CHAPTER – 5

ELECTRICAL PROPERTIES

CHAPTER-V

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I. INTRODUCTION :

A semiconductor is often defined as having an electrical conductivity intermediate between that of an insulator and a metal. The properties of semiconductors which are generally termed as their electrical properties include (1) Electrical conductivity, (2) The Hall coefficient which determines the carrier density and type (3) Hall mobility of the charge carriers under the influence of transverse electric field and magnetic field (4) Magnetoresistivity whereby semiconductors change their resistance when subjected to magnetic field. (5) The thermoelectric power in which a temperature difference maintained between the ends of the specimen gives rise to an EMF across the two ends. Among these, the electrical conductivity is the most basic and commonly measured property. The electrical conductivity of the vacuum deposited and heat treated thin films can give important information regarding the defect structure and density of defects present in the as-grown thin films and can throw light on the changes that take place during annealing process in the film. It is also possible to study the influence of deposition parameters on the defect density and structure of thin films by the conductivity measurement.

Bi_2Te_3 is a p-type semi conductor. At room temperature, the thermoelectric power perpendicular to the C - axis is 218 μV/k [3]. Its electrical resistivity is about 1.6×10^{-5} ohm. m[3]. At room temperature, the Hall coefficient and carrier concentration are 0.42×10^{-6} m^3/A.sec. and 1.75×10^{25} m^{-3}, respectively [3,4]. Electrical conductivity and thermoelectric power of its thin films increase with thickness and attain constant values of 0.3×10^5 ohm^{-1} m^{-1} and 200 μV/K, respectively, for thickness above ~2000Å[5]. The thickness dependence has been explained in terms of size effect. The absolute values of TCR and activation energy are 40×10^{-4} $°C^{-1}$ and 0.0287 eV, respectively[5]. Anisotropy of carrier density and its composition dependence in $Bi_{2-x}In_xTe_3$ has been studied by Kutasov et al [6], Horak et al[7].

Whereas an ample study can be found reported in literature on the transport properties of pure Bi_2Te_3 crystals and thin films, there are scarce reports so far on transport properties of doped Bi_2Te_3 crystals and thin films. The results obtained of measurements of transport properties of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ crystals and thin films carried out by the author are presented below, following a general overview of the phenomena involved.

II. GENERAL DISCUSSION :

According to quantum theory, electrical conduction in metals is due to electrons, while electrical resistivity results from the scattering of these electrons by the lattice. Because of their wave nature, electrons can pass through a perfect lattice without any attenuation. Actually no lattice is perfect. Electrons always undergo some scattering as they travel through a solid; the average distance that they travel between successive collisions being called the mean free path (mfp)[9]. Bloch showed that the mfp of an electron travelling through a perfect rigid lattice is infinite. In other words the electron can move without resistance in a perfect lattice. But lattice imperfections present in real samples give rise to electrical resistivity. Impurity atoms, vacancies, dislocations, grain boundaries and stacking faults are static defects while the dynamic imperfections are due to thermal motion of the atoms in the lattice. The vibrational modes of atoms are quantized and are called phonons. The number of phonons in a given lattice increases with temperature causing increasing electron-phonon collisions with increasing temperature and hence the resistivity increases according to the relation

$$\rho_o = \rho_{ph}(T) + \rho_i \qquad \text{........1}$$

where ρ_o = total resistivity, ρ_{ph} = temperature dependent resistivity due to phonons and ρ_i = resistivity due to impurities.

Normally the dimensions of bulk conductors are of several orders of magnitude larger than the mfp of conduction electrons. Hence the number of surface collisions are very small compared to the total number of collisions taking place in the bulk. However, the surface collisions cannot be neglected if one or more dimensions of the conductor approaches to or are less than the mfp, as in the case of thin films. Polycrystalline films are made up of small single crystals in contact with one another. Except for the size, the crystallites in polycrystalline films should be similar to larger single crystals. However, the additional scattering due to grain boundaries will reduced the effective carrier mobility compared to the bulk value and hence the measurements of electronic properties of films should yield results which represent the average of contributions of the crystallites and the grain boundaries as well as the average of anisotropies of the randomly oriented grains. As the size of the grains becomes smaller, the role of the grain boundaries becomes more important and the material begins to resemble an amorphous solid. Thus, an estimate of the maximum possible contribution to the resistivity from the grain boundaries may be arrived at by considering the resistivites of liquid metals. In the case of films, electrical resistivity depends on the growth stages the films undergo while being deposited and the films may be granular or island-like porous (network) or continuous. Each stage has its characteristic electrical properties.

Electrical conductivity of a granular film is of many orders of magnitude smaller than that of the bulk material. As the thickness of film becomes comparable in magnitude with the mfp of the carriers, the film boundaries impose a limitation on the movement of the carriers and thus the effective value of mfp. Physical effects arising because of this geometrical limitation on the mfp are termed as "mean free path" or "size" effects. Size effects in a film can also be studied by varying the mfp instead of the film thickness. This is achieved by a study of the temperature dependence of the film resistivity. At low temperatures, $T < \theta_D$, where θ_D is the Debye temperature, the mfp of the electrons in thin films may not be the same as that in the bulk. Further, because of the longer free path available at low temperatures, small angle electron phonon scattering becomes very effective.[10]

In the case of semiconductors, in the intrinsic range of temperature, the density of conduction electrons increases with temperature. This is because of the thermally activated transition of more and more electrons from donor levels to the conduction band or holes from the acceptor levels to the valence band. The energy required for this process is known as the resistivity activation energy. The conductivity is found to vary exponentially with the increase of temperature. The smaller the size of the particles (grains), the greater is the activation energy. The larger the distance between the particles, (i.e. the thicker is the grain- boundary) the lower is the tunneling probability.

In both the cases, the conductivity is lowered. The size of the particles and inter-particle separation are generally relatively greater for a lower melting point of the deposit material, a higher substrate temperature and a smoother substrate. Thus, given the deposition conditions, one can predict the conduction behaviour of granular films.

Many conventional methods for measuring resistivity are unsatisfactory for semiconductors because many metal-semiconductor contacts are usually rectifying in nature. Also there is generally minority carrier injection by one of the current carrying contacts. An excess concentration of minority carriers will affect the potential of the contacts and modulate the resistance of the material. The four probe methods overcome these difficulties and also offer several other advantages. They permit measurements of resistivity in samples having a wide variety of shapes, including the resistivity of small volumes within bigger pieces of the semiconductors. In a single crystal material, the resistivity may vary smoothly from point to point. Often, however, it is conventionaly stated that it is constant within small percentage and when the variation does in fact fall within this tolerance, it is ignored. Soldered probe contacts may disturb the current flowing in the sample, shorting out part of the sample and add to the ambiguity in the measurement of the probe spacing. Soldering directly to the body of the sample can affect the sample properties by heating and by contamination.

The thermoelectric power or thermal e.m.f. α is determined from the potential difference V produced when the semiconductor is placed between two metal contacts with a known temperature difference (T_1-T_2). The thermoelectric voltage V depends on the properties of the two materials in contact, but the absolute thermal e.m.f.s. for semiconductors are so much larger than for any pure metal, that the result is little affected by changing the metal contacts. Almost any metal can be used to determine the sign of the thermal e.m.f. The thermal e.m.f. α is a function of temperature, so temperature differences of about 10°C should be used, with the mean temperature covering a wide range. In many semiconductor samples α changes in sign from part to part, so we must be able to measure at least the sign of α using very small volumes. A pointed copper rod, kept at a fixed temperature by means of an electric heater and brought into contact with the semiconductor, can be used. The other electrode remains at room temperature and is placed at some distant point on the specimen. The sign of the potential difference is then determined by the properties of the small area heated by the point.

The thermal e.m.f. α also depends strongly on the carrier concentration n and the electrical conductivity σ ; α and σ are related by

$$\alpha = A - B \log \sigma$$

α varies with n from a few tenths of a μV per °C to 1000-1500 μV per °C in certain semiconductors; α also depends on the scattering mechanism and on the effective mass m^*.

The thermoelectric power was calculated using the formula[11].

$$\alpha(T) = \Delta V(T)/\Delta T \qquad \ldots\ldots 2$$

where ΔT is temperature gradient and $\Delta V(T)$ the thermo E.M.F. at absolute temperature, T.

