CHAPTER : 6

OPTICAL BANDGAPS IN TIN SULPHOSELENIDE SINGLE CRYSTALS

6.1 INTRODUCTION :

For high efficient solar energy conversion the fundamental band gap E_g is the most crucial optical parameter. It has been shown by Bucher [1] That E_g for single solar cells should be around 1.4 eV for maximum solar energy conversion. Semiconducting materials having band gaps near to this optimum value are therefore, considered as most suitable for photovoltaic applications. It is therefore, highly desirable that a determination of the optical band gap of the semiconducting material is made. Band gaps are usually classified in direct allowed and forbidden transitions [2], and both direct as well as indirect optical band gaps can be determined from the following methods :

1.   Optical absorption

2.   Photoelectrochemical methods

    (i)   Quantum yield η vs $h\nu$ plot

    (ii)   Action spectrum

    (iii)   Capacitance measurements

3.   Intrinsic conduction measurement at high temperature

4.   Photoemission

5.   Band structure calculations.

A great deal of work on the optical band gap measurements on the end members of the series SnS_xSe_{2-x} i.e. SnS_2 and $SnSe_2$ has been carried out by various investigators (See Chapter-1). However, the work on the intermediate compounds of the series i.e. $SnS_{0.5}Se_{1.5}$, SnSSe and $SnS_{1.5}Se_{0.5}$ is limited to that reported by Lee et al [3]. They attributed the energy gaps in their compound to the phonon assisted indirect transitions, but no attempt was made by them to determine the energies of the

phonons involved in the transitions. Further, since both direct as well as indirect transitions have been observed to take place in the end members SnS_2 and $SnSe_2$ it was considered highly desirable that a thorough analysis of the absorption spectrum obtained from the single crystals of the middle compounds of tin sulphoselenides is carried out. Therefore, looking to the importance of the optical band gap in semiconducting materials and because of the fact that no detailed study of this kind exists for SnS_xSe_{2-x} for (x = 1.5, 1 and 0.5), author has carried out a indepth study of the determination of optical band gaps in these materials by optical absorption. The results thus obtained have been described in this chapter and implications have been discussed

6.1.1 OPTICAL ABSORPTION :

An important technique for measuring the band gap of a semiconductor is the absorption of incident photon by the material. In this technique, photons of selected wavelengths are directed at the sample and their relative transmission is observed. Since the photons with energies greater than the band gap energy are absorbed while photons with energies less than band gap are transmitted, the technique provides an accurate measurement of the energy band gap.

If a beam of photons with E_g < hv falls on a semiconductor there will be some predictable amount of absorption determined by the properties of the material. The ratio of transmitted to incident radiation intensity is expected to depend on photon wavelength and the thickness of the sample.

When a photon beam of intensity I_o (photons/cm²sec) transmits through a slab of a medium of thickness x,the beam of photons attenuates

in accordance with the exponential law

$$I = I_o \exp(-\alpha x) \qquad 6.1$$

Where 'α' is called the absorption coefficient and has units of cm^{-1}. This coefficient 'α' can be obtained simply by measuring I_o/I of the intensities impinging and emerging from the sample.

Direct and Indirect Transitions :

The absorption process-taking place in a semiconductor can be described as an example of electronic transition processes, which are fully quantum mechanical in nature. These electronic transition processes give rise to interband absorption in solids, which are of two types, known as direct and indirect (interband) transitions Fig. 6.1.

In a direct transition, an electron in a Bloch energy band state below the Fermi level absorbs a photon and makes a vertical transition to an upper empty state in the conduction band. The characteristics of such transitions are defined by the following conditions :

$$\vec{k}_f = \vec{k}_i \qquad 6.2$$

$$E_c\left(\vec{k}_f\right) - E_v\left(\vec{k}_i\right) = \eta\omega \qquad 6.3$$

where $\vec{k}_i$ and $\vec{k}_f$ are, respectively, the initial and the final electron wave vectors in the valence E_v $(\vec{k})$ and the conduction E_c $(\vec{k})$ bands and $\hbar\omega$ is the photon energy. Equation (6.2) expresses conservation of momentum essentially, $\hbar\vec{k}_f = \hbar\vec{k}_i + \hbar\vec{Q}$, where $\vec{Q}$, the photon wave vector, is usually so small compared with the dimensions of the Brillouin zone that one may take $\hbar\vec{Q} \simeq 0$ Equation (6.3) expresses energy conservation.
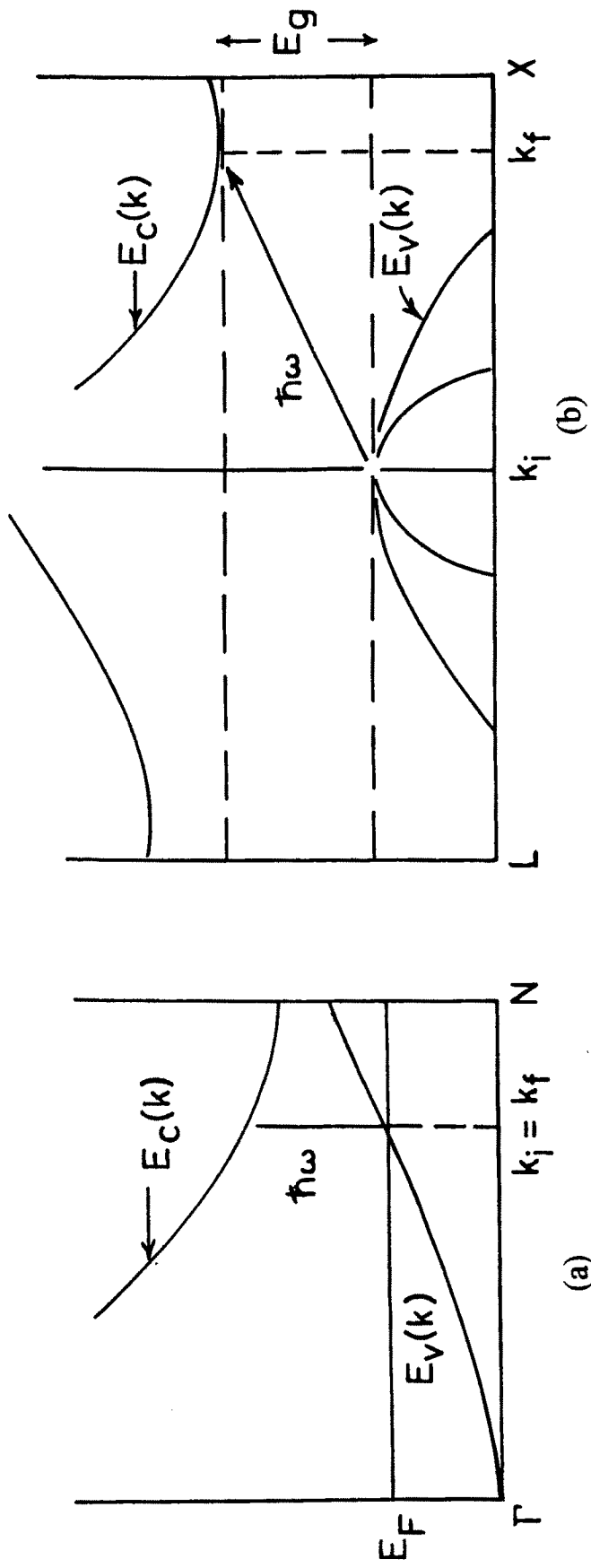
FIG. 6.1 Schematic diagram showing direct (a) and indirect (b) transitions.

In general, however, at high enough temperatures, phonons are present and can participate in the absorption process. Such phonon assisted transitions cannot be vertical because the phonon momentum $\hbar q$, must be added to the right hand side of equation (6.2) and similarly the condition in equation (6.3) has to include the energy of the absorbed (or emitted) phonon. The optical transition is accordingly said to be non-vertical or "indirect". Such indirect transitions are quite important in semiconductors and provide a means of determining the energy band gap separating the top of the valence band and the bottom of the conduction band when these band extrema occur at different values of the k vector.

Energy gap determination :

According to Bardeen et al [4], the relationships that exist for possible transitions across the energy gap of a semiconductor show that the absorption coefficient 'α' is proportional to

$$\frac{\left(h\nu - E_g\right)^r}{h\nu} \qquad\qquad 6.4$$

where $h\nu$ is the photon energy and 'E_g' is the band gap energy.

Indirect transitions require phonons for momentum conservation, and the absorption coefficient 'α' for them is expected to vary as [5].

$$\alpha = \sum_{l=1}^{2}\left\{B_{al}\frac{1}{\exp\left(E_{pl}/kT\right)-1}\left(h\nu - E_g' + E_{pl}\right)^r + B_{el}\frac{1}{1-\exp\left(-E_{pl}/kT\right)}\left(h\nu - E_g' - E_{pl}\right)^r\right\}$$

$$\ldots\ldots 6.5$$

Where B_{al} and B_{el} are temperature dependent coefficients associated with the absorption and emission of the lth phonon, $h\nu$ is the photon energy,

E_g' is the indirect energy gap, E_{pi} is the energy of the phonon assisting at the transition. From the expression for E_{pi}, phonon equivalent temperature 'θ_i' is defined as

$$\theta_i = E_{pi} / kT \qquad\qquad 6.6$$

The exponent 'r' in equations 6.4 and 6.5 depends upon the dimensionality of the bands and whether the transition is symmetry allowed or not. Possible values of 'r' are given in Table 6.1.

