CHAPTER 5

SINGLE CRYSTAL GROWTH OF LAYERED TIN MONO-SELENIDE SEMICONDUCTOR USING A CHEMICAL VAPOUR TRANSPORT TECHNIQUE

5.1 INTRODUCTION

Laminar semiconductors are attracting considerable interest because of the important opportunities they open up, particularly in optoelectronics. The primary consequence of the particular structure of laminar crystals is a pronounced anisotropy in physical properties, e.g.thermal, magnetic, optical and electrical. Despite the unusual interesting properties of laminar crystals, their semiconducting properties have been studied only extremely superficially. A great interest in these laminar crystals has developed markedly after it was demonstrated that they can be used as a solid state medium for writing reflection holograms [1].

Several investigators [2-7] and Chapter 4 of this thesis, have therefore taken up the synthesis of laminar semiconductor SnSe. In the majority of these cases the crystals always grew in the form of one large single crystal. Thin flakes needed for the physical property measurements are therefore obtained from a large size crystal by the method of cleaving. The process of cleaving may introduce a large number of defects. It is therefore desirable to evolve a method by which the crystals can be grown in the form of thin flakes so that they can be used as grown for the measurements.

The only report on the growth of SnSe in the form of thin crystals of thickness varying from 10 to 100 μm and having an area of 0.2 cm^2 is by Domingo et al [8]. They had used iodine as the transporting agent in their growth of SnSe. The exact details of the growth procedure adopted by them are however not available. Efforts tc grow SnSe in the form of thin flakes by iodine transport did not yield successful results. Author has therefore taken up the growth of these crystals by ammonium chloride (NH_4Cl) as the transporting agent. The growth and characterization of these crystals have been described in this chapter.

5.2 EXPERIMENTAL

5.2.1 Charge Preparation

The initial charge of SnSe required for growth by this technique was prepared in the same manner as described in Chapter 2 and Chapter 4 for the DVT technique.

5.2.2 Crystal Growth

10 gm of SnSe powder prepared as above was taken into a cleaned, etched and vacuum baked quartz ampoule of internal diameter 2.0 cm and length 26.0 cm.

A weighed quantity of (4 mg cm^{-3} of ampoule volume) of analar AR grade NH_4Cl was introduced into the ampoule in a sealed capillary tube made from ordinary corning glass. The ampoule was then evacuated to a pressure less than 10^{-5} torr and sealed at the constriction 3 mm in diameter.

The ampoule was vigorously vibrated to ensure that the capillary tube breaks and releases the NH_4Cl powder and the contents of the ampoule were mixed properly. The mixture was distributed along the length of the ampoule and was then placed in a two-zone horizontal furnace having the temperature profile as shown in Fig. 5.1 for 240 h. The ampoule was cooled to room temperature at the rate of 10 K

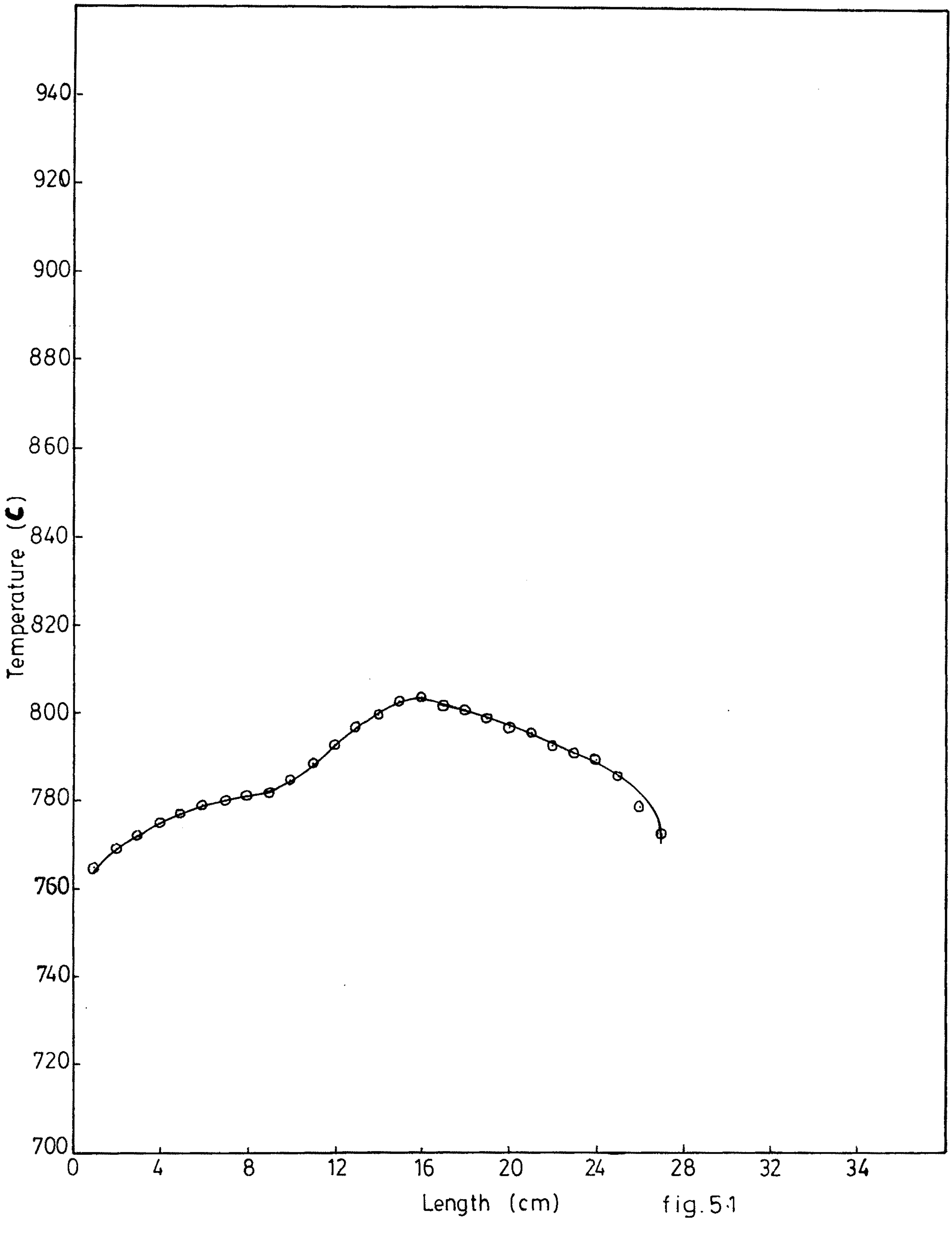

Temperature (C)
940
920
900
880
860
840
820
800
780
760
740
720
700
0
4
8
12
16
20
24
28
32
34
Length (cm)

fig.5·1

per hour. Upon breaking the ampoule, it was seen that good quality shining platelets grew directly over the distributed charge. Some of the large size crystals grown in the form of thin flakes by the above method are shown in Fig. 5.2.