For determining the carrier concentration normally the Hall effect is used. When a conductor is placed in a magnetic field perpendicular to the direction of current flow, a field E_y is developed across the specimen in the direction perpendicular to both the current, J_x, and the magnetic field, H_z. The field, called the "Hall field", is given by

$$E_y = \frac{J_x H_z}{ne} \qquad \ldots\ldots 3$$

where J_x is the current density and n is the number of carriers per unit volume. Thus the Hall field is proportional to the product of the current density and the magnetic flux density. The proportionality constant, R_H, known as the Hall coefficient is given by

$$R_H = \frac{E_y}{J_x H_z} = \frac{1}{ne} \qquad \text{.......4}$$

The product of Hall field and width of the film (i.e. dimension parallel to the field) is known as the Hall voltage. A measurement of the Hall voltage for a known current and magnetic field yields the value of carrier concentration. The measurement of the sign of the Hall voltage is a common technique for determining if the sample is p-type or n-type.

The carrier density (p) in the extrinsic region has been calculated using the relation [12].

$$P = \frac{3\pi}{8 R_H e} \qquad \text{.......4}$$

where R_H is the room temperature Hall coefficient and e is the electronic charge. The mobility, μ, of the charge carriers was determined from the relation [13].

$$\mu = 1/p\rho e \qquad \text{.......5}$$

where ρ = room temperature resistivity.

III. EXPERIMENTAL RESULTS :

A. Resistivity of the crystal and thin films :

Valde's four probe method has been used for the measurement of electrical conductivity of the crystals. The advantage of this technique is that one can use samples of any arbitrary shape. The problems of contact resistance, heating effect and contamination are avoided by using the four collinear pressure contacts on the surface. A schematic of the contact array is shown in Figure – 1.

A freshly cleaved sample with thickness approximately 0.5 mm was kept on the base plate of the sample holder. The four probes were allowed to rest under spring pressure on the middle of the sample. The current was adjusted to a desired constant value, I, through the two outer probes and the corresponding voltage, V, across the inner pair was measured. The whole set up was kept in an oven. The rate of heating was kept at about 5°C/min. The temperature was sensed by a thermometer of least count 1°C. The average distance between the successive probes was 2 mm. The resistivity is then calculated as :

$$\rho_0 = \frac{V}{I} \times 2\pi S \qquad \ldots\ldots 4$$

where, S = mean probe separation, ρ_0 = resistivity. Since the sample thickness was not too larger than the probe separation, a correction factor has

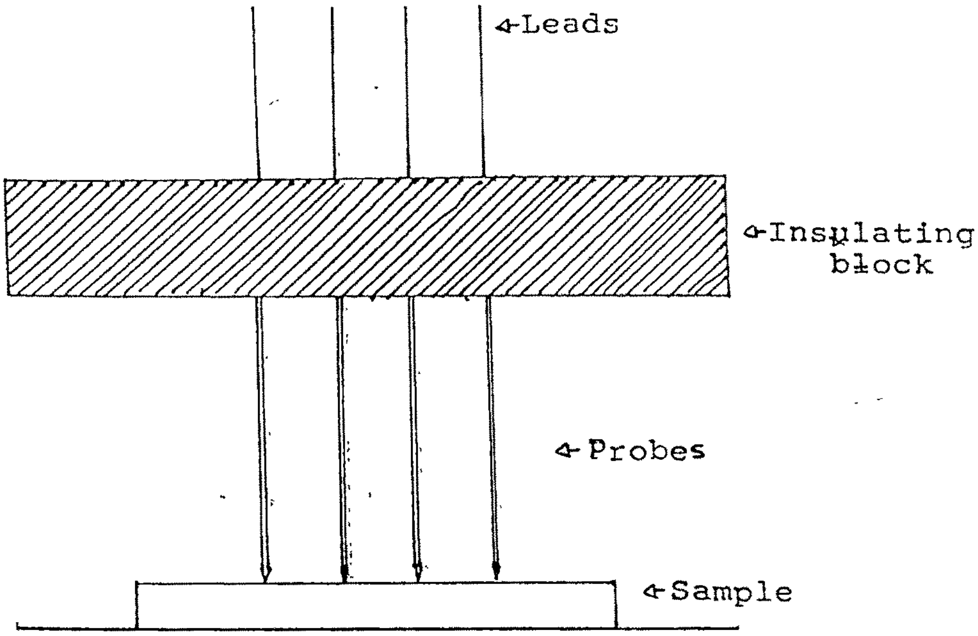

Figure - 1 : A schematic of the contact-array in Valde's set up.

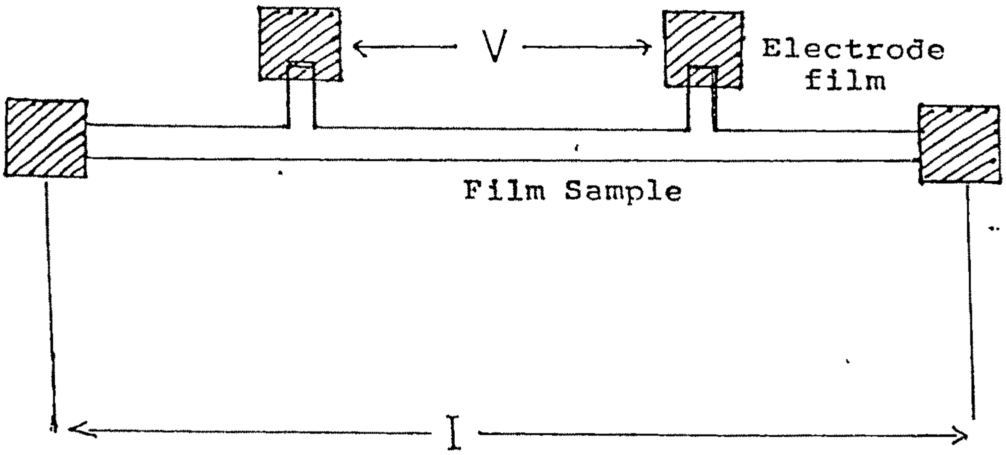

Figure - 2 : Linear four probe geometry.

to be applied giving resistivity to be

$$\rho = \frac{\rho_0}{G_7(w / s)} \qquad \text{.......5}$$

where, w = thickness of the sample and the correction factor G_7 (w / s) was obtained from the table for the appropriate value of (w/s)[1].

In the case of the thin film, since the resistance is usually high, Van der Pauw[13] method is not practical due to very small value of voltage which cannot be measured accurately using a microvoltmeter. So the linear four probe method described by Goswami[2] (Figure – 2) was used. The samples were prepared with rectangular geometry with a pre-evaporated aluminium film as the ohmic electrode. The length and breadth ratio of the film was kept more than 4 so as to avoid geometrical influence on the electrical characteristics. The resistivity was calculated using the formula.

$$\rho = \frac{Rwa}{l} \qquad \text{.......6}$$

where l is the length of the film, w is the width and a is the thickness of the film.

Electrical Resistivity of the single crystals :

The conductivity type of the crystal was tested by hot probe method. $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ exhibited p-type conductivity.

For electrical conductivity measurements, Valde's four probe technique was used along the cleavage surfaces of the crystals. The measurements were carried out at different temperatures in the range from 35°C to 130°C.

The room temperature conductivities of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ were measured to be 2.1×10^{-3}, 0.64×10^{-3} and 0.51×10^{-3} mho cm^{-1}, respectively. The temperature dependence of the conductivity σ of the three crystals is shown in the respective plots of log(resistivity) versus inverse temperature in Figure-3,4 and 5 . Similar trends at and near room temperature have been reported for p-type Bi_2Te_3 thin films[14] and p-type $Bi_2Te_{2.8}Se_{0.2}$ single crystals[15], indicating extrinsic conduction to be dominating. The plots obey the relation[16].

$$\rho = \rho_0 \exp (E\rho / K_B T)$$

where E_ρ = Resistivity activation energy, K_B = Boltzmann constant and T = absolute temperature. The activation energy values calculated from the corresponding slopes are found to be 0.011, 0.010, 0.012 eV respectively.Such a resistivity variation with temperature is explained by the presence of traps for electrons in the forbidden gap or by the formation of additional acceptors at high temperature [17,19-20]. The intrinsic conduction may set in at temperatures higher than those used in the present investigation.

