CHAPTER 4

TRANSPORT PROPERTIES OF MOLYBDENUM
SULPHOSELENIDES SINGLE CRYSTALS

4.1   Introduction

VI B - VI A group of compounds have been studied extensively for their electrical properties[1-3]. Studies have also been made on mixed systems such as $(Mo/W)Te_2$, $(Mo/W)Se_2$[4], $(Mo/W)(Se/Te)_2$[5] $(W/Mo/Ta)Se_2$[6]. However, no attempt has been made to investigate the variation of the properties like resistivity, Hall coefficient and thermoelectric power with composition for $Mo(S/Se)_2$ solid solutions in single crystalline form. The present chapter describes a study of such properties for these crystals, since the information thus provided will be useful in the fabrication of PEC cells with them.

4.2   Resistivity Measurement

The measurements of resistivity were performed with separate current 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 Pauw[7]. 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. 4.1) 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 ρ can then
be evaluated by using the relation

$$\rho = \frac{\pi d}{2 \ln 2} (R_1 + R_2) \, f(R_1/R_2) \qquad (4.1)$$

where d is the thickness of the sample. The function
$f(R_1 / R_2)$ is presented in a graphical form by Van-der-Pauw[11]
(Fig. 4.2). 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 diagram for resistivity measurement is shown in Fig. 4.4. The important features of the measurements are as follows.

1. Independent measurement of V and I.

2. Use of voltmeters with a high input resistance.

3. The use of low capacity leads from sample to current and voltmeter.

4.3 Hall Measurements

Hall mobility was determined by measuring the change of the resistance[7] $R_{BD.AC}$ where a magnetic field was applied perpendicular to the basal plane of the sample. Hall mobility μ_H is given by the relation

$$\mu_H = \frac{d}{B} \left(\frac{\Delta R_{BD.AC}}{\rho} \right) \qquad (4.2)$$

where B is the applied magnetic field , $\Delta R_{BD.AC}$ 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 specimen 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 magnetic field. A current was passed through the specimen with the help of batteries. The magnetic field applied was in the range of 3 K gauss to 5 K gauss.

4.4 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 the thermoelectric voltages for a semi-conductor is given in Fig. 4.3.

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
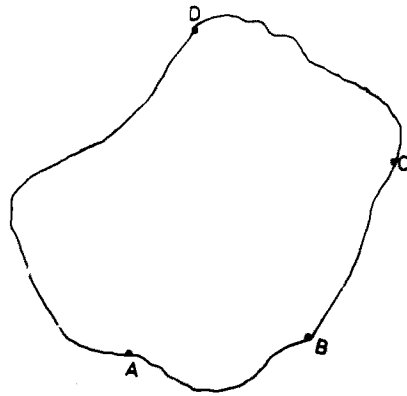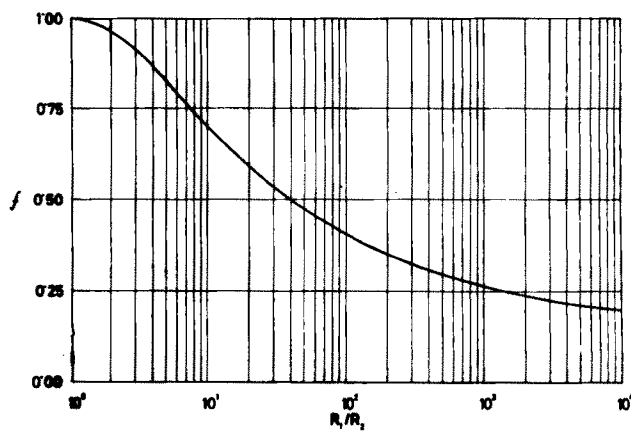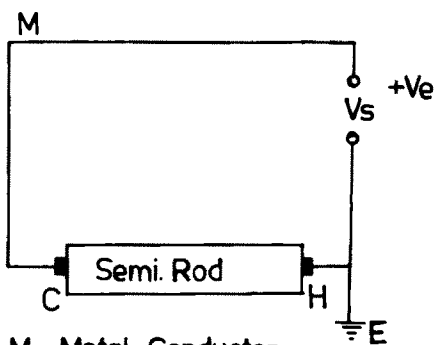
Fig. 4.1

Fig. 4.2

M— Metal Conductor

C —Cold Junction

H— Hot Junction

Fig. 4.3

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 upto 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 thermo-
        electric voltage is the contact potential
        difference between the metal and semiconductor
        which occurs at the two junctions.

        In the semiconductor as shown in Fig. 4.3,
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 differential method for different compositions. The sample holding assembly which has been fabricated in our University Service and Instrumentation Centre, is shown in Fig. 4.5. 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, which contacted the specimen. The same copper screw contacts were used as voltage probes. The entire system was mounted in an evacuated glass enclosure of 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.