5.2.3 Structural Characterization

Similar to SnSe crystals grown by DVT (Chapter 4), here also the single crystalline nature of the crystals was confirmed by taking an electron diffraction pattern from the grown sample. The crystals were then further characterised by X-ray powder diffraction (Fig. 5.3) taken from SnSe crystals by the method outlined in Chapter 2. The lattice parameters obtained from the XRD pattern shown in Fig. 5.3 are found to be a = 4.057 A, b = 4.230 A and c = 11.480 A. These values are in good agreement with the values reported for SnSe single crystals grown by DVT (chapter 4) and with the values obtained by [2] and [9]. As before (Chapter 4), the chemical composition of the grown crystals was confirmed through Energy Dispersive Analysis of X-rays (EDAX) using PHILLIPS, EM 400 T Analytical TEM/STEM system as described in Chapter 2.

5.2.4 DTA and TGA

Thermograms obtained from SnSe grown by the CVT technique were nearly identical to that obtained by DVT and

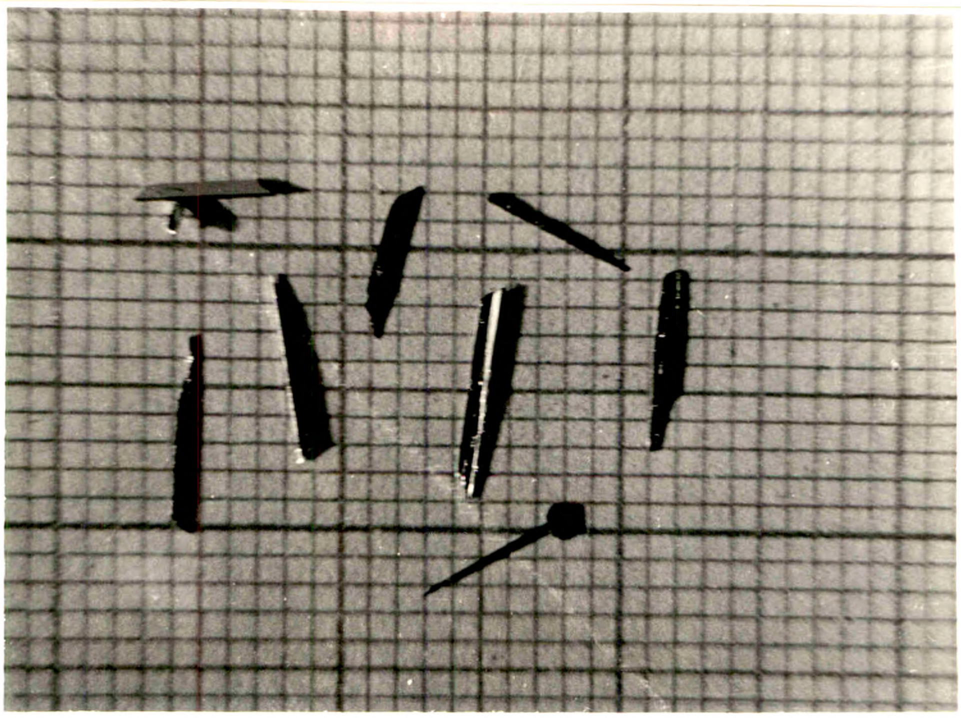


fig. 5.2.