The room temperature resistivity and activation energy measured for $Sb_{0.2}Bi_{1.8}Te_3$,$Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ crystals are given below in

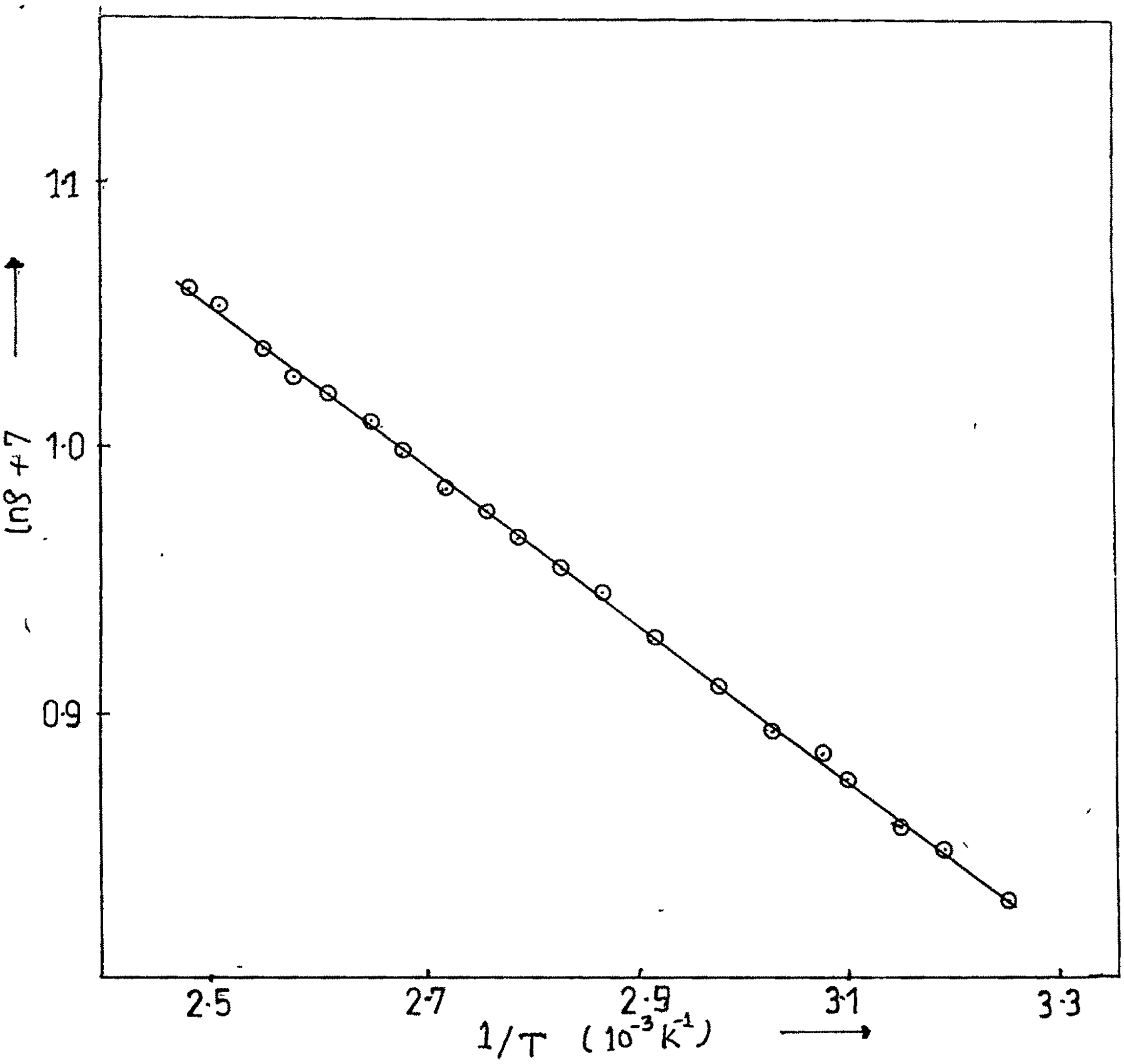

Fig. 3

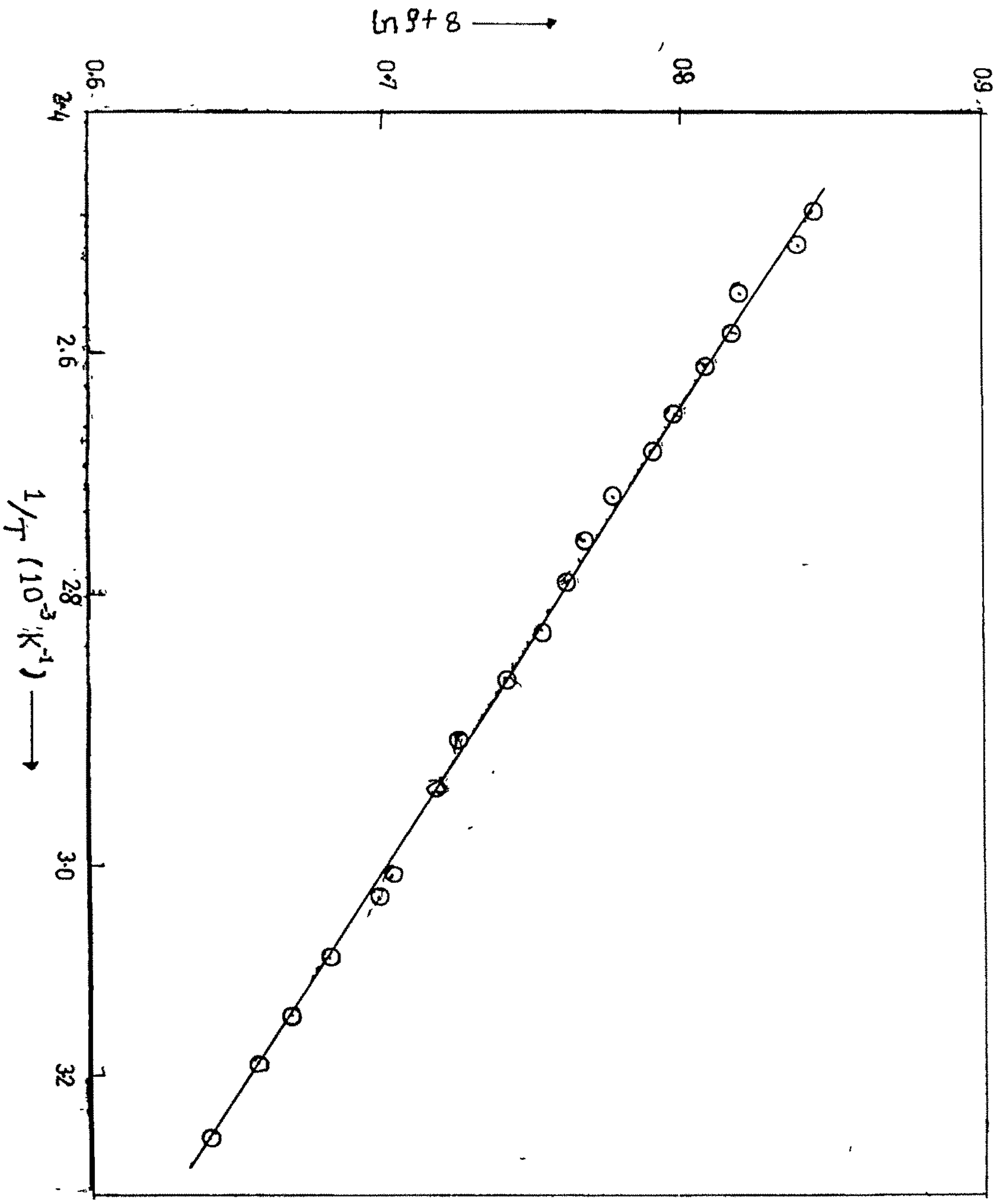

Fig. 4

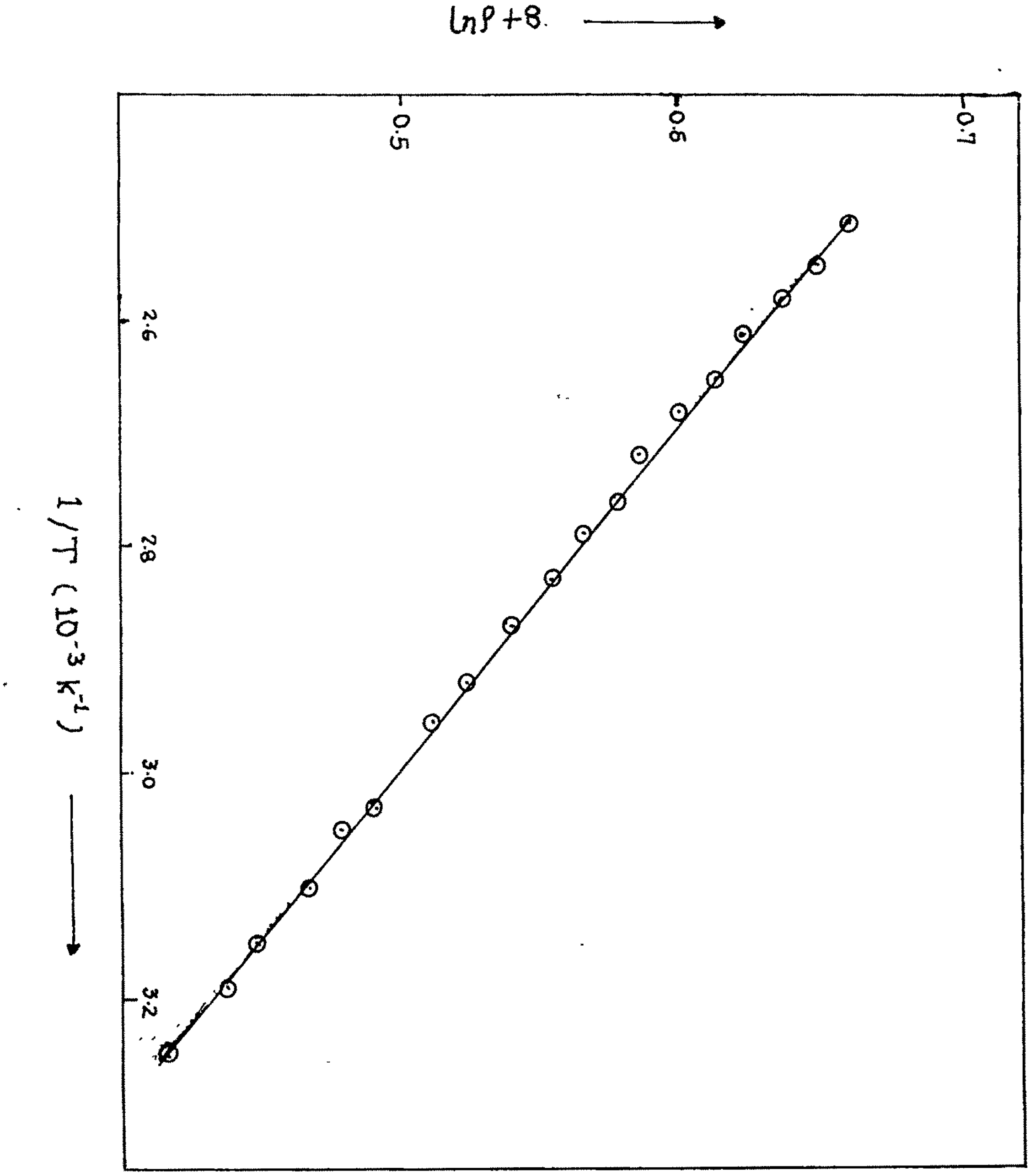

Fig. 5

table-1.

Electrical resistivity of the thin films :

The films of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ were prepared on cleaned glass substrates at room temperature (~313 K) using the thermal evaporation method under a pressure of 10^{-5} Pa. Thickness measurements were done by interferometry method. Aluminium film electrodes were deposited on the films. The film thickness and temperature dependences of resistivity have been studied. Films of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ of various thicknesses were obtained at room temperature. The resistivity as a function of temperature is shown in the plots of $\ln \rho$ vs $1/T$ of the films of different thicknesses shown in Figure – 6,7 and 8, respectively. It is observed that the resistivity decreases with increase in thickness. It is known that the resistivity will respond to the change in mfp of the carriers. The carriers will suffer a reflection at the surface when they happen to reach it. So the resistivity would increase whenever the specimen is thin enough to favour the collision with the surface or in other words, up to particular thickness the resistivity decreases with increase in thickness. The activation energy obtained as a function of film thickness is shown in Figures – 9,10 and 11, respectively, for the three materials. Similar variation of activation energy has been reported by Rahmankhan et al.[5] in the case of Bi_2Te_3 thin films.

Table – 1

Room temperature resistivity and activation energy.

Crystals	$\rho(\cap\ .\ \mathrm{cm})$	E_ρ(eV)
$Sb_{0.2}Bi_{1.8}Te_3$	2.10×10^{-3}	0.011
$Sn_{0.2}Bi_{1.8}Te_3$	0.64×10^{-3}	0.012
$Bi_2Te_{2.8}Se_{0.2}$	0.51×10^{-3}	0.010

