Chapter V

OPTICAL BAND GAP

CHAPTER - V

OPTICAL BAND GAP

I. INTRODUCTION :

The theoretical and experimental investigations of the optical behaviour of solids deal primarily with optical reflection, transmission and absorption properties, and their relation to the optical constants of the bulk and thin films. As a result of these studies, complex multilayer optical device systems with remarkable reflection, antireflection, interference and polarization properties have emerged for both laboratory and industrial applications. The absorption studies have led to a variety of interesting thin film optical phenomena which have thrown considerable light on the electronic structure of solids.

The optical measurement constitutes the most important means of determining the band structure of semiconductors. For absorption studies, photons of selected wavelength are directed at the sample and their relative transmission/absorption is observed. Optical properties of a thin film generally differ from those of the bulk. The difference are usually attributed to the microstructure of the films.

Principally there are several methods to determine the optical constants, such as Abbe's method, Spectroscopic methods, Polarmetric method and Critical angle method (1-4). The Spectroscopic method is probably the most widely used one for optical measurements. The most direct and the simplest method for determining the band structure is to measure the absorption spectrum.

There have been a few reports on the optical study on tin chalcogenides in bulk and thin film forms.

Garg et al (5) studied the optical absorption of SnSe single crystals grown by the Bridgman method. The absorption spectrum was obtained in the photon energy range of 0.5 to 1.3 eV for two light polarizations (E//a and E//b). The indirect energy gaps were obtained to be 0.9 eV for E//a and 0.89 eV for E//b, respectively. Yu et al(6) studied the absorption spectrum of SnSe crystal grown by vapour transport method. The crystals had been found to have an indirect band gap of 0.92 eV. Dang Tran Quan(7) measured the absorption coefficient of evaporated thin films of SnSe at 300°C over the photon energy range 0.8 to 1.3 eV. The analysis showed an indirect band gap of 0.96 eV and a direct band gap of 1.21 eV. W.Albers and J.Verberk(8) have found the indirect band gap of SnSe to be 0.9 eV and that of $SnSe_2$ to be 1eV. Bhatt et al(9) studied the optical band gaps of SnSe and $SnSe_2$ crystals grown by the Bridgman technique and have reported the indirect band gap of 0.94 eV and 1.01 eV for SnSe and $SnSe_2$, respectively. G. Valiukonis et al(10) have studied the electroreflectance and thermoreflectance spectra of SnSe crystal. They calculated direct band gap as 1.03 eV and

1.24 eV for light polarizations E//a and E//b, respectively.

II. GENERAL DISCUSSION :

It is apparent that a photon with energy $h\nu \geqslant E_g$ can be absorbed in a semiconductor, where E_g is the band gap of the semiconductor. Since the valence band contains many electrons and the conduction band has many empty states into which the electrons may be excited, the probability of photon absorption is high. Figure - 1 indicates an electron excited to the conduction band by optical absorption possibly gaining more energy than is common for conduction band electrons (almost all electrons in the band are near Ec unless the sample is heavily doped). Hence the excited electron loses energy to the lattice in scattering events until its velocity reaches the thermal equilibrium velocity of other conduction band electrons. The electrons and holes created by this absorption process are excess carriers ; since they are out of balance with their environment, they most eventually recombine. The excess carriers exist in their respective bands; however, they are free to contribute to the conductivity of the material.

A photon with energy less than E_g is unable to excite an electron from the valence band to the conduction band. Thus in a pure semiconductor, there is negligible absorption of photons with $h\nu < E_g$. This explains why some materials are transparent in certain wavelength ranges. We are able to "see through" certain insulators, such as NaCl crysatal, because a large energy gap exists in the material. If the band gap is about 2 eV, only long wavelength (infrared) and the red part of the visible spectrum are transmitted ; on the other hand a band gap of about 3 eV allows infrared and the entire visible spectrum to be transmitted. Band gaps of some common semiconductors relative to the optical spectrum is given in Figure - 2.

If a beam of photons with $h\nu > E_g$ 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 light intensity depends on the photon wave length and the thickness of the sample.

The intensity of light transmitted through the sample with thickness t is

$$I = I_0 e^{-\alpha t} \qquad \text{.... 1}$$

where α is the absorption coefficient, I_0 is the incident photon beam intensity and I is the transmitted intensity.

Near the absorption edge, the absorption coefficient is expressed as

$$\alpha \sim (\hbar\nu - E_g)^{\gamma} \qquad \text{....2}$$

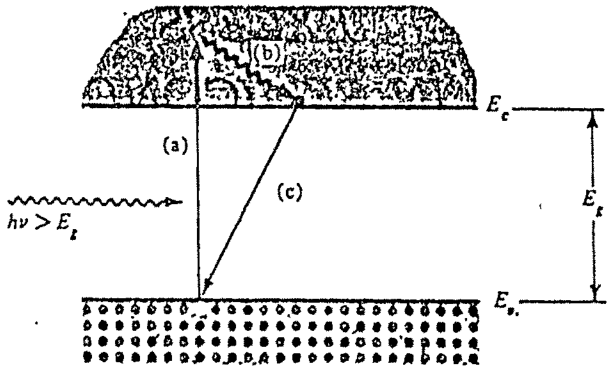

Figure – 1. Optical absorption of a photon with $h\nu > E_g$: (a) an EHP is created during photon absorption; (b) the excited electron gives up energy to the lattice by scattering events; (c) the electron recombines with a hole in the valence band.

