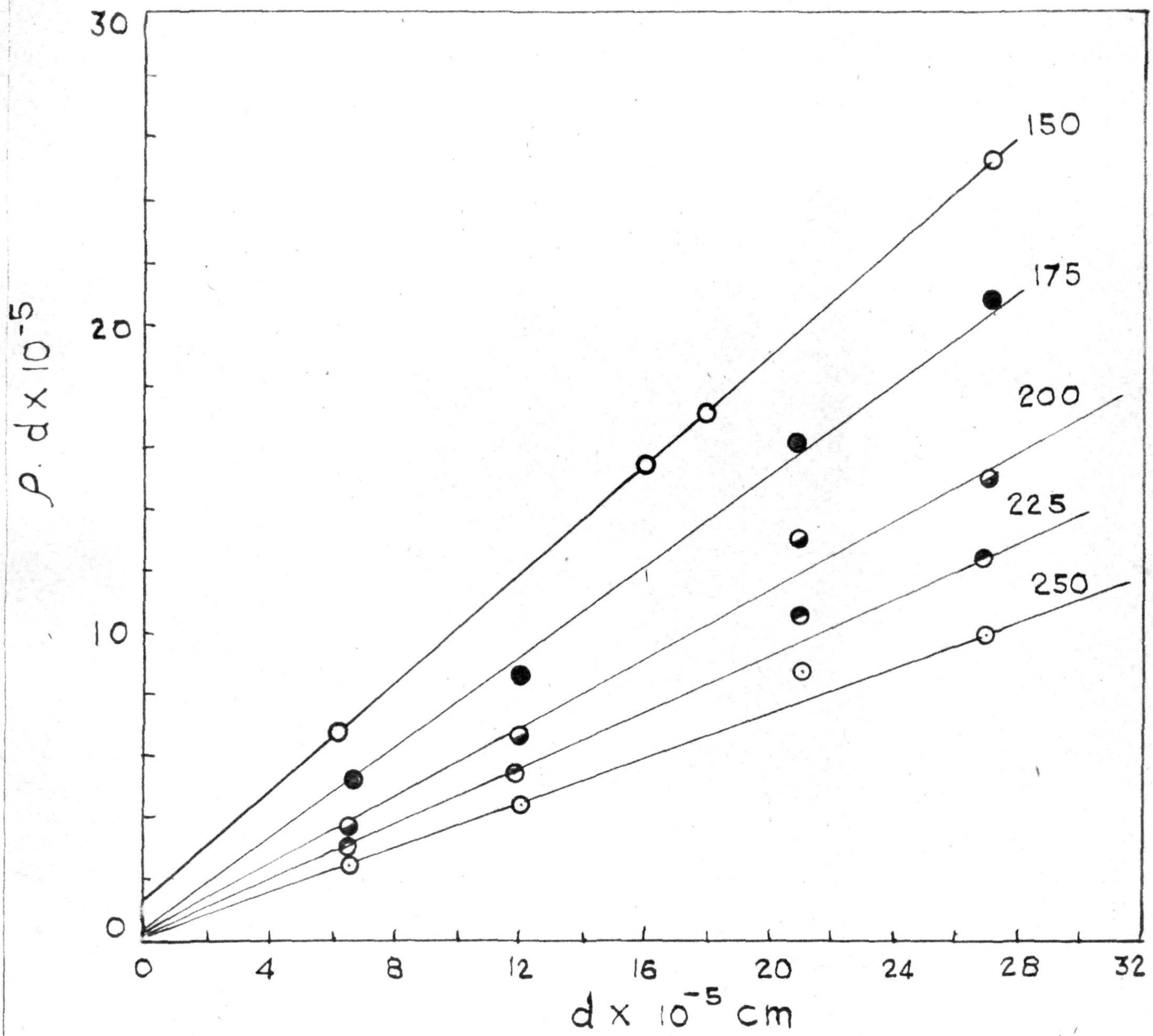


FIG-1A.

where the symbols have their usual meaning. The fig.15 shows the variation of log l_0 vs log T especially for PbTe. It can be seen from the fig.15 that the mean free path was found to decrease continuously with increase of temperature in both the cases viz. the curves (log l_0 vs log T) had negative slopes, especially for PbTe, it was -2.45 and for Pbse, -4.00. Assuming, that the effective mass of charge carriers is equal to the free electron mass, independent of temperature,

$$\mu \propto \frac{l_0}{\sqrt{T}}$$

for lead telluride, $\mu \propto T^{-2.95}$ and for lead selenide $\mu \propto T^{-4.5}$. The higher value of the power of T for lead selenide films, will be discussed later on in detail.

(v) Oxidation of lead sulphide films

Effect of oxidation :- Oxidation of lead sulphide films was also studied to some extent, since such films are being used in many devices. PbS films were oxidised at different temperatures under controlled pressure varying from atmospheric to 0.4 mm Hg in a temperature range 80°- 300°C. These oxidised films were subjected to resistance and thermoelectric power measurements in usual way. The fig.16 shows the variation of log μ vs 1/T for films; curve (A) for unoxidised 'p' type and (B) for oxidised film which was also 'p' type. The resistance of the film after oxidation was found to increase by two or three orders of magnitudes. It can also be seen that the adsorption effect

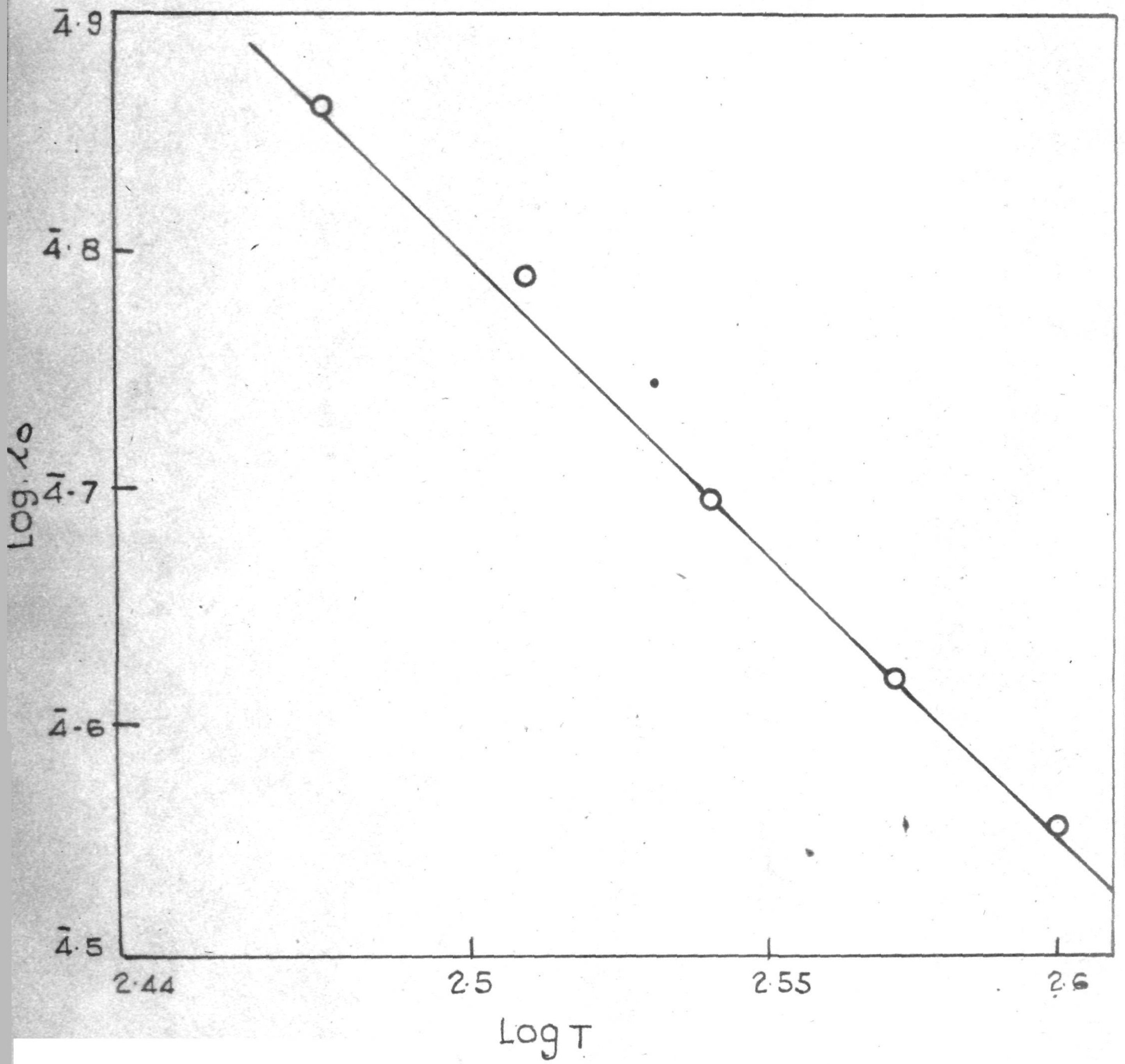


FIG- 15.

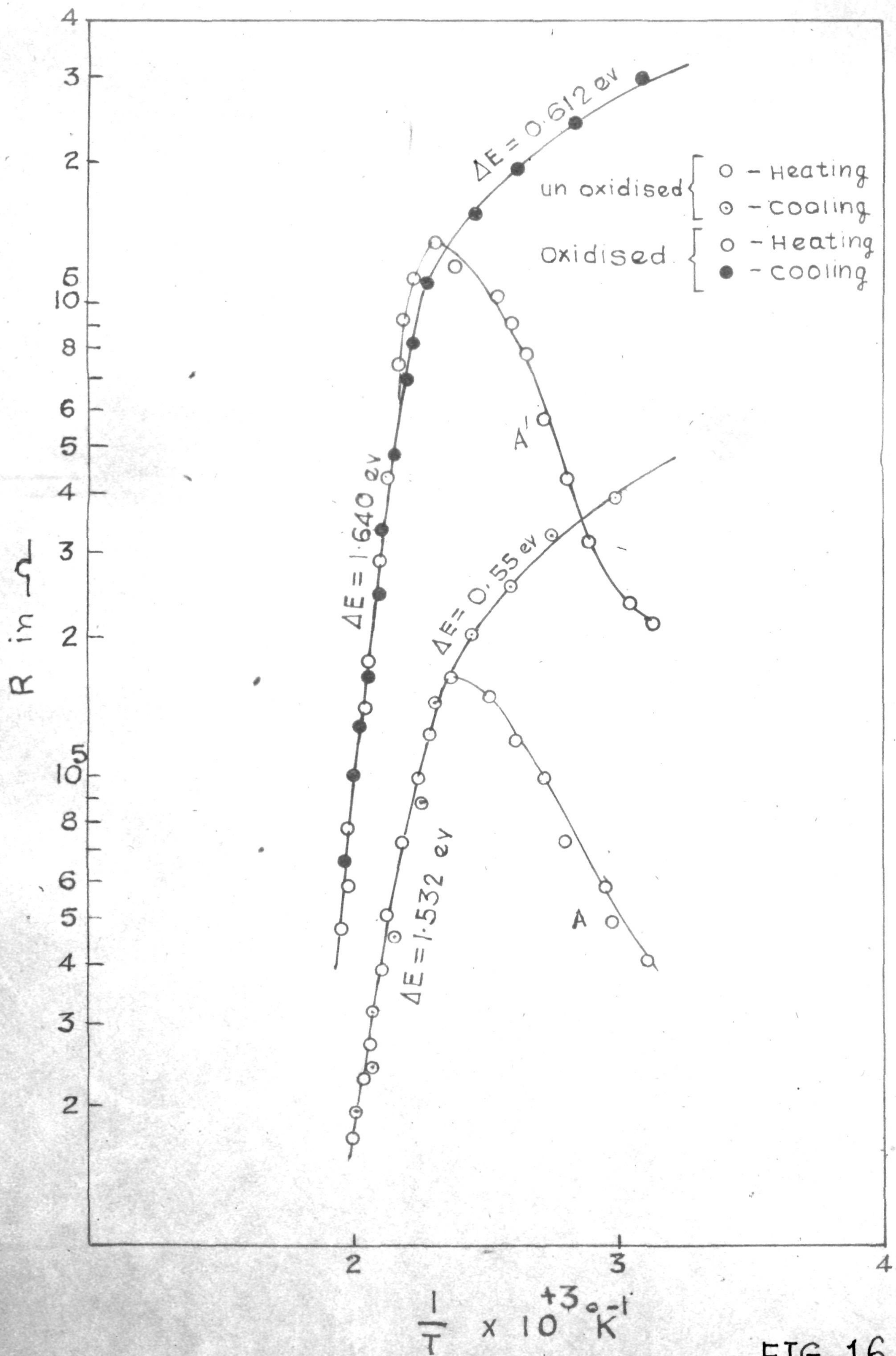


FIG- 16.

became more pronounced after oxidation though the general nature of the curve was similar to unoxidised samples. The other features of the curve during first heating and subsequent cooling and so on were similar to those observed for unoxidised PbS films. Higher was the temperature of oxidation, higher was the resistance and so also was the resistivity. Further if the sample was oxidised at temperature about 300°C, features of the curves were quite different from those of unoxidised PbS films, no doubt, due to the formation of oxide or sulphate layers. Activation energy was only slightly higher than those for unoxidised films. The oxidised films at different temperatures were also subjected to the thermoelectric power measurements. The fig.17 shows the variation of thermal e.m.f. with temperature for the films [oxidised, un oxidised] ~~at different temperatures~~. It can be seen that the magnitude of thermoelectric power increased with the increase of ~~oxidising~~ ~~temperature~~. It is interesting to point out here that no decreasing tendency of the thermal e.m.f. was observed up to the maximum temperature of our experiment for the film heated in air at about 300°C. It was noted that the oxidised film did not show the existence of the inversion temperature within the temperature range studied. All the p-type films showed same type of conductivity even though they were oxidised at higher temperatures.

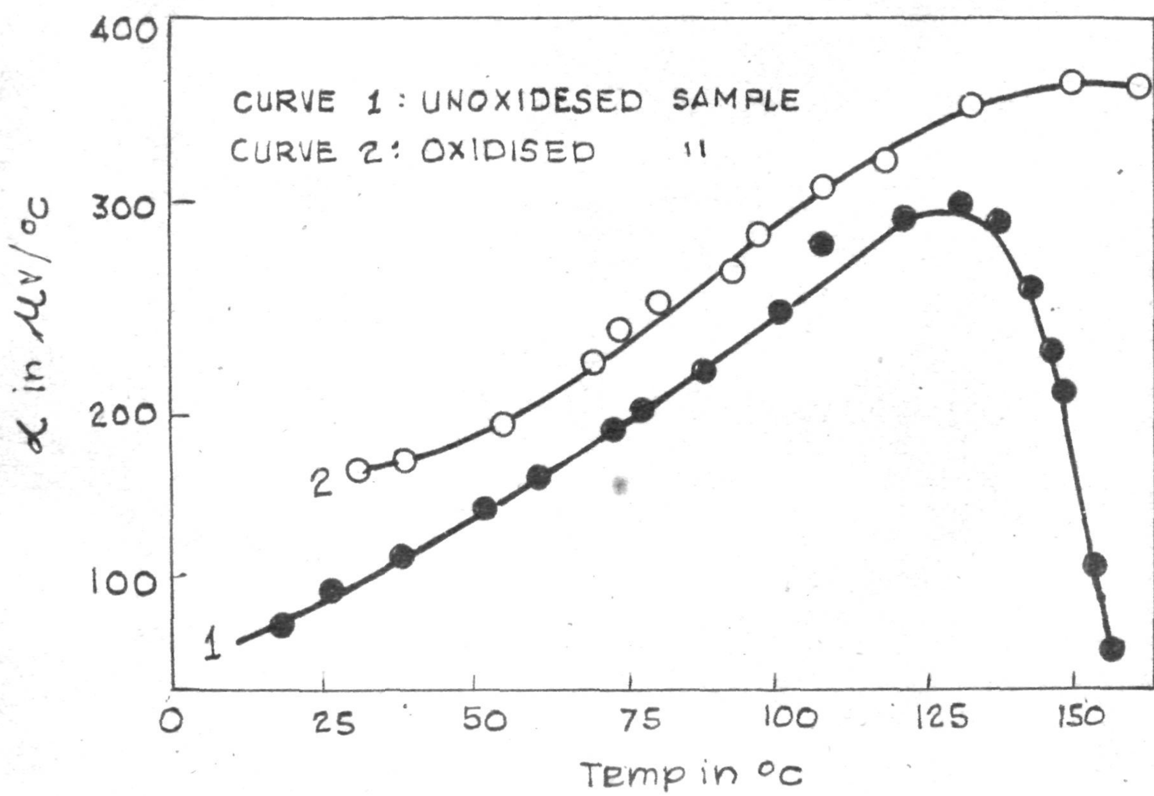


FIG-17.