By plotting graphs of $(\alpha h\nu)^{1/r}$ against $h\nu$ for various values of r given in Table 6.1, it is possible to determine which of the conditions given in the table dominate. Extrapolations of these plots to zero absorption will provide the appropriate values of the energy gaps of the tin sulphoselenide compounds.

6.2   EXPERIMENTAL :

The main aim of the work presented in this Chapter is to study the effect of variation of sulphur and selenium content in SnS_xSe_{2-x} on the optical band gap of this material, Therefore, all samples of $SnSSe$, $SnS_{1.5}Se_{0.5}$ and $SnS_{0.5}Se_{1.5}$ used in the present work were grown by the direct vapour transport technique using the slow cooling method (Chapter - 5). Since the crystals grew in the form of thin platelets, as grown samples were used to take the absorption spectrum. Thicknesses of the samples were measured with a micrometer or optical microscope. The 'a' and 'b' axis were contained in the plane of cleavage. The optical absorption spectra were obtained in an UV-VIS-NIR spectrophotometer (Chapter - 2)$_{in}$the range 350 nm to 1400 nm. For these measurements, thin crystals of thickness about 0.0035 cm were used. The samples were pasted on a thick black paper with a cut exposing the crystals to the

Table 6.1: Values of exponent 'r' for diffrent types of band gap transitions

Type of transition	Direct		Indirect	
	Two dimensional	Three dimensional	Two dimensional	Three dimensional
Allowed (Step function)	0	1/2	1	2
Forbidden	1	3/2	2	3

incident radiation. The reference used was a replica of the black paper having the cut in exactly the same position.

All measurements were performed at room temperature with the incident beam normal to the basal plane i.e. along the c-axis of the grown flakes. Measurements along the c-axis could not be performed since the specimens were too thin to be mounted along this direction.

6.3   RESULTS :

The absorption spectrum taken from a SnSSe single crystals in the form of a thin flake over the spectral range from 700 nm to 1400 nm is shown in Fig.6.2. A careful study of this spectrum reveals that an absorption edge is seen in the spectral range 700 nm to 850 nm. In order to analyse the results from this spectrum in the vicinity of the absorption edge on the basis of two as well as three dimensional models,values of absorption coefficient 'α ' were determined at every step of 2.5 nm. The interpretation of the results in the terms of direct and indirect transitions can be performed with the help of formulae (6.4) and (6.5) using the various values of r from Table 6.1, Fig.6.3 shows the spectral variation of $(\alpha h v)^{1/2}$ vs hv. Since the curve indicates discontinuous straight line it is quite plaussible that it represents indirect interband transitions involving the emission or absorption of phonons. In order to make an accurate determination of the points of discontinuities author has followed the method adopted by Koshkin et al [5] and Elkorashy [6]. Accordingly, from the graphical differentiation of the data presented in Fig.6.3, the dependence of the derivatives $\partial(\alpha h v)^{1/2} / \partial h v$ on hv has been shown in Fig.6.4. It can be clearly seen from this figure that the derivatives are step functions of energy with four steps well defined in the range
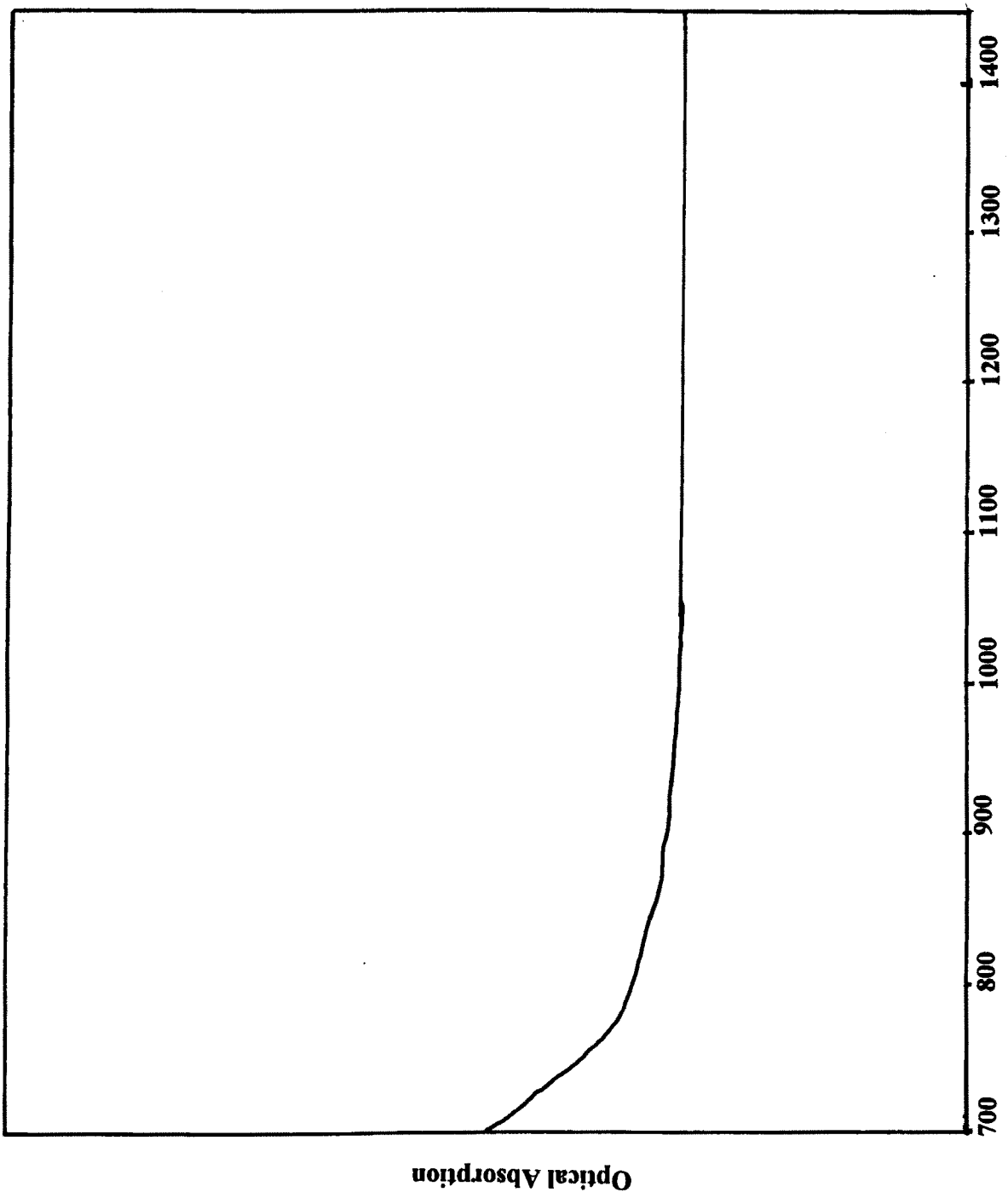
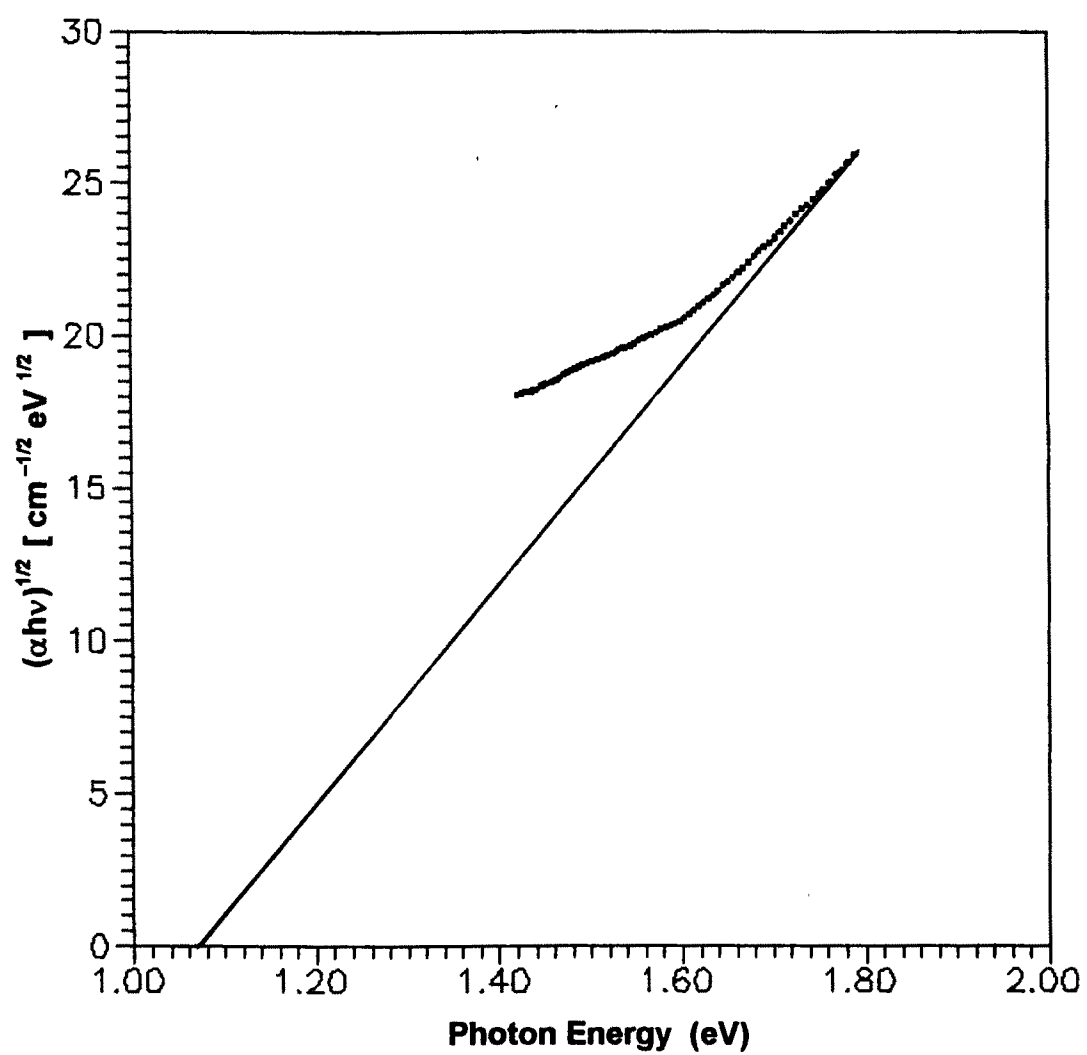FIG. 6.2 Absorption spectrum from a single crystal of SnSSe.