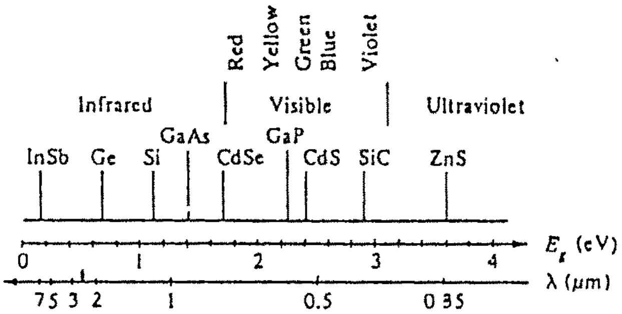

Figure - 2. Band gaps of some common semiconductors relative to the optical spectrum.

where $h\nu$ is the photon energy, E_g is the optical gap, γ is a constant which is equal to 1/2 and 3/2 for allowed direct transition and forbiddent direct transition, respectively [with K(min) = K(max) as in transitions (a) and (b) shown in Figure - 3]. It equals 2 for indirect transition [transition (c) shown in Figure - 3] where phonons must be incorporated. In addition, γ equals 1/2 for allowed indirect transitions to exciton states where an exciton is a bound electron - hole pair with energy levels in the band gap and moving through the crystal lattice as a unit.

The possible transitions are

1. Band to band.
2. Excitonic.
3. Between sub-bands.
4. Between impurities and bands.
5. Transition by free carriers within a band.
6. Resonance due to vibrational states of lattice and impurities.

The absorption is expressed in terms of a coefficient which is defined as the relative rate of decrease in light intensity $L(h\nu)$ along its propagation :