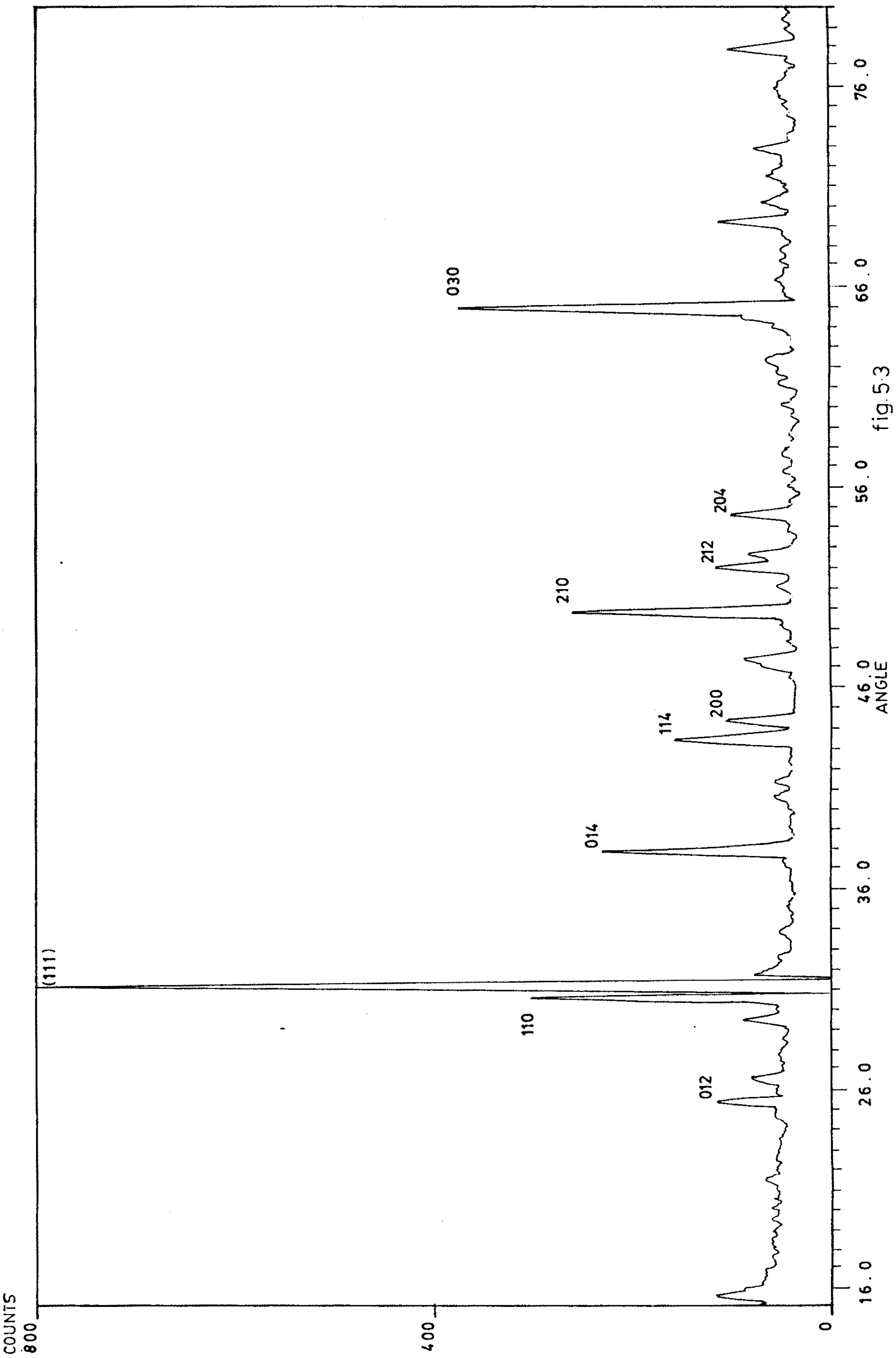

COUNTS
800
400
0
16.0
26.0
36.0
46.0
56.0
66.0
76.0
ANGLE
012
110
(111)
014
114
200
210
212
204
030

fig.5.3

do not provide any more information than already provided in Chapter 4 and hence have not been presented here.

5.2.5 Electrical Resistivity Measurements

The four-probe set up described in Chapter 2 was used to carry out the electrical resistivity measurements of the samples perpendicular to the c-axis. It was seen that the crystals had a negative temperature coefficient of resistivity, thereby suggesting a semiconducting behaviour for them.

A representative observation showing the variation of resistivity with temperature is shown in Fig 5.4. The values of activation energy obtained from the slopes of the graph are seen to be 0.06 eV in the temperature range 303-373 K and 0.22 eV in the temperature range 383-453 K.

5.2.6 Optical band gap measurements

The SHIMADZU UV-VIS-NIR RECORDING SPECTRO-PHOTOMETER UV-365 described in Chapter 2 was used to make the optical absorption measurements on as grown samples of SnSe in the wavelength range 1200 to 1500 nm. A plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ is shown in Fig. 5.5. As before, α is the absorption coefficient and $h\nu$ is the photon energy.