(vi) Doping of Iodine in Lead sulphide and Lead Telluride Films :-

It is well known that properties of a semiconductor can be altered by impurity doping in the host lattice. As a result, the charge carrier number, and hence the electrical properties, the type of the conductivity, the mean free path, mobility, thermal conductivity and such other properties are generally affected. PbS and PbTe films were doped with iodine to see its effect on semiconducting properties.

Doping method

PbS and PbTe films deposited on glass substrates by vacuum evaporation technique were kept in iodine vapour atmosphere for 10-12 hours in a desiccator. In order to have uniform diffusion of iodine (vapours), the films were heated at about 300°C about one and half hours in vacuo ($\simeq 10^{-3}$ mm Hg) at a temperature below the T_d so that no evaporation of the film took place. The colour of the films was found to change from blackish to reddish. The resistance was found to increase by two or three orders in magnitude.

Resistivity and activation energy

The iodine doped lead sulphide and lead telluride films were then subjected to the resistance measurements at different temperatures in the usual way.

The curves log R *vs* 1/T were plotted for iodine doped and undoped film (fig.18). It is seen that the resistance decreased continuously over the temperature range studied viz. 30°- 300°C. The curve (log R *vs* 1/T) changed its slope at about 130°- 150°C depending upon the thickness of the film. At higher temperatures, a steep fall of resistance was observed up to the maximum temperature 300°C. While cooling the curve followed more or less the same path over the temperature range 300°-150°C and then changed its slope, slightly higher than that of observed in the initial heating cycle. On continuous measurements, the heating and cooling curves followed the same new path obtained during the initial cooling. It is interesting to note here that the initial portion (A) as shown in fig.18 for undoped film, was absent in the present case. The resistance was also measured at room temperature in air immediately after the above measurements. It was noticed that the adsorption effect was considerably minimised. The activation energy was calculated in two regions of the temperatures. Similar results of shifting of the temperature at which the maximum thermoelectric power was occurred, were also obtained in the present case. Iodine doped lead telluride films were also subjected to resistance and thermoelectric power measurements. The fig.19 shows the variation of log R *vs* 1/T for different ~~PbTe~~ films of varying thicknesses. It can be seen that the value of the activation energy was slightly higher in the present case as compared to the undoped PbTe films of approximately same thickness.

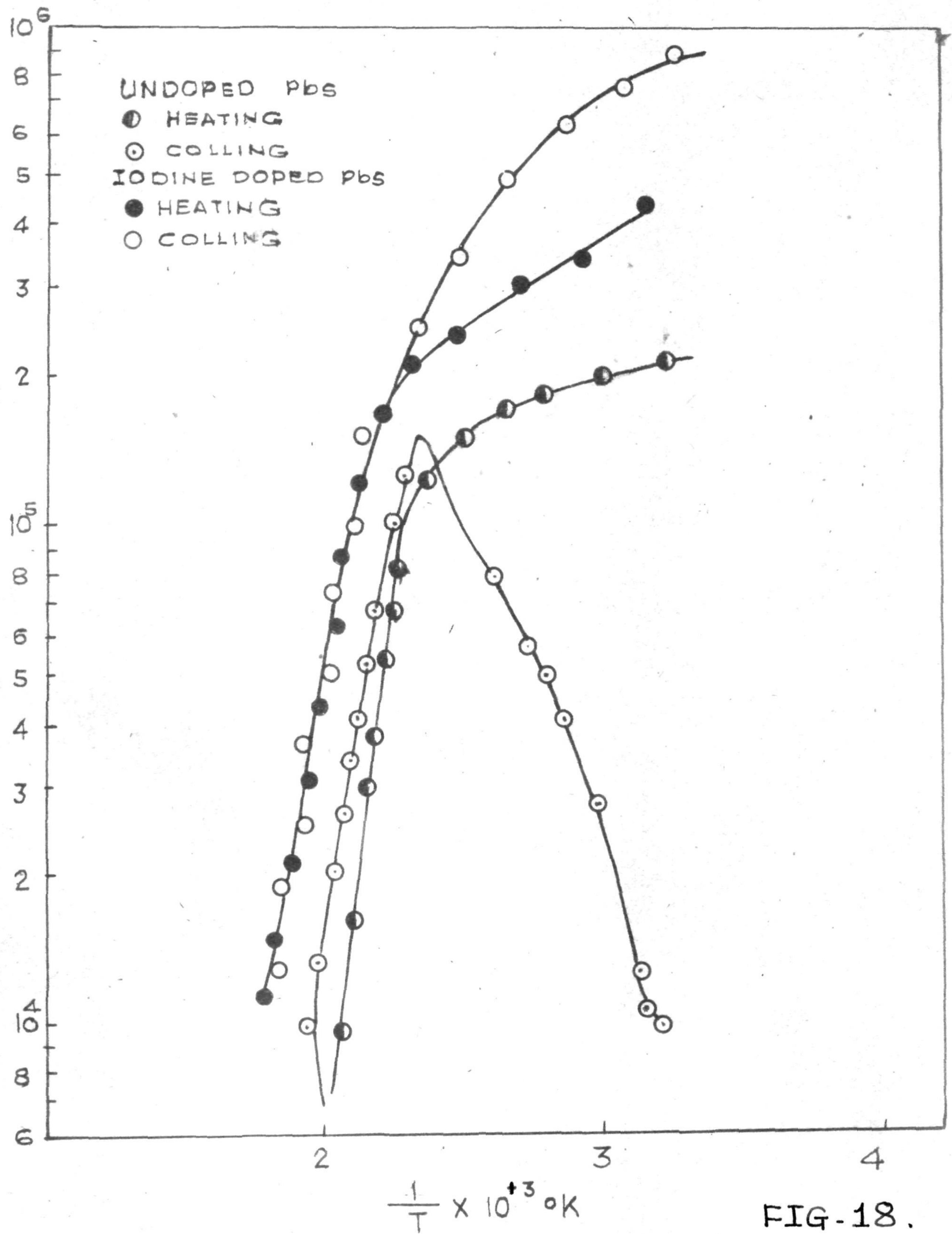


FIG-18.

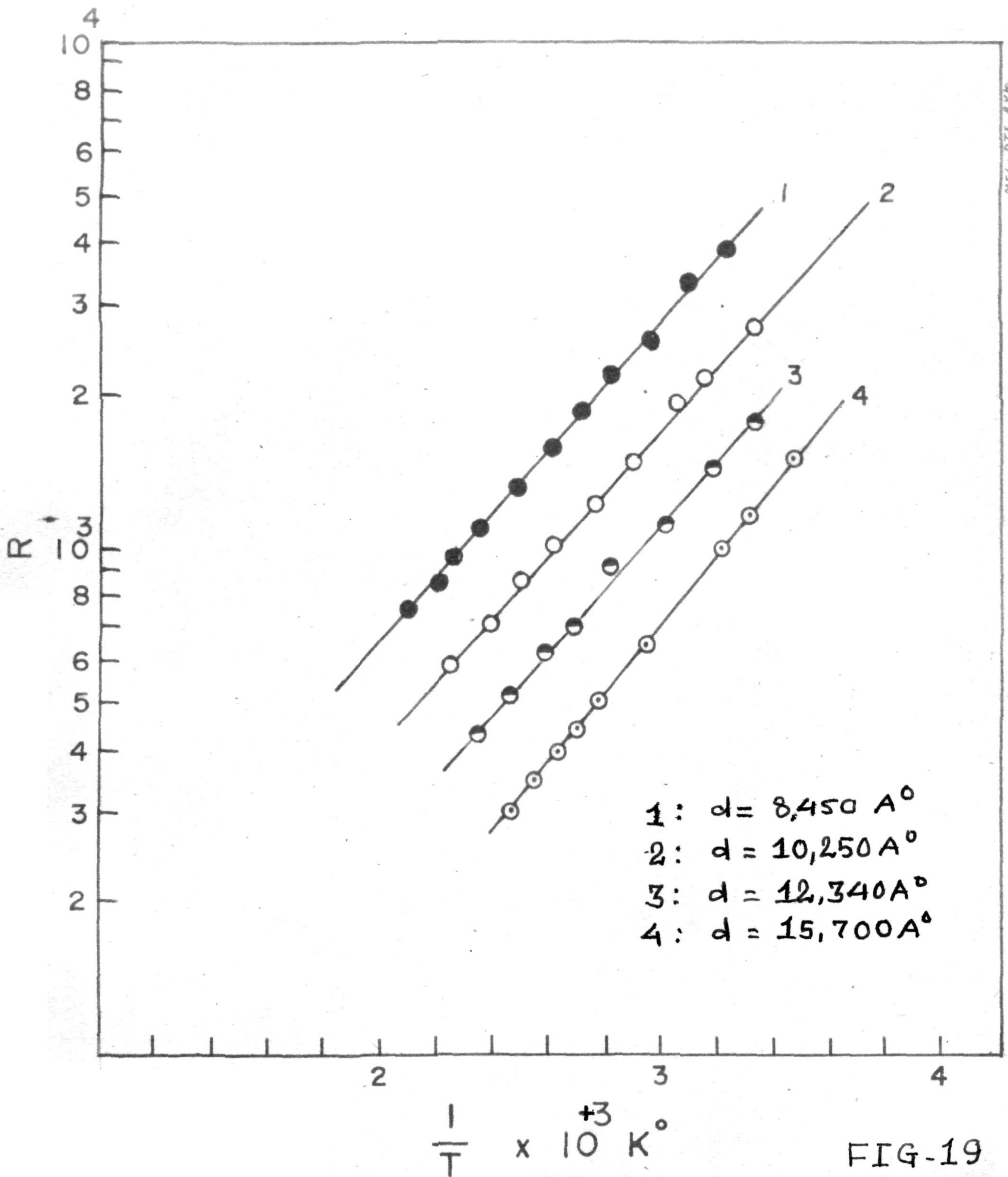


FIG-19

The thermoelectric power measurement showed that the corresponding values were slightly higher than those for undoped films. Fig.20 shows the variation of thermoelectric power at different temperatures for a doped and undoped lead telluride films of nearly same thicknesses. The general nature of the curve (α *vs* temperature) was similar in both the cases except their corresponding values were slightly different.

(vii) Hall coefficient (R_H) and mobility (μ_H)

Experiments were also carried out to find out the Hall mobility (μ_H) which is the product of Hall coefficient (R_H) and conductivity (σ) on films deposited at different substrate temperatures by measuring Hall coefficient and conductivity of the samples in a manner described by Deokar and Goswami (1965). Table No.6 shows R_H, σ, and μ_H for different films prepared at different substrate temperatures, more or less under the same deposition conditions. It is clearly seen that higher substrate temperatures favoured higher mobility (μ_H) in all cases mostly through the conductivity factor which was invariably higher with higher substrate temperatures.

Electron diffraction patterns were also taken from the deposits before and after measurements. There was practically no change in the patterns. The typical patterns for PbS, and PbSe are shown in figs. 21, and 22.

TABLE - 6

Substrate temperature °C	Film thickness Å	R_H (cm^3/coulomb)	σ ($ohm^{-1} cm^{-1}$)	μ_H (cm^2/volt sec.)
30	43,700	1.820	6.910	12.58
	32,000	1.748	6.125	10.07
	22,500	1.614	5.690	9.20
	14,750	1.592	5.155	8.20
	7,500	1.472	3.960	5.83
110	45,200	2.010	13.000	26.13
	36,100	1.930	12.200	23.58
	27,600	1.750	10.700	18.71
	12,400	1.620	9.300	15.07
	9,300	1.580	8.010	12.67
150	56,000	2.305	18.700	43.07
	37,730	2.270	15.75	35.75
	23,420	2.079	14.95	31.00
	12,800	1.767	13.08	23.00
	5,970	1.534	12.95	19.90

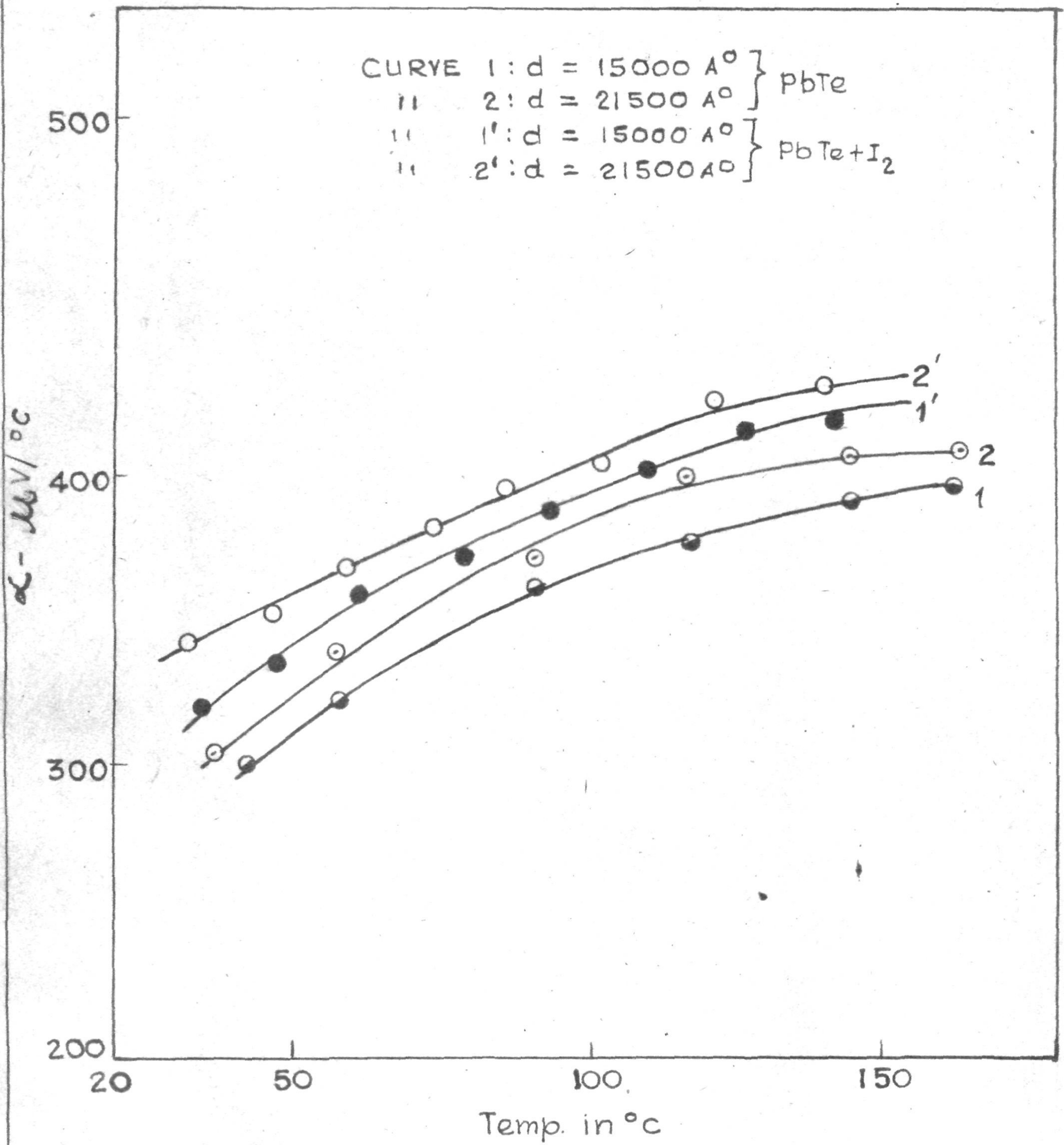


FIG. 20.

