

CHAPTER 5

TRANSPORT PROPERTIES OF THE $\text{MoSe}_x\text{Te}_{2-x}$ SINGLE CRYSTALS

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5.1 Introduction

VI B - VI A group of compounds have been studied extensively for their electrical properties¹⁻³⁾. Studies have also been made on mixed systems such as $(\text{Mo/W})\text{Te}_2$, $(\text{Mo/W})\text{Se}_2$ ⁴⁾, $(\text{Mo/W})(\text{Se/Te})_2$ ⁵⁾, $(\text{W/Mo/Te})\text{Se}_2$ ⁶⁾ and $\text{Mo}(\text{S/Se})_2$ ⁷⁾. However, no attempts has been made to investigate the variation of the properties like resistivity, Hall coefficient and thermoelectric power with composition for $\text{Mo}(\text{Se/Te})_2$ solid solutions in single crystalline form. The present chapter describes a study of such properties form these crystals, since the information thus provided will be useful in the fabrication of PEC cells with them.

5.2 Resistivity Measurements

The measurements of resistivity were performed with separate amount and voltage probes in order to eliminate contributions due to the contact resistances. The method most appropriate for measurements on plane parallel crystals of arbitrary shape is that described by L. J. Van der Pauw⁸⁾. For the evaluation of the resistivity of such a flat sample electrodes are taken in

an arbitrary way along the periphery of the sample (Fig. 5.1) and two resistance measurements are then carried out. When a current I_1 is passed through the contacts 1 and 2, a voltage V_1 appears across the contacts 3 and 4. The ratio V_1/I_1 is represented by a resistance R_1 . In an analogous way a resistance R_2 is determined by passing a current I_2 through the electrodes 2 and 3, while the voltage V_2 is measured across 1 and 4. The specific resistivity can then be evaluated by using the relation

$$\rho = \frac{\pi d}{2 \ln 2} (R_1 + R_2) f(R_1/R_2) \quad (5.1)$$

where d is the thickness of the sample. The function $f(R_1/R_2)$ is presented in a graphical form by Van-der-Pauw⁸⁾ (Fig. 5.2). According to the theory, the following conditions have to be fulfilled for the applicability of the method.

1. The contacts must be at the circumference of the sample.
2. The contacts must be sufficiently small

compared to sample dimensions.

3. Sample must be homogeneous in thickness.
4. There must be no isolated holes in the sample.

Experimental Set Up

Electrical connections for resistivity measurements were made by four copper wires at the periphery of the thin crystals and attached to the crystal surface by means of conducting silver paste. A ceramic switch, which enables rapid changing from one current voltage combination to other was used. The circuit was diagram for resistivity measurements is shown in Fig. 5.4. The important features of the measurements are as follows :

1. Independent measurements of V and I .
2. Use of voltmeters of a high resistance.
3. The use of low capacity leads from sample to current and voltmeter.

5.3 Hall Measurements

Hall mobility was determined by measuring the change of the resistance⁸⁾ $R_{BD.AC}$ when a magnetic field was applied perpendicular to the basal plane of the sample. Hall mobility u_H is given by the relation

$$u_H = \frac{d}{B} \left(\frac{R_{BD.AC}}{\rho} \right) \quad (5.2)$$

where B is the applied magnetic field,

$R_{BD.AC}$ is the change of the resistance.

$R_{BD.AC}$ due to the magnetic field.

Experimental Set Up

The specimen having an arbitrary shape was placed on the sample holder. The electrical contacts were made in the manner described for resistivity measurements. The specimen was then placed in a magnetic field in such a way that its surface was perpendicular to the direction of the magnetic field. A current was passed through the specimen with the help of batteries. The magnetic field applied was in the range of 6 K Gauss to 10 K Gauss).

5.4 Thermoelectric Effect

It is well known that if a metal is connected at its two ends with a second metal, and if one of the junctions is heated, a voltage is developed across the open ends of the second metal. A schematic circuit for the measurement of thermoelectric voltages for a semiconductor is given in Fig. 5.3.