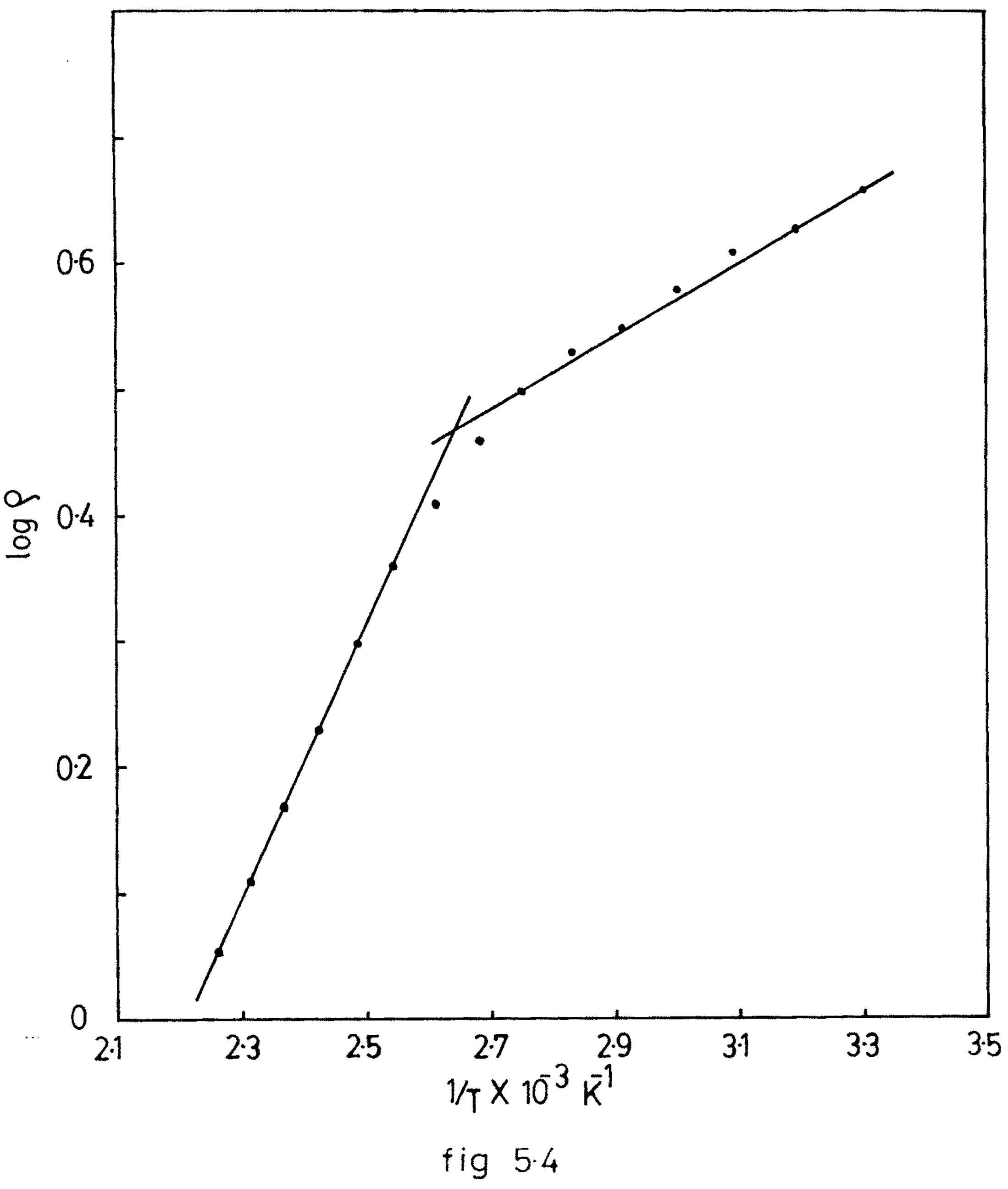
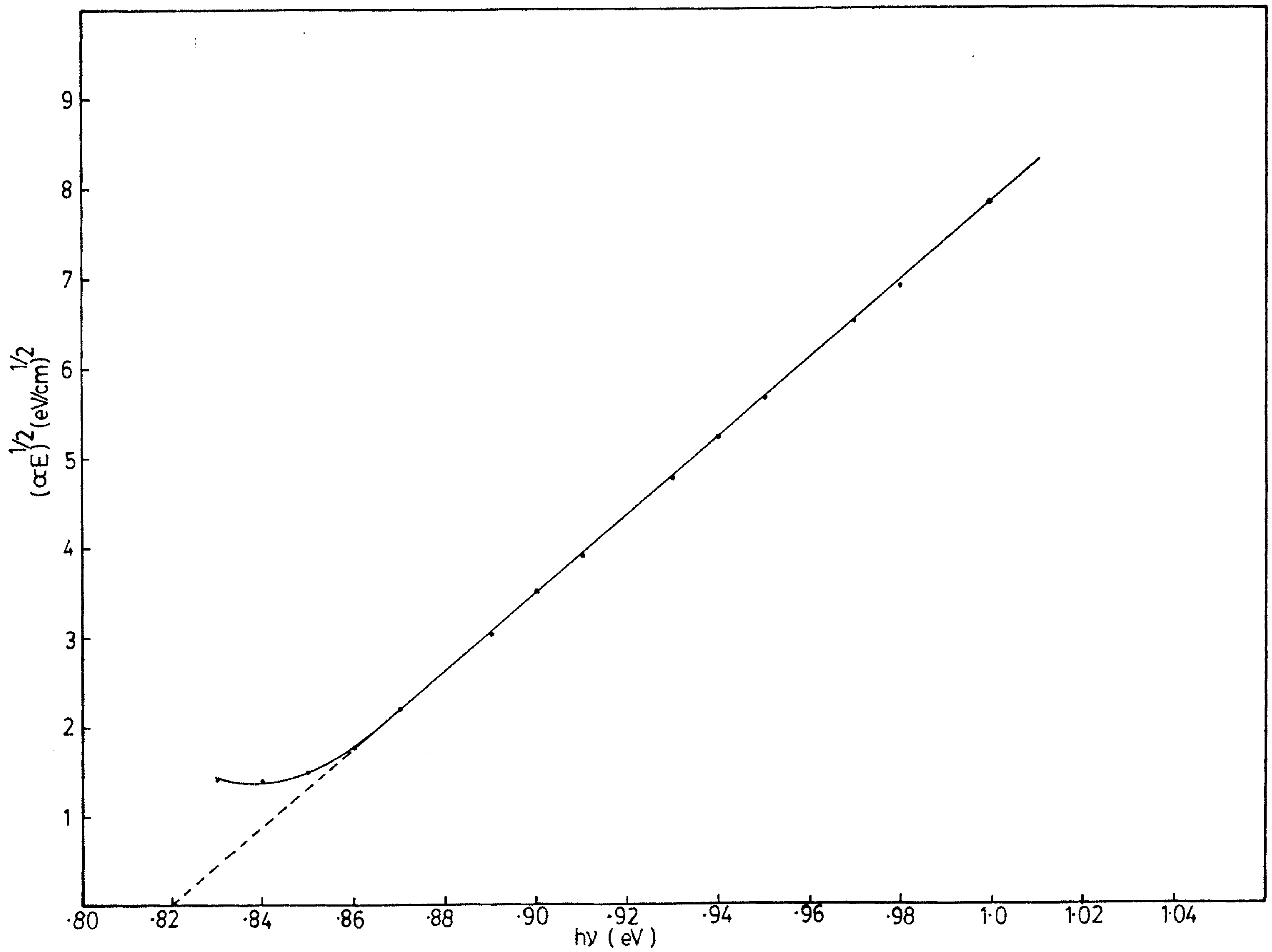


fig 5·4


$(\alpha E)^{1/2}$ $(eV/cm)^{1/2}$
9
8
7
6
5
4
3
2
1
·80
·82
·84
·86
·88
·90
·92
·94
·96
·98
1·0
1·02
1·04
hν (eV)

An indirect band gap of 0.82 eV could be obtained for these crystals. In addition, a direct band gap energy value of 0.921 eV could also be obtained (Fig. 5.6) in these crystals.

5.2.7 Thermoelectric Power Measurements

The importance of the measurement of thermo-electric power has already been pointed out in [10] and in chapter 4. The thermoelectric power measurements of the as grown samples of SnSe crystals were carried out with the help of "Differential Temperature Controller" developed by Scientific Solutions, Bombay (Chapters 2 and 4). The change in thermoelectric power with increase in temperature is also very clearly depicted in Figs. 5.7 and 5.8 for three different samples. The positive sign of the thermoelectric power for all the samples indicate their p-type semiconducting nature. The p-type nature of the crystals was also confirmed by carrying out the following experiment.