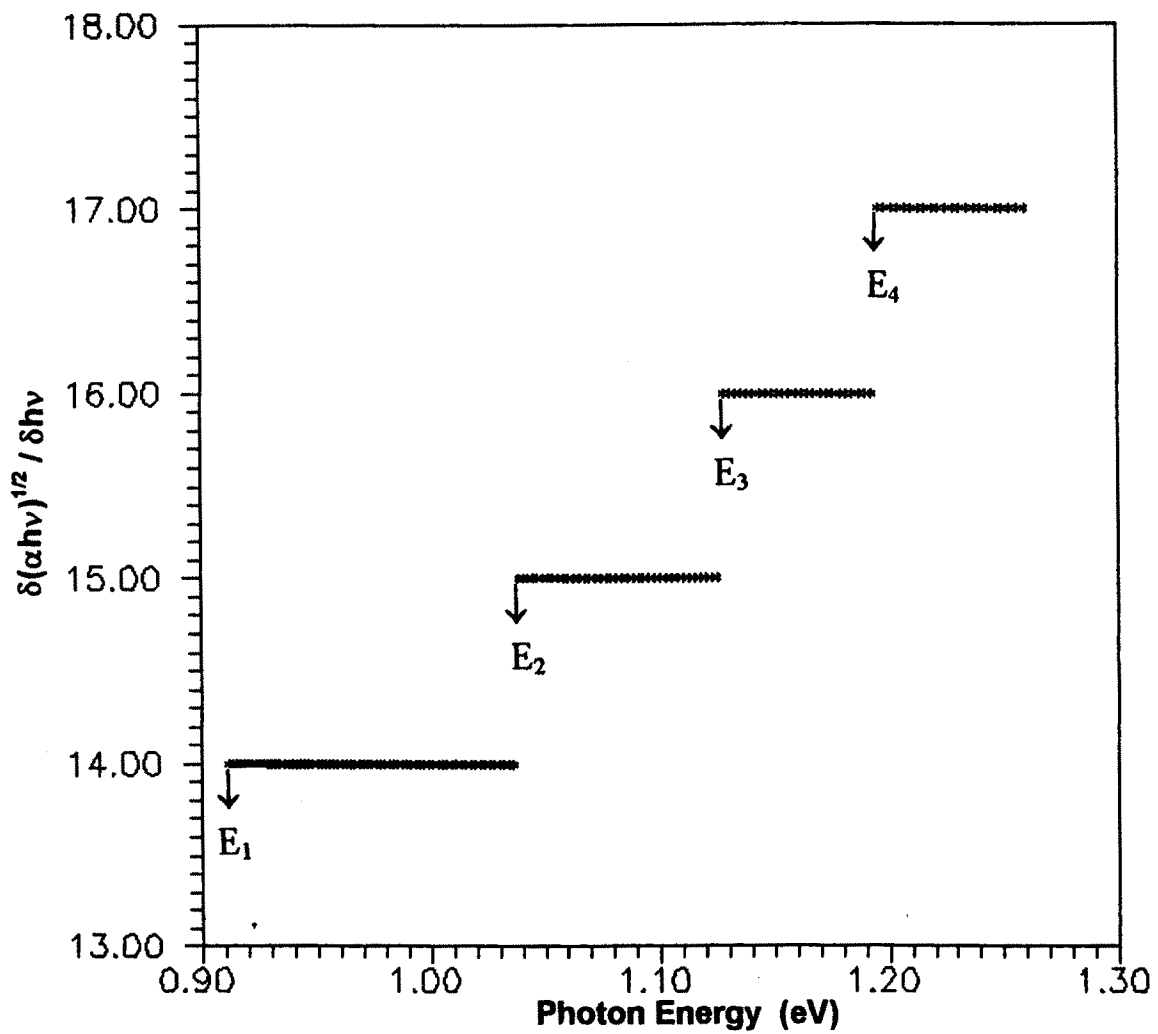FIG. 6.3 The spectral variation of the quantity (αhν) ½ for SnSSe single crystal.

FIG. 6.4 The spectral variation of the derivative $\delta(\alpha h\nu)^{1/2} / \delta h\nu$ obtained by graphical differentiation of the data presented in FIG. 6.3.

$$E_1 < E < E_2$$
$$E_2 < E < E_3$$
$$E_3 < E < E_4$$
$$E_4 < E$$

The values of E_1, E_2, E_3 and E_4 indicate the points of discontinuities in the plot of $\partial(\alpha h v)^{1/2} / \partial h v$ vs hv. The indirect energy gaps obtained from these values of E_1, E_2, E_3 and E_4 are given by

$$E'_g = \frac{E_1 + E_4}{2} = \frac{E_2 + E_3}{2} \qquad\qquad 6.7$$

and the phonon energies are given by

$$E_{p1} = \frac{E_4 - E_1}{2} \quad and \quad E_{p2} = \frac{E_3 - E_2}{2}$$

The values of indirect band gap E_g' and phonon energies thus obtained are given in Table 6.2. The value of E_g' can also be obtained from the intersection of the linear portion of the graph in Fig.6.3 with the energy axis for zero absorption. This value closely matches the value obtained from equation (6.7).

Further a graph of $(\alpha h v)^{1/3}$ vs hv is shown in Fig.6.5. It is seen that the nature of this curve widely differs from that shown in Fig.6.3. A graphical differentiation of the data presented in this figure and the intersection of the straight line portion of the graph with the energy axis for zero absorption will give widely different values. It is therefore, conjectured that the indirect transition represented by the absorption curve is an indirect allowed type.

Table 6.2 : Various parameters and constants obtained from the indirect band gap measurement for Sn S_x Se_{2-x} single crystals

Parameter	$SnS_{0.5} Se_{1.5}$	SnSSe	$SnS_{1.5} Se_{0.5}$
$Eg^*(eV)$	1.53	1.58	1.64
$E_1(eV)$	0.87	0.911	1.093
$E_2(eV)$	0.96	1.038	1.17
$E_3(eV)$	1.06	1.128	1.23
$E_4(eV)$	1.15	1.196	1.28
$E_g(eV) [C^*]$	1.01	1.069	1.19
$E_g(eV) [E^*]$	1.01	1.07	1.20
$E_{p1}(meV)$	141.7	142.3	096
$E_{p2}(meV)$	048.3	044.7	029
$\theta_1(K)$	1644	1650	1113
$\theta_2(K)$	560	518	336
$B_{a1}(cm^{-1} eV^{-1})$	856202.22	659788.96	631234.53
$B_{a2}(cm^{-1} eV^{-1})$	1976.22	84093.09	9950.27
$B_{e1}(cm^{-1} eV^{-1})$	76437.67	167254.12	59264.51
$B_{e2}(cm^{-1} eV^{-1})$	21770.52	87666.48	14186.78

