

---

CHAPTER 1

EXISTING INFORMATION ON TIN MONOSELENIDE

(SnSe) SINGLE CRYSTALS

---

## 1.1 INTRODUCTION

The orthorhombic IV-VI compounds (GeS, GeSe, SnS and SnSe) having interesting electronic and optical properties have been the subject of numerous investigations. These compounds are of interest, since they consist of structures intermediate between the three-dimensional materials, constructed of two-dimensional layers weakly bonded to each other to produce a three-dimensional material.

All the layer like chalcogenides crystallise in

the GeS structure which belong to the orthorhombic space group  $P_{mna}$  ( $D_{2h}^{16}$ ) and is closely related to the black phosphorous structure. The primitive cell contains eight atoms and covers two adjacent double layers. The atoms in a single layer are joined to three nearest neighbours by covalent bonds which form zigzag chains along the b-axis. All these crystals cleave exceptionally easily in the a-b plane since Van der Waals bonding predominates along the c-axis.

It is worth noting that whereas the III-V and II-VI alloys have often been studied in their monocrystalline form as well as in their polycrystalline form, only a few studies have been performed for the IV-VI group. So far in this group interest was focussed more on lead and germanium chalcogenides than on tin chalcogenides though the later are not less interesting.

Recently attention has been focussed on optical properties of layered semiconductors SnS and SnSe notably because of their use in holographic recording systems [1] and electrical switching [2].

A detailed survey of literature to be presented in this chapter will indicate that a great amount of attention is being paid to the optical properties and

electronic band structure of tin chalcogenides, particularly on SnSe. Information regarding characterisation of single crystals as well as thin films of tin chalcogenides is extremely scanty. A wide variety of techniques and growth conditions are possible to tailor these materials to the need of their electronic device applications. Still only a few attempts have been made to study and understand the growth kinetics during the preparation of these materials in crystalline form. For a proper evaluation and utilization of these tin chalcogenide semiconductors in any electronic device, studies need to be made on the influence of growth parameters and conditions on the transport properties and phenomena.

In order to carry out these studies in their right perspective a brief account of the existing information on tin monoselenides has been given below.

## 1.2 OCCURRENCE AND SYNTHESIS

Since the material tin monoselenide (SnSe) is not known to occur naturally, it has to be synthesised in the laboratory. A brief description of the various attempts made by earlier workers to grow the crystals has been given below.

Asanabe [3] and Albers [4] grew single crystals of SnSe from the melt while Mitchell [5] grew them from a vapour phase. Usually, the most frequent method for the synthesis of this material in the form of single crystals are the horizontal bridgman and vertical Bridgman-Stockberger techniques [6,7]. Garg et al [8] and Agnihotri et al [9] used a simplified Bridgman method to grow the single crystals of p-type SnSe. Elkorashy [10], Valiukonis et al [1] and Julien et al [11] have also used the Bridgman technique for the growth of their SnSe samples. Bhatt et al [12] and Merdan [13] prepared the single crystals of tin chalcogenides by the Bridgman Stockberger technique.

Domingo et al. [14] used an iodine transport method in a close vycor tube to grow crystals of good optical quality while Maier and Daniel [15] and Yu et al [16] used a closed tube vapour phase technique (without any transporting agent) for the successful growth of the crystals. Logothetidis et al [17,18] grew single crystals of SnSe by sublimation from polycrystalline material.

Details of the growth techniques used by [8, 9, 12, 14-16] are shown in Table 1.1.

Yellin and Ben-dor [19] studied the synthesis of selenides of Sn at temperatures considerably below the