Two contacts were taken on the semiconducting sample in the manner described in Fig. 5.9. When one of the contact was heated, the majority carriers in the sample moved from the hot junction towards the cold junction. Considering the p-type nature of the sample, it can be said that holes (being the majority carriers) would move away

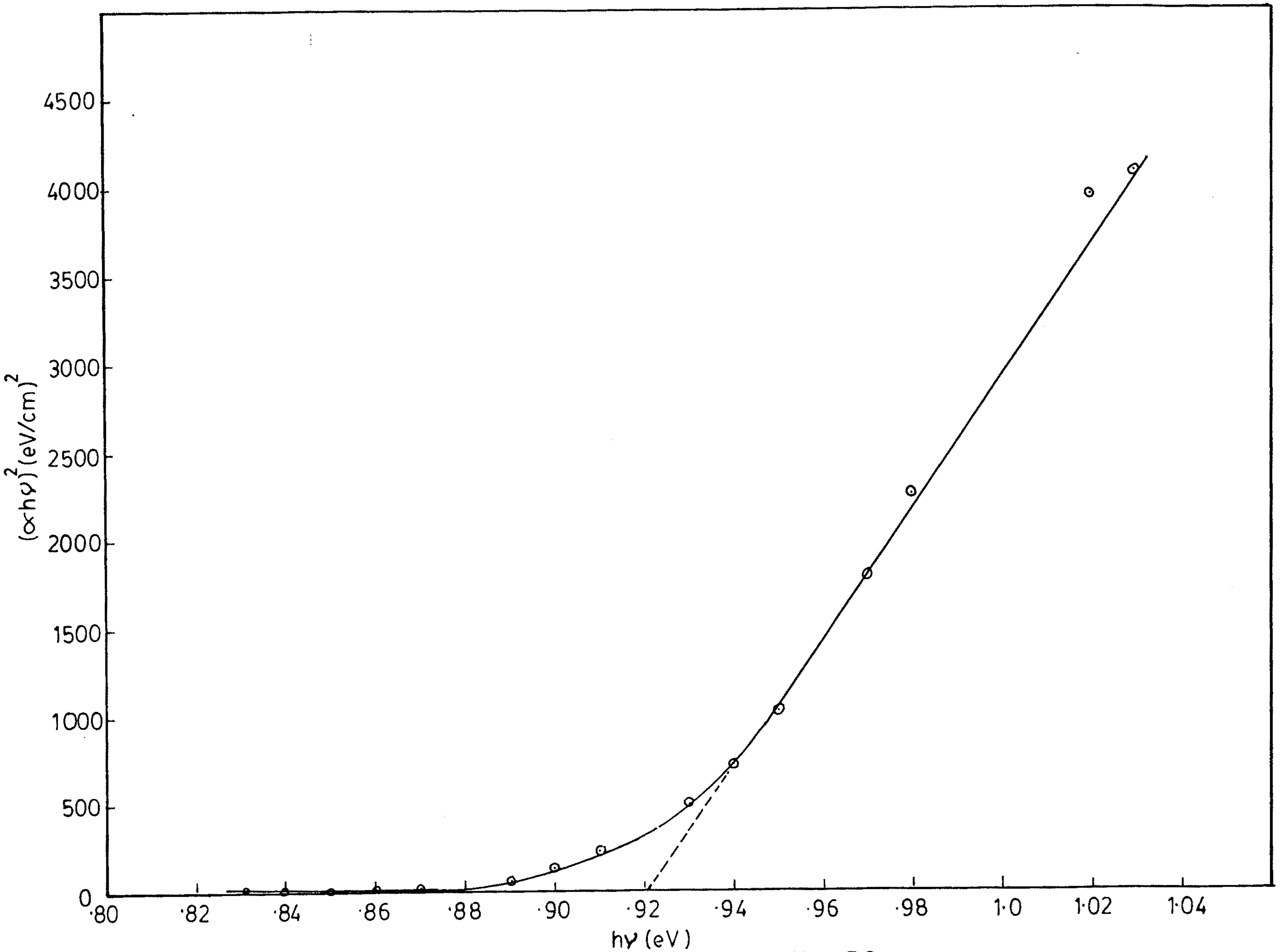

4500
4000
3500
3000
2500
2000
1500
1000
500
0
$(\alpha h\nu)^2 (eV/cm)^2$
·80
·82
·84
·86
·88
·90
·92
·94
·96
·98
1·0
1·02
1·04
hν (eV)