FIG-21.

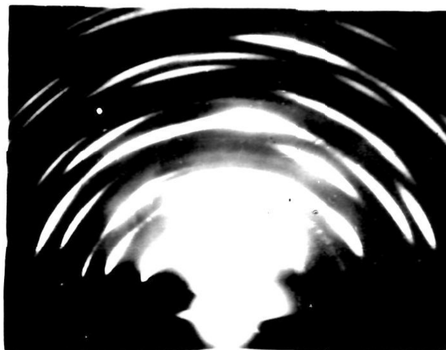


FIG-22.

D. Discussion

Resistivity and activation energy

It is known that the electrical resistance of metals is mainly due to the imperfections in their lattices (Bloch, 1928). In case of macroscopic metals the electrical resistance appears as a result of the scattering of electrons by thermal vibrations of lattice and also lattice defects such as missing atoms, interstitials impurity atoms etc. The resistance can therefore be divided into two parts (a) ideal part, strongly dependent on the amplitude of thermal vibration of the ions and hence strongly on temperature and (b) called "residual" resistance, strongly dependent on the lattice defects but independent of temperature as long as annealing effect is not taken into account. According to Matthiessen's rule,

$$\rho_{total} = \rho_{ideal} + \rho_{residual}$$

when annealing of lattice defects is carried out, an irreversible change of resistance takes place. Thomson (1901) and Swann (1914) introduced the concept of the effect of thickness on the mean free path in estimating resistivities of metal thin films. They suggested that the resistivity would be higher for the films having thicknesses lower than the mean free path and above that the resistivity would correspond to the bulk resistivity. The total resistance in case of films is given by

$$\rho_{total} = \rho_{ideal} + \rho_{residual} + \rho_{thickness}.$$

According to Neugebauer and Webb (1962) thickness is greatly depended upon the island size and distance between them. These factors are often depended upon the nature of substrate, its temperature, geometry of the substrates with respect to the source of vapour and sometimes also the distance between the substrate and source during the deposition of the films. Thickness dependent part may be considered to consist of $\rho_s + \rho_m + \rho_d$ where s is due to size effects, m is due to island size and d is due to distance between islands (Shah and Naik, 1964).

In the vacuum deposited films there is often a high density of defects, such as dislocations, stacking faults, microtwins etc. as reported by many workers (Pashley, 1959; Mathew, 1959; Phillips, 1960) and these will no doubt affect the resistivity. The small grain size and adsorption of gases will also produce high concentration of defects and scattering centers.

The resistivity for all the lead sulphide, lead selenide and lead telluride films investigated ranged from 1 to 0.5 ohm-cm. It was found to increase with the decrease of the film thickness and the rate of evaporation. From the fig.2 it can be seen clearly that the curves had two distinct different slopes. The curve corresponding to low rate of evaporation had higher slope than that for higher rate. This suggests that the film of similar thickness prepared under the condition of different

rates of deposition had a different structure as far as the porosity, number of defects etc. were concerned. Bennett and Scott (1950) in their study on thin metallic films observed a similar behaviour of resistivity of films with rate of deposition. Levinstein (1949) pointed out the connection between the structure of the film and phenomena of critical density of conduction on which the resistivity of the film depends. Presence of residual gases produce more porous and disordered films. The relation between the size of the islands and number of impinging atoms has been given by Neugebauer (1964), $\frac{\partial r^*}{\partial N} < 0$; $\frac{\partial \Delta F^*}{\partial N\downarrow} < 0$; where r^* is the critical radius of an aggregate, ΔF^* is the free energy of formation of such an aggregate of critical size and $N\downarrow$ is the number of impinging atoms. From the above relation it can be seen that with the increase of deposition rate the islands of smaller size will be formed and also the rate of formation of smaller islands will be higher. This shows that in case of high rate of evaporation a continuous film will be formed at lower film thickness resulting in lower resistivity. Our experimental results also corroborate this conclusion. Though the conductivity of metal depends more on the mean free path, in case of semiconductors, it depends more on the carrier concentration. In the present investigation particularly for lead telluride films, the size effect is not an important factor on the conduction mechanism since the film thicknesses were much higher than the mean free path of charge carriers.

In all the three compounds studied, the temperature of discontinuity was found to be much more lower than the melting points of the corresponding bulk materials. The evaporation of films at lower temperature than those of the bulk can be explained in the following way: In case of film state the surface to volume ratio of the material is very high and consequently there will be high total surface energy. This will result in the aggregates of becoming less stable and leading to a higher vapour pressure than from the corresponding bulk material. This will no doubt result in evaporation of the film at lower temperature.

The measurements of the resistance above room temperature up to a temperature well below the T_d temperature showed that the initial rapid fall in resistance might be due to the annealing out of the some of the defects. The resistance measurement during the initial heating process particularly for PbS and PbSe above room temperature showed an increase of resistance with the rise of temperature up to 130°-175°C depending upon the thickness of the film and above this temperature a fall in resistivity with rise in temperature. During subsequent heating and cooling the rise in resistance observed initially this appears especially for PbS films. This initial behaviour is no doubt very peculiar. It has been confirmed that this behaviour was due to the adsorption phenomena which could be removed by heat treatment or keeping the film under

dynamical vacuum. Lead sulphide film on subsequent heating and cooling showed semiconducting behaviour viz. decrease of resistance with increase of temperature throughout the temperature range studied indicating thereby the creation of electron-hole pairs viz. an intrinsic behaviour. From the fig.4 it can be concluded that PbS films showed extrinsic behaviour with $\Delta E = 0.6$ eV, below 130°- 175°C. The value of ΔE is, no doubt, depending also on the defects associated with deposited film in addition to impurity effect. The initial slow fall of resistance with increase of temperature may be due to the effect of some of the impurities which further ionized with the rise of temperature. It seems from the fig.4 that above 130°- 175°C the number of electrons in the conduction band and number of holes left behind in the valence band were comparatively higher than the holes supplied from impurity atoms and as a result the effect of decrease of mobility due to the impurity scattering and defects was swamped out leading to an increase in electrical conductivity, in tunneling transmission coefficient with rise of temperature as pointed out by Neugebauer (1962).

In case of PbSe films, the resistance after initial heating was found to increase a little and then decreased with the rise of temperature. This increase in resistance might be due to the presence of some adsorption (chemical or physical or both) effect which might not be removed by vacuum and heat treatment.

Similar sort of variation in resistance with temperature in this temperature range was also observed by Hirahara and Murakami (1954) in case of p-type of lead selenide single crystal having 0.3% excess of selenium. But the cause seems to be different from the one mentioned above. In case of bulk material, this behaviour may be interpreted as the effect of the scattering due to the lattice vibrations and impurity centers, since the carrier concentration assumed to be constant over the temperature range i.e. 30°- 175°C. For lead telluride films, no such behaviour was observed at all over the temperature range studied.

It has already been mentioned in our results that the activation energy measured for different films of varying thickness was higher for thinner films than bulk and vice versa. As already been discussed, the activation energy greatly depends on the island structure of the film. But in real films we have not only to consider the island structure form during the initial stage of the growth of the film but also to take into account other features, namely the gradual increase in the size of islands and their final merging to one another with the formation of innumerable discontinuties and eventually developing high surface asperities depending upon the evaporation conditions when the thickness of the film was high. These factors, it is believed, will also considerably affect the activation energy. The slight ~~decrease~~

decrease of activation energy with the increase of film thickness can be interpreted by the fact that the mean atomic spacing decreases with increasing thickness.

The expression for conductivity in thin metallic films given by Neugebauer can be further improved for semiconducting films introducing the exponential term in equation 25, since the carrier concentration increases exponentially with the rise of temperature provided the energy required to create electron-hole pairs should not be more than few kT. The conductivity for thin semiconducting films is,

$$\sigma = A' \exp. \left\{ -\frac{4\pi d}{h}\sqrt{2m\phi} + \frac{2e^2/\epsilon r + \Delta E_g}{2kT} \right\} \quad \ldots\ldots \quad (41)$$

The measured value from the curve log R *vs* 1/T will correspond to $\Delta E = \left\{ 2e^2/\epsilon r + \Delta E_g \right\}$.

<u>Temperature coefficient of resistance</u>

The present study on PbS, PbSe and PbTe showed negative temperature coefficient of resistance. The negative maxima and minima were observed in almost all of the films studied. The TCR varies from -0.7×10^{-2} to -1.15×10^{-2}. The maxima and minima could be explained easily on the island structure model. According to them TCR is given by the relation,

$$TCR = \frac{d(d)}{dT} \left\{ \frac{4\pi\sqrt{2m\phi}}{h^2} + \frac{1}{d} \right\} - \frac{C}{T^2} \quad \ldots\ldots \quad (42)$$

where $C = \frac{2e^2/\epsilon r + \Delta E_g}{2k}$ and the other symbols have their usual meaning. Since with the increase of temperature the distance between island goes on decreasing and therefore the term d(d)/dT must have a negative sign. Therefore the final expression for TCR will be

$$TCR = -\frac{d(d)}{dT}\left\{\frac{4\pi\sqrt{2m\phi}}{h^2} + \frac{1}{d}\right\} - \frac{C}{T^2} \quad \ldots\ldots \quad (43)$$

In the lower temperature region, the contribution from the first term will be negligible and the main contribution will be only from C/T^2. At about 40°-60°C for PbTe, the distance between islands might be decreasing and thereby the resistance of the film decreased rapidly resulting in higher negative values of TCR with increase of temperature. The contribution to TCR was mainly from the first term in equation No.43. At still higher temperatures only the term C/T^2 might be effective.

Thermoelectric power

As mentioned in the results, the thermoelectric power at room temperature for all the lead family compound films was found to be positive. It is possible that the p-type characteristic might be due to the excess of S, Se and Te in PbS, PbSe and PbTe respectively. Hitenberger (1942) showed that excess of S in PbS would lead to p-type characteristics. In energy band representation, the excess of sulphur atom induces an acceptor level very close to the upper edge of the valence band.

The equation for thermoelectric power in case of p-type of carriers can be obtained by putting $n = 0$ in equation 29 . It is well known that the position of the Fermi level depends upon the concentration and type of the impurities. In the present case, it will lie below the middle of the forbidden energy band. With the increase of temperature Fermi level will rise towards the middle of the forbidden energy gap and at certain temperature depending upon the concentration of impurities, attains its ultimate value. Eventually, the thermoelectric power will increase up to the temperature at which Fermi level attains its ultimate value.

It has been observed in the present study on PbTe films that thermoelectric power increased slowly with rise of temperature and finally showed a slight decreasing tendency. The slight increase in positive thermoelectric power appears to be due to an increase in effective mass with temperature as reported by Johnson (1962), Smirnov et al. (1961) and Johnson (1964) in bulk PbTe samples. The decreasing tendency on further rise of temperature may be due to the more electron-hole pair creation process.

The results for thermoelectric power in case of PbS and PbSe differ considerably from those of PbTe. It has already been mentioned that the positive thermoelectric power slowly increased to maximum value and then dropped steeply to zero and on further increase in temperature became negative

and at still higher temperature increased with negative sign. On cooling similar charge occurred with the difference the values obtained during cooling cycles were different. This change of positive thermoelectric power, to negative thermoelectric power indicates that the material which was originally p-type, changes to n-type due to thermal condition. A similar behaviour was also observed previously by Avafa et al. (1956) in case of bulk lead sulphide compound. The initial rise in thermoelectric power may be due to the increase in the position of the Fermi level as mentioned before. In another way it can be said that below 130°- 175°C depending upon the film thickness, the contribution to the thermoelectric power from the holes is more as compared to the electrons. Above 130°- 175°C the decrease of thermoelectric power with increase of temperature indicates that the contribution from the first term in equation 29 became appreciable. At the inversion point, the contribution from electrons and holes created due to the thermal ionization became equal resulting in zero thermoelectric power. In such case,

$$n\mu_e\left[(5/2-S) + \ln(N_c/n)\right] = p\mu_h\left[(5/2-S') + \ln(N_v/n)\right].$$

Since no intentional impurities were introduced into the samples the change of sign of α was no doubt due to the temperature effect. Since the carrier concentration is characteristic of the material, it appears that the change of sign is linked with the mobility of the charge carriers which is generally affected by the temperature.

The negative sign of thermoelectric power particularly observed at higher temperatures, for PbS and PbSe films, must be due to the higher mobility of electrons than holes as reported by Brebrick and Scanlon (1954), since in intrinsic range the electron and hole concentration are approximately same.

The inversion occurred at lower temperature for the thicker films indicating thereby that the thicker films became intrinsic at lower temperatures. This temperature for thinner films was however found to be higher indicating the higher concentration of impurities most likely the defects.

Mobility

The mobility relation $\mu \propto T^{-n}$ reported by many workers was also found to be valid in our studies on films. Many investigators reported the value of 'n' to vary between 2.5 to 3. Whilst Smirnov et al. (1961) found, for PbSe, the value of n = 3.5 to 4. For PbTe and PbSe the value of 'n' was 2.95 and 4.5 respectively. Since evaporated films consist of many defects such as stacking faults, dislocations, twinnings, grain boundaries etc. the probability of scattering will be much more compared to the bulk material of the same thickness, consequently the mobility of the thin films would considerably be less and hence 'n' will be more as found in the present studies. The mobility of charge carriers in films deposited at room temperature of varying thickness was found to be less than 10 cm^2/volt-sec

Generally the mobility for bulk material varies from 100 to 400 cm^2/volt-sec. This considerable decrease in mobility in thin films may be attributed as mentioned above to the defects viz. the presence of stresses and strain, imperfections etc. generally introduced during the growth of the films. In the present study as the thickness became low the mobility for lower film thickness seems to be associated with the presence of more defects. It will be worth mentioning that Lavy (1952) observed $\mu_n = 2$ cm^2/volt-sec. and $\mu_p = 20$ cm^2/volt-sec. for lead telluride films, Silverman and Levenstein (1954) also observed a very low mobility in case of PbTe films. Halvorsen (1950) reported that the mobility for p-type PbS films of 1-μ thickness was less than ten. The higher values of mobility with increase of substrate temperature during the deposition as obtained in the present investigation may be due to the increase in size of the crystallites (Finch and Wilman, 1937; Levinstein, 1949). At high substrate temperature, the surface diffusion and annealing out of the internal imperfections such as stacking faults, dislocations etc. takes place and the overall effect will cause an increase in mobility of the charge carriers with the increase of substrate temperature. The reverse will be the case for deposits formed at lower substrate temperature.

It is not easy to see the reason for the low values of Hall coefficient for thin films compared to the bulk. But it is likely that the values may arise out of the concellation of effects of majority and minority carriers which were always present in the films studied.