Table 1.1 Compound Preparation and crystal growth techniques for SnSe

Compound preparation procedure	Crystal Growth Technique	Crystal size
(a) Direct synthesis from the elements above 1173 K for 2 days. Second firing at the same temperature for 6 h [8]	<b>Bridgman Technique</b> $T_H = 1273 \text{ K} \rightarrow T_L = 873 \text{ K}$ Quartz tube = 20 cm x 2.2 cm. Tube lowered with a speed of 0.3 cm/hr. Annealing at 923 K for 1 day [8]	3 cm long and 1.5 cm diameter [8]
(b) Direct synthesis from the elements at 100 K above the melting point for 48 h. Kept at 773 K for 20 h and slowly cooled to room temperature in 10 h. [12]	<b>Bridgman Technique</b> Double wall quartz ampoule with inner ampoule = 20 cm x 1.8 cm Kept ampoule with material at 1173 K for 2 days. Lowered at the speed of 0.3 cm/h. Crystal was annealed at 923 K for 1 day. Cooled to room temperature at a rate of 20 K/h. [9]	Not reported
(c) Synthesised from 6 N purity Sn and 5N purity Se at 1173 K for 4 h for further purification a dynamic vacuum sublimation from 993 K to 693 K - 793 K was used [15]	<b>Bridgman - Stockbarger Technique</b> $T_H = 1193 \text{ K} \rightarrow T_L = 943 \text{ K}$ Quartz tube = 25.0 cm x 1.2 cm Tube lowered with a speed of 0.7 cm/hr. [12]	3 to 4 cm in length and 1.2 cm diameter [12]

Table 1.1 (contd.)

<u>Iodine Transport Technique</u>		Crystals of good optical quality having area cm <sup>2</sup> thickness from 10 to 100 um [14]
T <sub>H</sub> = 923 K	T <sub>L</sub> = 723 K	
Transporting agent = small quantity of iodine [14]		
<u>Closed tube vapour phase technique</u>		
T <sub>H</sub> = 1093 K		
Temperature gradient of 0.25 K/cm longitudinally and 1 K/cm transversally		upto 1 cm <sup>3</sup> in diameter[15]
<u>Quartz Tube</u>		
12 cm x 2.5 cm [15]		
T <sub>H</sub> = 1073 K	T <sub>L</sub> = 1043 K	1 cm long and 1.0 cm diameter [16]
<u>Quartz tube</u>		
18 cm x 1.8 cm [16]		

melting point of the compounds. According to them a complete reaction could be obtained within a period of few days.

Shinohara et al [20] obtained an array of lamellar SnSe-SnSe<sub>2</sub> structure by unidirectional solidification. In this array SnSe and SnSe<sub>2</sub> were respectively p- and n-type semiconductors. A crystallographic relationship between the two phases in the solidified state was determined by them using the technique of transmission and scanning electron microscopy.

N. Erdem et al [21] carried out the preparation of SnSe using a vapour transport technique which avoided the very high pressures developed in the sealed capsule technique during melting. In their vapour transport technique, a vapour liquid reaction took place above 823 K. This reaction proceeded rapidly and produced a dendritic compound between 823 K and 923 K, the product was a mixture of SnSe and SnSe<sub>2</sub>. But with increase in temperature, the proportion of SnSe<sub>2</sub> was reduced. At temperatures above 973 K, only SnSe was formed but the morphology still remained dendritic.

