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CHAPTER 11

HIGH PRESSURE STUDIES OF SnSe SINGLE CRYSTALS

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### 11.1 INTRODUCTION

The IV-VI binary compounds of the type  $A^{IV} B^{VI}$  are divided into two main groups according to their crystal structure. SnTe, PbS, PbSe and PbTe belong to the  $O_{hh}^5$  (Fm 3m) space group with NaCl type lattice [1]; GeS, GeSe, SnS and SnSe belong to the  $P_{mna}$  ( $D_{2h}^{16}$ ) space group with orthorhombic structure [1]. This orthorhombic subgroup of IV-VI compounds consists of structures intermediate between three- and two-dimensional materials, constructed of two-dimensional layers weakly bonded to each other to produce a three-dimensional material [2].

Attention has been focussed on the optical properties of layered semiconductors SnS and SnSe, notably because of their use in holographic - recording systems [3]. These materials are also useful because of their applications in optoelectronics [2] and electrical switching [4].

Recently, influence of temperature and pressure on the electronic transitions in SnS and SnSe semiconductors has been undertaken by Martin and Cosmo [5]. Peters and McNeil [6] have made use of Mossbauer spectroscopy and Hydrostatic high pressure techniques to examine the bonding of the Sn atoms in SnSe. However, there are no reports on the effect of pressure on the thermoelectric power and the electrical resistivity of these materials. A study of the effect of pressure on the thermoelectric power and the electrical resistivity of SnSe single crystals grown by a modified direct vapour transport technique and a chemical vapour transport technique has been undertaken and this chapter describes the results thus obtained.

## 11.2 EXPERIMENTAL PROCEDURE

Thin samples of DVT grown single crystals of SnSe [Chapter 4] were prepared by the method of cleavage from a large crystal. Since CVT grown crystals [Chapter 5]

were thin enough, they were used as such in the experiments.

For the room temperature measurements of electrical resistivity as a function of pressure upto 100 Kbar, pressure was generated with a Bridgman type tungsten carbide opposed anvil apparatus with in situ Bi pressure calibration [Chapter 10]. Similarly the simultaneous measurement of room temperature resistivity and thermoelectric power of these SnSe single crystals as a function of pressure were taken upto 75 Kbar. As already described in chapter 10, the measurements were made in a Bridgman anvil apparatus and as before here also Bismuth I-II and Bismuth III-IV transitions at 25.5 and 76.7 Kbar were used for the pressure calibration.

### 11.3 RESULTS AND DISCUSSION

#### 11.3.1 Variation of electrical resistivity with pressure in SnSe Single crystals

The variation of electrical resistivity with pressure at room temperature (303 K) for a typical SnSe single crystal is shown in Fig. 11.1. The decrease in resistivity with an increase in pressure was indicative of a reduction in the energy gap of the material. However, two distinct regions of response, one corresponding to the low pressure range of 0-65 Kbar and the other corresponding to a