$$\alpha(h\nu) = \frac{1}{L(h\nu)} \frac{d(h\nu)}{dx} \qquad .....3$$

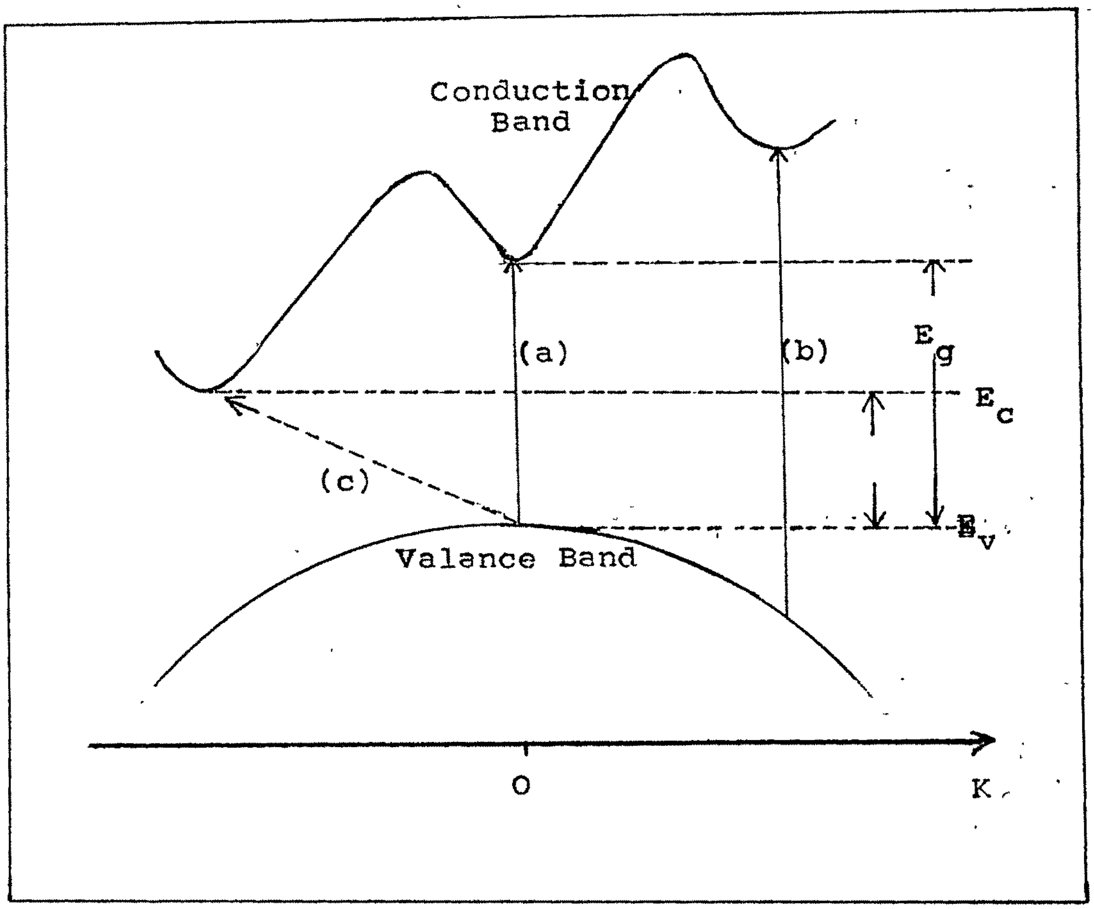

Figure - 3 : Optical transitions.
(a) and (b) Direct transitions.
(c) Indirect transition involving phonons.

where $L(h\nu)$ is incident light intensity, α is the absorption coefficient(11, 25).

The basic theory of direct and indirect transitions in semiconductors is formulated by Bardeen et al(12). The direct transitions are generally supposed to be taking place from valence band to conduction band under the selection rule :

$$K - K' + \left(\frac{2\pi i}{\lambda}\right) = 0 \qquad \ldots .4$$

where K and K' are the wave vectors of electron before and after transition, respectively. λ is the wavelength of the photon and i is the unit vector along the direction in which the photon travelled before it is absorbed. This can be simplified to $K'=K$, since $2\pi/\lambda$ is small compared to either K or K'. This shows that only vertical transitions are allowed. Other transitions, if taking place, will be of very small probability. Thus the steep edge in absorption spectra is attributed to the highly possible direct transitions. The weak lingering absorption in the tail region is considered to be due to indirect transitions involving the participation of phonons in the process and this will happen when the wave-vectors at the minima of the conduction band energy surface do not coincide. A phonon is emitted or absorbed depending on whether the energy of photon is more or less than the indirect band gap energy.

For direct transition, the absorption coefficient relates to the photon energy as

$$(\alpha h\nu) = B\,(h\nu - E_g)^x \qquad \text{.....5}$$

where x = 1/2 for allowed transitions and x = 3/2 for forbidden transitions; E_g is the direct energy gap and B is a parameter that depends on the transition probability.

For indirect transition.

$$(\alpha h\nu) = A(h\nu - E_g \pm Ep)^x \qquad \text{.....6}$$

where x = 2 for indirect allowed transitions and x = 3 for forbidden transitions. E_g is the band gap and Ep is the absorbed or emitted phonon energy(13,14,15). At room temperature, transitions, both with phonon emission and phonon absorption, will contribute to the absorption.

III. EXPERIMENTAL RESULTS :

3.1 Optical band gap of bulk materials :

The dual beam UV-VIS-NIR spectrophotometer (Shimadzu UV-365) was used for the optical measurements. Freshly cleaved thin crystals having thickness about 0.5 to 1 mm were mounted on the sample holder side and on the other side, reference sample having the same aperture as that of sample holder was fixed. Using specular reflectometry attachment the absorption spectrum was recorded.

3.1.1 **SnSe, $SnSe_2$ and SnSe-$SnSe_2$ eutectic crystals :**

The optical absorption was measured in the wavelength range 500 nm to 2000 nm and the absorption spectrum was recorded. By analysing the spectrum, absorption coefficient was calculated as a function of photon energy. The plots of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$ and $(\alpha h\nu)^2$ vs $h\nu$ were used to evaluate the optical band gaps. The plots of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$ for SnSe, $SnSe_2$ and SnSe-$SnSe_2$ eutectic are given in Figures 4,5,6, respectively and those of $(\alpha h\nu)^2$ vs $h\nu$ for SnSe and $SnSe_2$ are given in Figure 7 and 8, respectively. The plots are observed to be linear in the region of strong absorption near the fundamental absorption edge. Hence by extraploting the linear portion to $h\nu = 0$, the band gap was evaluated. The values of direct and indirect band gaps so obtained are given in Table - 1. These values correspond to the values obtained by other workers(5,16,17). In the case of SnSe-$SnSe_2$ eutectic crystals, it was observed that the plots of $(\alpha h\nu)^2$ vs $h\nu$ in the range of energies used, does not exhibit linearity in the higher energy range. This probably indicates that the direct transitions do not occur in these crystals.