### 1.3. CRYSTAL STRUCTURE

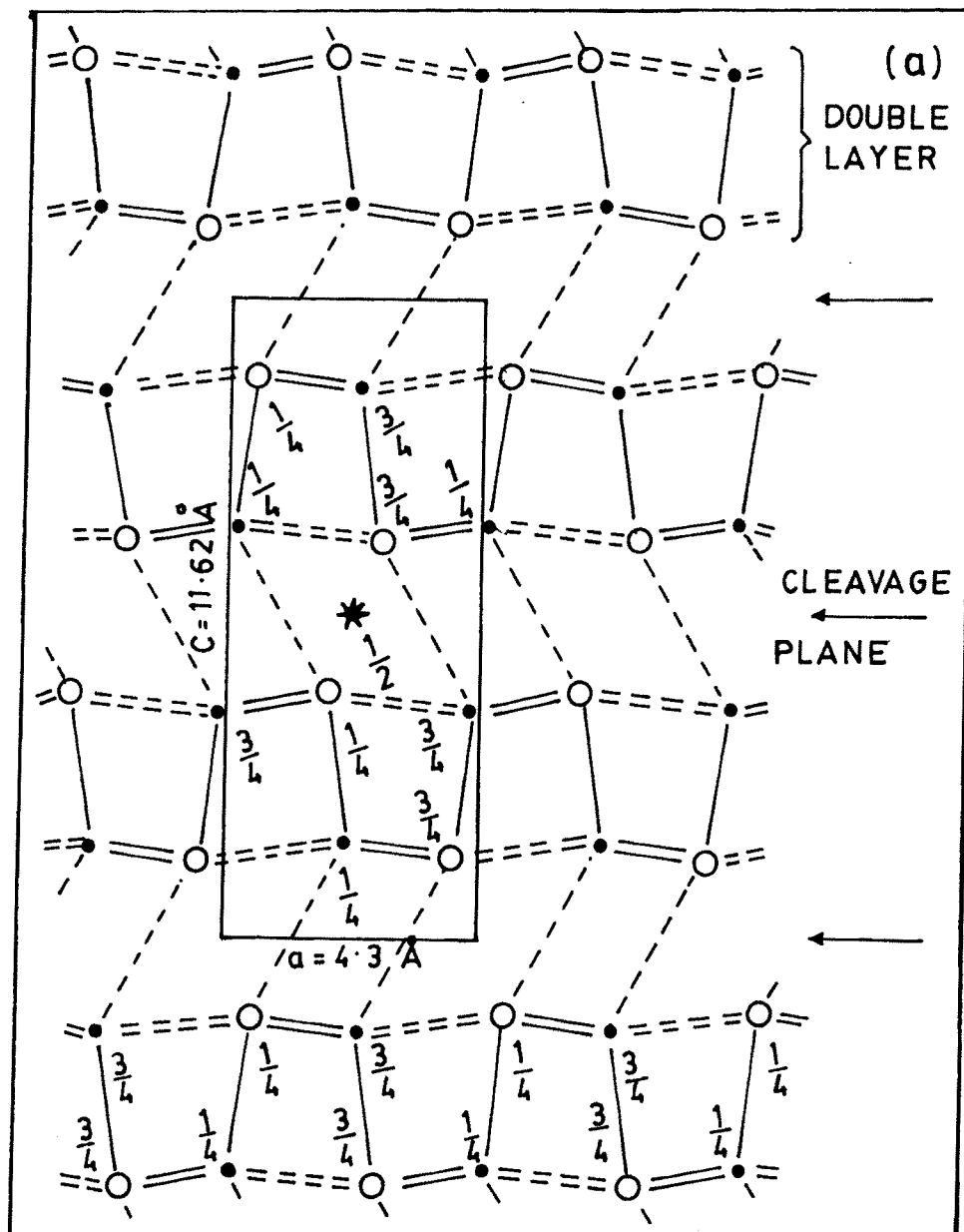
SnSe crystallises in the simple orthorhombic