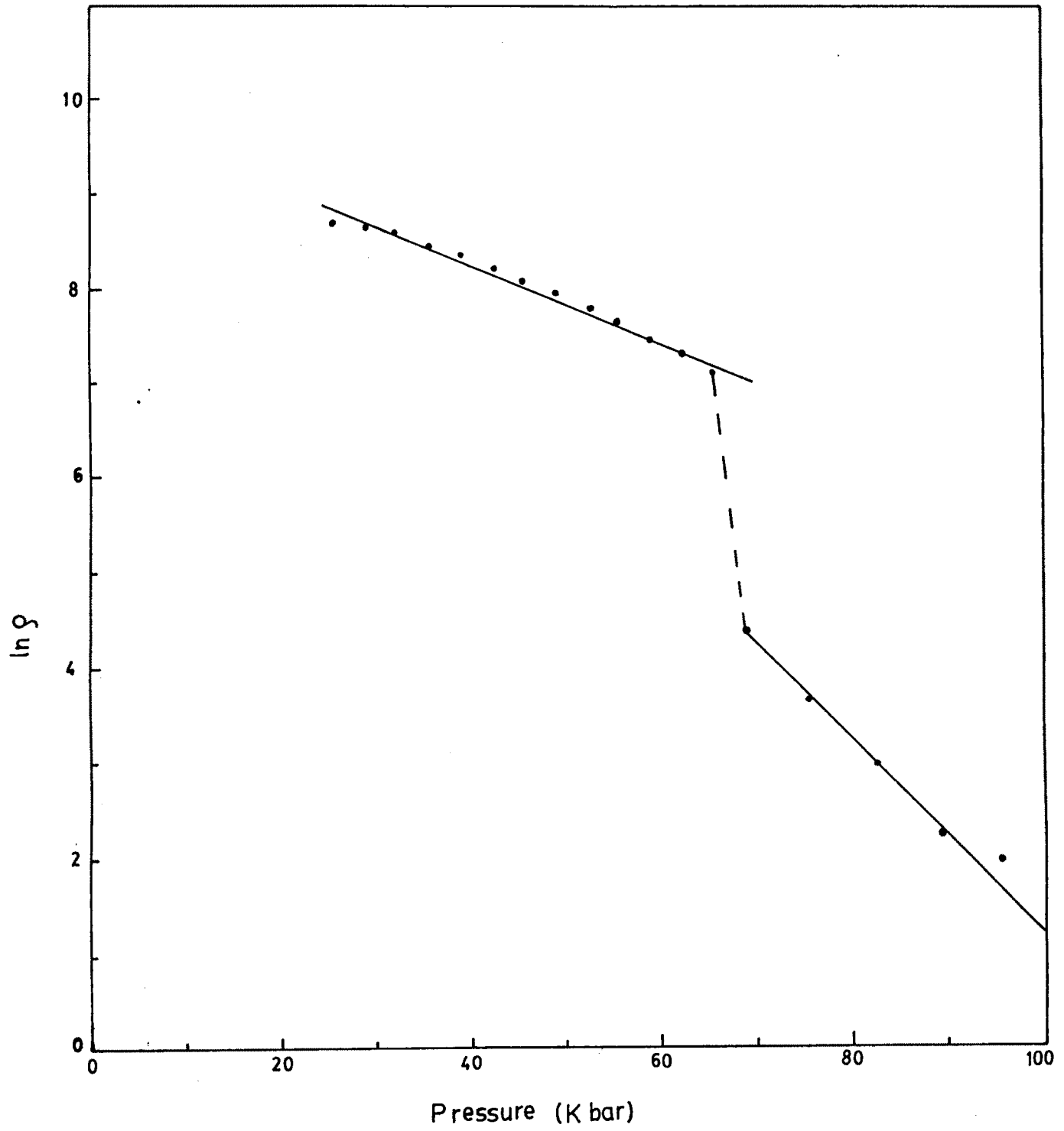


fig. 11-1

relatively high pressure range of 65-100 Kbar can be seen in Fig. 11.1. This could not be attributed to a phase transition, as no such transitions were found to occur in SnSe upto 340 Kbar [7]. The effect of pressure on the energy gap may be deduced from Fig. 11.1 for a two-band semiconductor model, making the usual assumption that the mobility and effective mass are constant.

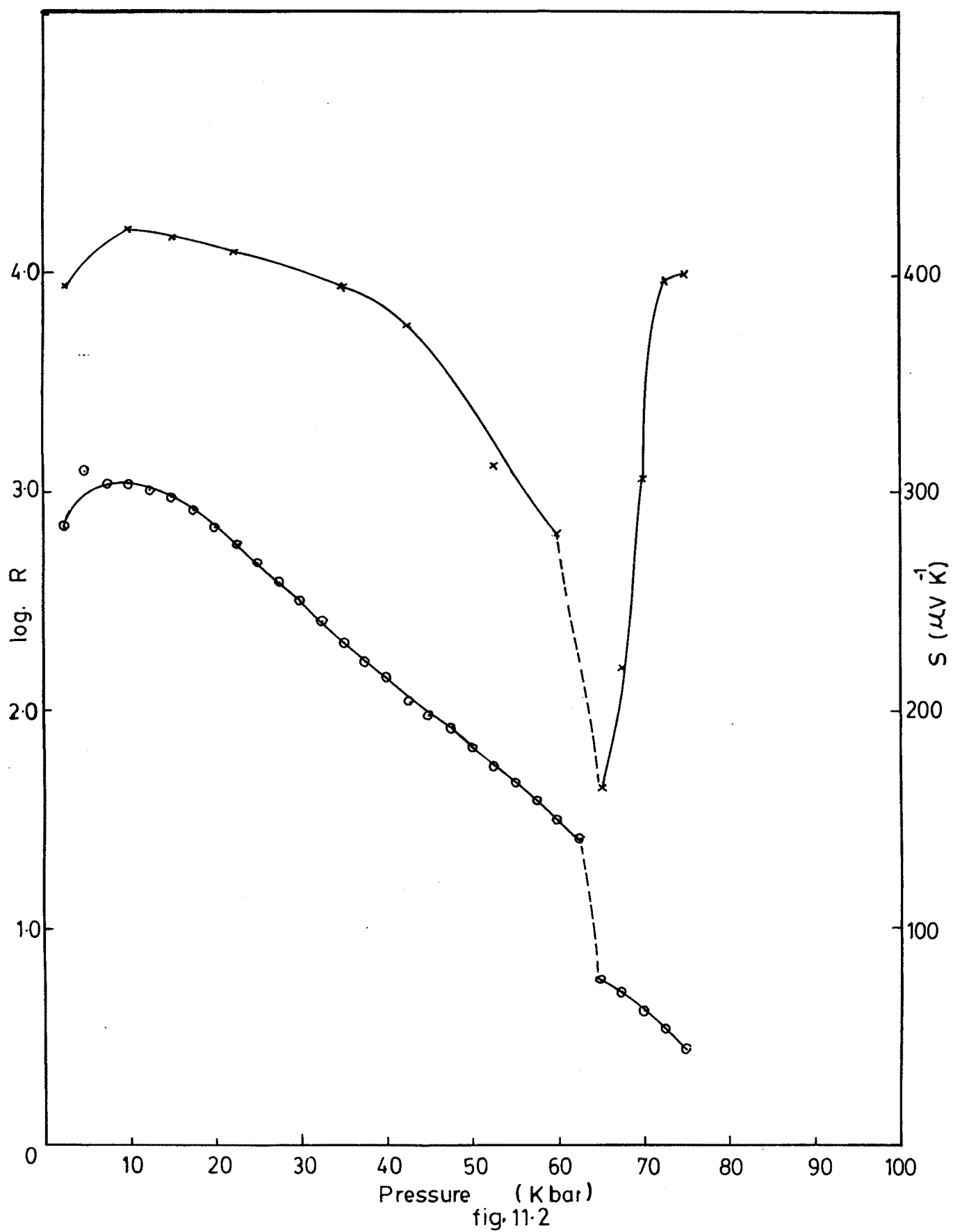
$$\frac{dE}{dP} = 2kT \frac{d \ln \rho}{dP}$$