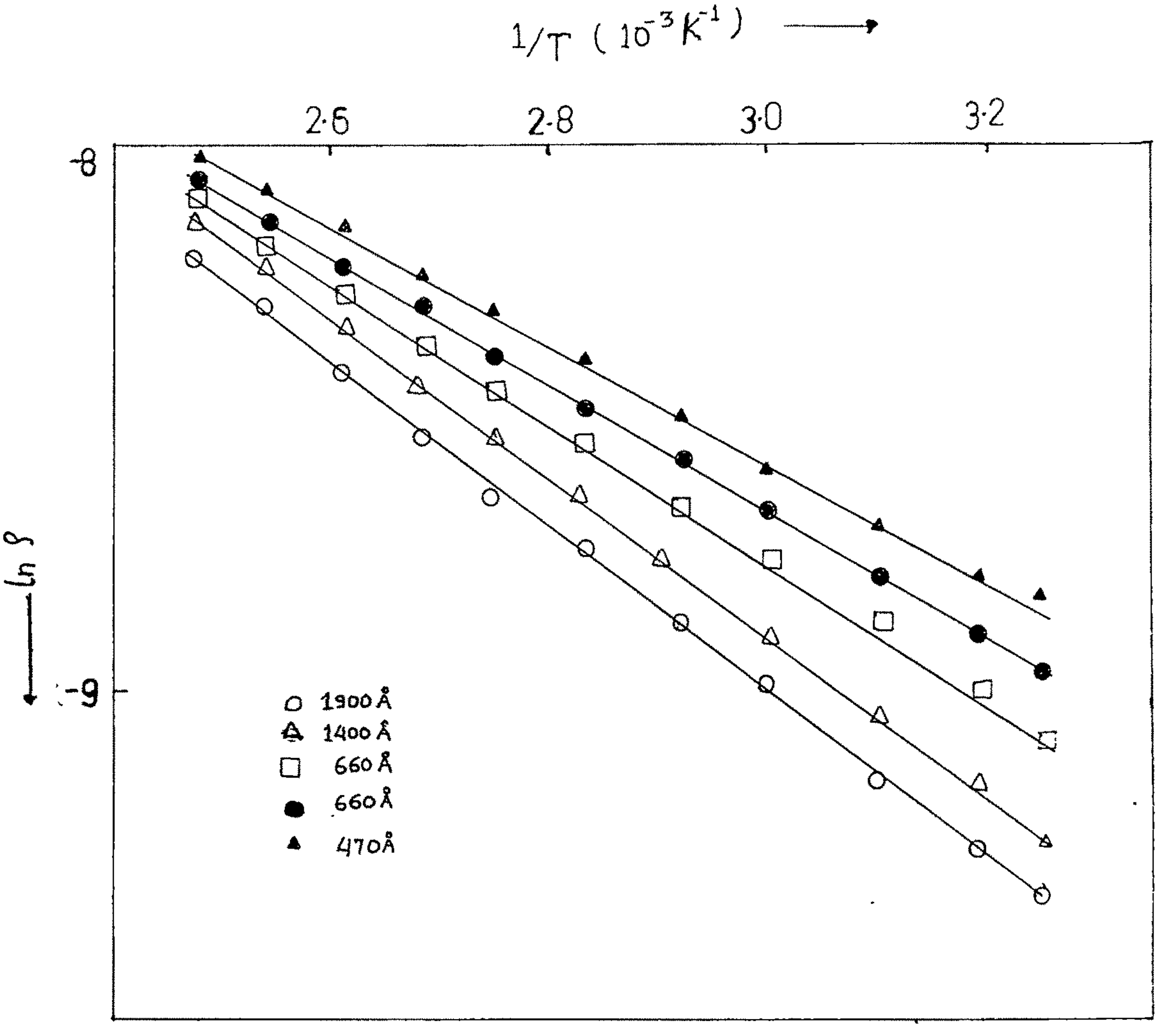

Fig. 6

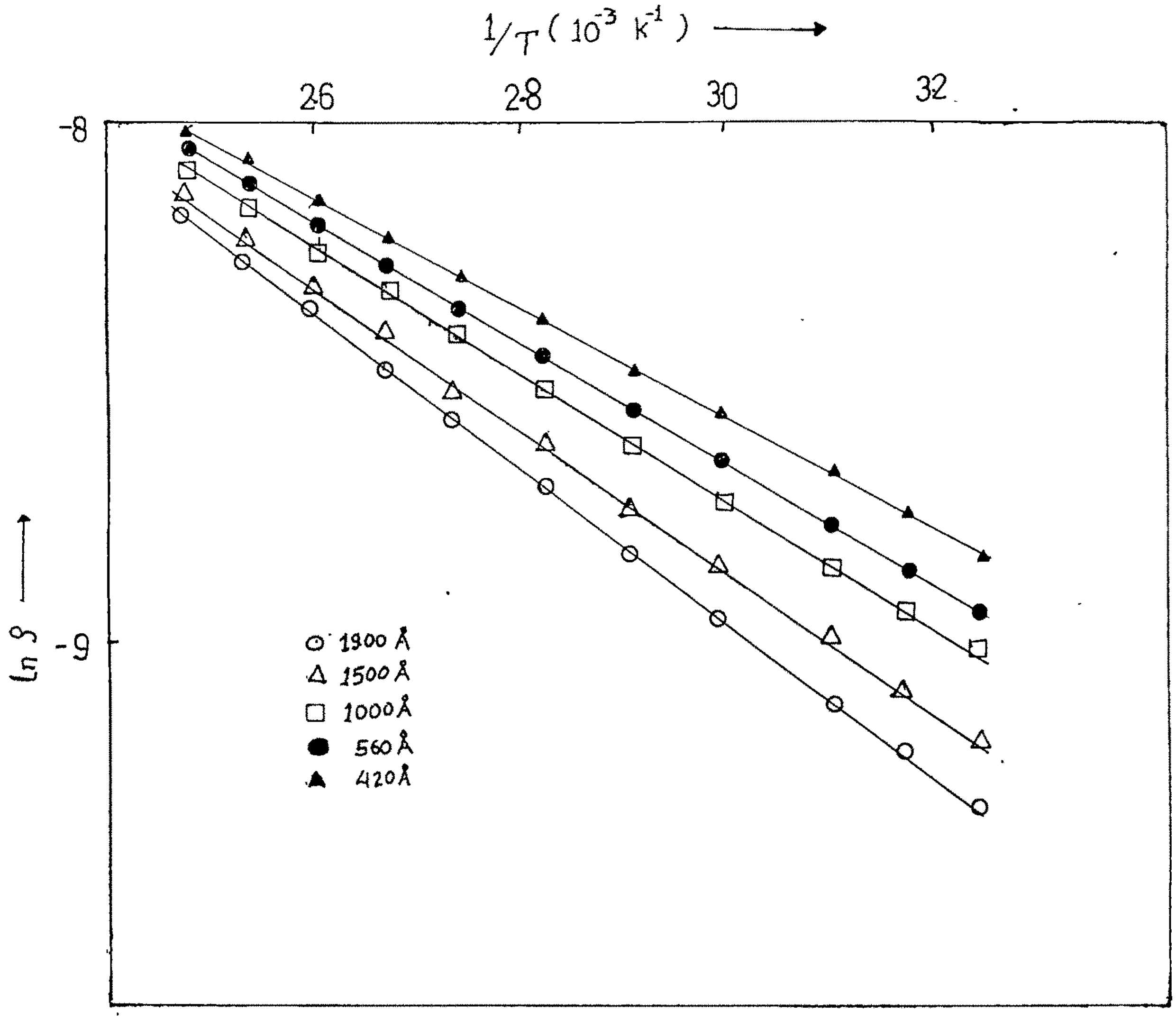

Fig. 7

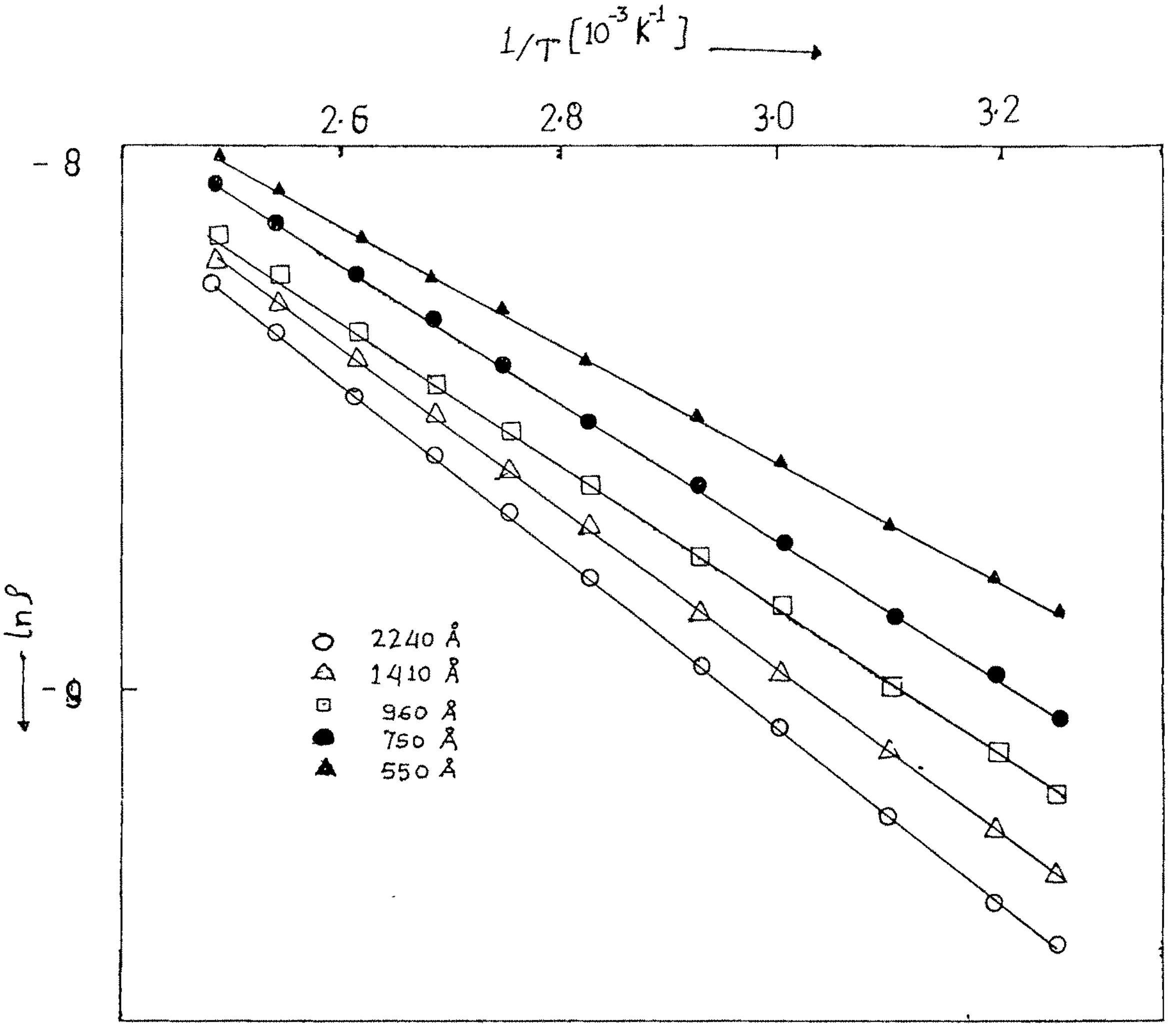

Fig. 8

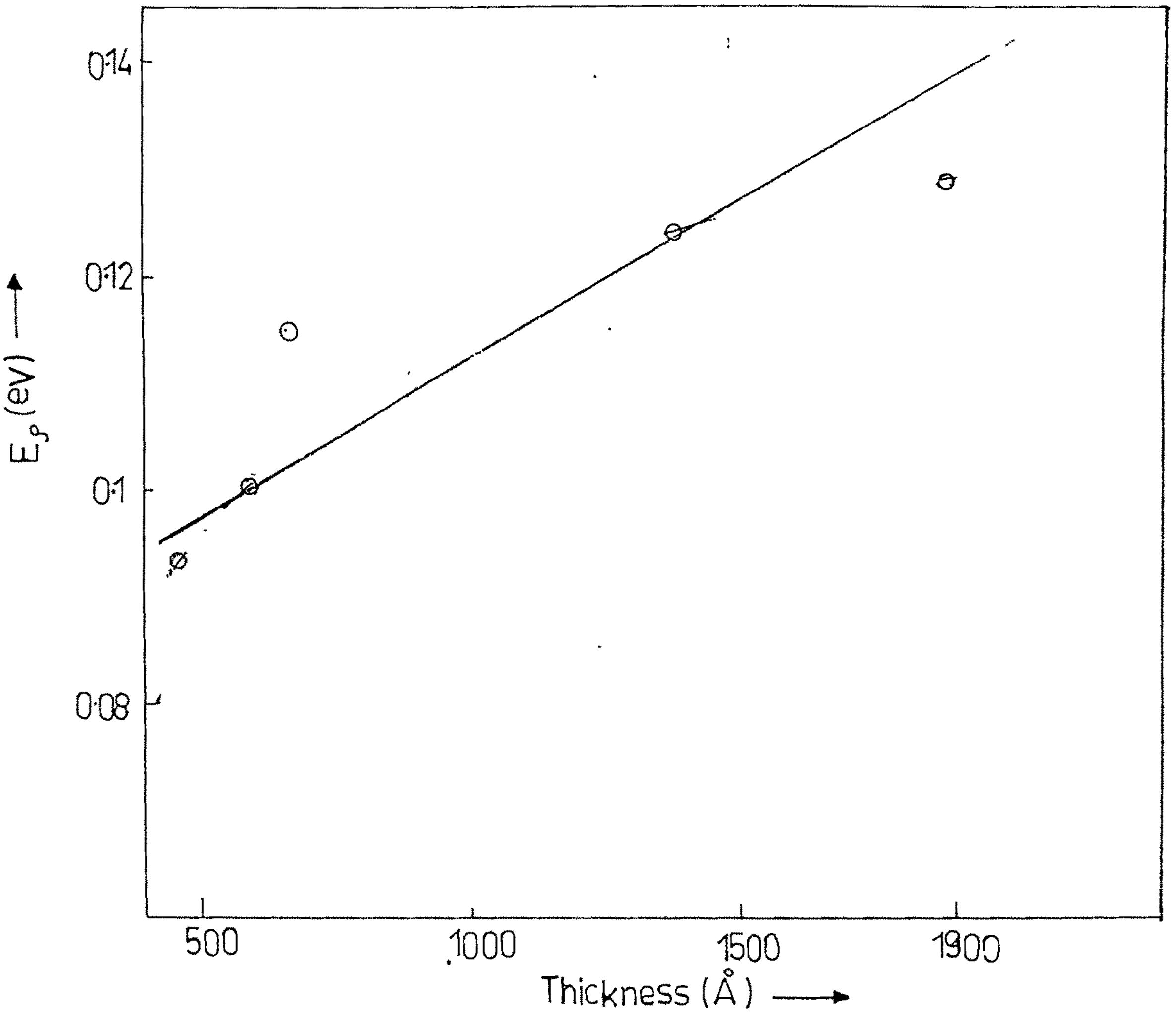

Fig. 9

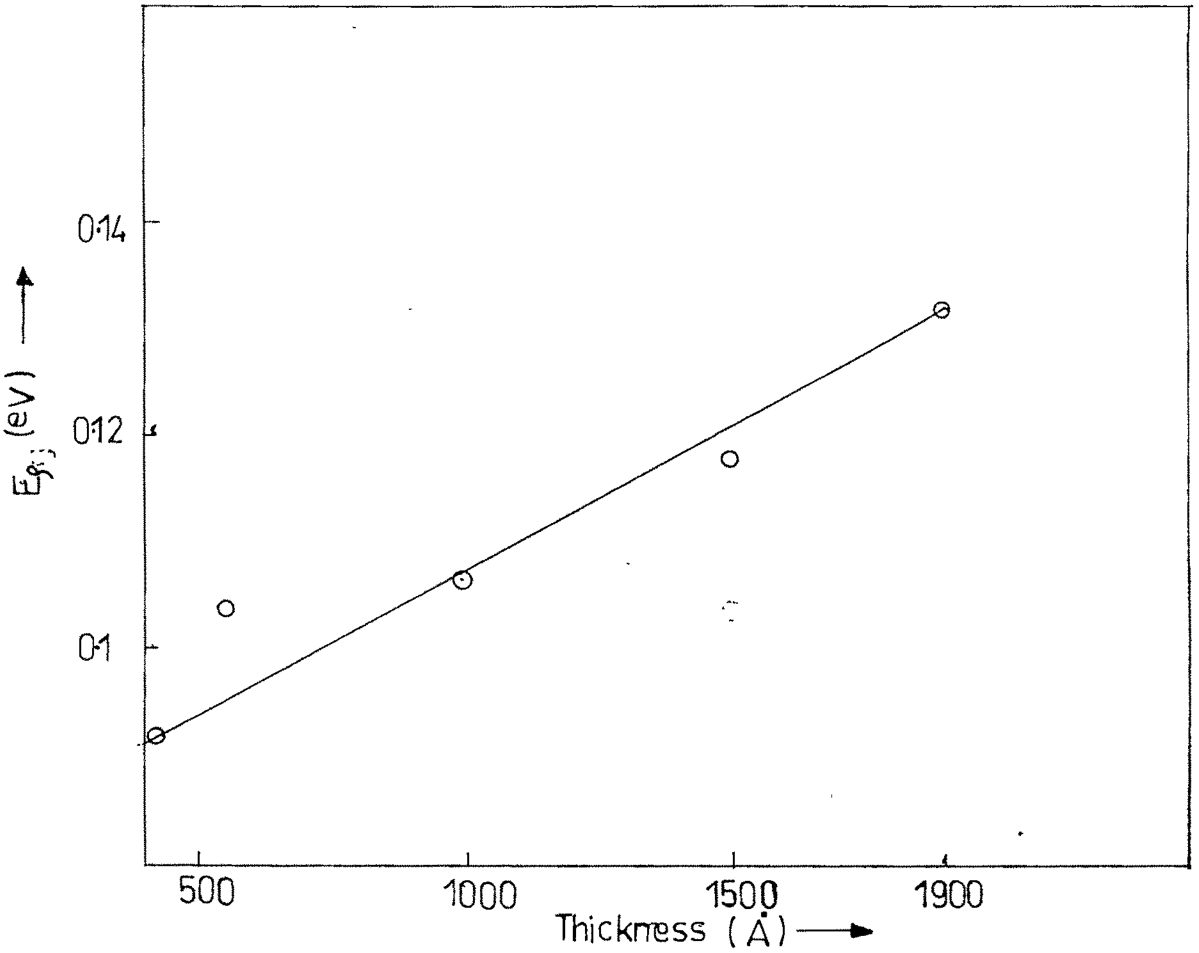

Fig. 10

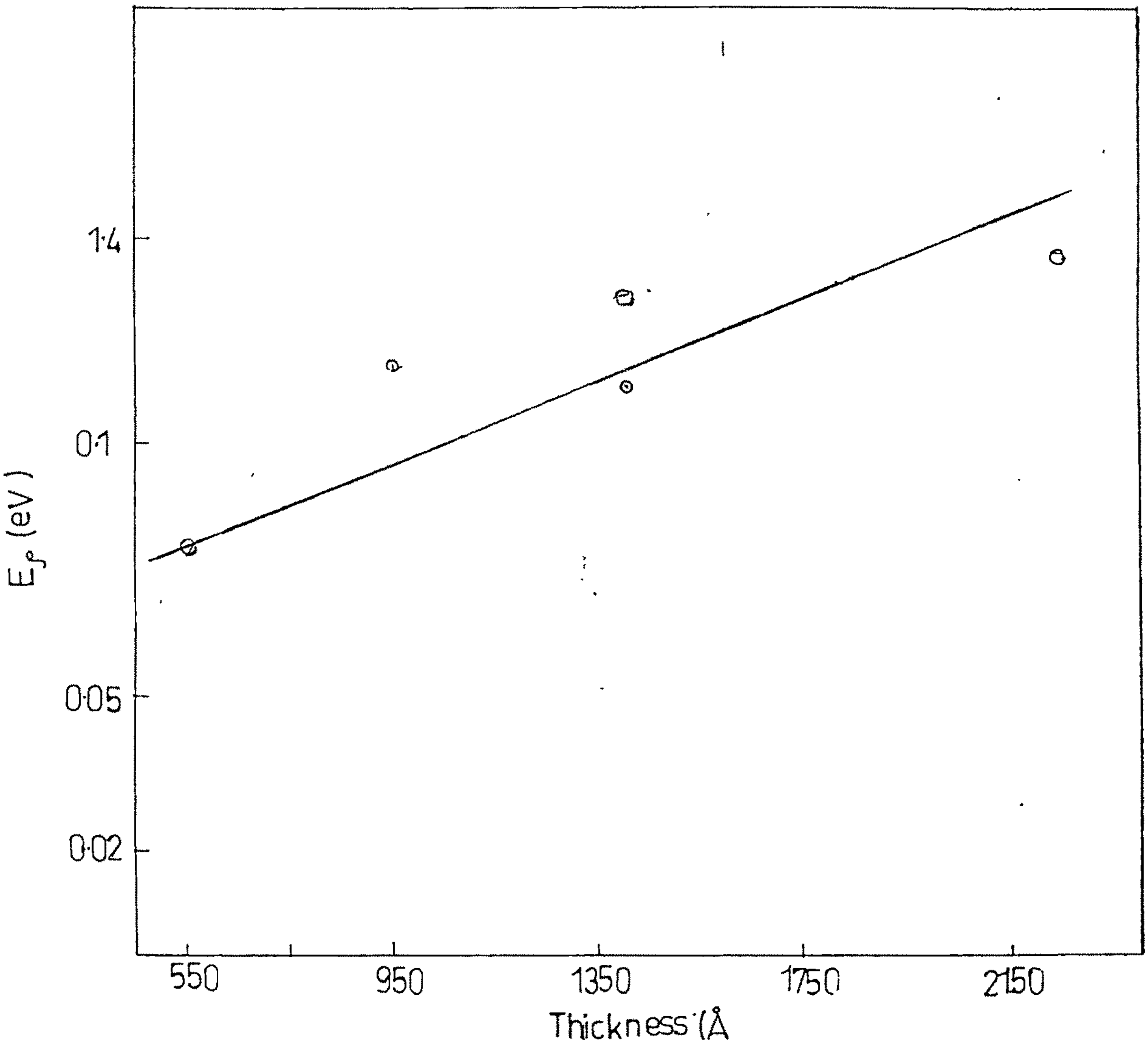

Fig. 11

B. Hall Measurement :

The Hall measurements were carried out at room temperature, using Van der Pauw method[21] . The probes 1 & 2 (as shown in Figure 12) were connected to a power supply with a digital current meter in series and across the probes 3 & 4, a digital microvoltmeter was connected to measure the voltage. The crystal was placed between the poles of a strong electromagnet giving a field of