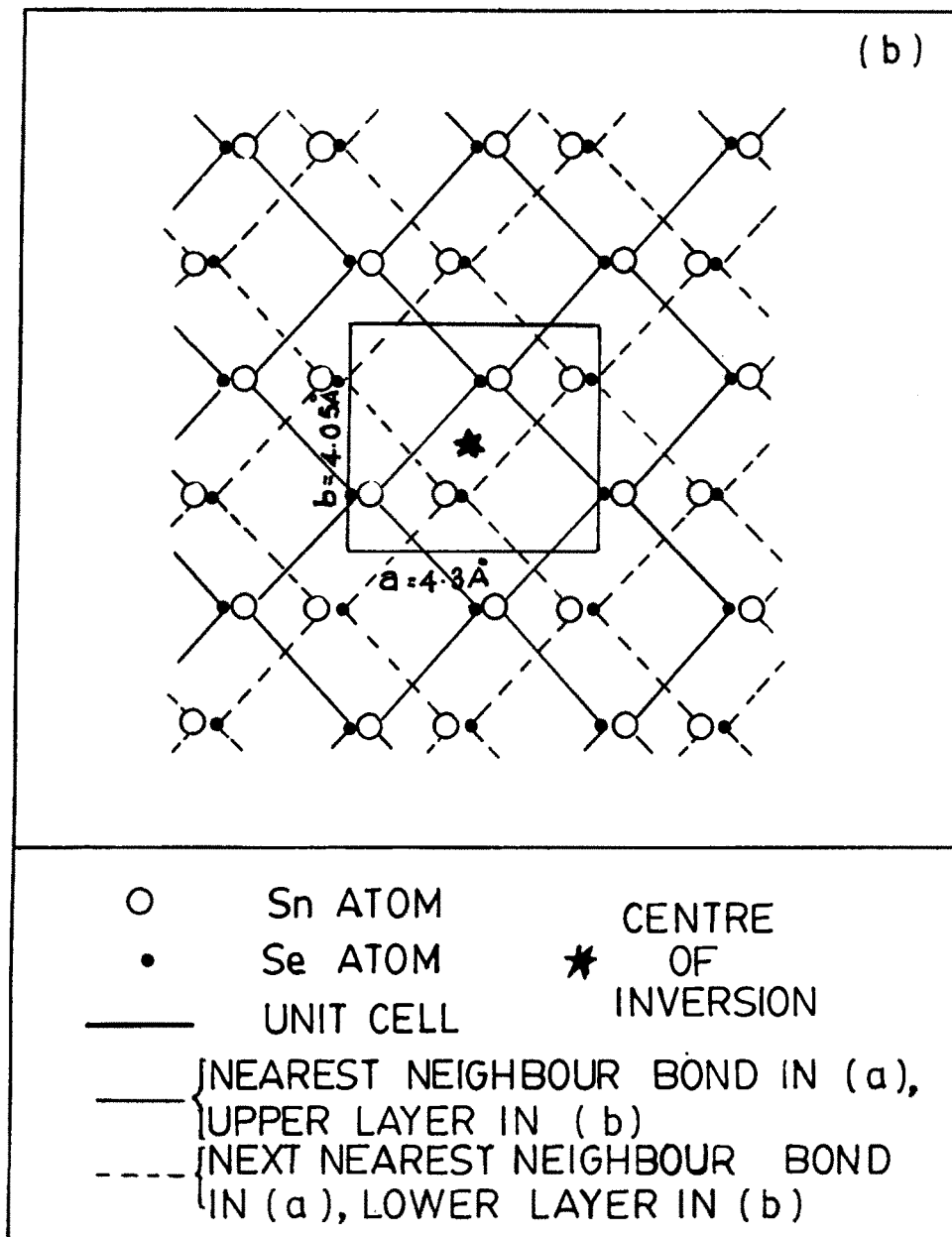
bravais lattice with structure B 29 [22,23] and lattice constants  $a = 4.19 \text{ \AA}$ ,  $b = 4.46 \text{ \AA}$  and  $c = 11.57 \text{ \AA}$  [24,25]. The unit cell contains eight atoms placed in positions given by [26] the scaled co-ordinates  $\pm (u, 1/4, v)$  and  $\pm (1/2 + u, 1/4, 1/2 - v)$  in compliance with the symmetry of the space group  $P_{nma} (D_{2h}^{16})$ . Measured values of parameters  $u$  and  $v$  are

$$\begin{array}{ll} u(\text{Sn}) = 0.118 & v(\text{Sn}) = 0.103 \\ u(\text{Se}) = -0.145 & v(\text{Se}) = 0.479 \end{array}$$

The Sn and Se atoms are arranged in two adjacent double layers stacked along the  $c$ -axis as shown in Figs. 1.1 and 1.2. Within either double layer each atom has the co-ordination environment of a heavily distorted octahedron and the lattice can be thought of as a deformed NaCl type [22]. Each atom forms six dominant heteropolar bonds, the strongest of which are in three bonds to nearest neighbours in the same double layer. Three weaker bonds are to further neighbours, two of which are in the same double layer, one to an atom in the next layer [22]. Table 1.2 gives the lengths of these six bonds for SnSe. Also included in the table is a quantity  $\Delta$  which is a measure of the deviation from an ideal NaCl type structure ( $\Delta = 0$ ).  $\Delta$  is the difference between the average of the three longest bond



SnSe structure projection on (010) plane  
fig. 1.1



SnSe structure projection on (001) plane.

fig. 1-2

**Table 1.2** Bond lengths of the six Heteropolar bonds in SnSe (in Å°)

SnSe		
Sn (1)	Se	2.77
(2)	Se	2.82
(2)	Se	3.35
(1)	Se	3.47*
$\Delta = 0.59$		

\* The Sn-Se bond marked with an asterisk is the bond between double layers [27]

lengths [22].