If metal contacts are applied to the two ends of a semiconductor rod, and if one junction is maintained at a higher temperature than the other, a potential difference is developed between the two electrodes. This thermoelectric or Seebeck voltage is produced partly because :

1. The majority carriers in the semiconductor diffuse from hot to the cold junction, thus giving a potential difference between the ends of specimen. This voltage builds up to a value such that the return current, just balances the diffusion current when a steady state is reached.

2. Other part which contributes to the thermoelectric voltage is the contact potential difference between the metal and semiconductor which occurs at the two junctions.

In the semiconductor as shown in Fig. 5.3, if the charge carriers are predominantly electrons, the cold junction becomes negatively charged and if the carriers are positive holes, the cold junction becomes positively charged. The magnitude of the developed voltage V_s is proportional to the difference in temperature between the hot and cold junction if the temperature difference is small. From the sign of the thermoelectric voltage, it is thus possible to deduce whether a specimen exhibits n-type or p-type conductivity.

Experimental Set Up

The Seebeck coefficients were measured by using an integral method. The specimen holder which has been fabricated in our University Science and Instrumentation Centre, (U.S.I.C.), is shown in Fig. 5.5. Large single crystals were used for the measurements. A thermal gradient was imposed across the sample by placing it between two

nichrome wound heaters on copper blocks. Chromel-alumel (40 SWG) thermocouples were fixed on to copper screw, while contacted the specimen. The same copper screw contacts were used as voltage probes. The entire system was mounted in an evacuated glass enclosure at pressure less than 10^{-4} torr. Proper care was taken to avoid any pick up of electrostatic and other signals by proper shielding. A multimeter (Philips PM 2502) was used to measure the developed thermo e.m.f.

5.5 Results and Discussion

A detailed study of d.c. resistivity (ohm.cm.) as a function of crystal composition reveals that the resistivity increases non-linearly with the increasing selenium content in the solid solution $\text{MoSe}_x\text{Te}_{2-x}$ ($0 \leq x \leq 2$) as shown in Fig. 5.6. The room temperature (30°C) resistivities of MoSe_2 and MoTe_2 have been obtained as 9.5 and 0.25 ohm. cm. respectively. These results are in agreement with those reported by earlier workers^{4,9)}.

Analogous behaviour is observed in the case of $\text{WSe}_x\text{Te}_{2-x}$ system⁵⁾.

In order to judge the semiconducting nature of $\text{MoSe}_x\text{Te}_{2-x}$ ($0 \leq x \leq 2$), Hall effect measurements were carried out. Hall mobility, u_H was determined using Van der Pauw's method for various compositions at room temperature. The Hall coefficient, R_H and carrier concentration, n were also calculated assuming the single carrier conduction model using the relations,

$$u_H = R_H/\rho \quad \text{and}$$

$$n = -\frac{1}{eR_H} \quad (5.3)$$

where e is the electronic charge. The variation of u_H , R_H and n with the composition of $\text{MoSe}_x\text{Te}_{2-x}$ is shown in Fig. 5.7. It is observed that the Hall mobility increases with an increasing selenium content. As resistivity also increases with the increasing selenium content, in the crystal, it is concluded that the Hall coefficient increases and hence carrier concentration decreases as we go from MoTe_2 to MoSe_2 .

It is interesting to note that the optical bandgap determined from spectral response (Chapter 7) of the crystals increases with the increasing

selenium content in the $\text{MoSe}_x\text{Te}_{2-x}$ system. It may be noted that the atomic radius reduces as we go from Te (1.37 Å) to Se (1.17 Å) leading to changes in the band strengths and hence in the structure. Further the electronegativity of the atoms increase from Te (2.1) to Se (2.4) meaning thereby an increase in the ionic nature of the bonding. As a result, an increase in the resistivity and a decrease in the effective carrier concentration should be expected which is in agreement with the experimental observations.