fig. 5·6

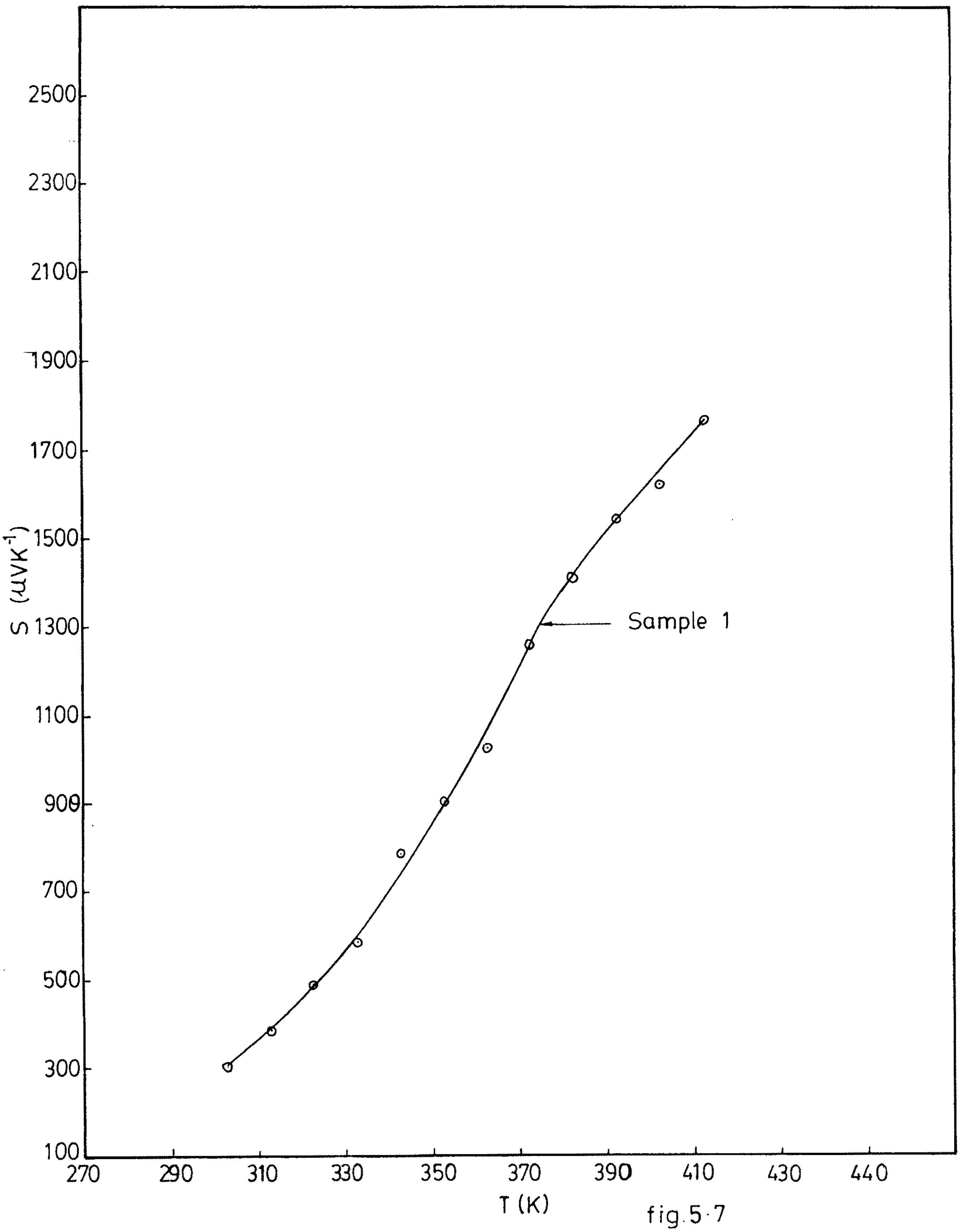

2500
2300
2100
1900
1700
1500
1300
1100
900
700
500
300
100
S (μVK⁻¹)
270
290
310
330
350
370
390
410
430
440
T (K)
Sample 1

fig.5·7

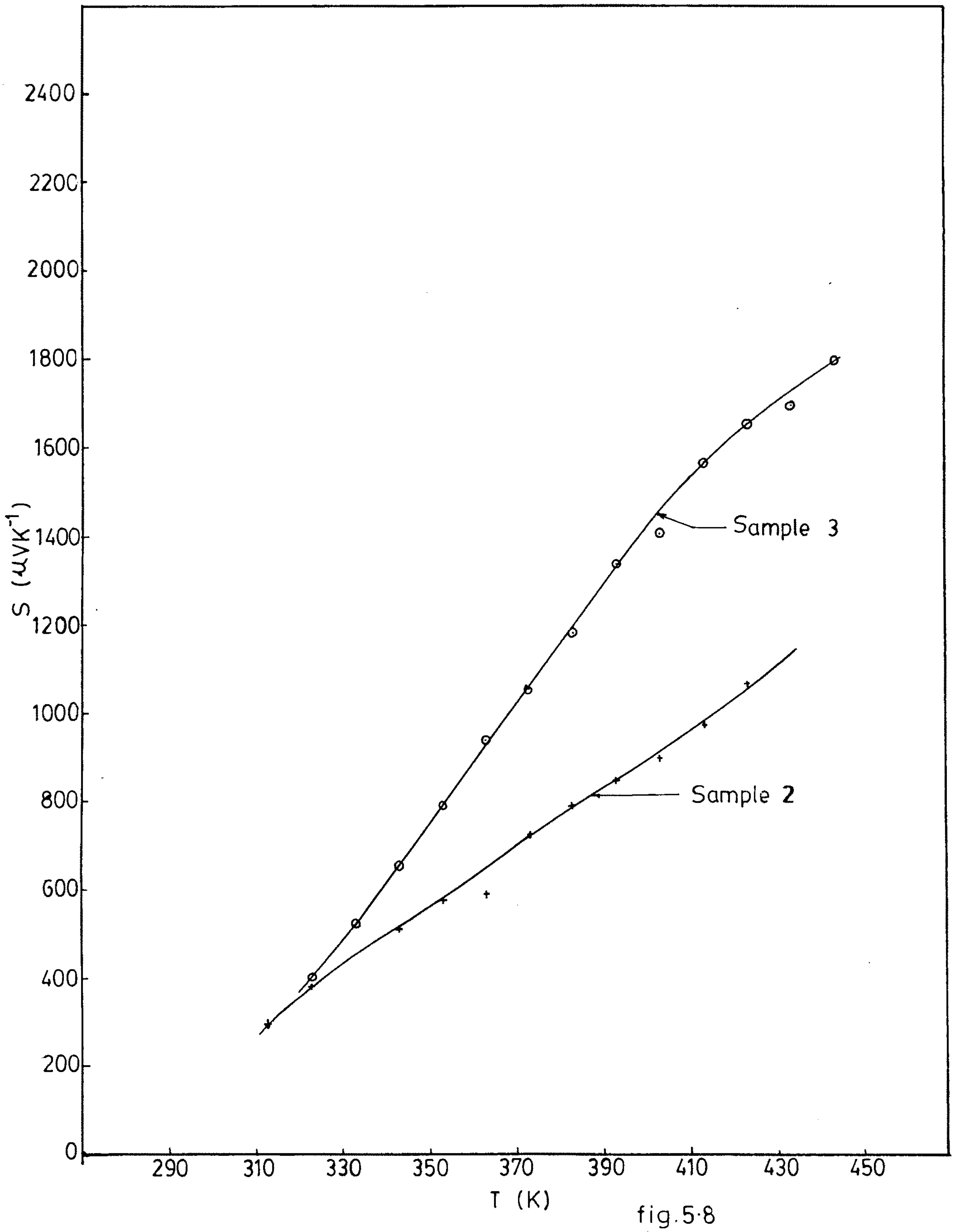

2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
S (μVK^{-1})
290
310
330
350
370
390
410
430
450
T (K)
Sample 3
Sample 2