about 18 K gauss maximum. The current and voltage were measured with and without the magnetic field. A large number of samples were measured at the room temperature.The Hall coefficient, mobility and carrier concentration of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ crystals are listed in Tabel-2. The Hall coefficient was found to be positive indicating that the majority charge carriers are holes.

C. Thermoelectric Power Measurements :

The thermoelectric power measurements were carried out on freshly cleaved surfaces of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ single crystals, using Differential temperature method. The temperature difference between the hot and the cold junction was kept constant at 5K. The measurements were carried out in the temperature range from 308 to 403 K. The sign of thermal EMF and the results of the hot probe tests show that the $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ single crystals are all of p-type in agreement with the Hall coefficient results. Fig. 13,14 and 15 gives the plots

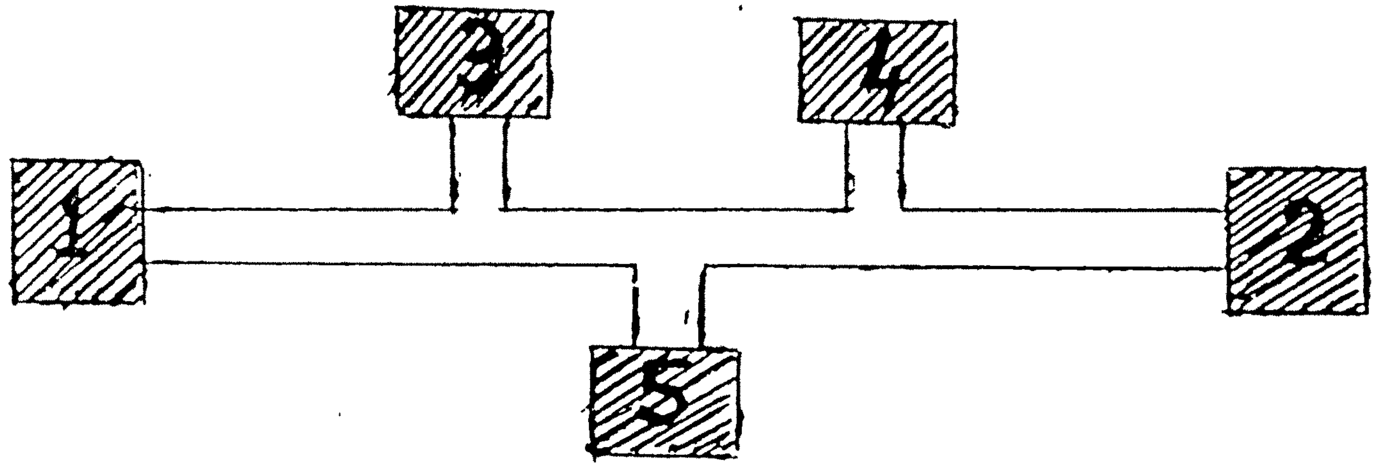

Figure - 12 : Goswami's linear probe geometry used for Hall measurement.

Table – 2

Crystals	Hall Co-efficient Cm^3/coul	Carrier mobility cm^2/v.sec	Carrier Concentration 10^{19} cm^{-3}
$Sb_{0.2}Bi_{1.8}Te_3$	0.7795	315	0.945
$Sn_{0.2}Bi_{1.8}Te_3$	0.6897	914	1.07
$Bi_2Te_{2.8}Se_{0.2}$	0.6192	1030	1.19