E_g^* (eV) — Direct band gap from extrapolation

E_g (eV) $[C^*]$— Indirect band gap from calculation

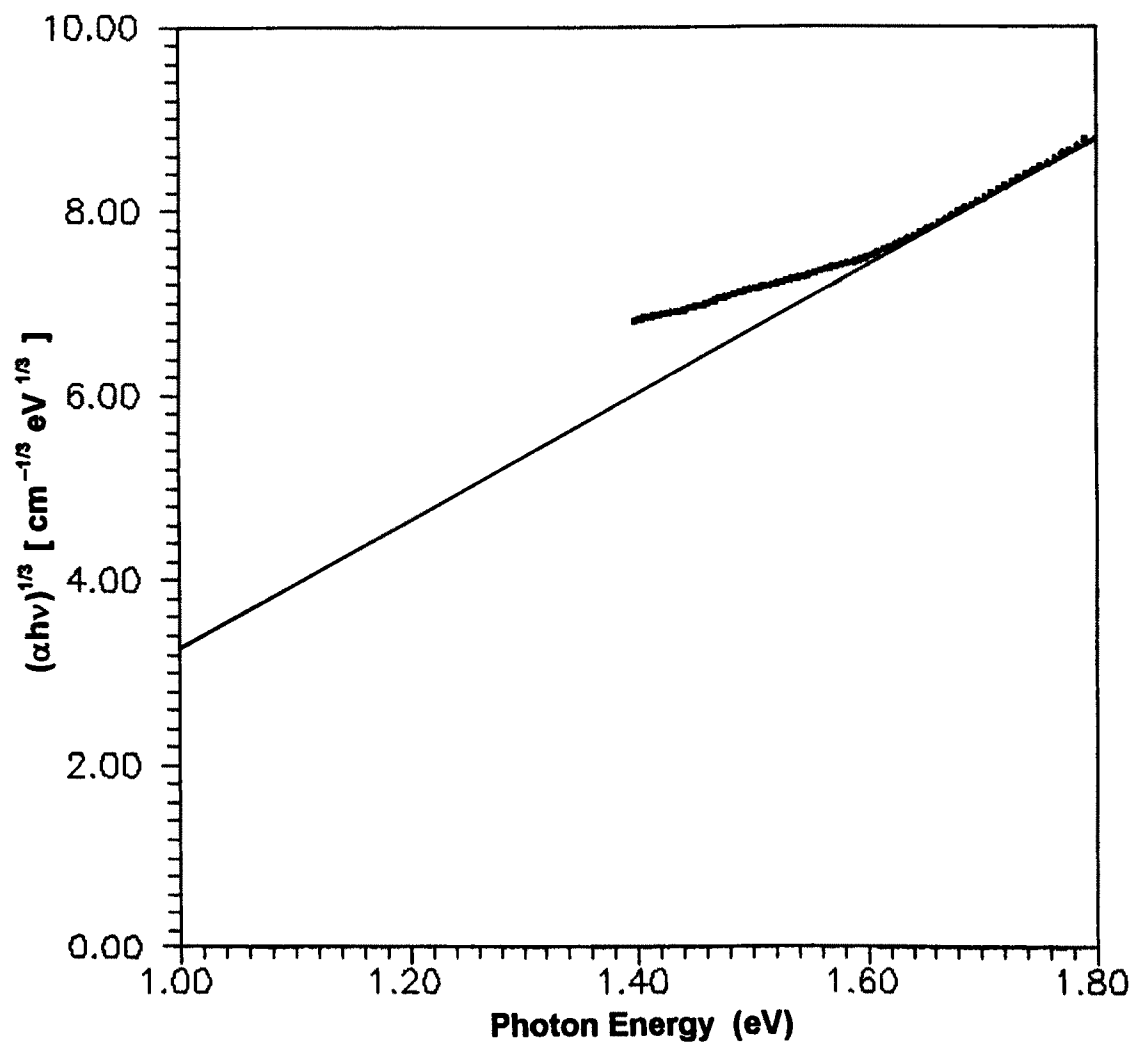E_g (eV) $[E^*]$— Indirect band gap from extrapolation

FIG. 6.5 The spectral variation of the quantity $(\alpha h\nu)^{1/3}$ for SnSSe single crystal.

In order to analyse the data from the absorption curve on the basis of two dimensional model, variation of $\alpha^{1/2}$ vs hv was studied. In this case, it was not at all possible to fit the experimental results on a straight line. It was therefore, inferred that the two dimensional model does not work in the present case.

Taking the values of $E_g{}'$ and $E_{p/}$ at room temperature from Table 6.2 the constants B_{a1}, B_{a2}, B_{e1}, B_{e2}, θ_1 and θ_2 have been determined with the help of formulae (6.5) and (6.6) for r = 3. All these values are presented in Table 6.2.

For the determination of the direct band gap E_g, the best fit for all the experimental points was observed in the case of $(\alpha hv)^2$ vs hv plot (Fig.6.6). The value of E_g obtained from the intercept of the straight line portion of the curve on the hv axis comes out to be 1.58 eV (Table 6.2).

In order to see the effect of making tin sulplhoselenide rich in sulphur or selenium content on the absorption spectra of tin sulphoselenide (SnSSe), UV-VIS-NIR spectra were obtained for $SnS_{0.5}Se_{1.5}$ and $SnS_{1.5}Se_{0.5}$ in the spectral range 700 nm to 1450 nm. Similar to SnSSe values of 'α' were determined from the absorption spectra and the graphs of $(\alpha hv)^{1/2}$ vs hv for single crystals of $SnS_{0.5}Se_{1.5}$ and $SnS_{1.5}Se_{0.5}$ are shown in Figs.6.7 and 6.8 respectively. Graphical differentiation of the data presented in these figures was carried out and the graphs of $\delta(\alpha hv)^{1/2}/\delta hv$ vs hv are shown in Figs.6.9 and 6.10.

The values of E_1, E_2, E_3 and E_4 indicating the points of discontinuities in these figures, the values of the indirect band gap $E_g{}'$ and the phonon energies '$E_{p/}$' and 'E_{p2}' obtained in the manner similar to SnSSe are represented in Table 6.2. The values of indirect band gap $E_g{}'$ obtained from the extrapolation of the straight line portions of the graphs
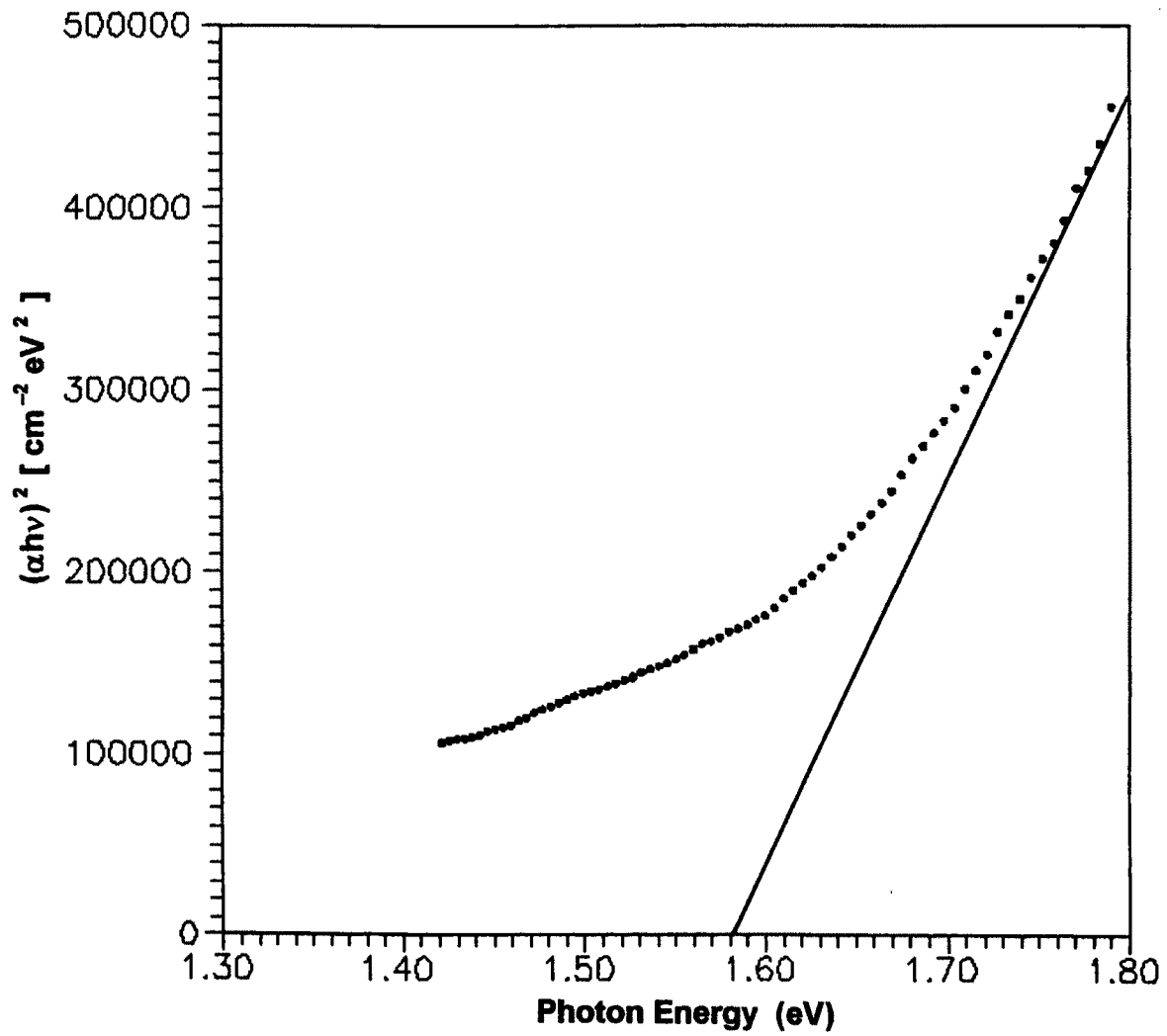
FIG. 6.6 The spectral variation of the quantity $(\alpha h\nu)^2$ for SnSSe single crystal.

in Figs. 6.7 and 6.8 are also given in Table 6.2. In the case of sulphur rich and sulphur deficient compounds also, it was seen that the experimental data could not be analysed from the graphs of $(\alpha h\nu)^{1/3}$ vs $h\nu$, thereby indicating that the indirect transitions represented by the absorption curves are indirect allowed type. Similarly the data obtained from their absorption curves could not be analysed on the basis of two dimensional model.

Taking the values of $E_g{}'$ and $E_{p/}$ for $SnS_{0.5}Se_{1.5}$ and $SnS_{1.5}Se_{0.5}$ from Table 6.2, the constants B_{a1}, B_{a2}, B_{e1}, B_{e2} and θ_1 and θ_2 for these compounds were estimated as before and are given in Table 6.2.