The highly layered structure typical of all orthorhombic chalcogenide crystals, causes a strong anisotropy of the physical properties of these compounds and determines a marked difference between the cubic and non-cubic IV-VI crystals, even though the orthorhombic structure can be regarded as a distortion of the cubic structure [28].

#### 1.4 ELECTRICAL PROPERTIES

Asanabe [3] showed that according to electrical measurements, SnSe was p-type with carrier density at 300 K as  $\sim 10^{18} \text{ cm}^{-3}$ . The doping was believed primarily due to the deviation from the stoichiometry with Sn vacancies as the acceptor source in SnSe. An excess of Sn would therefore change the type of conductivity of SnSe from p-type to n-type. Crystals grown by Maier and Daniel [15] were also p-type and the apparent net hole concentration was found to be dependent on the composition of the source material or on the annealing process. Hall mobility in their experiments showed a strong decrease with increasing temperature. Above 200 K it followed a power law  $\mu_p(T) \propto T^{-2.2}$  to  $T^{-2.4}$  indicating that lattice scattering mainly by optical phonons was predominant.

Variation of carrier concentration and conductivity with temperature in the temperature range [30 - 300 K] was investigated by Yu et al. [16]. It was observed by them that carrier concentration varied very little with temperature. The dependence of mobility on temperature studied in the range 10 K to 1000 K showed that mobility was proportional to  $T^{-2.24}$  for  $T > 130$  K and to  $T^{-1/3}$  for  $T < 130$  K. The former relation indicated the dominance of lattice scattering at higher temperatures while impurity scattering was considered as the main mechanism for the scattering process at lower temperatures. Julien et al [11] confirmed the semiconducting character of their SnSe crystals by means of resistivity and Hall effect in the temperature range 90 to 300 K.

A comprehensive investigation of electrophysical properties (Hall effect, electrical conductivity and thermoelectric power) of SnSe was carried out by Glazov et al [29] in a wide range of temperatures in solid and liquid states. An analysis of the experimental results and of calculations carried out using the modern electron theory demonstrated that SnSe like GeSe and PbSe exhibited semiconductor - semiconductor melting which was partly due to retention of the band structure of the crystal in a wide range of temperatures above the melting points.

Chun et al. [30] observed polarity dependent memory switching in devices of SnSe with aluminium contacts. Low-level switching (1V/1mA) with reversed polarity and high level (100 V/10 mA) polarised memory switching were observed in the devices. The low-level switching involved an electronic process while high level switching was associated with an electrothermally driven mass transport.

### 1.5 ELECTRONIC BAND STRUCTURE

Car et al. [26] have calculated the electronic bands of SnSe along all high symmetry lines of the Brillouin zone using a local empirical pseudopotential method. They were able to obtain a band structure consistent with optical and photoelectric data.

The electronic properties of SnS, SnSe and SnTe were investigated by Singh and Gupta [31]. They discussed a correlation between the evaluated values of ionicity and the reported values of isomeric shift.

The electronic structure of SnSe was studied using the first principle scalar relativistic LMTO-ASA method in the local-density approximation by Duan et al. [32]. The calculated results were compared with the experiment and other non-self consistent calculations.

Photoelectron partial-yield and constant-initial-state (CIS) spectra of the layered semiconducting SnSe single crystals was investigated by Taniguchi et al. [33] using synchrotron radiation. Energies of the experimental DOS peaks obtained by them compared favourably with the conduction band features derived from interband optical absorption spectra.

Terra and Guenzburger [34] have used cluster method for the band structure calculations of SnSe to obtain the density of states and related parameters. They compared their results from band structure calculations with experimental measurements to get a valuable insight into the electronic properties of tin monochalcogenides.

Gashimzade et al. [35] calculated the band structure of SnSe by the Equivalent-Orbital Linear Combination of Atomic Orbitals (EOLCAO) method in the single layer approximation. The results of band structure and density of states obtained by them were in good agreement with earlier calculations carried out by the pseudopotential method. The experimental and theoretical values of energy gaps along the symmetry lines  $\Lambda$  and  $V$ , electron effective mass near the extremes on the  $\Lambda$  and  $V$  lines and the hole effective mass near the extremes on the  $\Lambda$  and



V lines for SnSe obtained by them are shown in Table 1.3.