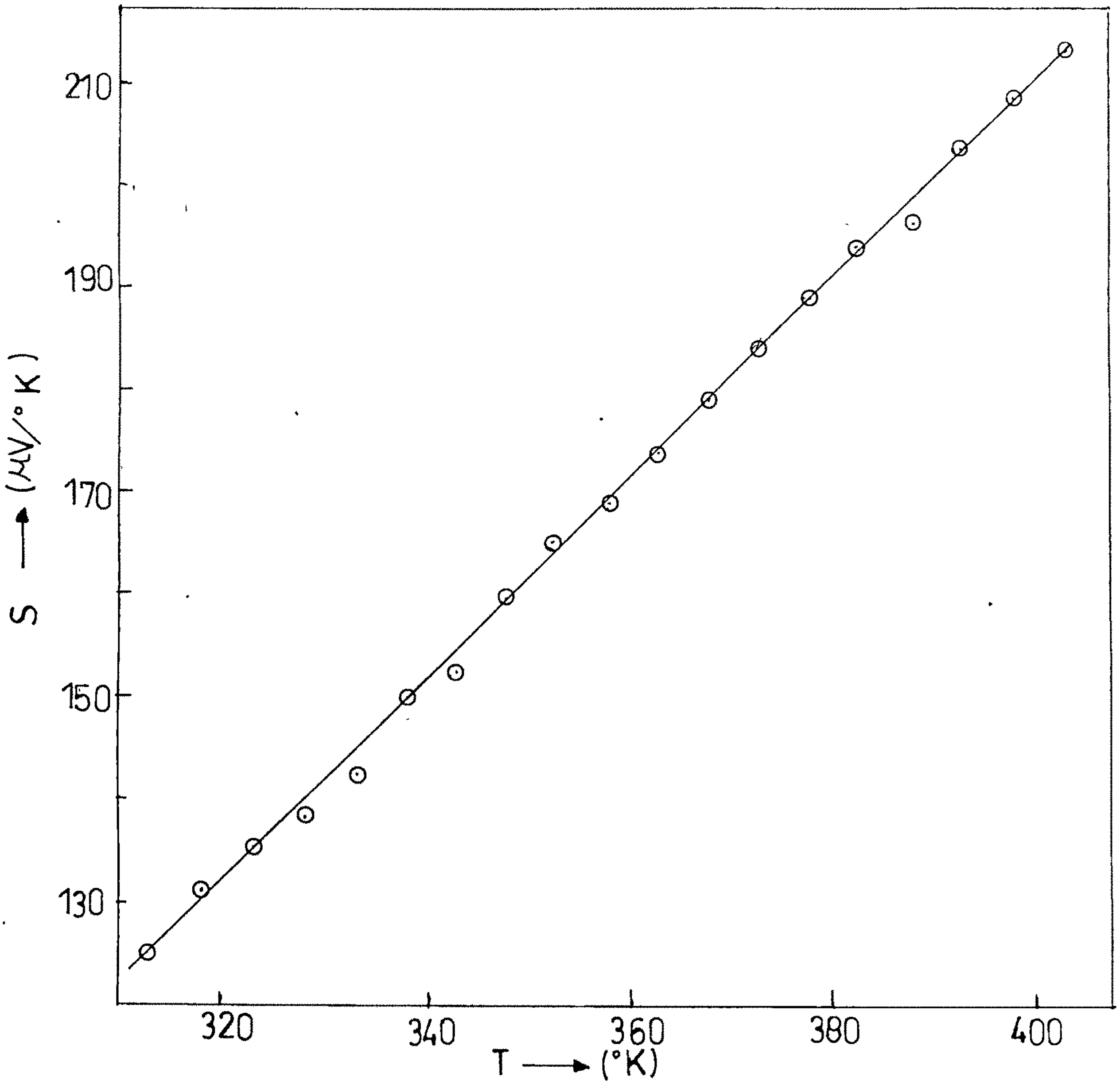

Fig.13

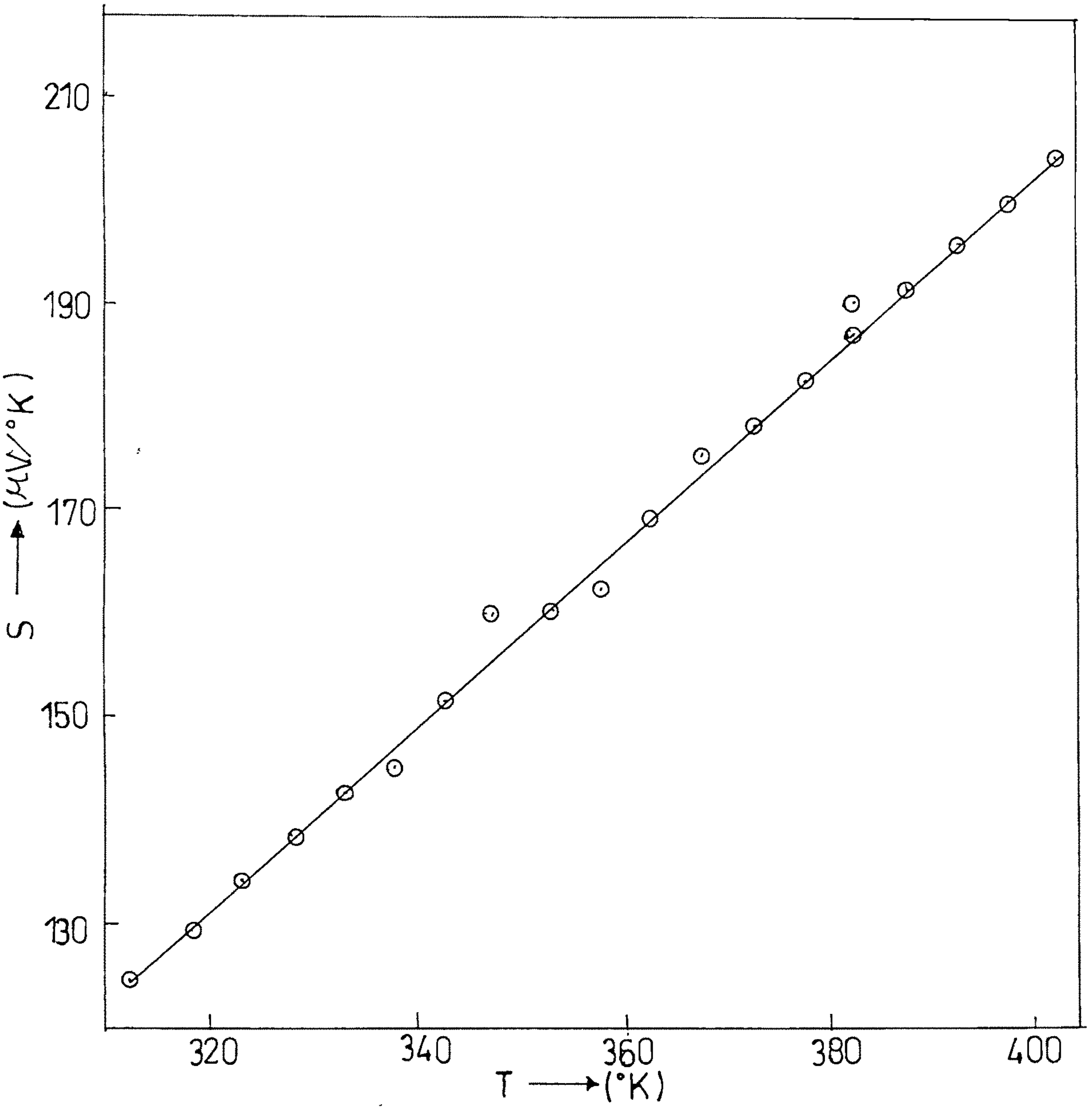

Fig. 14

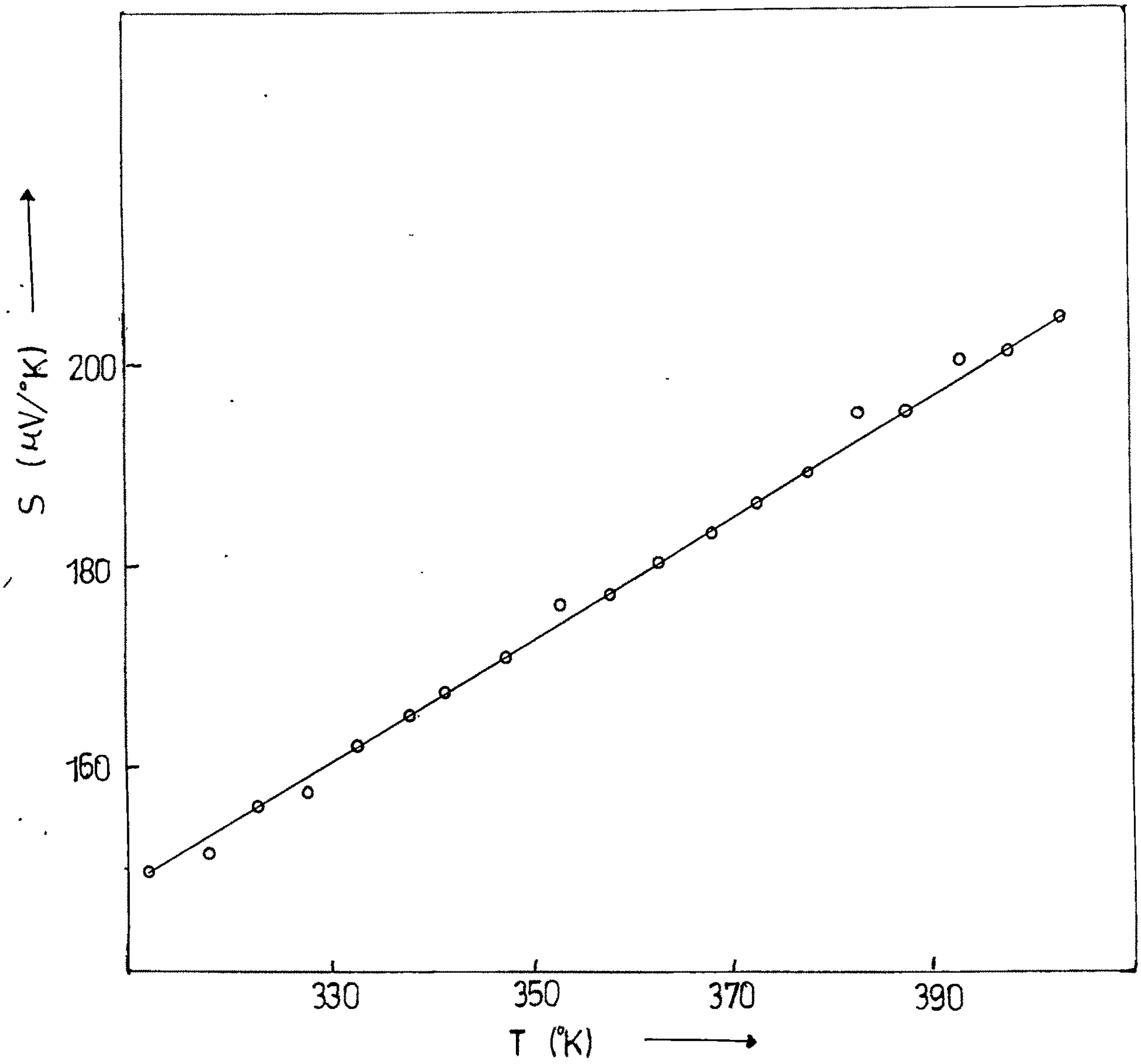

Fig. 15

of the thermoelectric power versus temperature, obtained for these crystals. The plots indicate that thermoelectic power increases linearly with increasing temperature, agreeing with the behaviour expected of a typical degenerate semiconductor [13].

CONCLUSIONS :

1. The signs of Hall coefficient and thermal EMF and the results of the hot probe tests show that all the crystals were of p-type, with carrier concentration of the order of 10^{19}cm^{-3}.

2. The room temperature resistivity of the single crystals of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ are 2.1, 0.64 and .51 x 10^{-3} Ω.cm, respectively.

3. The electrical resistivity of thin films of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ has been found to be thickness dependent. It decreases with thickness.

4. Hall co-efficient, carrier concentration and mobility of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ were found to be 0.7795 cm^3/coul, 315 cm^2/v.sec and 0.945x10^{19}cm^{-3}, 0.6897 cm^3/coul, 914 cm^2/v.sec and 1.07x10^{19}cm^{-3} and 0.6192 cm^3/coul, 1030 cm^2/v.sec and 1.19x10^{19}cm^{-3} respectively.

5. Addition of any of Sb, Sn and Se is found to increase the carrier mobility and hence decrease the resistivity of Bi_2Te_3 whereas it decreases the carrier concentration to a significant extent. Among these, Se addition is the most effective in improving these parameters.

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