For the determination of the direct band gap for sulplhur rich and sulphur deficient compounds in SnSSe, the best fit for all the experimental points was observed in the case of $(\alpha h\nu)^2$ vs $h\nu$ plots. These curves for $SnS_{0.5}Se_{1.5}$ and $SnS_{1.5}Se_{0.5}$ are shown in Figs.6.11 and 6.12 respectively. The values of direct band gap E_g obtained by the extrapolation of the straight line portions in these curves on $h\nu$-axis for zero absorption are 1.53 eV and 1.64 eV respectively.

6.4   DISCUSSION :

It is quite clear from the analysis of the absorption data (based on three dimensional model) presented above that both direct and indirect symmetry allowed transitions give a good account of the absorption edge in SnSSe and sulphur rich $(SnS_{1.5}Se_{0.5})$ and sulphur deficient $(SnS_{0.5}Se_{1.5})$ compounds of tin sulplhoselenides. Analysis based on two dimensional model is unable to provide a consistent explanation and thus inspite of the high anisotropy, true two dimensional behaviour seems unlikely for these compounds.
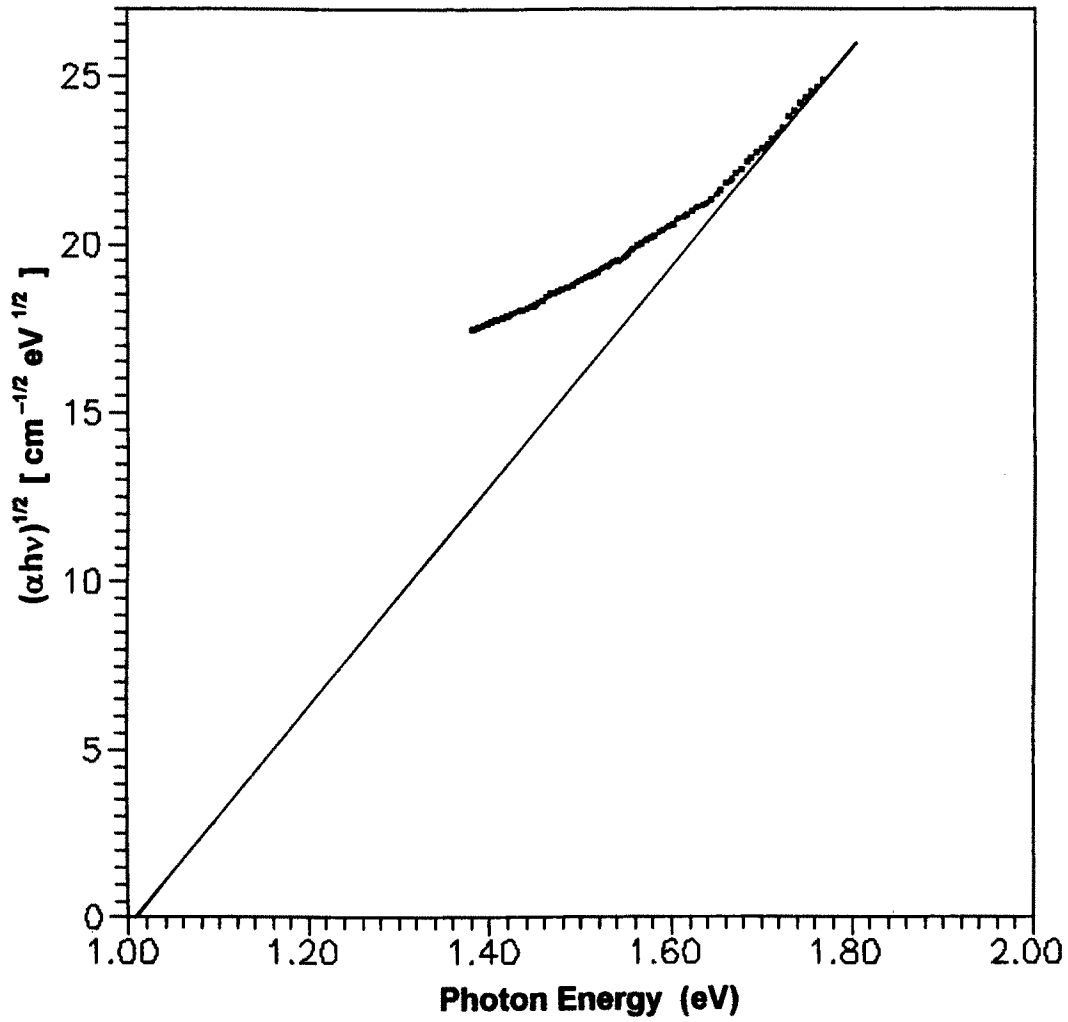
FIG. 6.7 The spectral variation of the quantity $(\alpha h\nu)^{1/2}$ for $SnS_{0.5}Se_{1.5}$ single crystal.