3.2 **Optical band gap of thin films :**

To carry out the absorption measurements on the thin film, the film on substrate and a blank identical substrate as

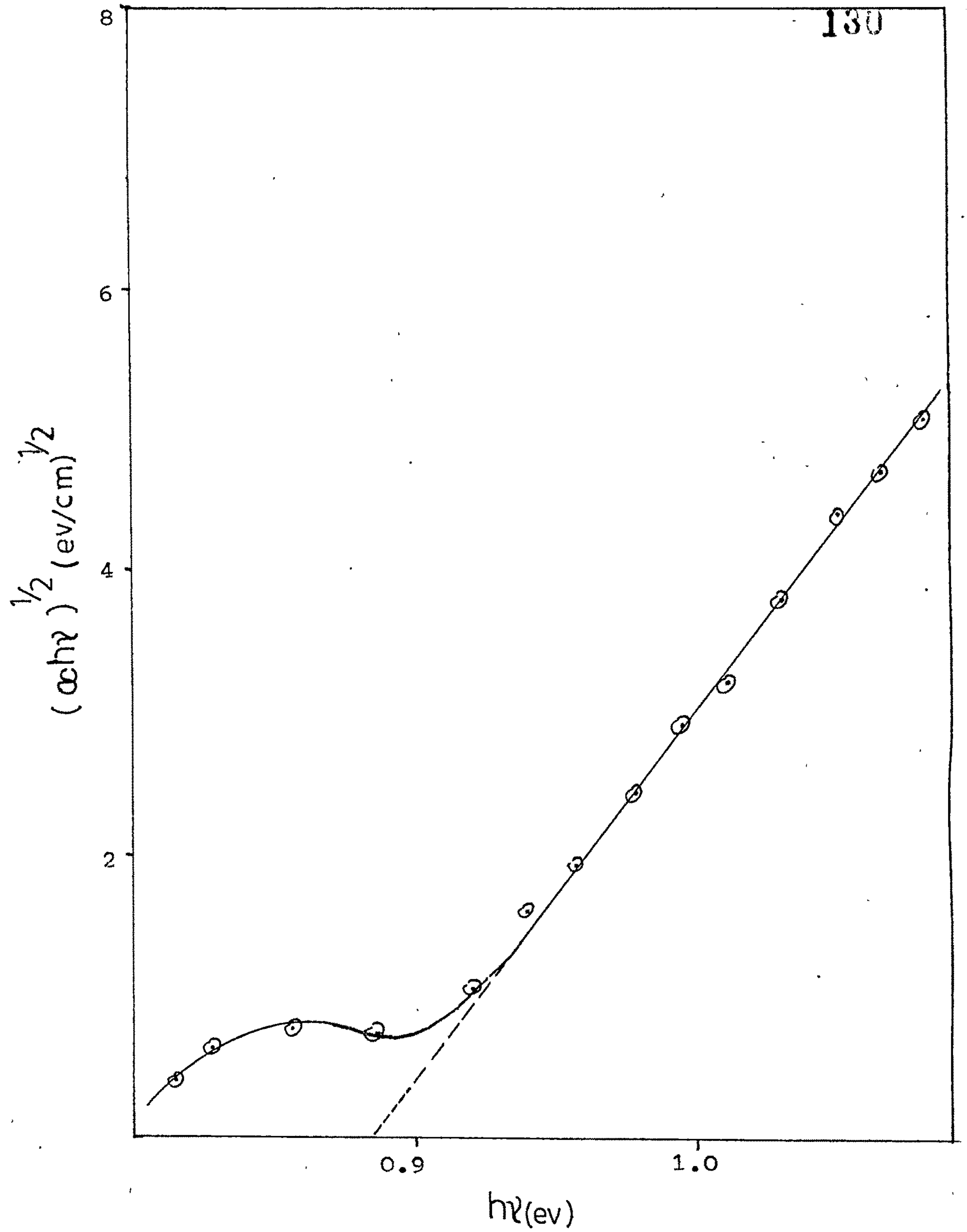

Figure - 4 : Plot of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$; SnSe crystal.