4.5   Results and Discussion

A detailed study of variation of the d.c. resistivity, ρ (ohm cm) as a function of crystal composition reveals that the resistivity increases non-linearly with increasing sulphur content in the solid solution MoS_xSe_{2-x} ($0 \leq x \leq 2$)   as shown in Fig. 4.6. The room

Fig. 4.4   Schematic circuit diagram for measurement
            of resistivity.

            S - Specimen

            P - Battery

            V - V.T.V.M.

            SW- Switch

Fig. 4.5   Sample holder assembly for TEP measurements

            H, H - Heaters,   S - Sample

            Th, Th-Thermocouples, M - Mica sheet

            E, E - Electrodes.

Fig. 4.6   Variation of resistivity (ρ) as a

            function of composition 'x' of
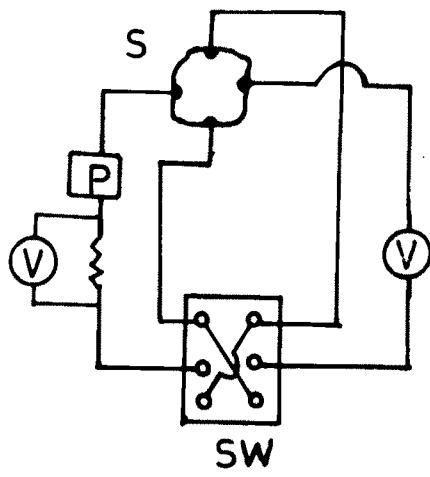
            MoS_xSe_{2-x}, $0 \leq x \leq 2$ at $30°C$.

S

P

V

V

SW

Fig. 4.4

E   Th   Th   E

S

M

H   H

Sample holder

Fig. 4.5

ρ (ohm-cm)

12

8

4

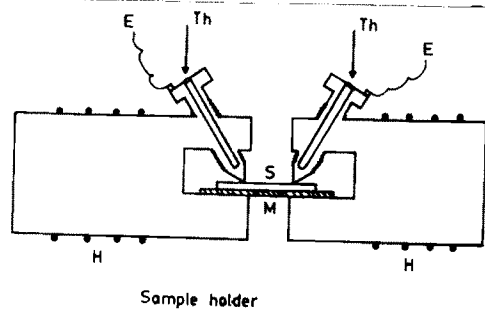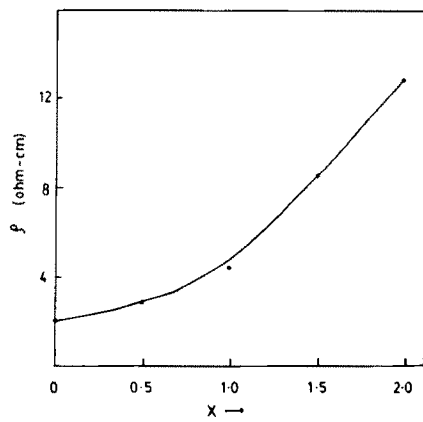0   0·5   1·0   1·5   2·0

X ⟶

Fig. 4.6

temperature (30°C) resistivities of $MoSe_2$ and MoS_2 have been obtained as 1.98 and 12.91 ohm cm. These results are in agreement with those reported by earlier workers[8-11] and the resistivity value is found to increase as the sulphur content increases in the solid solution. Analogous behaviour is observed in the case of $MoSe_xTe_{2-x}$ and WSe_xTe_{2-x} systems where the resistivity is found to increase with increasing selenium content.

In order to judge the semiconducting nature of molybdenum sulphoselenides, Hall effect measurements were carried out. Hall mobility, μ_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,

$$\mu_H = R_H / \rho \qquad \text{and} \qquad n = -\frac{1}{e R_H} \qquad (4.3)$$

where e is the electronic charge. The variation of μ_H, R_H and n with the composition of MoS_xSe_{2-x} is shown in Fig. 4.7. It is observed that the Hall mobility increases with increasing sulphur content. As the resistivity also increases with increasing sulphur content in the crystals,

it is concluded that the Hall coefficient increases and hence the carrier concentration decreases as we go from $MoSe_2$ to MoS_2.

It is interesting to note that the optical band gap determined from spectral response (Chapter 7) of the crystals increases with increasing sulphur content in MoS_xSe_{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) to S (1.04 Å) leading to changes in the bond strengths and hence in the structure. Further, the electro-negativity of atoms increases from Te (2.1) to Se (2.4) to S (2.5) meaning thereby an increase in the ionic nature of 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 data of resistivity and Hall effect measurements are summarised in Table 4.1.