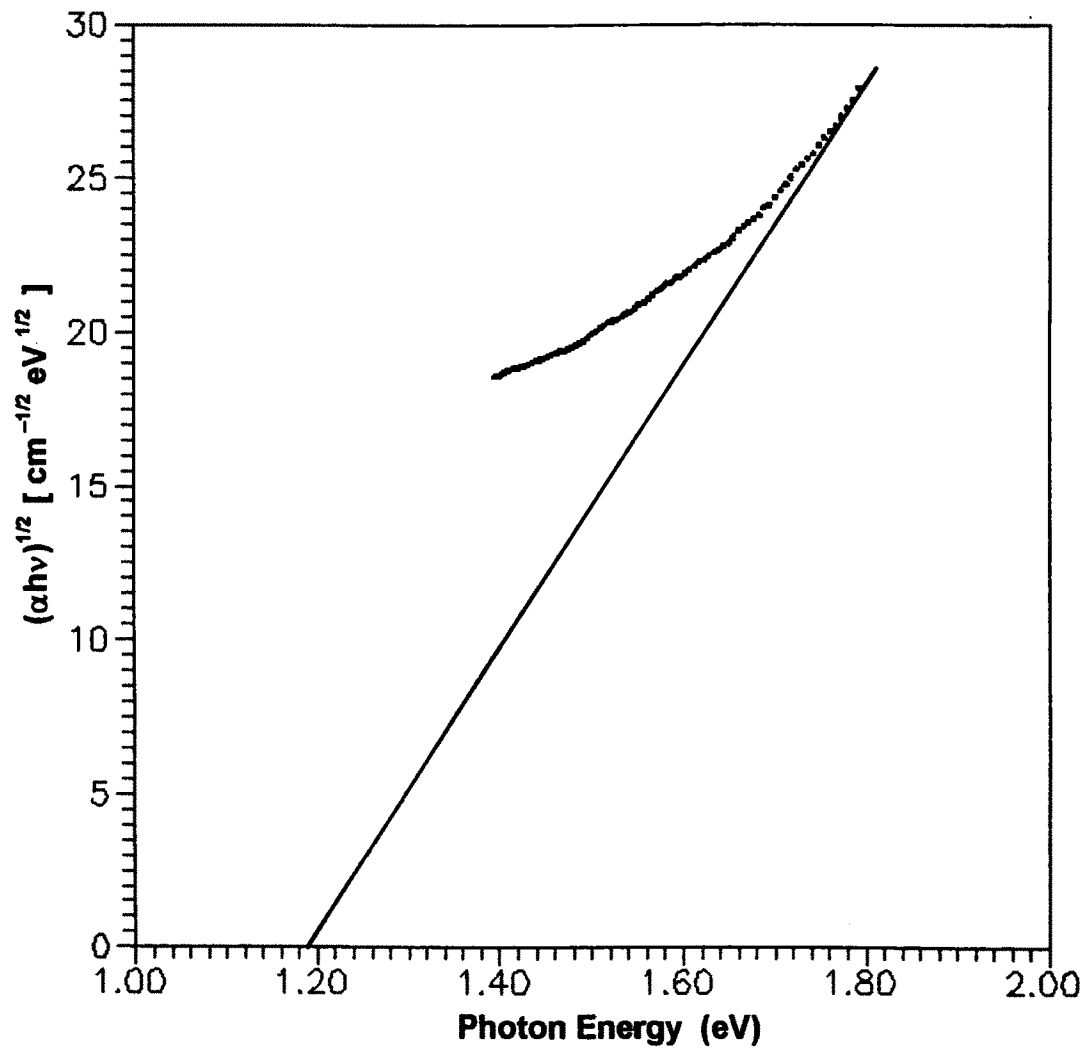FIG. 6.8 The spectral variation of the quantity $(\alpha h\nu)^{1/2}$ for SnS $_{1.5}$Se $_{0.5}$ single crystal.
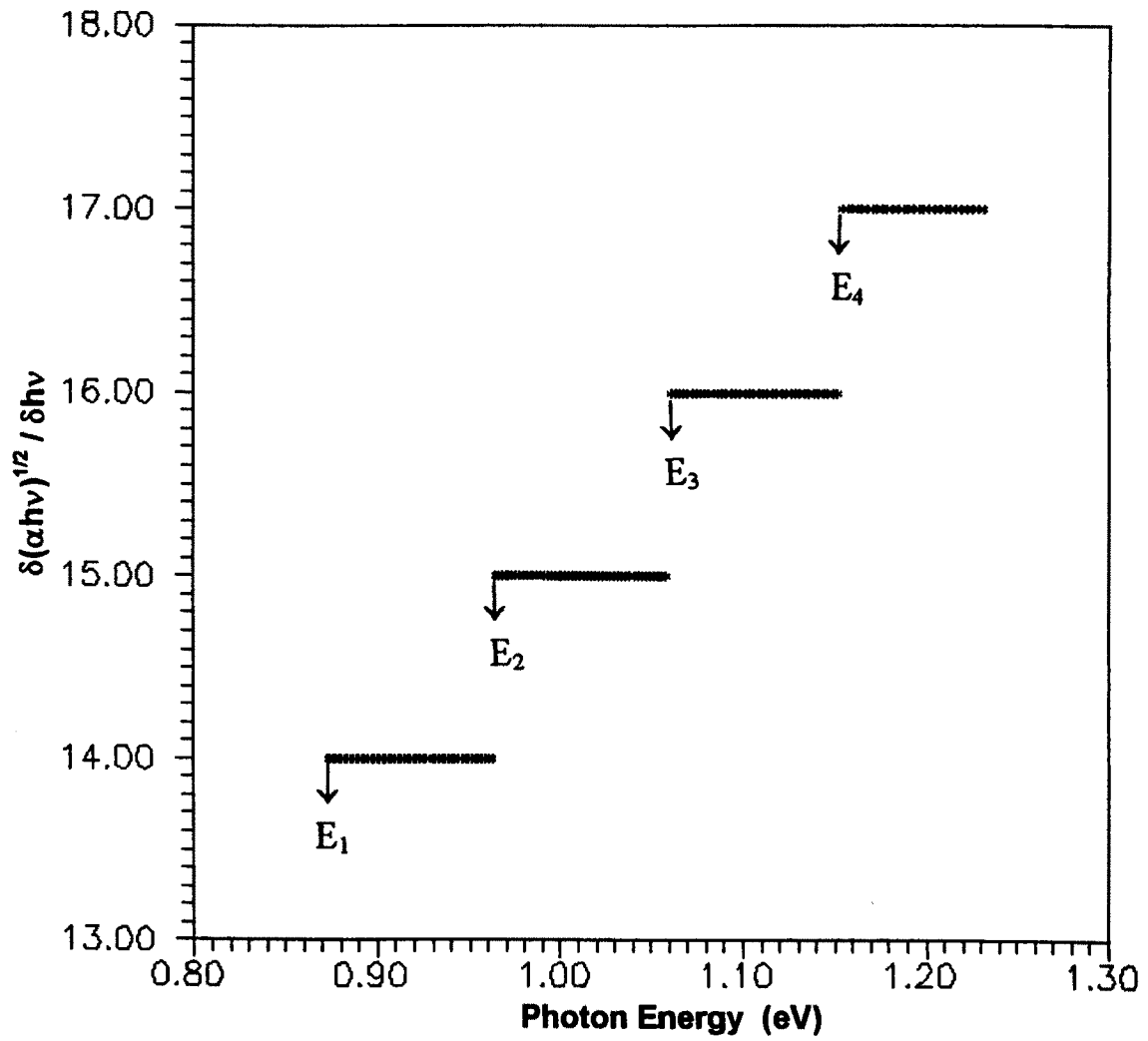
FIG. 6.9 The spectral variation of the derivative $\delta(\alpha h\nu)^{\frac{1}{2}} / \delta h\nu$ obtained by graphical differentiation of the data presented in FIG. 6.7.
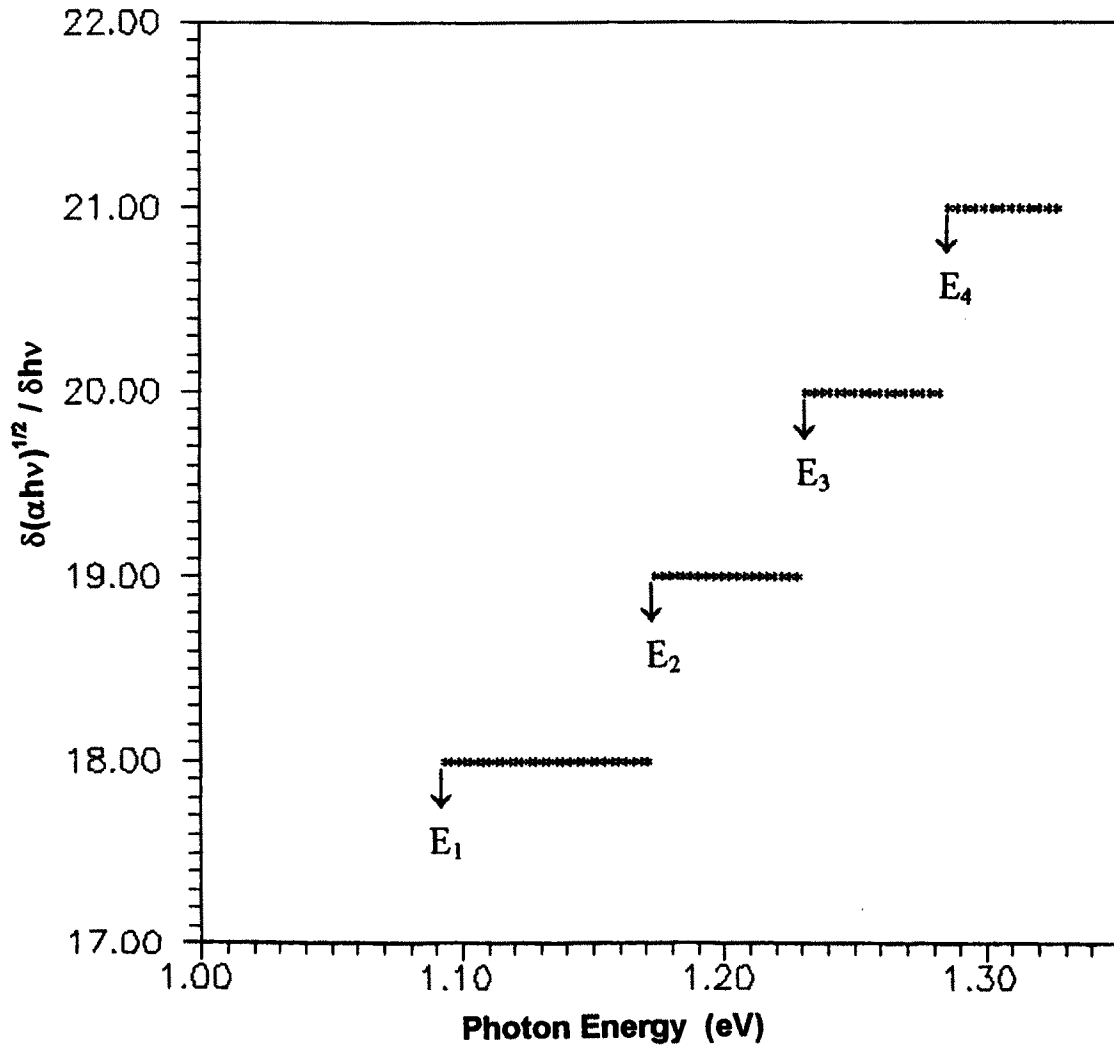
FIG. 6.10 The spectral variation of the derivative $\delta(\alpha h\nu)^{1/2} / \delta h\nu$ obtained by graphical differentiation of the data presented in FIG. 6.8.

in Figs. 6.7 and 6.8 are also given in Table 6.2.[t] In the case of sulphur rich and sulphur deficient compounds also, it was seen that the experimental data could not be analysed from the graphs of $(\alpha h\nu)^{1/3}$ vs hν, thereby indicating that the indirect transitions represented by the absorption curves are indirect allowed type. Similarly the data obtained from their absorption curves could not be analysed on the basis of two dimensional model.

Taking the values of E_g' and E_p for $SnS_{0.5}Se_{1.5}$ and $SnS_{1.5}Se_{0.5}$ from Table 6.2, the constants B_{a1}, B_{a2}, B_{e1}, B_{e2} and θ_1 and θ_2 for these compounds were estimated as before and are given in Table 6.2.

For the determination of the direct band gap for sulplhur rich and sulphur deficient compounds in SnSSe, the best fit for all the experimental points was observed in the case of $(\alpha h\nu)^2$ vs hν plots. These curves for $SnS_{0.5}Se_{1.5}$ and $SnS_{1.5}Se_{0.5}$ are shown in Figs.6.11 and 6.12 respectively. The values of direct band gap E_g obtained by the extrapolation of the straight line portions in these curves on hν-axis for zero absorption are 1.53 eV and 1.64 eV respectively.