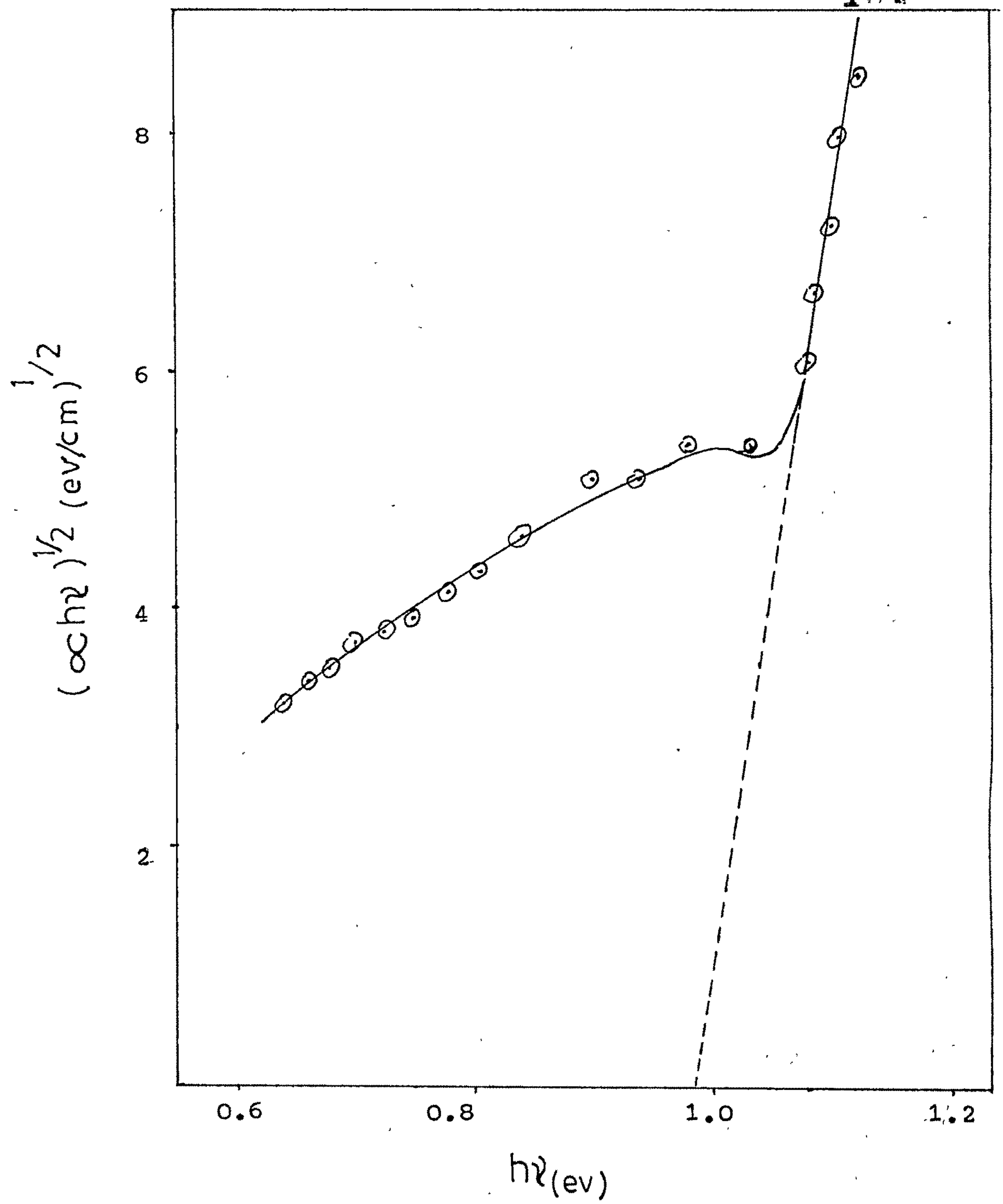

Figure - 5 : Plot of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$; $SnSe_2$ crystal.