Oxidation of PbS and Iodine doping in PbS and PbTe Films

The results of oxidation of PbS films showed that resistance increased by two or three orders in magnitude. The higher values of resistance for oxidised film appears to be due to the absorption of oxygen and sometimes oxidation of films, Wilman (1942) found by electron diffraction that the surface layer consisted of PbS, $PbSO_4$ and other compounds. Minden (1955) suggested that these sort of films might be composed of two layers next to the substrate viz. (i) conducting layer and (ii) the upper layer of the film which was supposed to be non-conducting. He suggested the formation of $PbSO_3$, PbO and removal of SO_2. Due to the adsorption of oxygen as well as formation of new phases on the surface of the film, the resistivity would increase considerably. The results of thermoelectric power measurements suggested that the type of the material remained unchanged after oxidation of the film. The slight higher values of thermoelectric power observed might be due to the formation of new compound such as $PbSO_3$ and PbO (Minden, 1955), or $PbO \cdot PbSO_4$ (Berlaga et al. 1956), Bode and Levinstein (1954) showed that the n-type material changed to p-type after oxidation.

Resistivity measurements on iodine doped PbS and PbTe films showed a considerable increase in resistivity at room temperature. The higher values of iodine-doped films might be due to the formation of layer of I_2 on the surface of the

films which had generally very low conductivity. It can be seen clearly from the measurements on Iodine-doped films of PbS that the adsorption effect was considerably reduced. It is not easy to interpret this peculiar behaviour of such films. It is evident that Iodine layer so formed might prevented the penetration or diffusion of moisture and gases through the film possibly by occupying active sites. It has been reported previously that the halogens doping in lead sulphide group generally gave n-type of material (Bloem et al., 1954). But the present study showed that the Iodine did not change the type of the material in case of PbS and PbTe films. The thermoelectric power measurements gave a slightly higher values. The general trend of the result was similar.

CHAPTER - IV

STUDIES ON BISMUTH TELLURIDE AND BISMUTH SELENIDE FILMS

A. Introduction

It is well known that the bismuth telluride and bismuth alloys are frequently used in thermoelectric devices. The experimental data on materials which had been used in thermoelectric devices up to 1954 is given in papers by Telkes (1947, 1954), Forsberg (1953) and Horing et al. (1947). Bismuth telluride is supposed to be one of the best intermetallic compounds used in thermoelectric devices. The work of Haken (1910) on Bi-Te system showed that the pure Bi_2Te_3 (52 Bi - 48 Te) always gave n-type conductivity whereas impure compound showed p-type conductivity, with thermoelectric power varying from 120 - 170 $\mu V/^{\circ}C$.

Later on Goldsmid and Douglas (1954) showed that p-type Bi_2Te_3 could be used to produce thermoelectric cooling. After 1954, many investigators studied the semiconducting parameters of Bi_2Te_3 single crystals and polycrystals. Tsidil'kovskii (1955) and Amirkhanov et al. (1957) measured the thermomagnetic effects over the temperature range 120°- $700^{\circ}K$ and reported that in most of the samples the carrier concentration was of the order of 10^{18} - 10^{19} cm^{-3}. Lagrenaudie (1957) confirmed that Bi_2Te_3 was a semiconductor and applied the same bonding model as reported by Kreb (1954) for lead sulphide. He also reported

that the thermoelectric power of his sample having the carrier concentration 1.6 x 10^{18} cm^{-3} decreased with the rise of temperature and for $n = 1.7 \times 10^{19}$ cm^{-3}, it was almost constant over the temperature range 130°- 475°K and then had a decreasing tendency. Goodman (1959) proposed a new model as was used for CdI_2. Gordyakova and Sinani (1958) investigated the effects of impurities in Bi_2Te_3. They also reported that the electrical conductivity and thermoelectric power changed considerably with doping. Drabble and Wolfe (1956) suggested the multivalley band structure. The measurements of Drabble et al. (1958) and Drabble (1958) showed that both the conduction and valence bands had either three or six extremas and they deduced that the constant energy surfaces of electrons were spheroidal. The effective mass from Hall and Seebeck data were reported to be as 0.45 m_o and for holes 0.51 m_o. Many investigators also measured the electron and hole mobility (Goldsmid et al., 1958; Satterthwaite and Ure, 1957). The electron hall mobility of Bi_2Te_3 was found to be 310 cm^2/volt-sec. and hole mobility was about 400 cm^2/volt-sec. at 300°K (Satterthwaite and Ure, 1957; Drabble, 1958; Harman et al., 1957). The temperature dependence of mobility from resistivity and Hall effect measurements varied as T^{-n} varied from 1.63 to 3 for electron mobility and 1.5 to 2.3 for hole mobility. The activation energy varied from 0.16 to 0.2 eV for bulk material.

Goldsmid (1957) made the thermoelectric power measurements on both n- and p-type materials and reported that thermoelectric power was independent of an axial direction i.e. found to be isotropic in the range $150^\circ - 300^\circ K$. He found $\alpha = 190 \mu V/^\circ C$ for n-type and $\alpha = 170 \mu V/^\circ C$ for p-type Bi_2Te_3. From the graphs of Seebeck coefficients against lnT, the slope corresponded to $167 \mu V/^\circ C$ for n-type and $150 \mu V/^\circ C$ for p-type material in the above temperature range. He also stated that the effective mass increases with increasing degree of degeneracy. Goldsmid (1958) and Mansfield & Williams (1958) measured the Seebeck coefficient in the intrinsic range of temperature and Goldsmid determined the ratio of electron to hole mobility as 1.2 and $m_n^* / m_p^* = 0.9$. Bowley et al. (1958) studied the magneto-thermoelectric effects.

Goldsmid (1958), Walker (1960) also measured the thermal conductivity of a number of p- and n-type specimens of varying composition over the temperature range $150^\circ - 300^\circ K$ and at lower temperature i.e. $2^\circ K$ (McDonald et al., 1959). Measurements of thermal conductivity as a function of temperature also been reported by Satterthwaite and Ure (1957). Over the temperature range they found $K_L = 5.1 \times T^{-1}$ W cm^{-1} deg^{-1}. Optical properties of Bi_2Te_3 single crystals have been reported in a series of papers by Austin (1958, 59, 60). He reported that the thermal energy gap at room temperature was 0.13 eV and had a temperature coefficient -0.95×10^{-4} eV/ $^\circ C$.

Carlson (1959) studied the diffusion of copper in Bi_2Te_3 and his results were in agreement with the theory of diffusion given by Zener (1951). Boonpaa (1964) correlated the type of material and c/a ratio for Bi_2Te_3. The results were corresponding to those previously reported by Francombe (1958), Vasenin and Konovalov (1957).

Lange (1939) determined the positions of the atoms in the rhombohedral C_{33} type of Bi_2Te_3. Dongus (1951) reported a hexagonal structure with a = 4.35, C = 5 x 0.05 Kx whilst Shigotomi and Mori (1956) reported a = 6.79, c/a = 1.4. In the view of Francombe (1958), Bi_2Te_3 had a marked anisotropy between the axial expansion coefficients. According to Sato (1963), changes in structure of Bi_2Te_3 took place during the mechanical grinding process. Recently Francombe (1964) from electron diffraction study on sputtered thin films of Bi_2Te_3 reported a modified hexagonal structure which corresponds to pseudocubic structure.

Many investigators have attempted to study the semiconducting properties of Bi_2Se_3 single crystals and also of polycrystals. In 1950, Gibson and Moss have estimated the value of the activation energy (ΔE) = 0.4 eV. According to Black et al. (1951) the value of ΔE was 0.35 eV, and the temperature coefficient of optical energy gap was -2×10^{-4} eV/$^{\circ}$C. Whilst Hashimoto (1958) have observed ΔE = 0.2 eV for polycrystalline Bi_2Se_3 and the activation energy of donor static

was 0.003 eV. He also reported for BiSe polycrystals, $\Delta E = 0.4$ eV. Austin and Sheard (1957) estimated the value of $\Delta E = 0.27$ eV. Joffe and Stil'ban measured the thermoelectric power, figure of merit and thermal conductivity. They found $\alpha = -200\ \mu V/^{\circ}C$, $Z = 1.6 \times 10^{-3}$ to $1.4 \times 10^{-3}\ deg^{-1}$ and $\kappa = 14 \times 10^{-3}\ W\ cm^{-1} deg^{-1}$. Konorov reported $\alpha = 70\ \mu V/^{\circ}C$. Gordyakova et al. (1958) reported the mobility in Bi_2Se_3, $\mu = 725\ cm^2$/volt-sec.

It is interesting to state that the bulk material obtained from the stoichiometric composition of Bi and Se, is generally n-type. According to Donges (1951) an alloy Bi_2Se_3 annealed at 475°C for several days had a hexagonal structure. Parravano and Caglioti (1930), Schubert et al. (1953) and Schubert & Fricke (1953), Konorov (1956), reported hexagonal structure for Bi_2Se_3. In view of Semiletov (1954), Semiletov and Pinsker (1955) reported from their electron diffraction study Bi-Se system had three phases viz. Bi_2Se_3, Bi_3Se_4 and BiSe. Recently Gobrecht et al. (1964) studied the structural and electrical properties of Bi_2Se_2 and Bi_2Se_3. They have observed a high anisotropy for Bi_2Se_3 ($\sigma a/ \sigma c = 10$) as compared to Bi_2Se_2 ($\sigma a/ \sigma c = 2$) as far as the conductivity was concerned. In this laboratory Dhere (1965) made a detailed study on the crystal growth process of Bi_2Te_3 and Bi_2Se_3 films on (100), (110) and (111) faces of NaCl and also on (0001) of mica.

These studies, no doubt, give some insight into the electron transport process in the bulk material. It is also evident that no such studies have been made on the semiconducting

and physical properties of thin films. In the following, some study has been undertaken on the measurements of semiconducting parameters in order to get some insight into the electron transport processes.

B. Experimental

(a) Preparation of bismuth telluride :- Bismuth telluride in the bulk was prepared by melting bismuth and tellurium in atomic proportion (2:3) in vacuo in a sealed silica tube by heating to about 1000°C for about six hours and cooling later on. The bismuth metal used was supplied by Johnson Matthey and Co. and the tellurium (metal) powder by Riedel-de haenag, Seelze-Hannover, of Germany. The method of preparation was similar to that of lead selenide.

(b) Preparation of bismuth selenide :- Bismuth selenide was also prepared in a similar way in atomic proportion (2:3) by taking bismuth and selenium. Selenium was obtained from British Drug House and was of 99% purity. The maximum temperature of heating was about 700°C. The other stages were similar to that of Bi_2Te_3.

C. Results

(i) Resistivity and activation energy :- Before carrying out the measurements of the other parameters, the discontinuity temperature of both the Bi_2Te_3 and Bi_2Se_3 films were found out and was about 225°C and 300°C respectively. The Bi_2Te_3 films were then annealed at temperature about 200°C. In the case of

Bi_2Se_3 films no annealing was carried out, the reason for which will be discussed in the results.

(a) <u>Bismuth telluride films</u> :- The resistance measurements were made in the temperature range of -17°C to 200°C. The fig.23 shows the variation of log R vs 1/T for different film thicknesses. It can be seen from the curves that the resistance decreased continuously with the rise of temperature through-out the temperature range. However, the curve log R vs 1/T changed its slope at about 30°C and on further rise of temperature up to the maximum temperature of our experiment, the slope remained constant. The activation energy was calculated for both the regions i.e. from -17°C to 30°C and 30° to 200°C and the results are shown in table No.7 for films of varying thickness. It can be seen from the fig.23 that the Bi_2Te_3 films showed intrinsic behaviour above room temperature. The activation energy calculated over the temperature range 30°-175°C was slightly higher than that of bulk material, reported by other investigators.

The study was also made on the films prepared under different evaporating conditions, namely with the rate of evaporation. The resistivity measurements at room temperature on such films showed that the resistivity increased with the decrease of rate of evaporation and vice verse. Measurements at higher temperature also indicated that the general trend of the results was similar for different rates of evaporation

TABLE - 7

BISMUTH TELLURIDE.

Film No.	Film thickness Å	(Δ E) eV above room temperature	(Δ E) eV below room temperature
A (fast rate of evaporation)	2,090	0.2700	0.237
	3,650	0.368	0.230
	5,732	0.365	0.225
B (slow rate of evaporation)	8,325	0.380	0.255
	10,300	0.377	0.250
	12,100	0.360	0.240

TABLE - 8

BISMUTH SELENIDE

Film No.	Film thickness Å	Activation energy (Δ E) eV
1	2,340	0.440
2	5,910	0.399
3	11,010	0.360
4	15,670	0.355
5	21,790	0.349

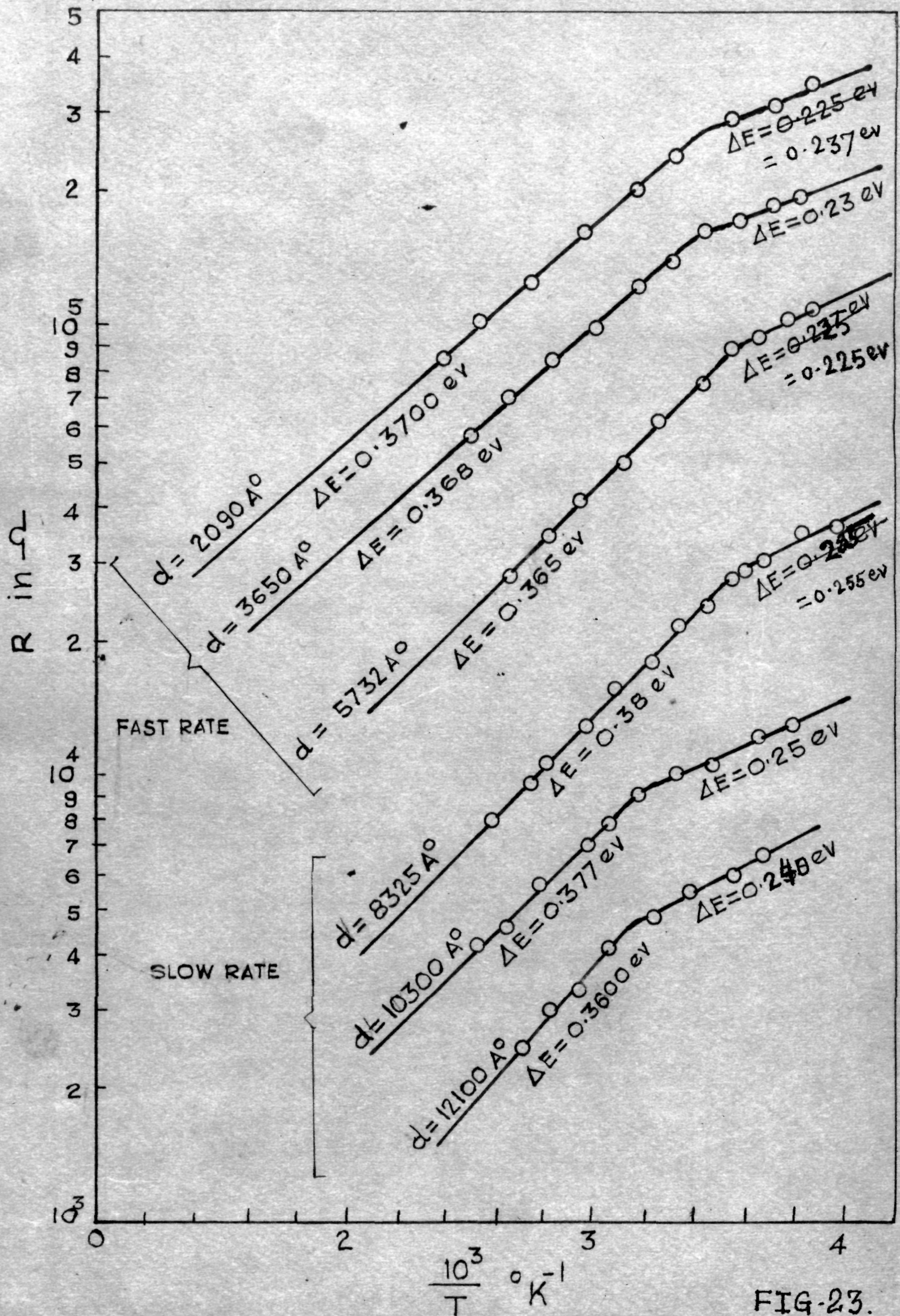


FIG-23.

i.e. the nature of the curve (log R *vs* 1/T) was independent of the rate of evaporation though the resistivities for different film thicknesses at the same temperatures were different for different rates of evaporation. Activation energy was also found to be affected a little with the rate of evaporation. It increased slightly with the decrease of the rate of evaporation and vice versa.