The thermoelectric measurements were made in the temperature range 40 to $200°C$. The variation in the Seebeck coefficient S with temperature is shown in Fig. 4.8. It is observed that the Seebeck coefficient increases initially with temperature and then decreases to a constant value. The nature of the variation is identical for all

Fig. 4.7   Variation of Hall mobility (μ_H), Hall co-
            efficient (R_H) and carrier concentration
            (n) as a function of composition 'x' of
            MoS_xSe_{2-x}, $0 \leq x \leq 2$, at $30°C$.

Fig. 4.8   Seebeck coefficient 'S' as a function
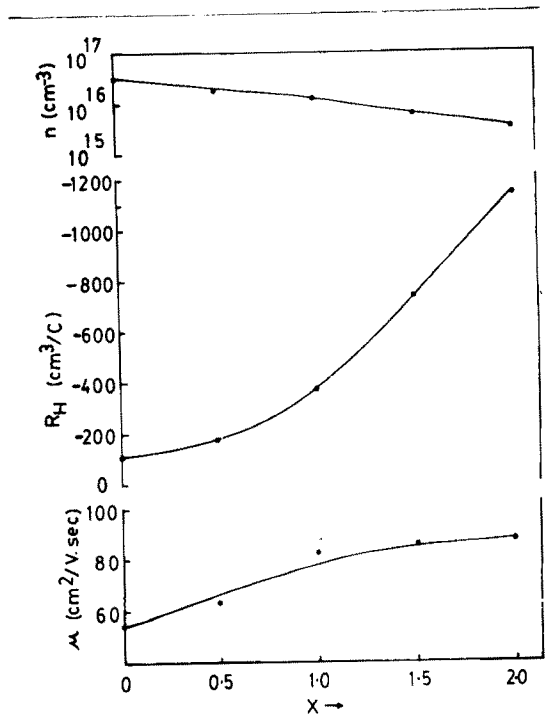   of temperature for molybdenum sulpho-
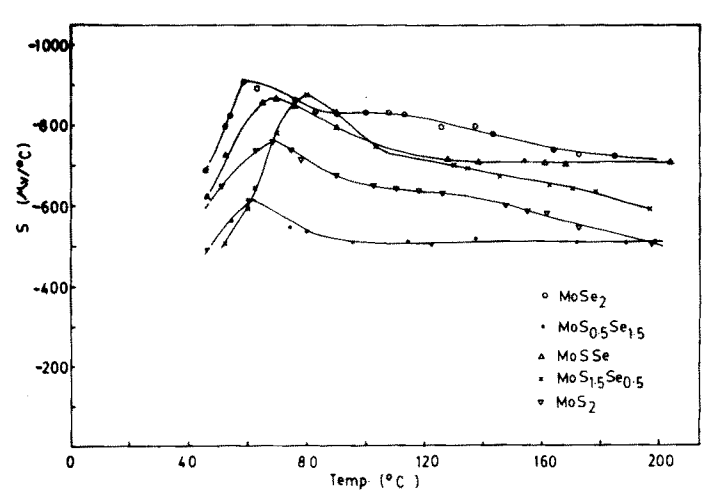   selenide system.

Fig.4.7

Fig. 4.8

Table 4.1

Data obtained on resistivity and Hall effect measurements for compositions in the MoS$_x$Se$_{2-x}$ series

Composition X	D. C. resistivity at 30 C ρ (ohm·cm)	Hall mobility μ_H (cm^2/V.s.)	Hall coefficient R_H (cm^3/C)	Carrier concentration n (cm^{-3})
0.0	1.98	54.8	-108.7	5.73×10^{16}
0.5	2.82	62.3	-175.7	3.55×10^{16}
1.0	4.42	83.7	-370.2	1.69×10^{16}
1.5	8.63	85.8	-740.7	8.85×10^{15}
2.0	12.91	87.9	-1136.3	5.5×10^{15}

compositions in the MoS_xSe_{2-x} system except that the peak value of Seebeck coefficient occurs at different temperatures. The existence of peak in the Seebeck coefficient versus temperature plot and its relation to the variations in the concentration and mobility of charge carriers need further investigations for the adequate explanations. However, it is worth noting that the Seebeck coefficient had a negative value for all compositions of solid solutions throughout the temperature range under the present investigation indicating the crystals to be n-type.

4.6   Conclusion

1.   The resistivity measurements have shown in general that the resistivity increases with the increasing amount of sulphur in molybdenum sulphoselenide series.

2.   Hall effect measurements indicate, improved mobility with substitution leading to an increasing amount of sulphur.

3.   Thermoelectric investigation finds all

compositions in the series to be n type
semiconducting materials. This fact has
also been confirmed by Hall effect
measurements.

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