fig.5·8

For n-Type Semiconductor Samples

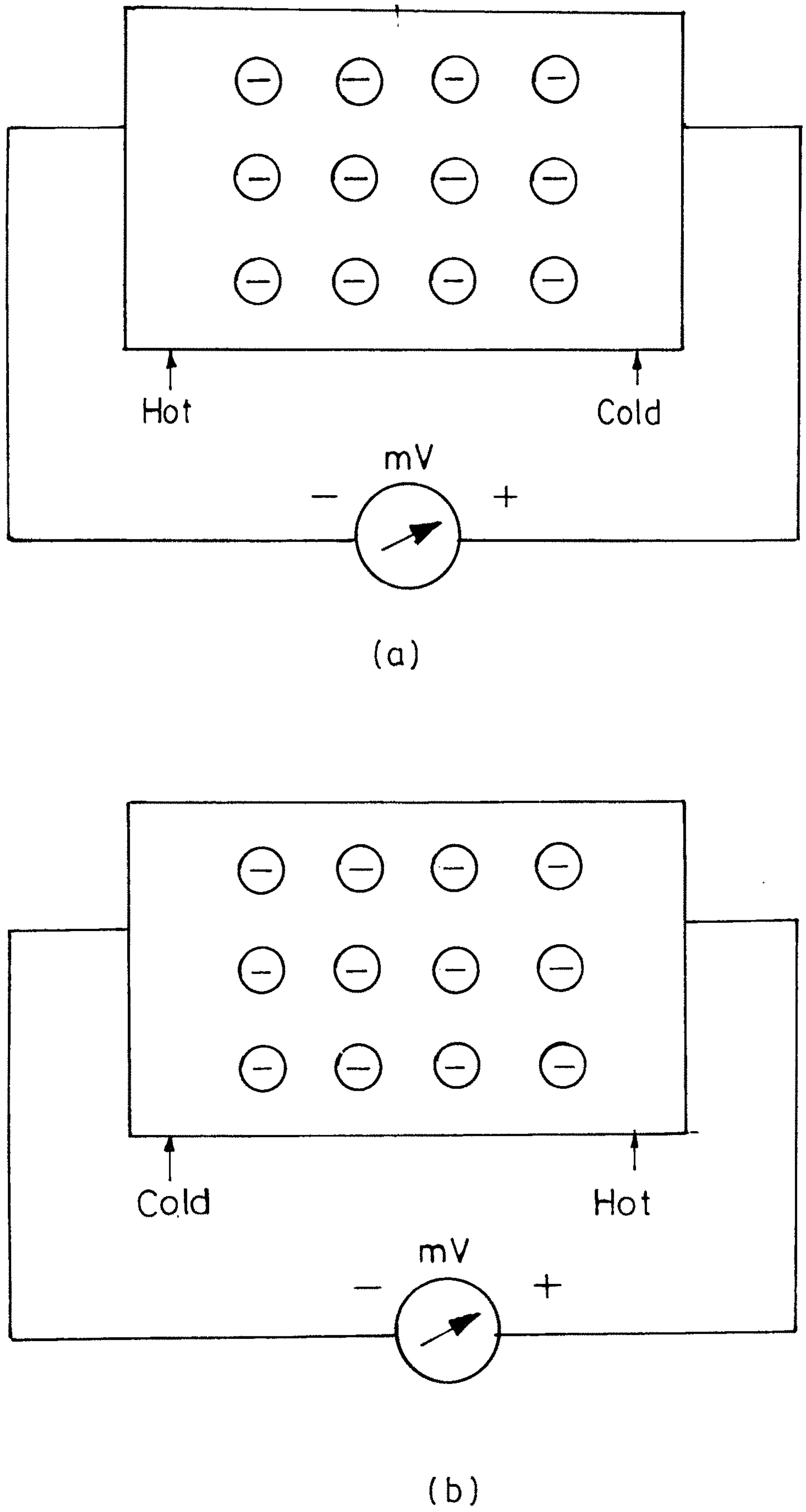
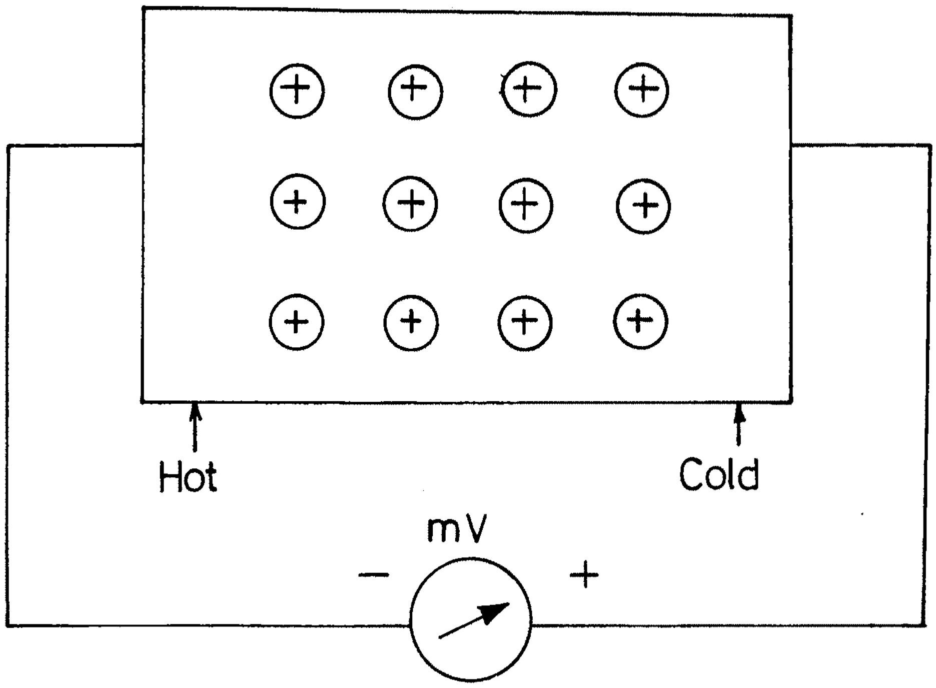
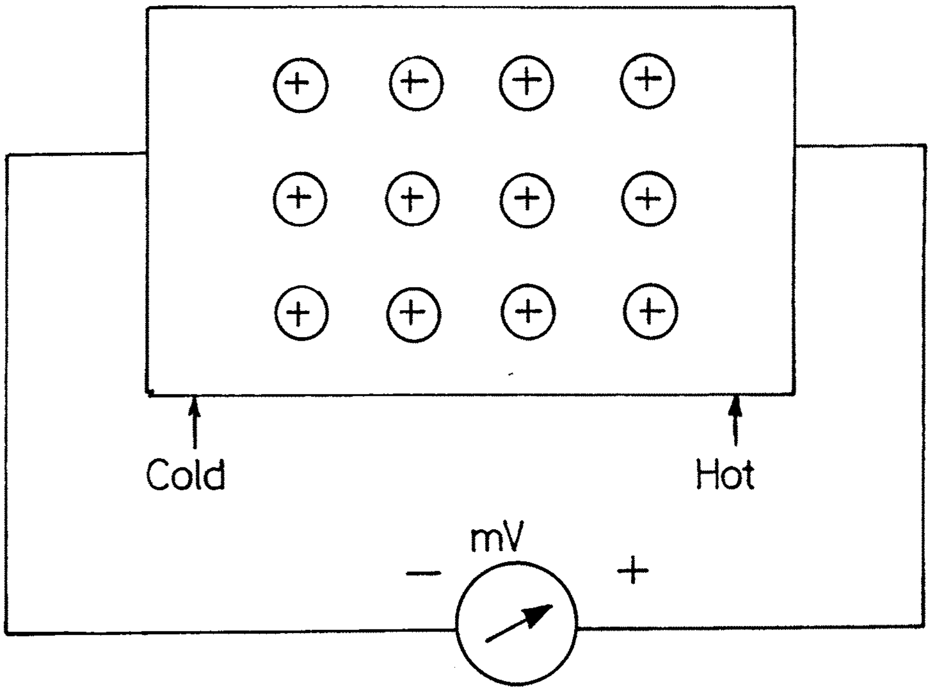