(b) Bismuth selenide films :- Preliminary experiments on resistance measurements with temperature showed some interesting features in log R *vs* 1/T curves, which were not present in case of Bi_2Te_3 and lead chalcogenides. A typical curve, (fig.24) showed that during the heating cycle the resistance decreased continuously with the rise of temperature up to a region slightly below the temperature of discontinuity. During the cooling cycle it was observed that the curves did not follow the heating path but continued in entirely a different one, nearly parallel to the 1/T axis (fig.24). If the resistance measurement was again carried out, it followed the cooling path provided the maximum temperature was more or less the same as before. If, however, during the initial heating cycle, heating was stopped at an intermediate temperature, the cooling curve again followed, depending upon the maximum temperature, a new path different from the heating curve. The typical curves for log R *vs* 1/T are shown in fig.25 for different maximum temperature of heating. In all cases, fresh heating curves followed exactly the previous cooling curves provided the maximum temperature was not exceeded.

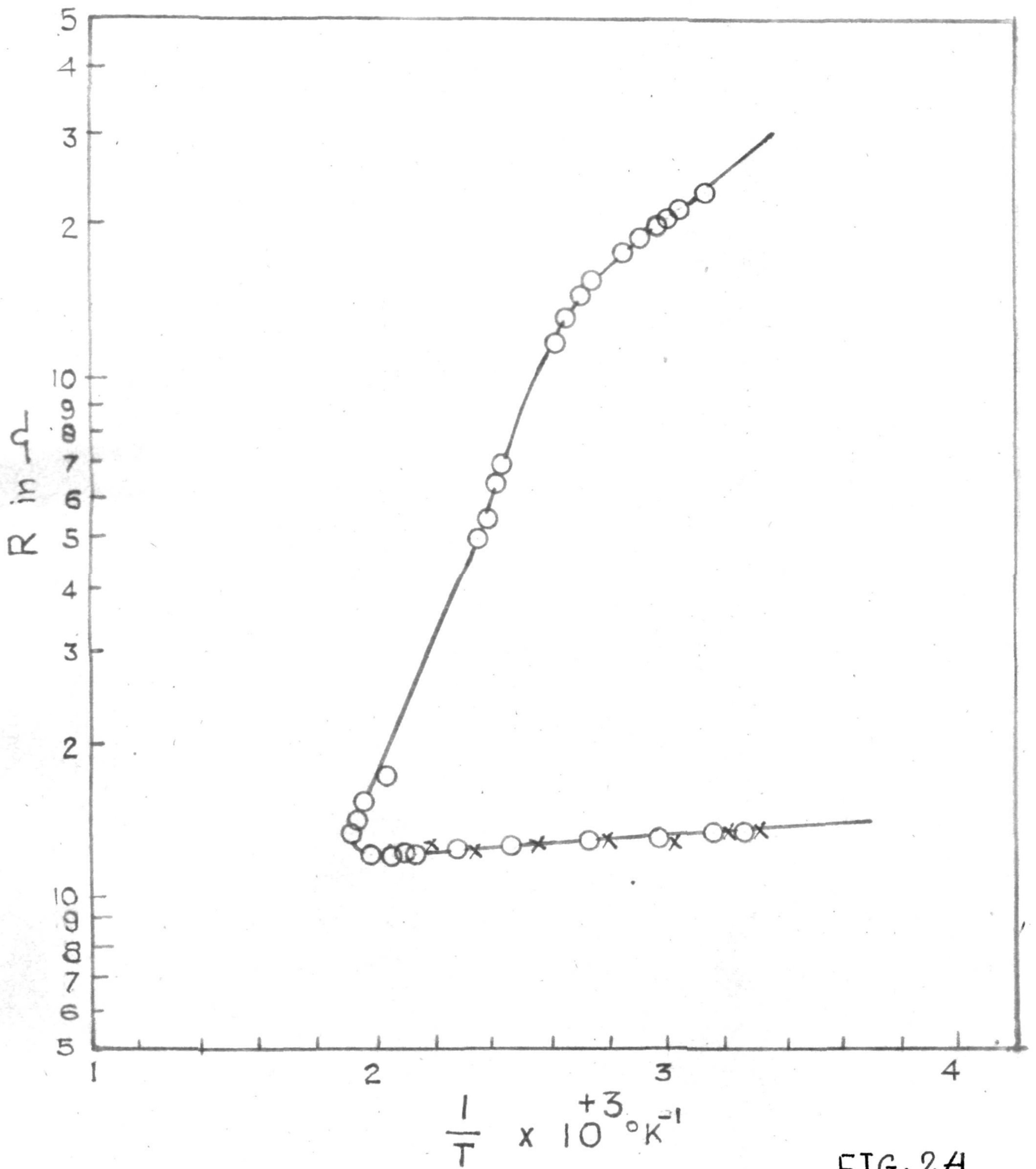


FIG. 24.

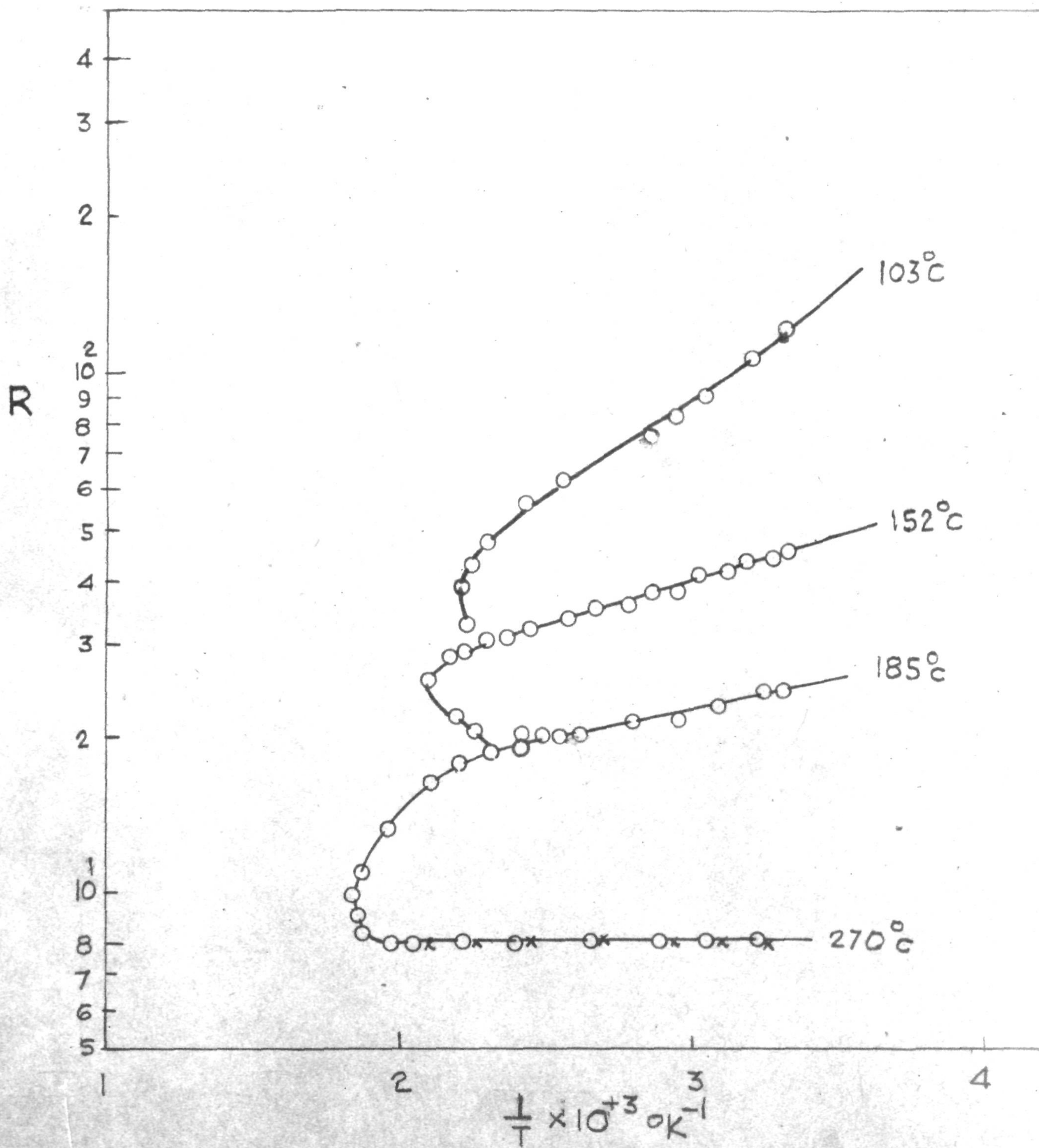


FIG-25.

It thus appeared that the cooling curve which more or less showed the effect of annealing was dependent eventually on the temperature o annealing. Since slopes also varied with this annealing temperatures, the usual annealing process carried out for other thin films was purposely avoided in the case of Li_2Se_3 films. The values of activation energy for different film thicknesses were measured over the temperature range 30°-$100^{\circ}C$. The table No.8 shows the variation of activation energy with the film thickness. It can be seen from the fig.25 that the slope of the cooling curve decreased with the increase of the maximum temperature of heating and finally approached to zero at about $250^{\circ}C$ as the resistance was practically constant during the cooling process from $250^{\circ}C$ to the room temperature. It can be seen from the above studies that once a cooling curve is obtained corresponding to the maximum temperature of heating the cycle will be repeatable provided the maximum temperature was not exceeded. This was confirmed by making eight or ten different runs below the maximum temperature of heating on the same film.

The activation energy for the same film in different temperature regions was calculated by using the expression (40). The results for (ΔE) for different temperature of maximum heating are presented in table No.9. The fig.26 for ΔE vs T_h indicates that the activation energy decreased with the increase of maximum temperature of heating. From the above

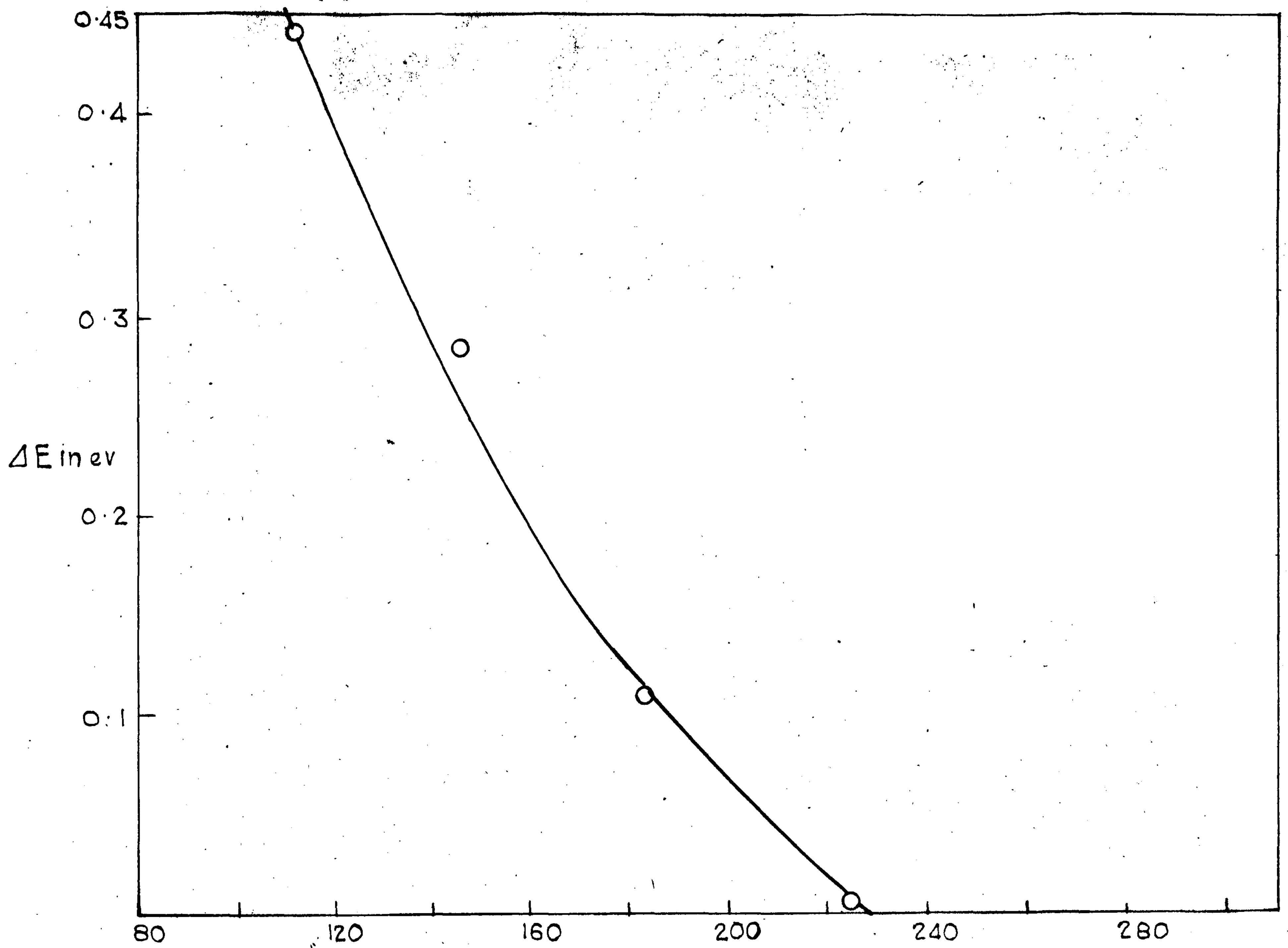


FIG-26.

figure, the rate of decrease of (ΔE) with the rise of maximum temperature of heating was calculated. The results are shown in table No.9. It was found that the rate of decrease of activation energy with the maximum temperature of heating was about 5×10^{-3} eV/°C in the temperature range 30°- 155°C and above 155°C it was found to be equal to 3×10^{-3} to 2×10^{-3} eV/°C.

(ii) <u>Thermoelectric power measurements</u>

Before preparing the films, the bulk materials were subjected to the thermoelectric test. The bulk material Bi_2Te_3 was found to be p-type whereas Bi_2Se_3 was showing n-type behaviour.

(a) <u>Bismuth telluride films</u> :- The measurements of thermoelectric power were made over the temperature range -18°C to 175°C. The fig.27 shows the typical curve for the variation of thermoelectric power with temperature. It indicates that ($\propto$) increased slowly with the rise of temperature and at about 125°C remained constant and then showed a decreasing tendency with the further rise of temperature as was observed in the case of PbTe films. The maximum value obtained for Bi_2Te_3 films was about 240 μV/°C. The table No.10 shows the magnitude of thermoelectric power at different temperatures for varying film thicknesses. Here again thinner films had higher values than the thicker films.