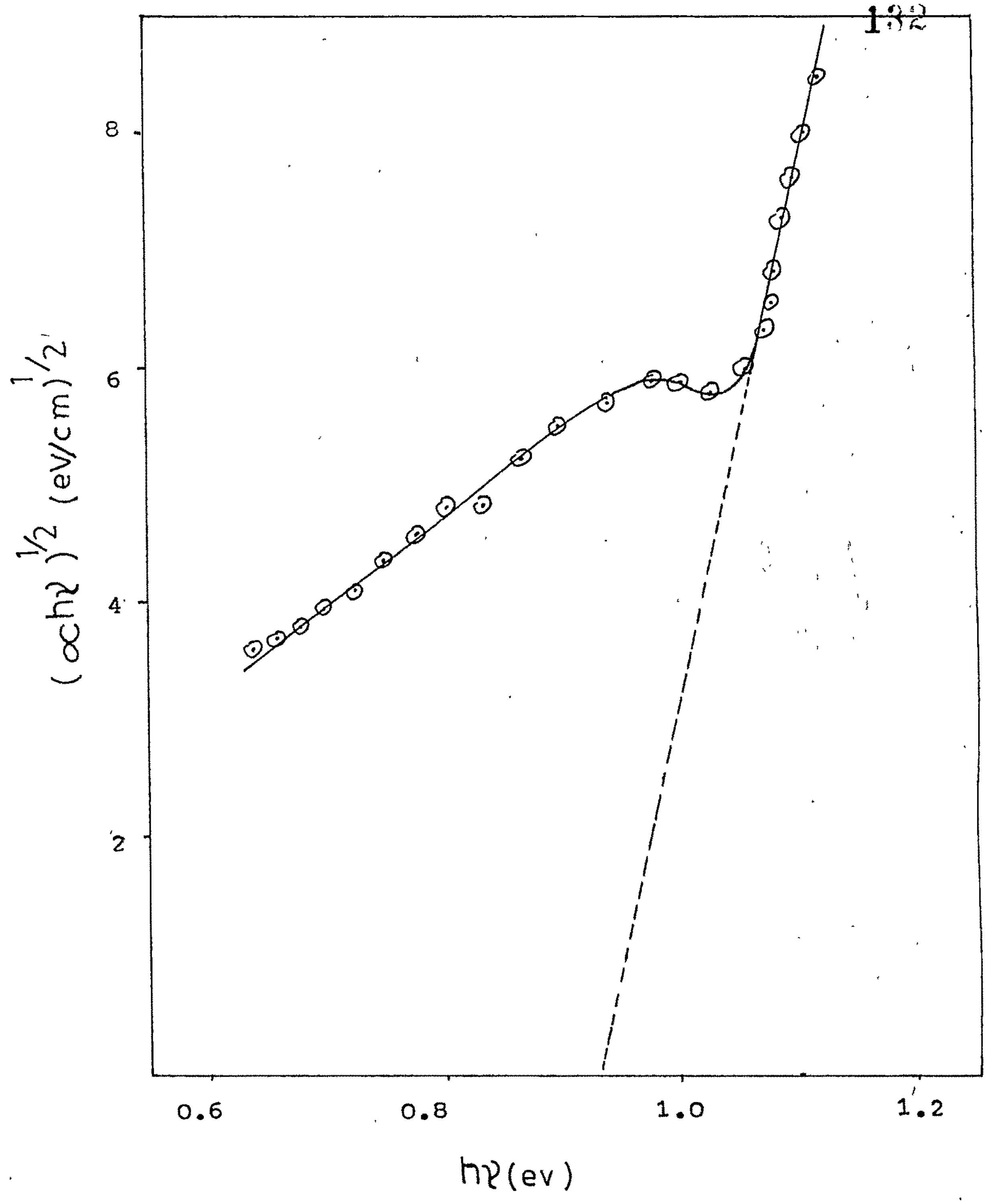

Figure - 6 : Plot of ($\alpha h\nu$)$^{1/2}$ vs $h\nu$; SnSe-SnSe$_2$ eutectic crystal.

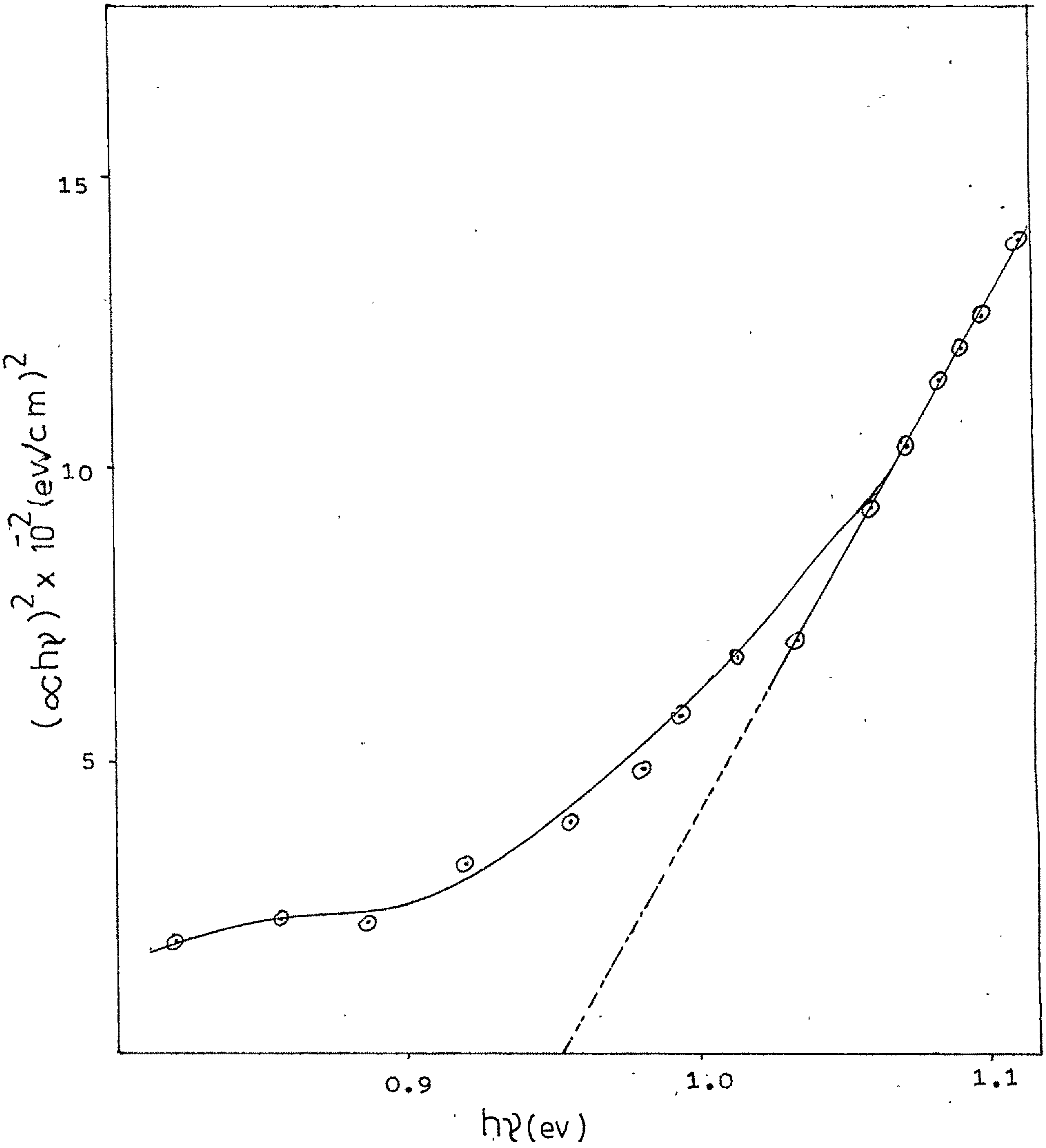

Figure - 7 : Plot of $(\alpha h\nu)^2$ vs $h\nu$; SnSe crystal.