The thermoelectric measurements were made in the temperature range 40° to 290°C . The variation of in the Seeback coefficient 'S' with temperature for $\text{MoSe}_x\text{Te}_{2-x}$ system is shown in Fig. 5.8. It is observed that the Seeback coefficient increases initially with temperature and then decreases to a nearly constant value. The nature of variation is identical for all compositions in the $\text{MoSe}_x\text{Te}_{2-x}$ system except that the peak value of Seeback coefficient occurs at different temperatures. The existence of a peak in the Seeback coefficient versus temperature plot and its relation to the variation in concentration and mobility of charge carriers need further investigation for an adequate explanation. However, it is worth noting that the

Seebeck coefficient had a negative value for all compositions of the solid solutions throughout the temperature range under the present investigation indicating the crystals to be n-type semiconductors.

5.6 Conclusions

1. The resistivity measurements have shown in general that the resistivity increases with the increasing amount of selenium in $\text{MoSe}_x\text{Te}_{2-x}$ series.
2. Hall effect measurements indicate, improved mobility with substitution leading to an increasing amount of selenium.
3. Thermoelectric measurements find all the compositions in the series to be n-type semiconductors. This fact has also been confirmed by Hall effect measurements.

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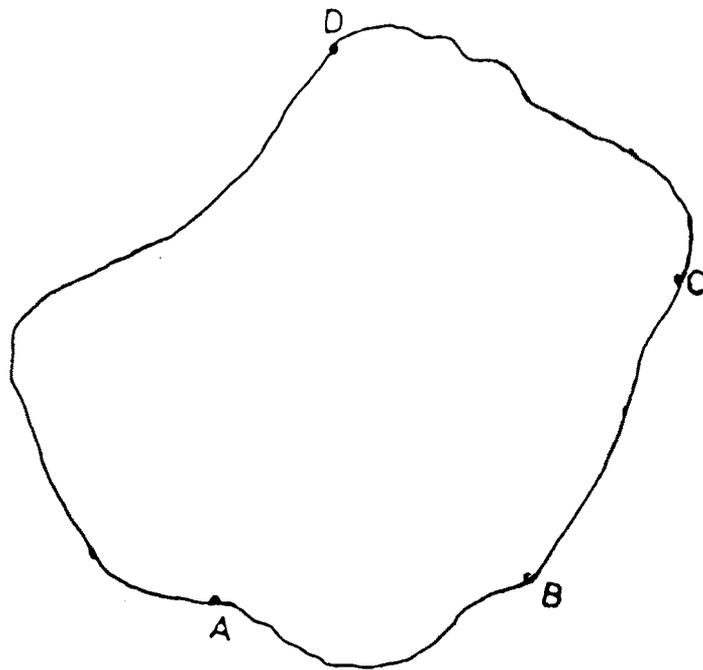


Fig. 5.1 Sample of arbitrary shape with four small contacts at arbitrary places of the circumference to measure the specific resistivity and Hall effect.