TABLE - 9

Maximum temperature of heating $^{\circ}K$	Activation energy (ΔE) eV
125	0.390
145	0.260
155	0.215
170	0.160
180	0.120
200	0.060
225	0.005

TABLE - 10

Bismuth telluride			Bismuth selenide		
Thickness	Temperature	α $\mu V/^{\circ}C$	Thickness	Temperature	α $\mu V/^{\circ}C$
7,500	25	162	9,300	25	80
	50	188		50	100
	75	204		75	112
	100	218		100	120
	125	228		125	120
13,300	25	132	15,700	25	74
	50	166		50	92
	75	187		75	100
	100	182		100	105
	125	186		125	105
22,000	25	120	24,120	25	72
	50	140		50	76
	75	152		75	78
	100	160		100	78
	125	167		125	78

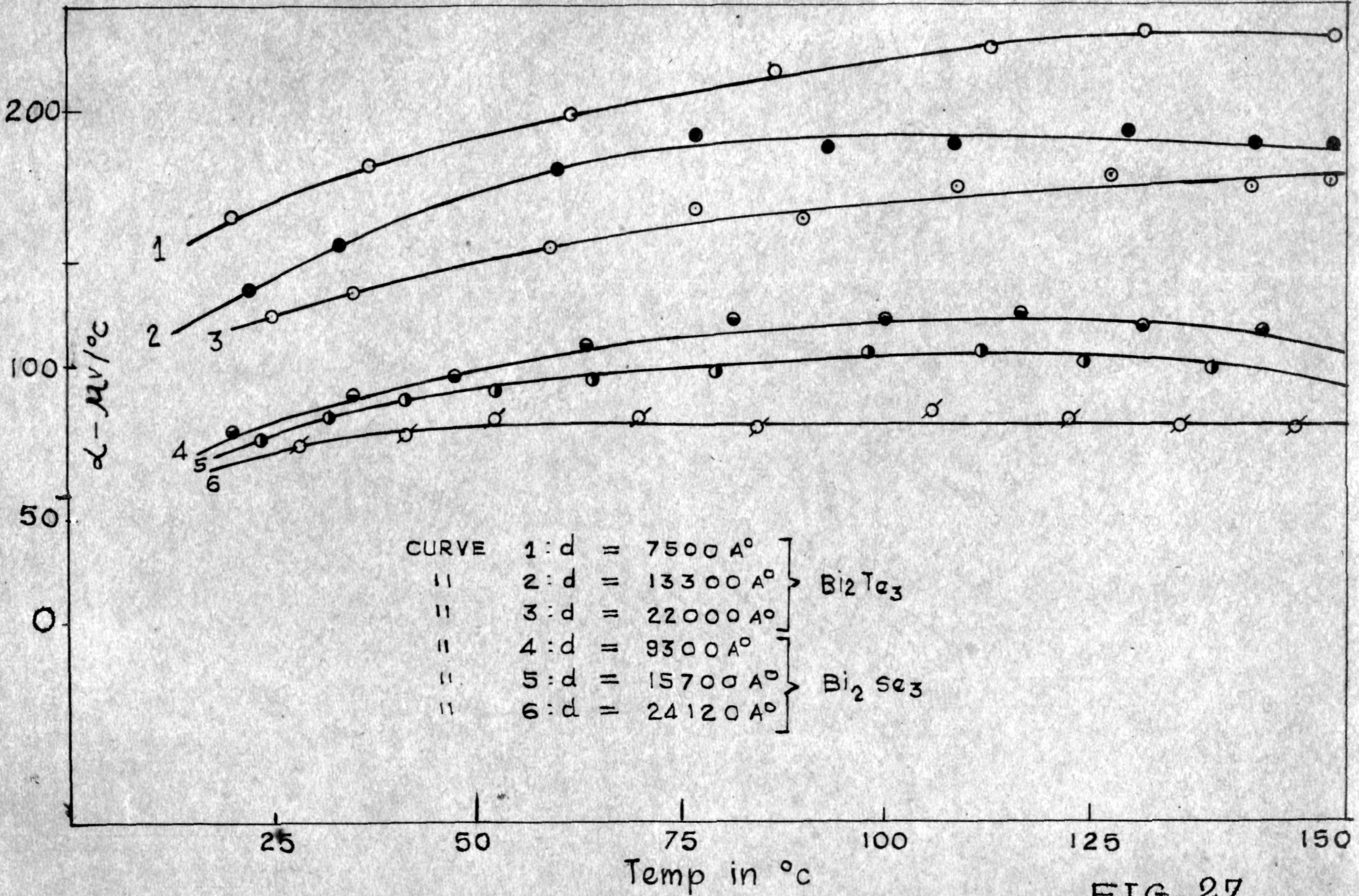


FIG-27.

All the Bi_2Te_3 films prepared by vacuum evaporation technique were found to be p-type over the temperature range studied.

(b) Bismuth selenide films :- The thermal e.m.f. generated due to the temperature difference between the two ends of the film was measured. The typical curve of thermal e.m.f. against temperature of the hot end shows a continuous rise of thermal e.m.f. with temperature up to the maximum temperature of our experiment. With a better control of temperature, no hysteresis type of loop was observed between the heating and cooling cycle. But the resistance measurements in different temperature range showed the irreversible changes. In order to see the effect of irreversibility on the thermal e.m.f. the film was first heated to certain temperature and measurements were made below this temperature. In a similar way the same film was heated at different temperatures and within those temperature ranges the thermal e.m.fs. were measured. The different typical curves for thermal e.m.f. vs temperature are shown in fig.28 which shows that the corresponding values of the thermal e.m.fs. decreased a little with the maximum temperature of heating. The thermoelectric power ($\propto$) was calculated at different temperatures in different temperature ranges. The fig.27 for $\propto$ vs T shows similar sort of variation with temperature as observed in case of Bi_2Te_3 films.

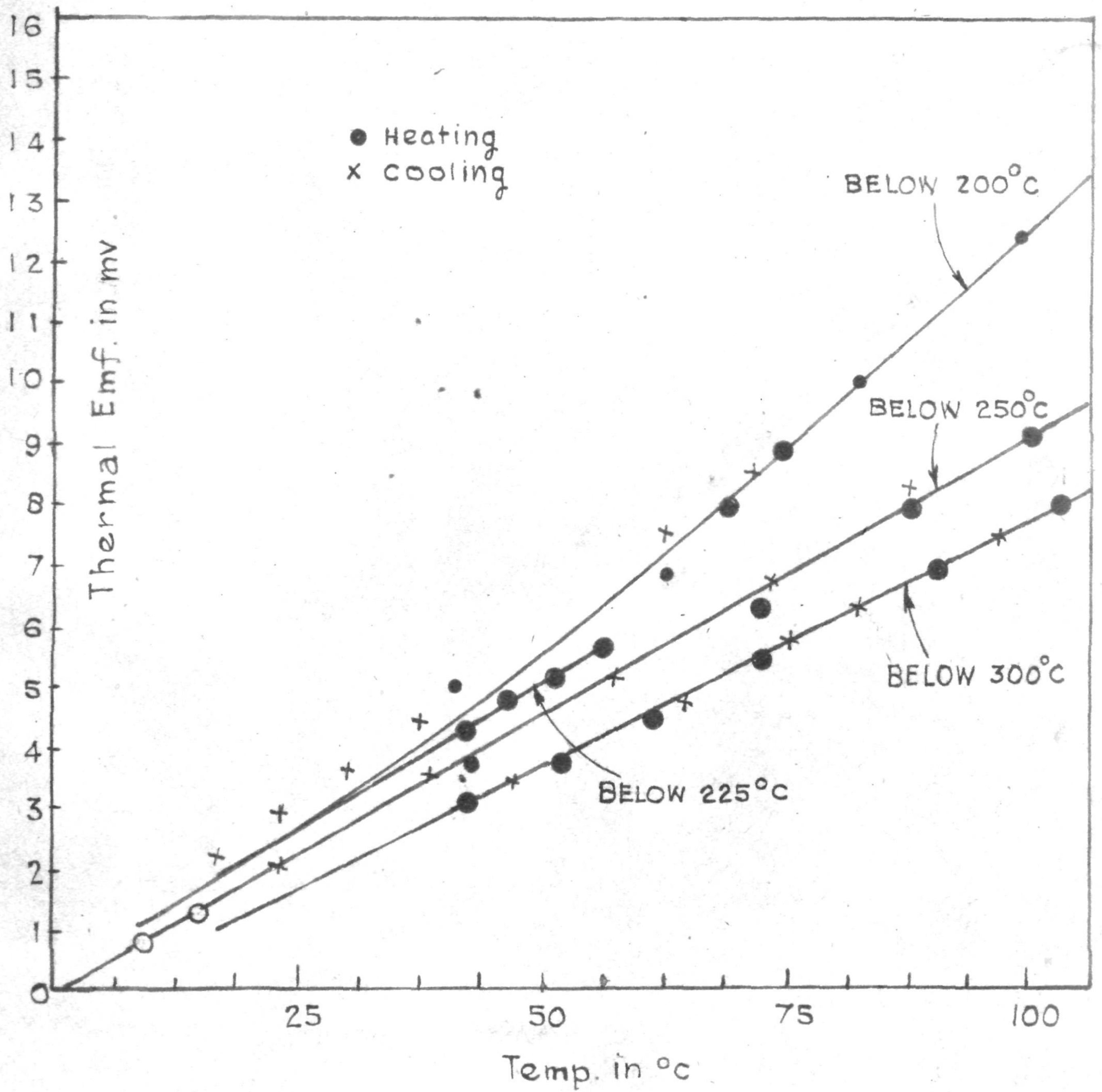


FIG. 28

The thermoelectric power in the same temperature region for different film thickness was calculated and results are shown in table No.10. The table shows that the thermoelectric power increased with the decrease of the film thickness. Normally, the value of (α) varied from 70 to 80 $\mu V/^{o}C$ for most of the Bi_2Se_3 films. All the films under investigation, were found to be n-type unlike Bi_2Te_3. This may be due to the presence of excess of selenium.

(iii) Temperature coefficient of resistance

This parameter for Bi_2Te_3 and Bi_2Se_3 films was measured in the usual way described previously (Chapter III). The temperature range was between 30° - $175^{o}C$. The fig.29 shows the typical curves for TCR *vs* temperature for Bi_2Te_3 and Bi_2Se_3 films and the results are shown in table No.11.

It is seen that TCR had a negative sign and its negative value decreased with the rise of temperature up to temperature $\simeq 60^{o}C$ for Bi_2Te_3 films. On further increase of temperature the negative TCR also increased up to the maximum temperature of our experiment which was less than the annealing temperature. For Bi_2Se_3 films, the smaller value of the negative TCR, however, occurred at temperature much lower than that of Bi_2Te_3 films.

It is of interest to mention here that even though measurement of the TCR for Bi_2Se_3 films was carried out before annealing the films' nature of the curves were similar to that of Bi_2Te_3. This has been confirmed in numerous specimens of Bi_2Se_3 films.

TABLE - 11

Bismuth selenide		Bismuth telluride	
Temperature °C	TCR deg^{-1}	Temperature °C	TCR deg^{-1}
30	1.02×10^{-2}	29.5	1.25×10^{-2}
35	0.92×10^{-2}	35.0	1.12×10^{-2}
43	0.66×10^{-2}	40.0	1.09×10^{-2}
54.5	0.56×10^{-2}	50.0	1.00×10^{-2}
63	0.53×10^{-2}	60.0	0.88×10^{-2}
73.5	0.54×10^{-2}	80.0	0.76×10^{-2}
97.5	0.60×10^{-2}	100.0	0.85×10^{-2}
-	-	120.0	0.97×10^{-2}
-	-	130.0	1.05×10^{-2}

TABLE - 12

BISMUTH TELLURIDE

Temperature °C	Mean free path (l_o) cm.
25	6.08×10^{-5}
50	5.97×10^{-5}
75	5.90×10^{-5}
100	5.57×10^{-5}
125	2.05×10^{-5}

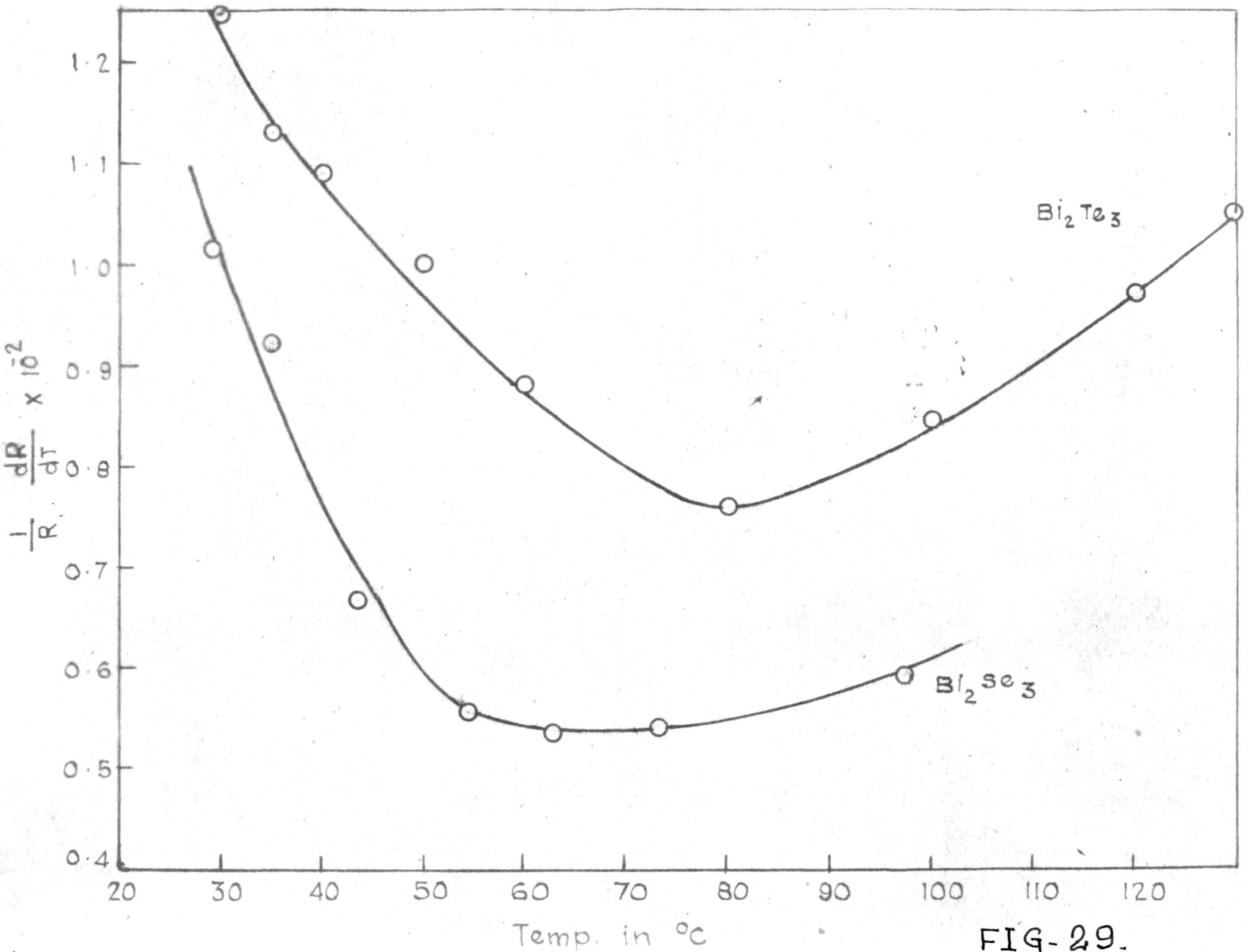


FIG-29.