fig. 5·9 (contd.)

- ype semicon uctor Samples.



(c)



(d)

Connection of millivoltmeter to sample of which one end is hot and other is cold.

(a) n-type sample for −ve voltage.

(b) n-type sample for +ve voltage.

(c) p-type sample for +ve voltage.

(d) p-type sample for −ve voltage.

fig. 5·9

from the hot junction giving rise to a negative potential. The appearance of negative potential for all the samples used above confirmed their p-type semiconducting nature.

Observations presented in Figs. 5.7 and 5.8 clearly show that in all cases the thermoelectric power progressively increased with increase in temperature, thereby indicating a typical non-degenerate semiconducting behaviour.

5.3 DISCUSSION

Single crystals of SnSe were found to grow in the form of thin platelets and needles. All of them showed a mirror like metallic lustre. The lattice parameters obtained from X-ray diffraction studies were found to be in good agreement with the reported values and the values described in Chapter 4. The crystals were found to be nearly stoichiometric as judged from their EDAX analysis,

The role played by NH_4Cl introduced in the ampoule as transporter can be understood as follows :

It is well known that the molecule NH_4Cl decomposes into NH_3 (ammonia gas) and HCl (gaseous) at elevated temperatures. The liberated HCl gas forms a product $SnCl_4$ reacting with Sn. The reaction product $SnCl_4$ act as transporting agent for Sn, yielding synthesis of single crystals of SnSe at the growth end of the ampoule.

The activation energies of 0.06 eV in the temperature range 303-373 K and 0.22 eV in the temperature range 383-453 k are nearly of the same order as those obtained in the case of SnSe single crystals grown by DVT method. The low values of activation energy suggest that here also the extrinsic i.e. impurity conduction is present in the observed range of temperature.

Using the relation (4.2), for the thermoelectric power, one can estimate the carrier concentration and the mobilities and their variation with temperature. However, a close look at the equation (4.3) for log p suggests that value of thermoelectric power hardly affects the value of carrier concentration. Therefore the variation of log p and consequently of log μ with temperature will not be different from that obtained in chapter 4 for the DVT grown samples.

Moreover relation (4.3) will only provide a rough estimate of the carrier concentration. For an accurate determination of the carrier concentration and mobility, one has to carry out the measurement of Hall parameters on the grown samples. This will be taken up in next chapter on anisotropic measurements.

The optical absorption measurements have provided a clear cut evidence for the existence of indirect and direct band transitions in CVT grown SnSe single crystals. This is in confirmation with the results reported in the literature and in Chapter 4.

5.4 CONCLUSIONS

Single crystals of tin monoselenide have been successfully grown in the form of thin platelets by a Chemical Vapour Transport technique using analar AR grade NH_4Cl. The single crystalline nature of the material has been confirmed from the electron diffraction studies. The stoichiometry of the grown crystals has been verified from the EDAX analysis. The electrical resistivity and Seebeck coefficient measurements have shown that the crystals are p-type semiconductors. The optical absorption measurements have suggested that both direct and indirect transitions take place across the energy gap. The values of optical band gap E_g determined in the present work are in agreement with the reported values in the literature.

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CAPTIONS TO THE FIGURES

Fig. 5.1 Temperature distance profile in the furnace for the synthesis of SnSe single crystals.

Fig. 5.2 As grown single crystals of SnSe.

Fig. 5.3 X-ray diffractometer trace of SnSe.

Fig. 5.4 Variation of electrical resistivity with temperature.

Fig. 5.5 Optical absorption $(\alpha h\nu)^{1/2}$ as a function of photon energy '$h\nu$'.

Fig. 5.6 Optical absorption $(\alpha h\nu)^{2}$ as a function of photon energy '$h\nu$'.

Fig. 5.7 Variation of thermoelectric power with temperature (Sample 1).

Fig. 5.8 Variation of thermoelectric power with temperature (Samples 2 and 3).

Fig. 5.9 Schematic diagram for testing the type of carriers by hot probe technique.