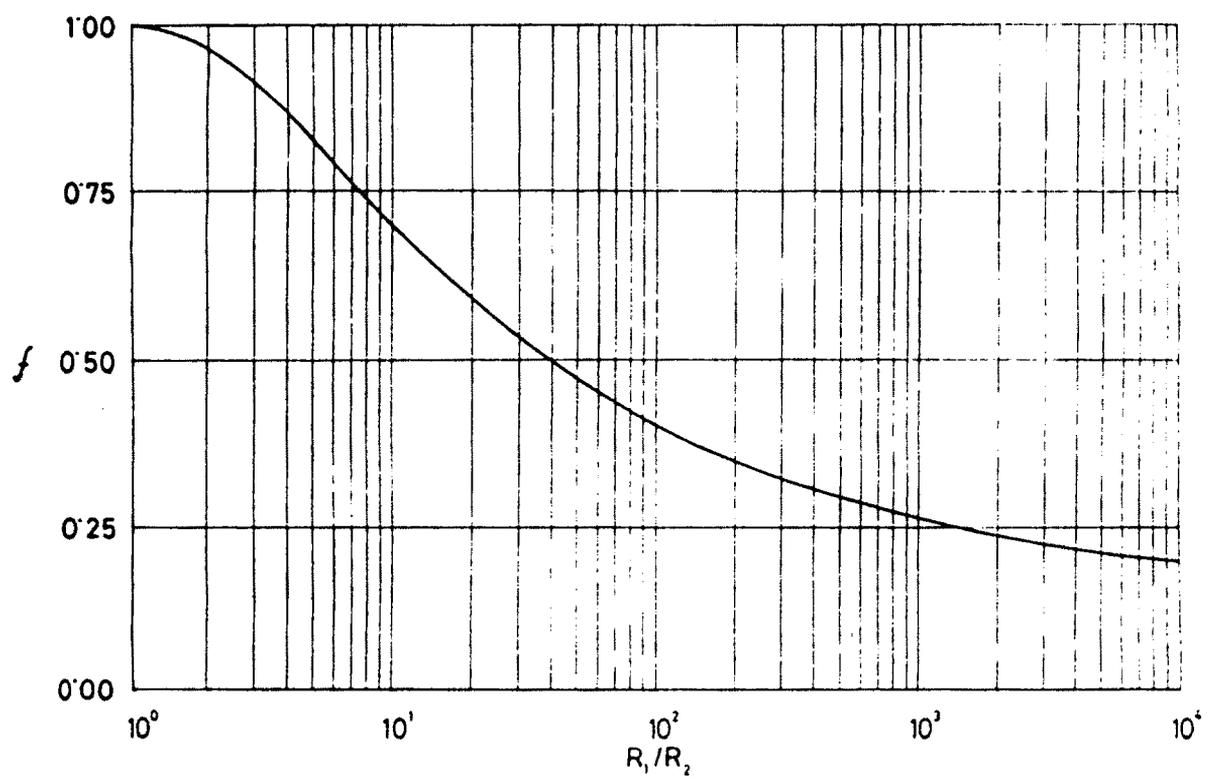


Fig. 5.2 The function f used for determining the specific resistivity of the sample, plotted as a function of R_1/R_2

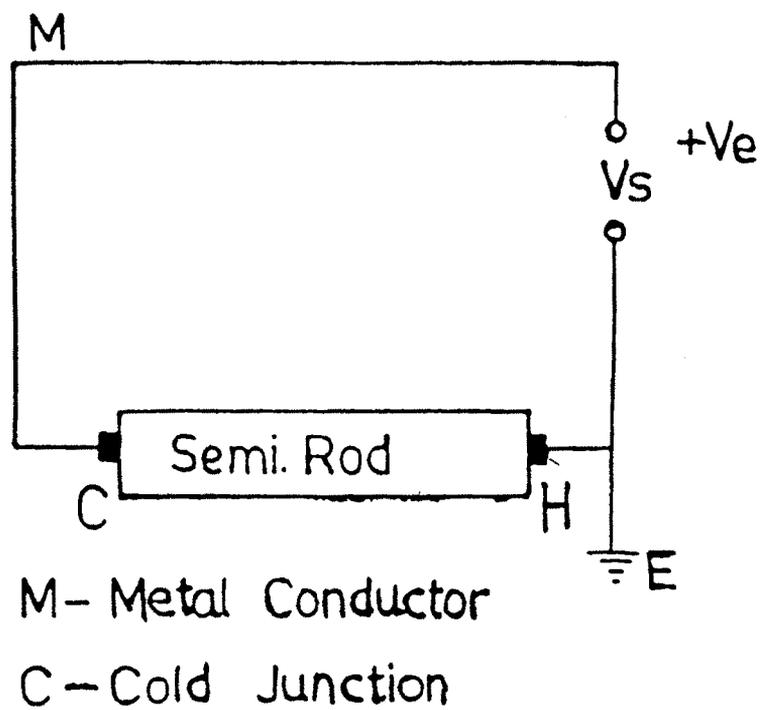


Fig. 5.3 Schematic circuit for the measurement of the thermoelectric voltage for semiconductor