6.4 DISCUSSION :

It is quite clear from the analysis of the absorption data (based on three dimensional model) presented above that both direct and indirect symmetry allowed transitions give a good account of the absorption edge in SnSSe and sulphur rich ($SnS_{1.5}Se_{0.5}$) and sulphur deficient ($SnS_{0.5}Se_{1.5}$) compounds of tin sulplhoselenides. Analysis based on two dimensional model is unable to provide a consistent explanation and thus inspite of the high anisotropy, true two dimensional behaviour seems unlikely for these compounds.
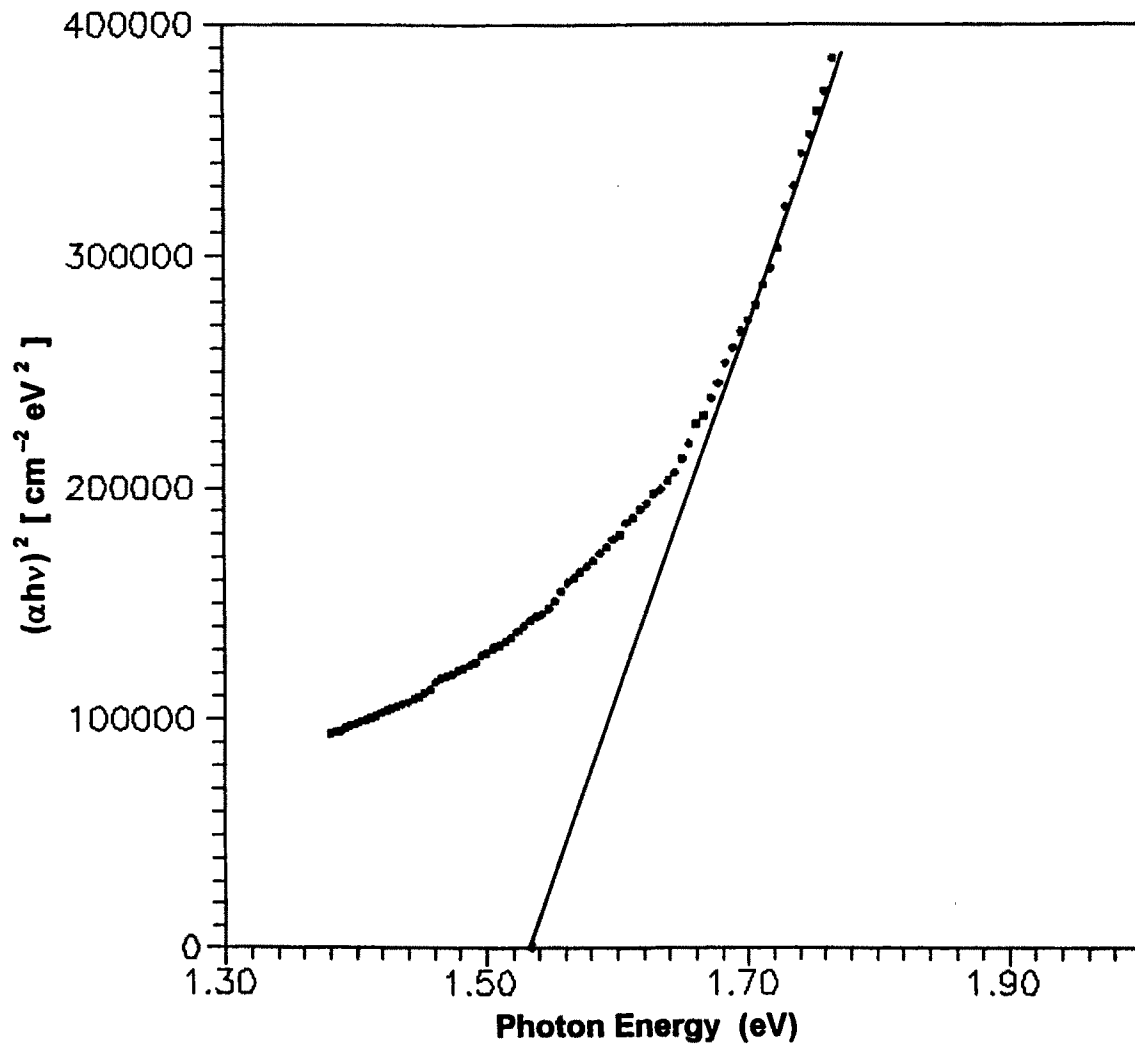
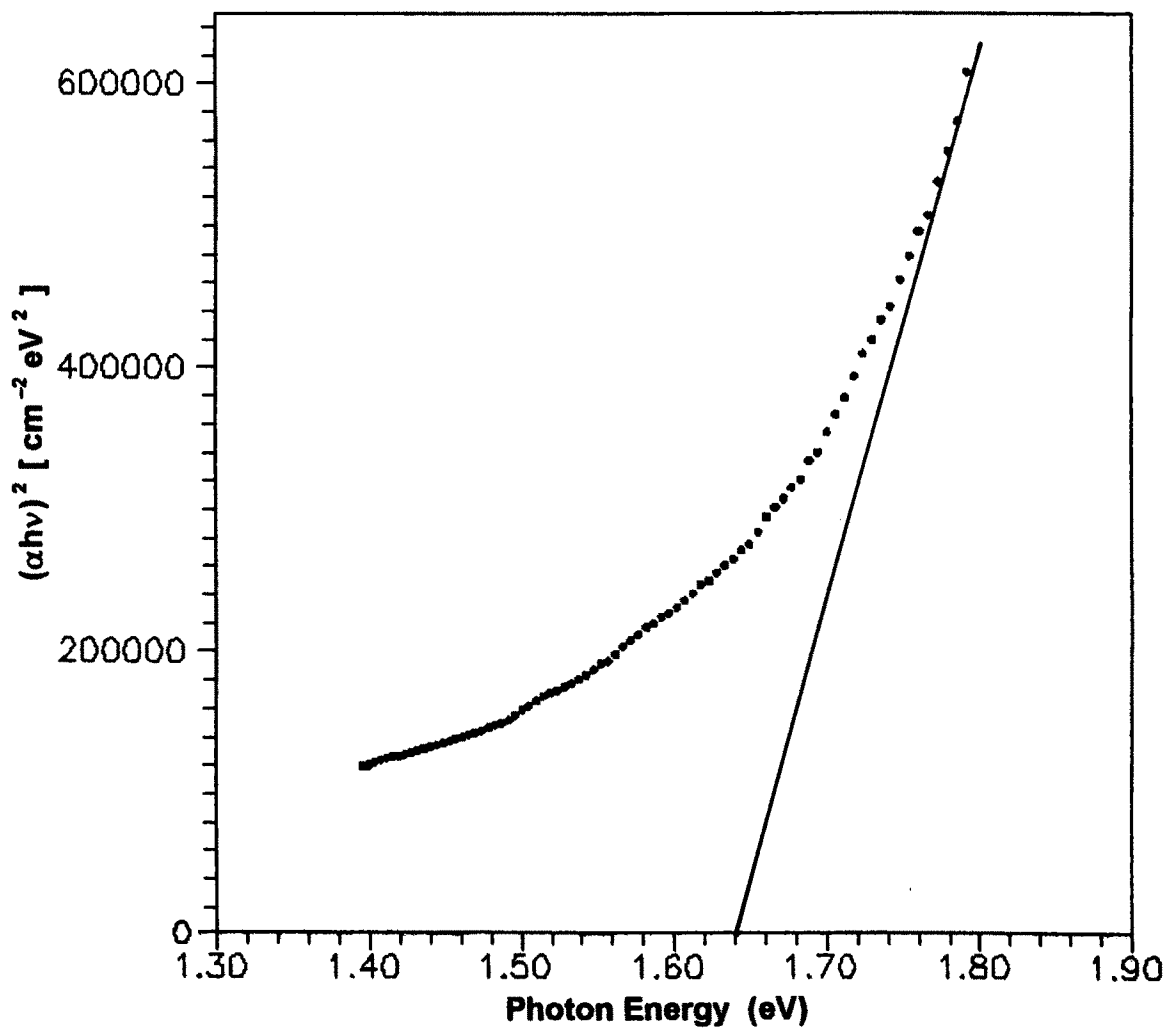FIG. 6.11 The spectral variation of the quantity $(\alpha h\nu)^2$ for SnS $_{0.5}$Se $_{1.5}$ single crystal.

FIG. 6.12 The spectral variation of the quantity $(\alpha h \nu)^2$ for SnS $_{1.5}$Se $_{0.5}$ single crystal.

The increase of phonon energy (Table 6.2) with increasing concentration of selenium in $SnS_{2-x}Se_x$ is consistent with the results of Harbec and Jandl [8] who observed that phonon frequency increases with increasing concentration of $SnSe_2$ in $SnS_{2-x}Se_x$.

The values of direct and indirect band gaps (Table 6.2) obtained in the present investigation do not match with the results of Lee et al [3], since these investigators only obtained the values of band gap from the plots of ($\alpha h\nu)^{1/2}$ vs $h\nu$, but did not show the variation of $(\alpha h\nu)^2$ vs $h\nu$. Our work differs from them in the sense that we have made a complete analysis of the absorption data using the three dimensional model and conclusively shown that the estimates of indirect band gaps obtained from the extrapolation of the $(\alpha h\nu)^{1/2}$ vs $h\nu$ curves with the zero absorption match with those obtained from the graphical differentiation of the data.