## 1.6 OPTICAL PROPERTIES

Elkorashy [10], Garg et al. [8], Lukes et al. [36] and Julien et al. [11] measured optical absorption in single crystals of tin monoselenide. Elkorashy [10] found that absorption near the fundamental edge was due to indirect forbidden transition with the involvement of two phonons in the process. The energy gap and phonon energies found by him were 0.948 eV and 54 and 21 MeV for  $\vec{E}$  parallel to  $\vec{a}$  and 0.902 eV and 41 and 20 MeV for  $\vec{E}$  parallel to  $\vec{b}$ . While Garg et al observed that the transition involved the participation of only one phonon. The values of energy gap and phonon energy found out by them were 0.94 eV and 0.022 eV for  $\vec{E}$  parallel to  $\vec{a}$  and 0.891 eV and 0.009 eV for  $\vec{E}$  parallel to  $\vec{b}$ . Lukes et al. [36] got the values of energy gap for indirect transitions as 0.907 eV for  $\vec{E}$  parallel to  $\vec{a}$  and 1.01 eV for  $\vec{E}$  parallel to  $\vec{b}$  at 295 K. They could also identify two direct transitions, first direct transition for  $\vec{E}$  parallel to  $\vec{b}$  with  $E_{od} = 1.051$  eV and the other direct transition for  $\vec{E}$  parallel to  $\vec{a}$  with  $E_{1d} = 1.236$  eV.

The existence of direct transitions was also very elegantly shown by Valiukonis et al. [1,37] from the

**Table 1.3** Energy gaps, electron and hole effective masses of SnSe

Property	Experimental		Calculated	
	$\Lambda$	$V$	$\Lambda$	$V$
Experimental and theoretical value of energy gaps along the symmetry lines $\Lambda$ and $V$	1.05	1.24	1.13	1.22
Property	$\lambda(a)$	$\lambda(c)$	$V(a)$	$V(c)$
Electron effective mass near the extremes on the $\Lambda$ and $V$ lines	0.34	5.29	-2.86	0.37
Hole effective mass near the extremes on the $\Lambda$ and $V$ lines	0.35	-10.87	3.15	0.52

electroreflectance, thermorefectance and absorption spectra of the SnSe crystals. The direct energy gaps obtained by them were 1.05 eV for  $\vec{E}$  parallel to  $\vec{b}$  and 1.24 eV for  $\vec{E}$  parallel to  $\vec{a}$ . From the study of the hydrostatic pressure dependence of the fundamental absorption edge of GeS, GeSe, SnS and SnSe crystals in polarised light, Valiukonis [1] showed that the pressure coefficient of the energy gap for SnS and SnSe was almost two times larger than that of GeSe and GeS.

Elkorashy [38,39] measured the refractive index 'n' of SnSe single crystals from the reflectance spectra and by the interference method in the transparent region. He calculated the extinction coefficient k from the measured absorption coefficient. Using these values of n and k he calculated the real and imaginary parts of the complex dielectric constant ( $\epsilon_r, \epsilon_i$ ). He showed that SnSe single crystals exhibited birefringence. Assuming that the binding in SnSe was partly ionic and partly covalent, he could satisfactorily fit his results of the optical constants to the model of a single effective oscillator.

A dielectric function ( $\epsilon$ ) spectra for two principal polarisations parallel to the layer plane from 0.5 to 28 eV was obtained in as early as 1977 by Eymard et al.

[40] from a combined analysis of optical transmission and electron energy loss spectra for SnSe. Their calculated reflectivity spectra were found to be in good agreement with the experimental ones from 1.5 to 6 eV. The spectra of the imaginary part of the dielectric permeability constant obtained by Valiukonis et al. [41] in their studies of the electroreflectance spectra from SnSe was explained by them with the help of a pseudopotential method.

The dielectric function for orthorhombic SnSe was measured ellipsometrically by Logothetidis and Polatoglou [42] in the 1.26 - 5.6 eV photon energy region. The effect of the air exposure on both the dielectric function and the ellipsometric angles as well as the structure of the surface were studied by "null" ellipsometry and electron microscopy respectively. The results indicated the formation of an amorphous overlayer cleavage.

From the measured values of transmittance and reflectance, Elkorashy [43] determined the absorption coefficient of SnSe single crystals in the temperature range from liquid nitrogen temperature to the room temperature. He showed that optical energy gap increased linearly with temperature in the temperature range 92 K to 300 K.