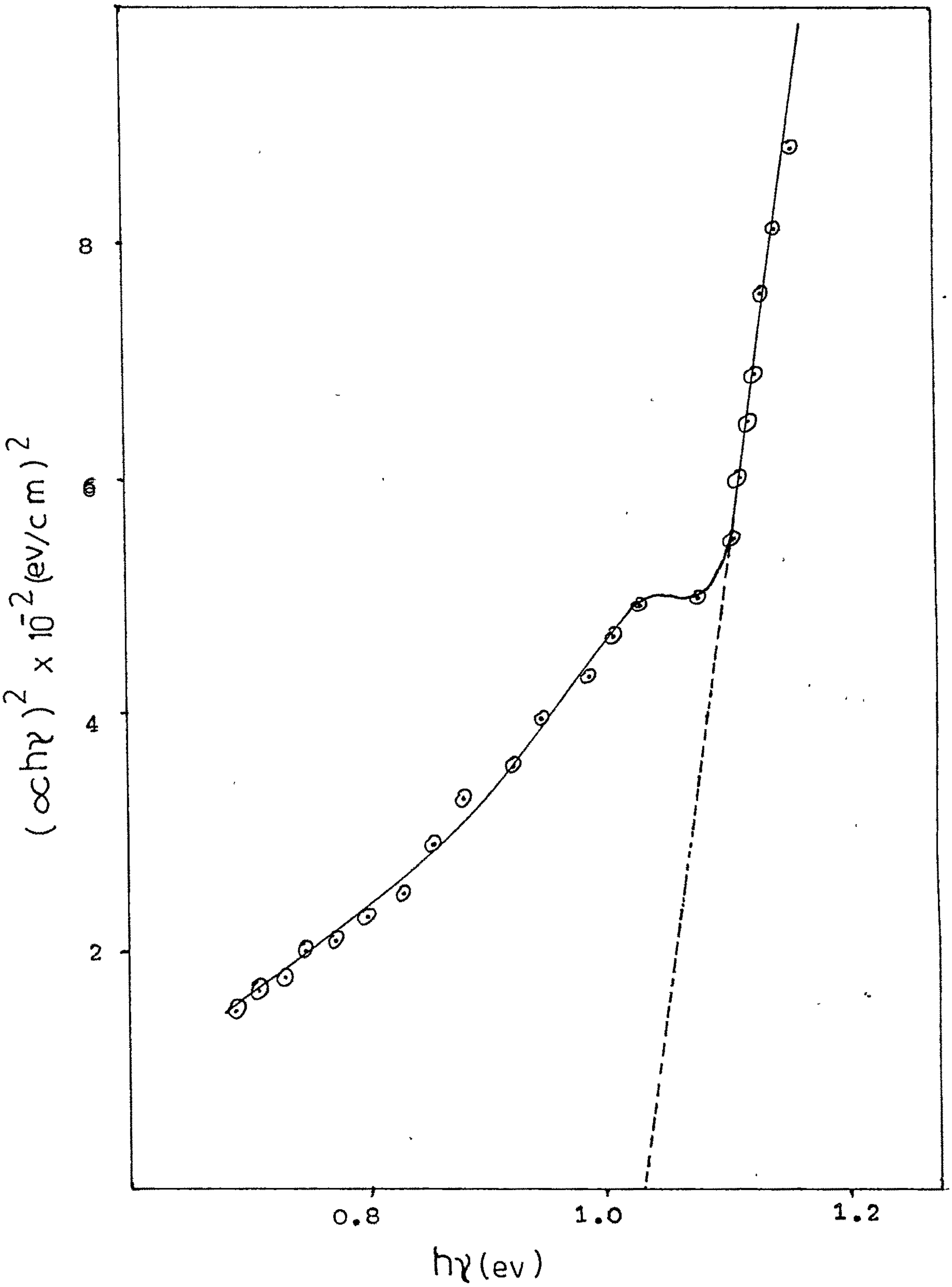

Figure - 8 : Plot of $(\alpha h\nu)^2$ vs $h\nu$; $SnSe_2$ crystal.

reference were placed in their respective positions in the sample compartment of the spectrophotometer. The absorption data was used to study the band gap and its dependence on different parameters like film thickness, deposition temperature and anneal-temperature.