A careful study of the data presented in Table 6.2 indicates that both direct as well as indirect band gaps increase with increase of sulphur content in SnS_xSe_{2-x} single crystals. For direct band gaps in mixed III-V semiconducting materials it is customary as shown by Van Vechten and Bergstresser [9] to express the composition dependent energy gap as

$$E(x) = E(0) + bx + cx^2$$

with 'c' called the bowing parameter. For direct and indirect band gaps in the present work if we fit $E(x)$ to this expression, we get the results shown in Table 6.3. Figs.6.13 and 6.14 show the dependence on x of the direct and indirect band gaps respectively. In these figures optical direct and indirect band gaps of SnS_xSe_{2-x} single crystals have been plotted against x

Table 6.3 : Band gap of SnS_xSe_{2-x} for various values of x
Least - Squares fit to $E(x) = E(0)+bx+cx^2$

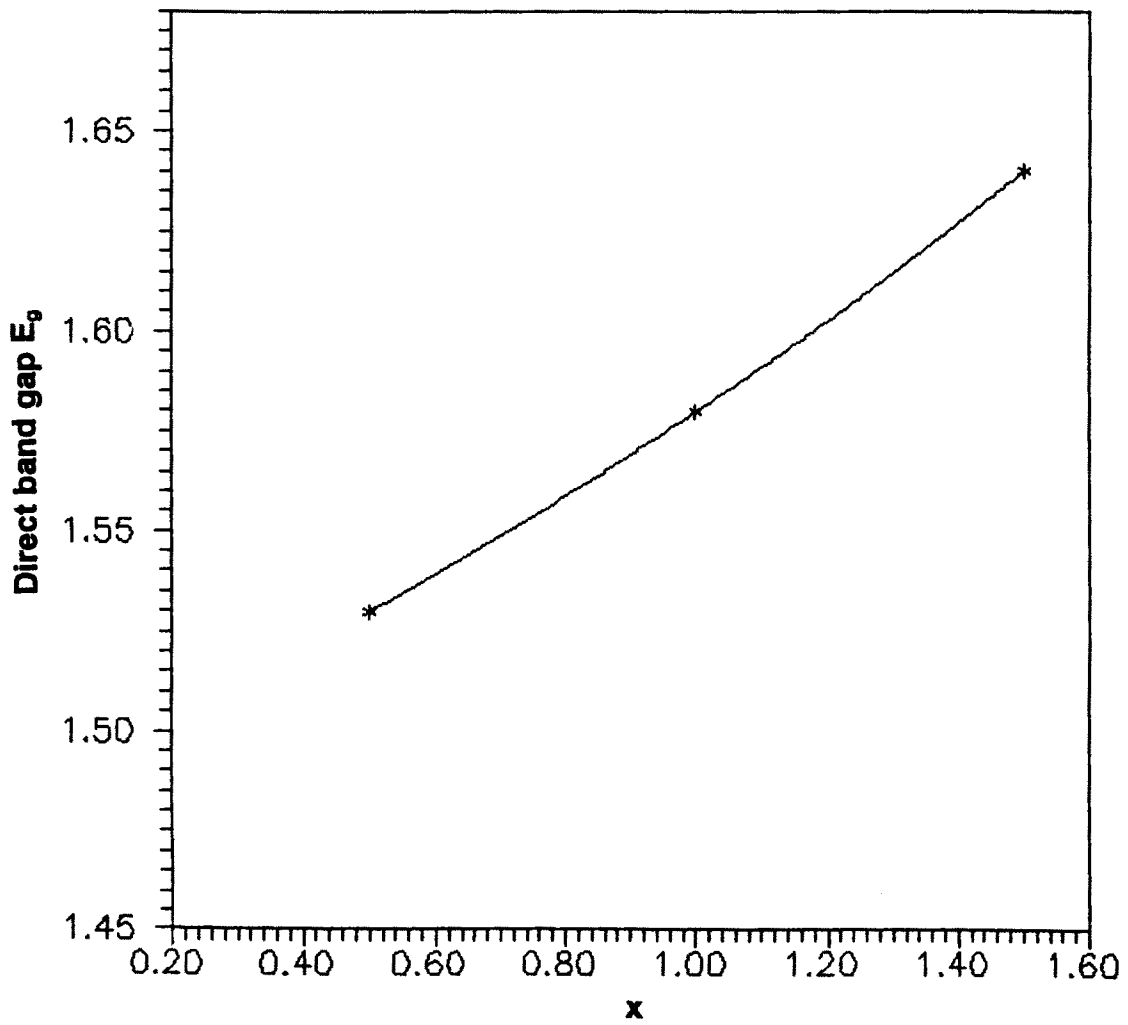|	T (^{0}K)	E_0 (eV)	b (eV)	c (eV)
Direct band gap	300	1.49	0.07	0.019
Indirect band gap	300	1.02	-0.089	0.14

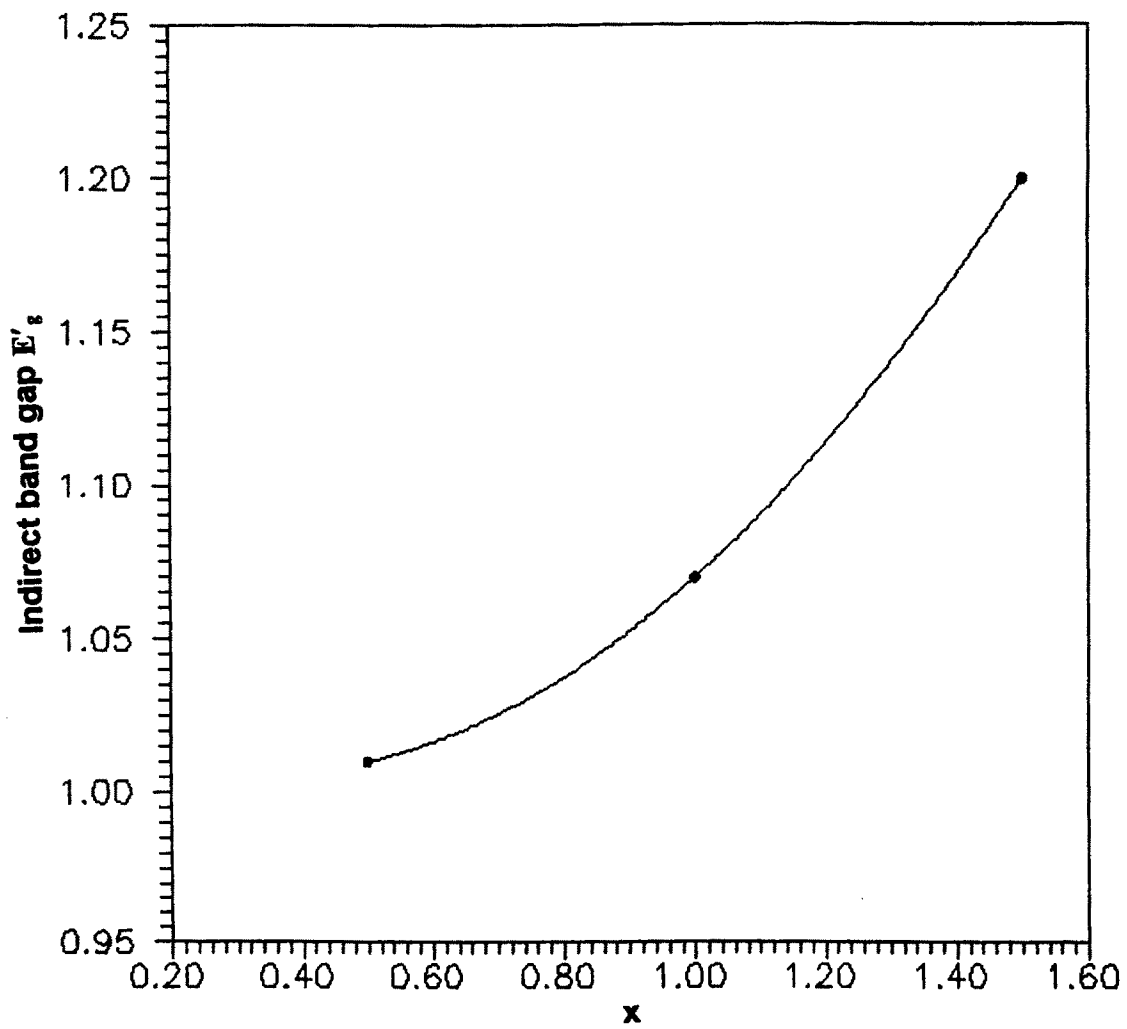FIG. 6.13 Graph showing the dependence of direct band gap E_g on x in $Sn\ S_x\ Se_{2-x}$.

FIG. 6.14 Graph showing the dependence of indirect band gap E'_g on x in
Sn S_x Se $_{2-x}$.

at 300 K. The curves are least square fit to

$$E(x) = E(0) + bx + cx^2$$

The change in energy gap with x is smooth. There are no abrupt slope changes, indicating a different band maximum might be replacing that for Sn Se$_2$ as x increases. Thus it can be concluded that the band edges are the same in all these compounds. There is no change in the nature of the valance band maximum or conduction band minimum.

Although the values of band gaps do not agree with those reported by [3], the increase in band gap with the increasing amount of sulphur is consistent with them. The increase in band gap with increase in sulphur content (i.e. x in SnS$_x$Se$_{2-x}$) can be linked with increase in resistivity with x (Chapter - 5). This conjecture is also supported by the electrical property measurements reported in Chapter - 5.

Failure to give a consistent analysis of the absorption data on two dimensional model suggests that although the material tin suphoselenide has been pointed out as highly anisotropic, it should possess some conductivity along the c-axis because of the presence of high density of stacking faults in them.

6.5   CONCLUSION :

The analysis of new accurate measurements of the optical absorption in SnS$_x$Se$_{2-x}$ single crystals for x = 0.5, 1.0 and 1.5 single crystals near the fundamental absorption edge has shown that both direct as well as indirect allowed transitions take place in these materials. The indirect transition involves two different phonons. Author has come to the conclusion that it is the three dimensional model which gives an

accurate analysis of the absorption data and the two dimensional model cannot be used satisfactorily to describe the main optical properties of tin sulphoselenide single crystals.

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