Lukes and Dubb [44] have summarised and

166779

...  
systematised the results on the optical properties of single crystals of GeS, GeSe, SnS and SnSe in the form of a book. They have discussed and interpreted the results obtained by various workers.

Liebegall and Schwartz [45] obtained upper-valence band spectra for several cubic and orthorhombic  $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$  single crystals using photoemission spectroscopy. They presented some electronic distribution curves to demonstrate the shift of the valence band with increasing  $x$ .

Berg et al. [46] carried out the investigation of the XPS valence band structure from Sn chalcogenides. Their measurements allowed an identification of the symmetry of the valence orbitals from intensity variations of the valence band maxima.

## 1.7 IMPORTANCE

The monoselenides of tin have attracted considerable attention in the recent years on account of their semiconducting nature. SnSe is an important material for infrared optoelectronic devices [47]. Technically they are useful as infrared and visible radiation detectors [48]. Tin monoselenides are also of interest to holographic recording systems [49] and electrical switching [2].

REFERENCES

- [1] G. Valiukonis, D. A. Guseinova, G. Krivaite and  
A. Sileika,  
Phys. Stat. Solidi (b), **135** (1986) 299.
- [2] D. I. Bletskan, V. I. Taran and M. Yu. Sichka,  
Ukr. Fiz. Zh., **21** (1976) 1436.
- [3] S. Asanabe,  
J. Phys. Soc. Japan, **14** (1959) 281.
- [4] W. Albers, C. Haas, H. Ober, G. R. Shrodder and  
J. D. Wasscher,  
J. Phys. Chem. Solids, **23** (1962) 215.
- [5] D. L. Mitchell,  
Diss. Syracuse Univ., Syracuse N.Y. (1959)
- [6] P. W. Bridgman,  
Proc. Am. Acad. Arts Sci., **60** (1925) 305.
- [7] Stockbarger,  
Rev. Sci. Instruments, **7** (1936) 133.
- [8] A. K. Garg, A. K. Jain and O. P. Agnihotri,  
Ind. J. Pure and Appl. Phys., **21** (1983) 276.

- [9] O. P. Agnihotri, A. K. Jain and B. K. Gupta,  
J. Cryst. Growth, **46** (1979) 491.
- [10] A. M. Elkorashy,  
J. Phys. Chem. Solids, **47** (1986) 497.
- [11] C. Julien, M. Eddrief, I. Samaras and M. Balkanski,  
Mat. Sci. and Engg., **B 15** (1992) 70.
- [12] V. P. Bhatt, K. Gireesan and G. R. Pandya,  
J. Cryst. Growth, **96** (1989) 649.
- [13] M. Merdan,  
Doga Turk Fizik Astrofizik Dergisi, **14** (4) (1990)  
413.
- [14] C. Domingo, R. S. Itoga and C. R. Kannewurf,  
Phys. Rev., **143** (1966) 536.
- [15] H. Maier and D. R. Daniel,  
J. Electron. Mat., **6** (1977) 693.
- [16] Y. G. Yu, A. S. Yue and O. M. Stafsudd,  
J. Cryst. Growth, **54** (1981) 248.
- [17] S. Logothetidis, L. Vina and M. Cardona,  
Phys. Rev. B, **31** (1985) 2180.

- [18] S. Logothetidis, P. Lautenschlager and M. Cardona,  
Phys. Rev. B, **33** (1986) 1110.
  
- [19] N. Yellin and L. Ben-Dor,  
Mat. Res. Bull., **18** (1983) 823.
  
- [20] K. Shinohara, T. Seo and S. Isomura,  
Sadhana, **11** (Pt. 3-4) (1987) 397.
  
- [21] N. Erdem, S. Onurlu and H. Yorucu,  
J. Mat. Sci. Lett., **8** (4) (1988) 483.
  
- [22] N. Kh. Abrikosov, V. F. Bankina, L. V. Poretskaya,  
L. E. Shelimova and E. V. Skudnova,  
Semiconducting II-VI, IV-VI and V-VI compounds,  
(Plenum Press, New York) (1969).
  
- [23] R. W. G. Wyckoff,  
Crystal Structures Vol. I, Inter Science Publishers,  
New York (1963).
  