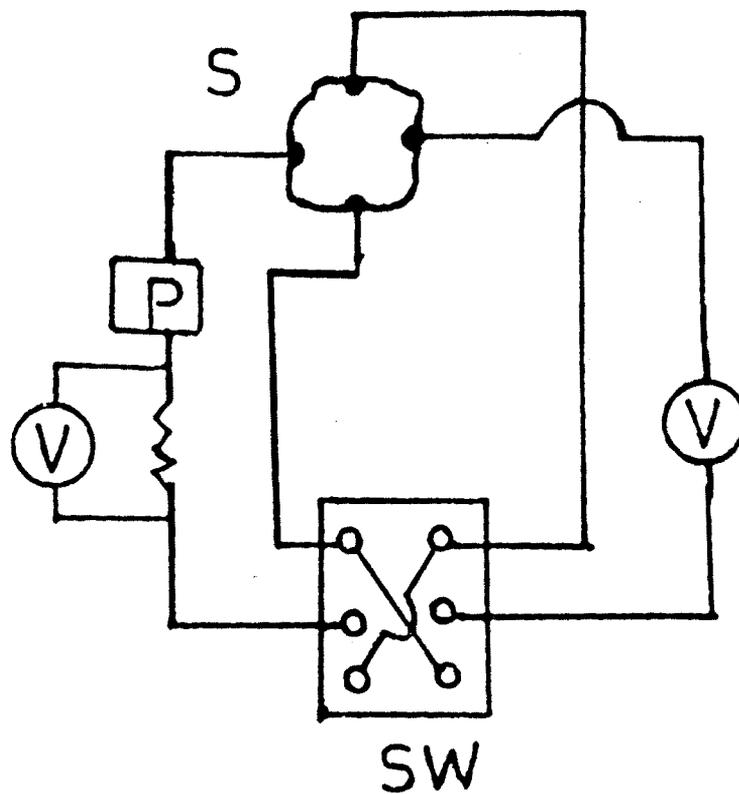


Fig. 5.4 Schematic circuit diagram for measurement of resistivity

S-specimen	P - Battery
V- V.T.V.M.	Sw- Switch

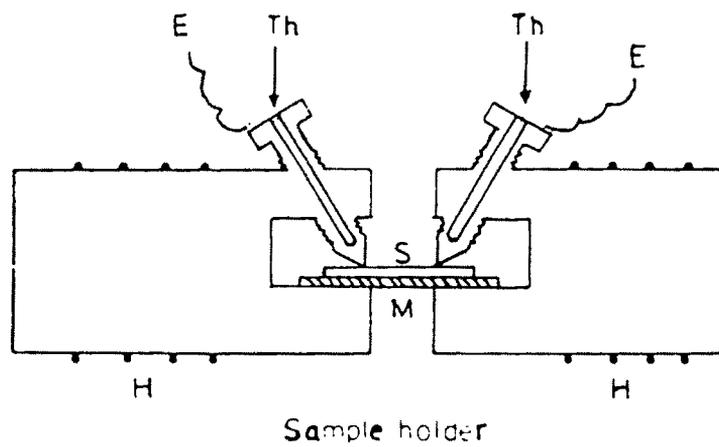


Fig. 5.5 Sample holder assembly for TEP
measurements

H,H - Heaters