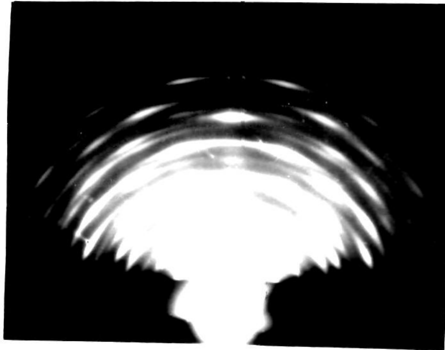


FIG - 31

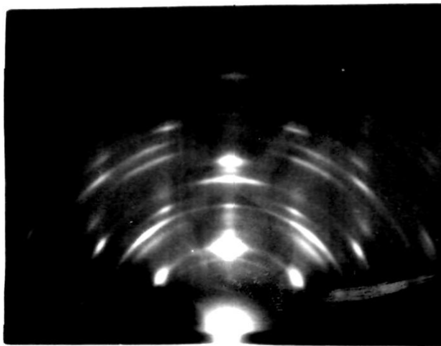


FIG - 32.

(iv) Mean free path

The mean free path of Bi_2Te_3 films was measured by employing the method previously used by Mayer (1959) as mentioned in the Chapter III.

The fig.30 shows the dependence of $\rho.d$ on 'd' at different temperatures. Though these curves show similar trend of results, the magnitudes of intercepts and ρ_{∞} at different temperatures were quite different. The table No.12 shows the value of mean free path at different temperatures. A typical curve for log (l_0) vs log (T) indicates that mean free path decreased with the increase of temperature obeying the law $T^{-\delta}$ where δ was found $\simeq$ 0.45. It was also found that the mobility obeys the law T^{-n}, where n = 0.95 i.e. $\mu \propto T^{-0.95}$.

Electron diffraction patterns were also taken from the deposits before and after measurements. The patterns obtained from the deposits after measurements were sharper than those for taken before measurements. This suggested an increase in the crystal size. The typical pattern for Bi_2Te_3 and Bi_2Se_3 are shown in figs.31,32.

D. Discussion

Resistivity and activation energy :- It has been observed during our present study that the resistivities at room temperature for Bi_2Te_3 and Bi_2Se_3 films were of the order of 0.1 to 0.05 ohm-cm. and 0.1 ohm-cm. respectively. These

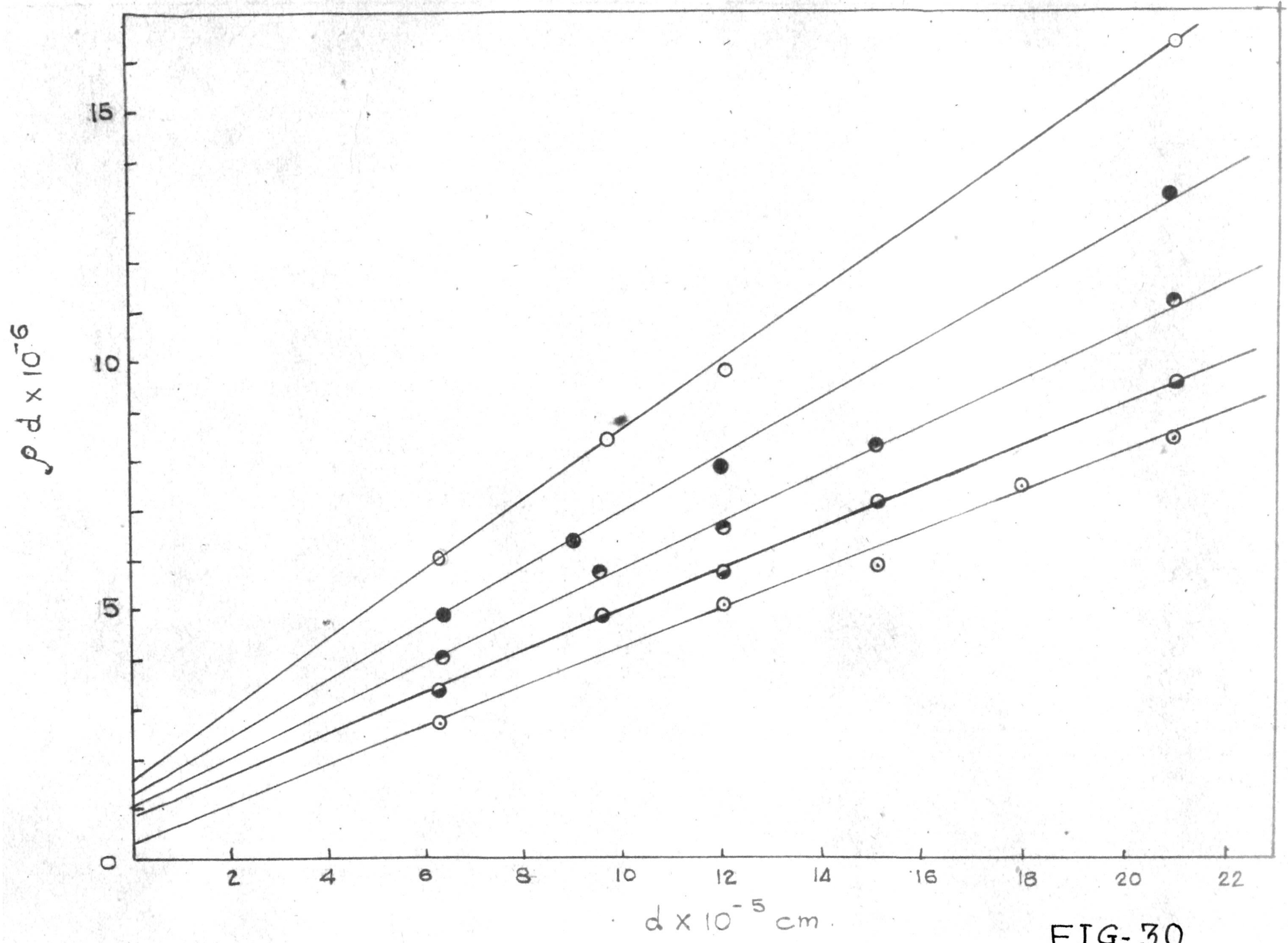


FIG-30.

values of resistivities were much higher than that of bulk as reported by many investigators (Blact et al., 1957; Joffe and Sti'bans, 1959; Knorov, 1956). Reasons for the higher resistivities in thin films have already been discussed in details in case of the chalcogenides of lead. The imperfections or defects etc. contribute generally to an increase of resistivities in thin films. It may be pointed out here that the conductivity of lead telluride and bismuth telluride films deposited at room temperature was of the same order for the same order of film thickness.

The general features of the curves, log R vs 1/T, for Bi_2Te_3 films above room temperature were similar to PbTe films. Below the room temperature the resistance, however, increased slowly with the decrease of temperature. A continuous fall in resistance with the increase in temperature as can be seen from fig.23, indicates the excitation of electrons from the valence band to the conduction band and also further ionization of the impurities. It is obvious from fig.23 that the intrinsic behaviour started above the room temperature. Below $30^{\circ}C$ all the films of Bi_2Te_3 studied showed extrinsic behaviour with an activation energy = 0.20 to 0.24 eV.

The resistivity data of Bi_2Se_3 films (fig.25) showed that certain transformation occurred in the films such that after a certain temperature irreversible changes in resistance were observed. This change was found to depend upon the maximum temperature of heating of films. Below this temperature

films were quite stable in the sense that the resistance measurements were reproducible. This peculiar behaviour of bismuth selenide films may be due to the dessociation of Bi_2Se_3 to BiSe. Electron diffraction study in this laboratory also confirms the above view (Dhere 1965). Owing to the removal of selenium from film during the heating process, the measurements of activation energy became difficult. The value of the activation energy at different points corresponding to the maximum temperature of heating was calculated. The results showed a wide variation in activation energy at different temperature range studied.

In case of Bi_2Te_3 films there were two different values of activation energy in two temperature ranges viz. (a) below room temperature and (b) above room temperature to the maximum temperature of experiment. In temperature region (b), the value for ΔE was found to vary from 0.3 to 0.39 eV and in (a) 0.20 to 0.24 eV over the thickness range 20,000 to 1,000 Å. Many investigators for example Black et al. (1957), Konorov (1956), Shigetomi and Mori (1956), Harman et al. (1957), Satterthwaite and Ure (1957) and Goldsmid (1958) reported 0.16, 0.3, 0.21, 0.16, 0.20 and 0.16 eV respectively for bulk Bi_2Te_3 at room temperature. It is interesting to point out that higher values of activation energy for thinner samples were also noticed by Black et al. (1957) in the case of bulk Bi_2Te_3. The values of activation energy observed in the present study on Bi_2Se_3 films, corresponded with those of Gibson and Moss (1950) for bulk Bi_2Se_3 with ΔE = 0.4eV. Hishimoto (1958) reported 0.35 eV for single crystals of Bi_2Se_3. The values of activation energy obtained in the present study would not only account for the energy required to excite an electron from the

valence band but also for the energy required to transfer an charge carrier from one neutral island to another and finally also for the energy required to anneal out some of the defects. As it has already been stated in the previous chapter, the activation energy is also affected considerably by the surface asperities. The higher values observed for thinner films could be explained on a similar line as discussed for lead chalcogenides films.

Thermoelectric power

The present study on thermoelectric power of thin Bi_2Te_3 films showed that the values obtained were slightly higher than that for the bulk material. It can be seen from the results that the Seebeck coefficient varied from 130 to 240 $\mu V/^{\circ}C$ over a temperature range 300°- $400^{\circ}K$. At higher temperatures, the thermoelectric power showed a little decreasing tendency. The continuous rise in thermoelectric power over the above temperature range might be represented by the relation, $\alpha = \frac{3}{2}\frac{k}{e}\ln T +$ const. It seems reasonable to suppose that the carrier concentration was constant viz. further ionization of impurities and electron-hole pair creation was not appreciable. Goldsmid (1958) observed similar sort of variation in thermoelectric power over a considerable range of temperature. The variation of thermoelectric power with temperature could be explained on a similar line as discussed in the case of lead telluride.

Since thermoelectric power depends greatly on the mobility which also varies with effective mass as given by

$$\mu \propto (m^*)^{-5/2}$$

From the above relation the variation of 'α' with temperature can be easily explained. Many investigators found that Seebeck coefficient varied from 170 to 210 $\mu V/^{\circ}C$ depending upon the nature of the material.

It is worth mentioning here that all the bismuth telluride films showed p-type behaviour as that of original bulk material. Depending upon the relative concentration of elements over the stoichiometric ratio 2:3, the type of materials will be determined. It is generally found that on exact composition 2:3 the material become p-type. Soonpaa (1964) suggested that the type of the material particularly of Bi_2Te_3, also depended upon the relative magnitude of lattice parameters viz. c/a ratio. In view of this suggestion, it will be worthwhile to carry out a detailed structural studies by electron diffraction and correlate the c/a ratio with the films characteristics.

Thermoelectric power measurements on Bi_2Se_3 films showed that the thermoelectric power was not constant over the temperature region studied. It decreased, however, with the maximum temperature of heating. The decrease in thermoelectric power might be due to the annealing out of the defects as mentioned before. Due to this, the effect of scattering mechanism

varies which affect the value of thermoelectric power though the value of it is not affected directly but through an energy dependent mean free path term in the thermoelectric power formulae. From resistivity and thermoelectric measurements in case of Bi_2Se_3 films, it can be safely concluded that, the degree of degeneracy increased with the increase of the maximum heating temperature. The present study showed that at room temperature thermoelectric power varied from 70 to 130 $\mu V/^{\circ}C$ depending upon the thickness of the film. According to Konorov (1956) and Black et al. (1957) thermoelectric power for bulk varied from 70-100 $\mu V/^{\circ}C$.

Temperature coefficient of resistance

The curve TCR vs temperature for Bi_2Te_3 and Bi_2Se_3 films, showed that it was neither a linear nor an independent of temperature. This behaviour could be explained on the basis of island structure model as discussed before. Simultaneous examination of equation (43) and the curve (TCR vs temperature) suggests that, the initial fall in the negative TCR up to about $55^{\circ}C$ to $+80^{\circ}C$ for Bi_2Te_3 and Bi_2Se_3 respectively might be due to the term C/T^2. Above these temperatures the contribution from the first term became appreciable and the effect of the term C/T^2 was completely swamped out. The present investigation on Bi_2Te_3 and Bi_2Se_3 films showed that the negative maxima were not clearly defined up to $175^{\circ}C$. A comparison with sulphide, selenide and telluride of lead showed that TCR was much more enhanced compared to Bi_2Se_3 and Bi_2Te_3 with temperature.

<u>Mean free path</u>

It is seen from the results that l_0 was found to be of the order of 10^{-6} cm. in Bi_2Te_3. The relation $\mu \propto T^{-n}$ was also found to be valid. It is interesting to note here that the value of 'n' was low ($n \simeq 0.96$). Goldsmid (1958), Shigetomi and Mori (1956) Vlasova and Stil'bans (1955), Satterthwaite and Ure (1957) reported the values of 'n' to be 1.94, 2.3, 2.5, 1.5 etc. respectively. These values indicate that the samples must have been in a degenerate state or had a large concentration of charge carriers i.e. $n > 10^{19} - 10^{20}$ cm^{-3}. The low value of 'n' might be depended upon the degree of degeneracy and the structure of the material under investigation.

CHAPTER - V

CRYSTAL GROWTH OF LEAD SELENIDE

A. Introduction

At present many workers are engaged in various parts of the world in the study of the optical and electrical properties of the films but relatively less attention is being paid to the nature of the films, their structure, crystal size and orientations etc. which are necessary for the understanding of their behaviour. Thin films because of their properties different from the bulk materials find wide slope of use in many fields especially in electrical devices and in optical instruments. The physical and electrical properties are completely dictated by the film structure. It is well known that the film structure is frequently quite different from the bulk as films commonly have a much higher defect density; sometimes they even have completely different crystal structure.

In order to see the effect of the structure and nature of the films on the electrical properties, an electron diffraction study was made on the lead selenide compound in detail and to some extent on lead telluride at different temperatures. The work done on physical, electrical and optical properties has already been reviewed in the chapter III.

Ramsdell (1925) reported NaCl type f.c.c. structure for lead selenide. Olshausen (1925) found the value of a_o = 6.162 Å and a_o = 6.14 Å (Goldschmidt' 1926). Lead selenide was reported to have NaCl type f.c.c. structure with a_o = 6.122 Å (A.S.T.M. 6 - 0356) and also a_o = 6.124 Å (A.S.T.M. 6 - 0354). Lead telluride was reported to have a hexagonal (NiAs type) structure with a_o = 6.439 Å (Ramsdell, 1925; Goldschmidt, 1926; Wyckoff, 1948). Feltynowski et al. (1955), from their electron diffraction study reported that the lead telluride has a f.c.c. structure with a_o = 6.36 Å. According to Feltynowski (1958), the lead telluride has a simple cubic structure with a_o = 6.21 Å (by electron diffraction method) and a_o = 6.34 Å (by X-ray study).

Recently Semilov et al and Voroniva (1965) have also studied the structural and electrical properties of lead telluride single crystal films. The epitaxial growth on mica has been studied by Yoshimi Makina (1964).

From the above survey it will be seen that not much work has been carried out on the epitaxial growth of PbSe and PbTe on the different faces of rocksalt. In the following study has been undertaken on the crystal growth process of PbSe on the different faces of NaCl.

B. Experimental

(a) Preparation of specimens :- The deposited films were prepared by vacuum evaporation technique. The apparatus as

shown in fig.33 consisted of a wide pyrex glass tube about 30 cms. in length, with rubber stoppers at two ends and two copper electrodes to heat the filament were inserted through one of the stopper. The tube was evacuated by a rotary oil pump through the other end. The ultimate vacuum obtained was of the order of 10^{-3} mm Hg. Substrates were generally placed at about 5-6 cms away from the filament. The substrates were heated to the required temperature by a tubular furnace which could be slided over the pyrex tube. In order to avoid the surface contamination the filament was initially flashed to white hot. When cooled the materials to be evaporated were put into it. When the substrates attained the required temperature the deposition was carried out by raising the temperature of the filament. The deposits were then cooled in vacuo, removed and examined by electron diffraction technique in the usual manner.