- [24] A. Okazaki and I. Ueda,  
J. Phys. Soc. Japan, **11** (1956) 470.
  
- [25] A. Okazaki,  
J. Phys. Soc. Japan, **13** (1958) 1151.



- [26] R. Car, G. Ciucci and L. Quartapelle,  
Phys. Stat. Solidi (b), **86** (1978) 471.
  
- [27] M. J. Peters and L. E. McNeil,  
Phys. Rev. B, **41** (9) (1990) 5893.
  
- [28] S. N. Dutta and G. A. Jeffrey,  
Inorg. Chem., **4** (1965) 1363.
  
- [29] V. M. Glazov, V. A. Kurbatov and A. I. Faradzhov,  
Sov. Phys. Semicond., **21** (3) (1987) 295.
  
- [30] Dongwoo Chun, R. M. Walser, R. W. Bene and  
T. H. Courtney,  
Appl. Phys. Lett., **24** (10) (1974) 479.
  
- [31] O. P. Singh and V. P. Gupta,  
Phys. Stat. Solidi (b), **136** (1) (1986) K 41.
  
- [32] Duan Wen-hui, Gubing-lin and Zhu Jia-lin,  
Acta Physica Sinica, **39** (3) (1990) 437.
  
- [33] M. Taniguchi, R. L. Johnson, J. Ghijsen and  
M. Cardona,  
Phys. Rev. B, **42** (6) (1991) 3634.

- [34] Joice Terra and Diana Guenzburger,  
Phys. Rev. B., **44** (16) (1991) 8584.
  
- [35] F. M. Gashimzade, D. G. Guliev, D. A. Guseinova  
and V. Y. Shteinshtayber,  
J. Phys. Condens. Matter, **4** (1992) 1081.
  
- [36] F. Lukes, E. Schmidt, J. Humlicek, P. Dub and  
F. Kosek,  
Phys. Stat. Solidi, (b) **137** (1986) 569.
  
- [37] G. Valiukonis, F. M. Gashimzade, D. A. Guseinova,  
G. Krivaite, M. M. Mamedov and A. Sileika,  
Phys. Stat. Solidi (b), **122** (2) (1984) 623.
  
- [38] A. M. Elkorashy,  
J. Phys. Chem. Solids, **51** (4) (1990) 289.
  
- [39] A. M. Elkorashy,  
J. De. Physique, **III** (1) (1991) 1169.
  
- [40] R. Eyemard and A. Otto,  
Phys. Rev. B, **16** (4) (1977) 1616.

- [41] G. R. Valiukonis, F. M. Gashimzade, D. A. Guseinova,  
G. Krivaite, M. M. Mamedov, G. S. Drudzhev and  
A. J. Sileika,  
Sov. Phys. Collect (USA), 25 (1) (1985) 29.
- [42] S. Logothetidis and H. M. Polatoglou,  
Phys. Rev. B., 36 (14) (1978) 7491.
- [43] A. M. Elkorashy,  
J. Phys. Chem. Solids, 50 (9) (1989) 893.
- [44] F. Lukes and P. Dub,  
Optical Properties of GeS, GeSe, SnS and SnSe.  
Published by Univerzita, J. E. Purkyne, V. Brne, Brno,  
Czechoslovakia (1988).
- [45] A. Liebegall and W. Schwartz,  
Nuovo Cimento B, 66 B (2) (1981) 173.
- [46] U. Berg, T. Chasse and O. Brummer,  
Phys. Status. Solidi (b), 108 (2) (1981) 507.
- [47] T. C. Harman and I. Melngailis,  
Appl. Sol. State Science, New York, 4 (1974) 1.

- [48] Lai-Sheng Wang, B. Niu, Y. T. Lee and D. A. Shirley,  
J. Chem. Phys., 92 (2) (1990) 899.
- [49] D. I. Bletskan, I. F. Kopinets, P. P. Pogoretskii,  
E. N. Sarkova and D. V. Chepur,  
Kristallografiya, 20 (1975) 1008.

**CAPTIONS TO THE FIGURES**

Fig. 1.1 SnSe Structure : Projection on (010) plane.

Fig. 1.2 SnSe Structure : Projection on (001) plane.