S - Sample

Th,Th- Thermocouples

M - Mica sheet

E,E - Electrodes

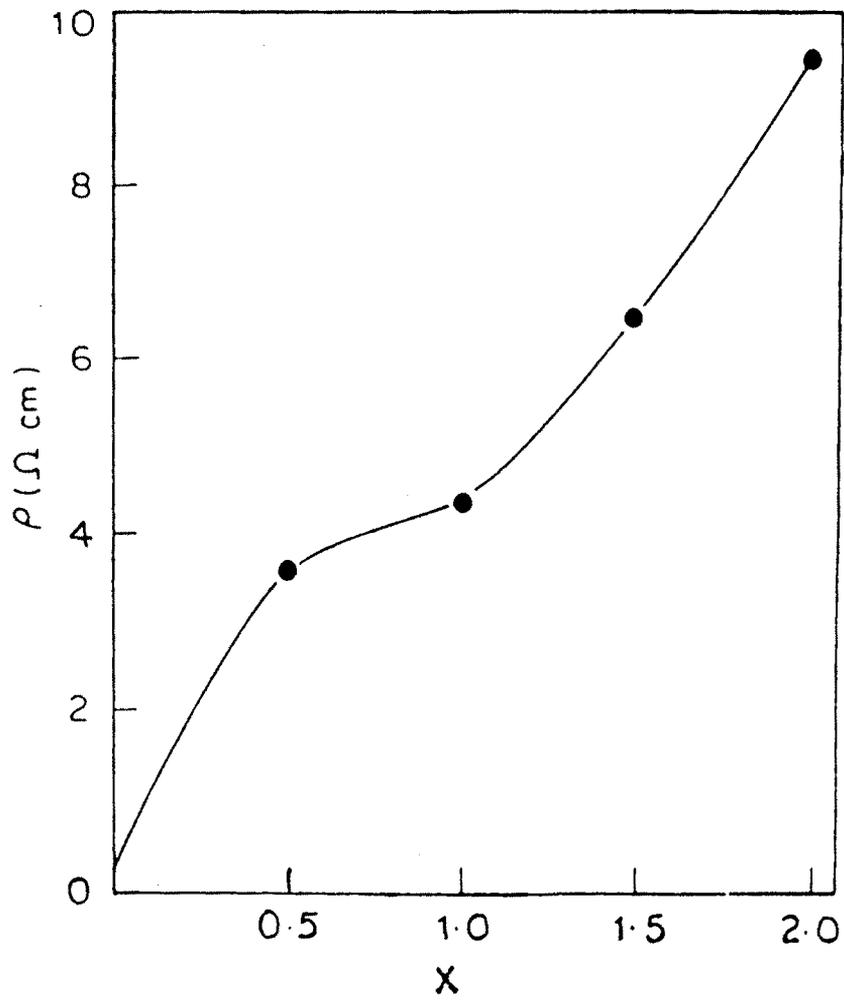


Fig. 5.6 Variation of resistivity (ρ)
 as a function of composition
 X of $\text{MoSe}_x\text{Te}_{2-x}$, $0 \leq x \leq 2$
 at $T = 30^\circ\text{C}$