The filaments were in the form of basket and prepared from kanthol or tungsten wires. The current used for heating the filament was controlled by a variac. The temperature of the films during deposition was measured by a suitable thermometer.

(b) <u>Preparation of substrates</u> :- The substrates used in the present investigation were (100), (110) and (111) faces of rocksalt crystals and amorphous glass pieces.

FIG - 33.

The (100) face was obtained by cutting single crystal with a clean and sharp edged knife by applying a little pressure along the cube edge direction. The untouched cleared surfaces were then used as substrates.

The (110) and (111) faces were prepared by grinding the crystals at appropriate angles with different grades of emery papers down to 0000. These were then etched in running distilled water, dried between clean filter papers and examined by electron diffraction technique. If necessary, they were reground and re-examined to get the necessary faces.

(c) Examination of specimens and interpretation of electron diffraction patterns

The specimens were examined both by reflection and transmission methods. The electron diffraction patterns were interpreted in the manner discussed by many workers (Finch and Wilman, 1937; Thomson and Cochrane, 1939; Beeching, 1936; Wilman, 1948a and 1949, 1948b, 1952; Pinsker, 1953 etc.) and hence are not given in detail.

The diffraction patterns obtained can be grouped in as follows: (1) Patterns due to single crystals or two-degree orientated deposit crystals mostly consisting of spots, (2) Ring patterns due to polycrystalline nature of the deposits, and (3) Reflection patterns consisting of arcs which did not change on the change of beam direction were due to one degree orientated deposits.

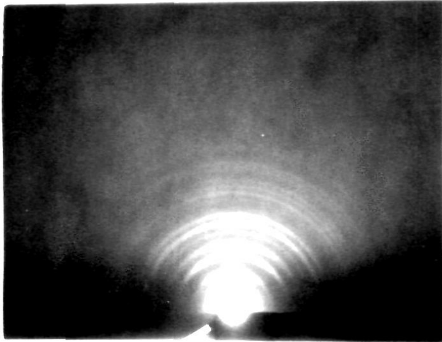


FIG. 34.

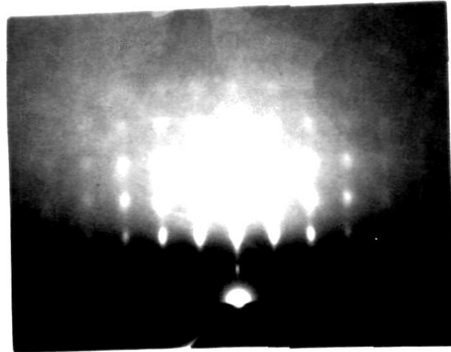


FIG-35.

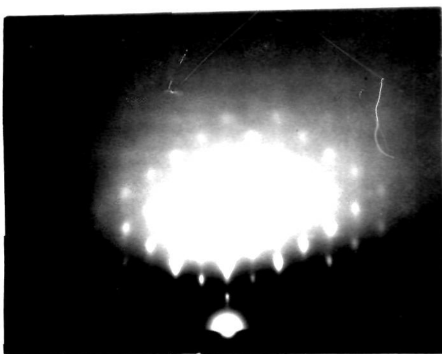


FIG-36.

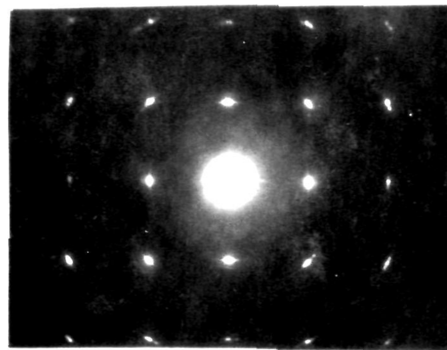


FIG-37

C. Results

(a) Lead selenide films

(i) On rocksalt

On (100) face : The deposits of lead selenide formed at different substrate temperature, on rock-salt cleavage face were studied in detail. The deposits at room temperature were polycrystalline in nature. The pattern (fig.34) was sharp consisting of reflections having either all odd or all even indices indicating thereby that the deposits developed a f.c.c. structure. The lattice parameter as was found to be a_o = 6.1 Å. Patterns obtained by reflections from deposits formed at 150°C consisted of spots as well as rings. The deposits with beam direction along ⟨100⟩ yielded a square type of arrangement of spots (fig. 35). The patterns, however, changed on rotation of the specimen such that 200, 400 reflection etc., and their higher order reflections were always in the plane of incidence in all cases. This suggested that the deposits developed 2-d(100) orientation. The pattern (fig.36) which beam along the cube face diagonal of the substrate showed centered $\sqrt{2}$ type rectangles which was in confirmation with the above view. Thus the deposits grew with parallel orientation. Similar results were also obtained in the case of deposits formed at 200°, 250°, 300°, 350° and 400°C. The pattern (fig.37) was obtained by transmission from the deposit formed at 400°C. The square type of arrangement of the spots clearly showed the formation of 2-d {100} orientation.

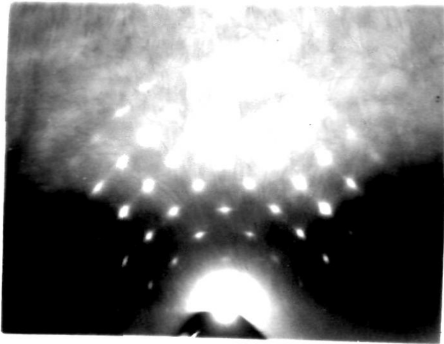


FIG-38

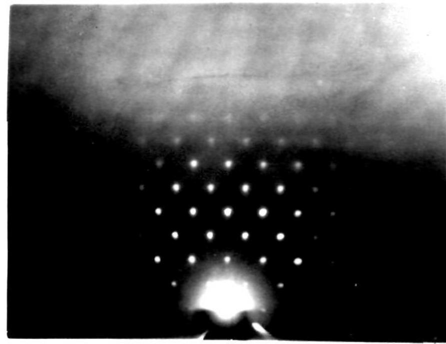


FIG 39.

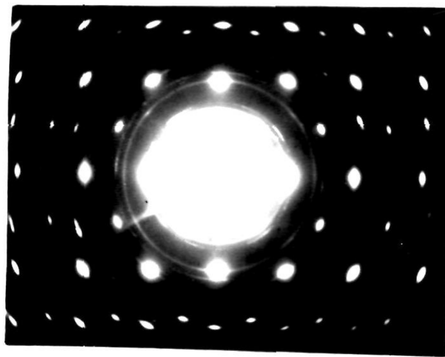


FIG-40.

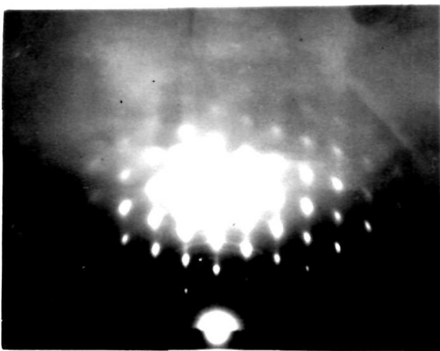


FIG-41.

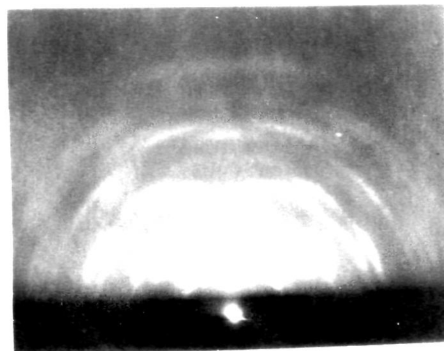


FIG-42.

<u>On (110) face</u> : Deposits on (110) rocksalt at room temperature were polycrystalline in nature. The deposits formed above 160°C gave sharp spots due to the increase in the size of crystallites.

From a close examination of the reflection pattern (fig.38) it is seen that the pattern consisted of square type of arrays of spots when the beam direction was along 100 of the substrate. The appearance of 220, 440 etc. reflections in the plane of incidence suggested the formation of 2-d $\{110\}$ orientation such that $\langle 100 \rangle$ of deposit $\langle 100 \rangle$ substrate. The above interpretation was found to be consistent with the pattern (fig.39) corresponding to the beam direction along $\langle 110 \rangle$ and also when the beam was also $\langle 111 \rangle$ of the materials. The corresponding transmission pattern (fig.40) showed an arrangement of spots 000, $2\bar{2}0$, $2\bar{2}2$ and 002 reflections and their higher orders forming rectangular network with $1\bar{1}1$, $3\bar{3}1$ etc. reflections at the centers of the rectangles. It is consistent with the reciprocal lattice for $\langle 110 \rangle$ axis of the deposits of crystals and hence the deposits developed 2-d $\{110\}$ orientation on NaCl (110) face.

<u>On (111) face</u> : The deposits formed at room temperature also showed the polycrystalline nature. At higher temperature the deposits gave sharp spot pattern (fig.41).

The pattern shows that the deposits grew epitaxially with 2-d {111} orientation, as 111, 222 etc. reflections were present in the plane of incidence. The asymmetric nature of the arrangement of spots suggested the parallel or anti-parallel orientation developed by the deposits.

(ii) <u>On glass</u> : The deposits formed on glass at room temperature were polycrystalline in nature. At about 200°C the deposit yielded patterns (fig.42) which remained unchanged even with the change of the beam direction. This suggested the formation of one degree orientation. It is seen that the reflections in the plane of incidence were 200, 400 and their higher order thereby suggesting the formation of 1-d {100} orientation were also obtained in case of deposits formed at 300°C. In this case the degree of orientation is more perfect than from deposits formed at lower temperature.

<u>Lead telluride</u> : The deposits formed at different substrate temperature on glass showed the similar orientation as observed in case of lead selenide films.

D. <u>Discussion</u>

The results on the evaporated films of lead selenide showed that these grew epitaxially on single crystal substrates such as NaCl, at higher temperatures but they had a tendency to be randomly disposed at or near about the room

temperature. It is well known that the atoms in vapour phase when start depositing on the substrate condense and try to occupy the positions which correspond to the minimum potential energy configuration provided the mobilities of the atoms are sufficient. At higher substrate temperature, they get sufficient mobility to arrange themselves in positions which correspond to the ideal position of minimum potential energy state. At lower substrate temperatures they would not have sufficient time to take up the ideal position and hence remain on the sites in the immediate neighbourhood of the deposition position. In the above cases it is seen that at higher temperatures the deposits had tendency to develop parallel orientations on all three faces of rocksalt. The orientation and the azimuthal directions were as follow :

$\{100\}$ $\langle 001 \rangle$ // (100) $\langle 001 \rangle$ NaCl
$\{110\}$ $\langle 001 \rangle$ // (110) $\langle 001 \rangle$ NaCl
$\{111\}$ $\langle 110 \rangle$ // (111) $\langle 110 \rangle$ NaCl

Lead selenide deposits developed perfect one-degree 100 orientation on glass above 150°C. The deposits formed on glass at room temperature showed the polycrystalline nature. At medium temperature, the presence of many rings in addition to the spots suggested an 1-d $\{100\}$ orientation.

The higher mobilities and lower resistivity of the films formed at higher temperature in case of lead telluride films were must be due to the increase in crystal size and annealing out of the some of the defects.

SUMMARY AND CONCLUSIONS

The present systematic study on the semiconducting properties of thin films of varying thicknesses on several semiconductors has shown some features not present in the bulk materials. Further the measurements of semiconducting parameters in thin films have been standardised for the first time and effects of various factors, such as thickness, rate of evaporation, substrate temperature on the different parameters viz. resistivity, thermoelectric power, Hall coefficient, TCR, mean free path etc. have been emphasised. The size effects, imperfection of surface asperities, higher concentration of defects which control the thin film properties in the same way as impurities in bulks have been established. Studies of surface structure simultaneously by electron diffraction in all the specimens, however, served as a control to correlate the semiconducting and structural properties. The change of resistivity with temperature of substrates opened up a new possibility of changing conductivity and hence a control in the electron transport process.

From the results, it can be seen that the films of lead and bismuth chalcogenides had lower conductivities, higher activation energies, higher thermoelectric power,

lower mobilities, rapid variation of temperature coefficient of resistance and variable Hall coefficient depending on the thickness of the film than those obtained for bulk materials. For all materials studied the resistivity decreased with an increase of film thickness and finally becoming nearly constant with greater thickness. The resistivity was also found to decrease with the rate of evaporation and substrate temperature during the growth of the film. The resistivity (ρ) normally observed was varying from 1 - 0.1 (PbS), 1 - 0.05 (PbSe), 0.1 - 0.01 (PbTe), 0.5 - 0.05 (Bi_2Se_3) and 0.5 - 0.01 (Bi_2Te_3) depending upon the thickness of the film. Lead sulphide and lead selenide showed considerable adsorption phenomena especially when exposed to atmosphere unlike lead telluride, bismuth selenide and bismuth telluride films. The activation energy was found to be 1.2 - 1.6 (PbS) at high temperature; 0.7 - 0.9 (PbSe); 0.22 - 0.44 (PbTe); 0.20 - 0.38 (Bi_2Te_3) and for Bi_2Se_3 0.29 - 0.45 eV, for various film thicknesses, the thinner films however giving higher values. Increase in the values of activation energy for films compared to bulk appeared to be associated with island structure and surface asperities etc. The thermoelectric power (α) varied similarly with thickness thus 150 - 375 (PbS); 340 - 450 (PbSe); 300-400 (PbTe); 140 - 200 (Bi_2Te_3) and for Bi_2Se_3 60 - 100 $\mu V/^{o}C$, but not much affected by the rate of evaporation and substrate temperature. An interesting feature in the thermoelectric

power of PbS and PbSe at higher temperatures ($\simeq 135^o - 200^oC$) was the change of positive value of '$\propto$' to negative one with the rise of temperature and its reversible character on cooling. This was, no doubt, related to the higher electron mobility over the hole mobility. Hall coefficient and hence the carrier concentration (n) for PbTe also varied with the film thickness and the evaporation conditions especially with the substrate temperature. Thicker films yielded higher values. All the films of PbS, PbSe, PbTe and Bi_2Te_3 were found to be p-type whilst Bi_2Se_3 showed n-type behaviour. The carrier concentration for PbTe and Bi_2Te_3 was $\simeq 2 \times 10^{17} - 5 \times 10^{17}$ cm^{-3} and $1 \times 10^{19} - 5 \times 10^{19}$ cm^{-3} respectively. The mean free path (l_0) calculated from the resistivity measurements was found to be of the order of 10^{-5} cm. in most cases. The mobility of PbTe films was found to vary from 5 to 12 cm^2/volt-sec. at room temperature and increased with the substrate temperature mainly through the conductivity factor. The relation $\mu = \mu_0 T^{-n}$ was found to hold good for lead and bismuth chalcogenides, and the values of 'n' were 2.95, 4.5 and 0.95 for lead telluride, lead selenide and bismuth telluride films respectively. For bulk material 'n' was found to be 2.5 for lead compounds and 1 - 1.5 for bismuth telluride. The negative TCR values changed with temperature passing through minima and maxima. The greater values of resistivity and reduced values of TCR suggested the utilization of these films in fabrication of resistors and building up microcircuitary.

The above studies on the semiconducting properties of thin films showed that the parameters observed for bulk material cannot be applied to the thin films. Further none of the theories can give complete account of characteristics observed in thin films. To explain satisfactorily one has to consider surface features, defects etc. which are peculiar to films. It is only these theories will be amenable to experimental verifications.

--x-x--

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