The pressure coefficients thus obtained were found to be  $2.15 \times 10^{-11}$  and  $5.01 \times 10^{-11}$  eV K bar<sup>-1</sup> for the 0-65 and 65-100 K bar pressure ranges, respectively. Peters and McNeil [6] observed that the interlayer spacing in SnSe changed more rapidly than the intralayer spacing at low pressures (below 300 Kbar) during their high pressure Mossbauer studies of SnSe. Since the interlayer bonds are much weaker than the intralayer bonds, the transition from a predominantly two-dimensional material to a more three-dimensional material can be the only explanation of the observation of two ranges of response in the resistivity variation with pressure [8].

### 11.3.2 Simultaneous variation of Thermoelectric Power and resistance with pressure

The pressure dependence of thermoelectric power and resistance at room temperature for a representative sample of SnSe single crystal grown by DVT technique is shown in Fig. 11.2. Similar to Fig. 11.1, the variation of resistance with pressure once again shows a transition at 65 Kbar. The variation of thermoelectric power with pressure however shows that thermoelectric power at first decreases monotonically with pressure upto about 65 Kbar. This initial decrease of thermoelectric power can be related to the decreasing unit cell parameters and energy gap upon application of pressure as in a normal non-degenerate semiconductor. The thermoelectric power is then found to increase from 65 Kbar onwards. This transition in the behaviour of thermoelectric power cannot be attributed to the development of any phase transition since as already pointed out in section 11.3.1 above; no such transitions are found to occur [7] in SnSe upto 340 Kbar.

Upon application of pressure, the increase in resonance scattering usually contributes to the increase in both resistance and thermoelectric power. However, in the present case the resistance is found to decrease even after the transitional pressure. Hence, the increase in





thermoelectric power cannot be attributed to the presence of a continuous valence transition in this compound. The transition can be appropriately explained by the appearance of some defects in the crystal structure of SnSe at high pressure in the presence of inhomogeneous strain. These defects can lead to the appearance of an acceptor level in the band structure. The contribution of acceptor carriers in thermoelectric power becomes more and more significant at higher pressures and leads to an increase in the magnitude of thermoelectric power as observed in the present case.

Similar results were obtained in the case of CVT grown crystals too.

#### 11.4 CONCLUSIONS

The electrical resistivity in SnSe single crystals has been found to be pressure dependent. The transition in resistivity behaviour observed at 65 Kbar has been explained on the basis of a transition from a predominantly two-dimensional material to a more three-dimensional one. Similar to resistivity, the thermoelectric power in SnSe single crystals is also found to be pressure dependent. The increase in thermoelectric power with pressure at the transition pressure of 65 Kbar has been explained in terms of defects which originate in the crystal structure of SnSe in the presence of inhomogeneous strain.

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**CAPTIONS TO THE FIGURES**

Fig. 11.1 Variation of electrical resistivity with pressure in SnSe single crystals.

Fig. 11.2 Thermoelectric power and resistance as a function of pressure for p-type DVT grown SnSe single crystals.