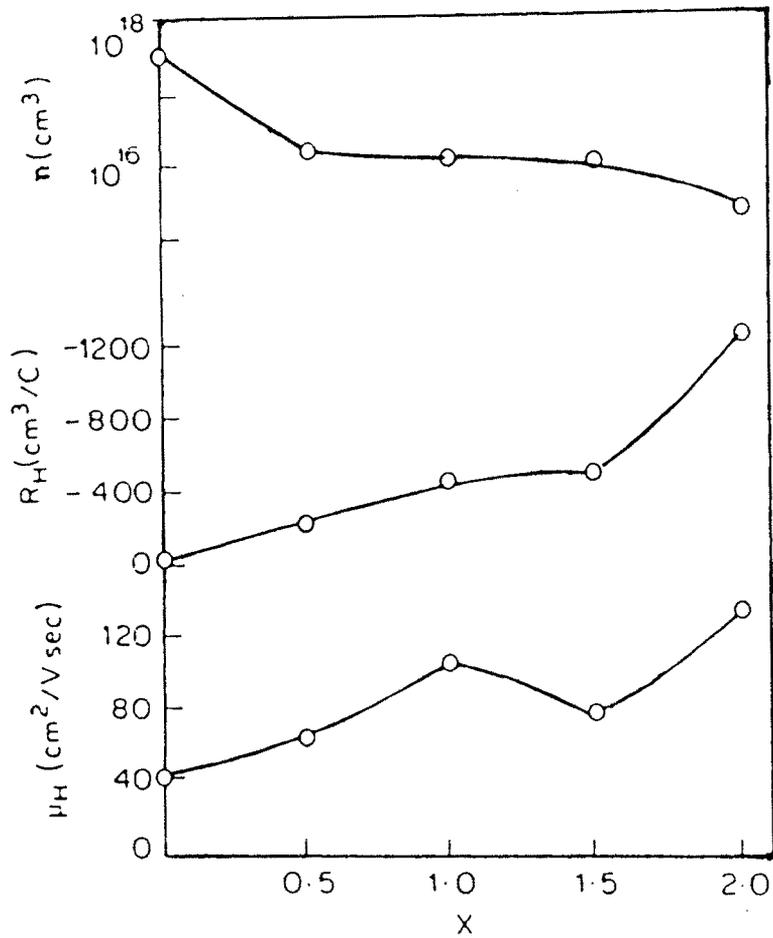


Fig. 5.7 Variation of Hall mobility (μ_H), Hall coefficient (R_H) and carrier concentration (n) as a function of composition 'X' of $\text{MoSe}_x\text{Te}_{2-x}$, $0 \leq x \leq 2$ at $T = 30^\circ\text{C}$.

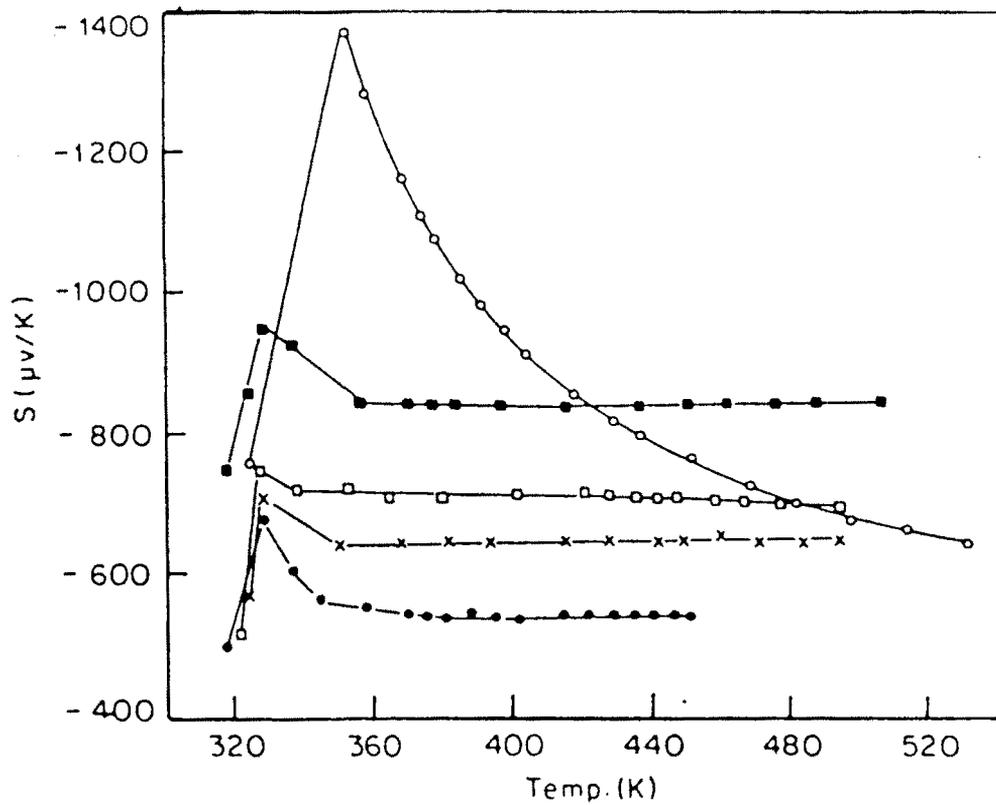


Fig. 5.8 Seebeck coefficient 'S' as a function of temperature for $\text{MoSe}_x\text{Te}_{2-x}$, $0 \leq x \leq 2$ system.