3.2.1 SnSe and $SnSe_2$ films :

The plot of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$ obtained for SnSe and $SnSe_2$ films (prepared by evaporation of the compound) are given in Figures 9 and 10, respectively. Similar plots for the films of different thicknesses were plotted and the band gaps obtained. The band gap varies as the inverse square of the film thickness as shown in Figures 11 and 12 for SnSe and $SnSe_2$, respectively. Table - 2 gives the values of the band gaps for SnSe and $SnSe_2$ films of different thicknesses. It is seen that with increasing film thickness the band gap decreases. Such thickness dependence of band-gap has been explained in terms of quantum size effect and dislocation density(18,19). Quantum size effect appears in semiconductors and semimetal films when their thickness is comparable with or smaller than the mean free path or effective de Broglie wavelength of the carriers. Because of the finite thickness of the film, the transverse component of quasi-momentum of carriers is quantized. Due to this quantization, the bottom of the conduction band and top of the valence band are separated by an additional amount ΔE given as

$$\Delta E = \frac{h^2}{8 m^* t^2} \qquad \text{.... 7}$$

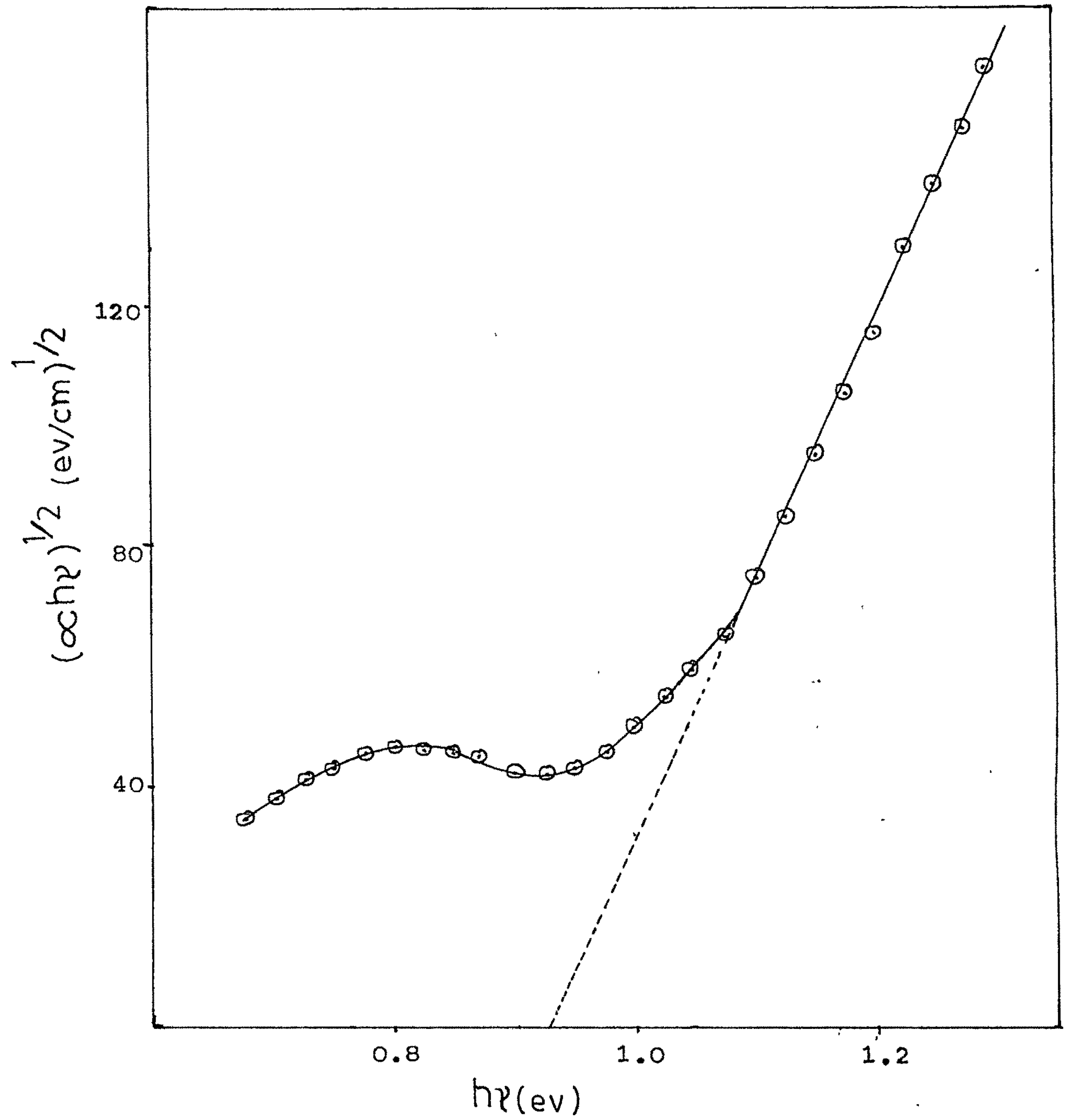

Figure - 9 : Plot of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$; SnSe directly evaporated film (t ~1000 Å)

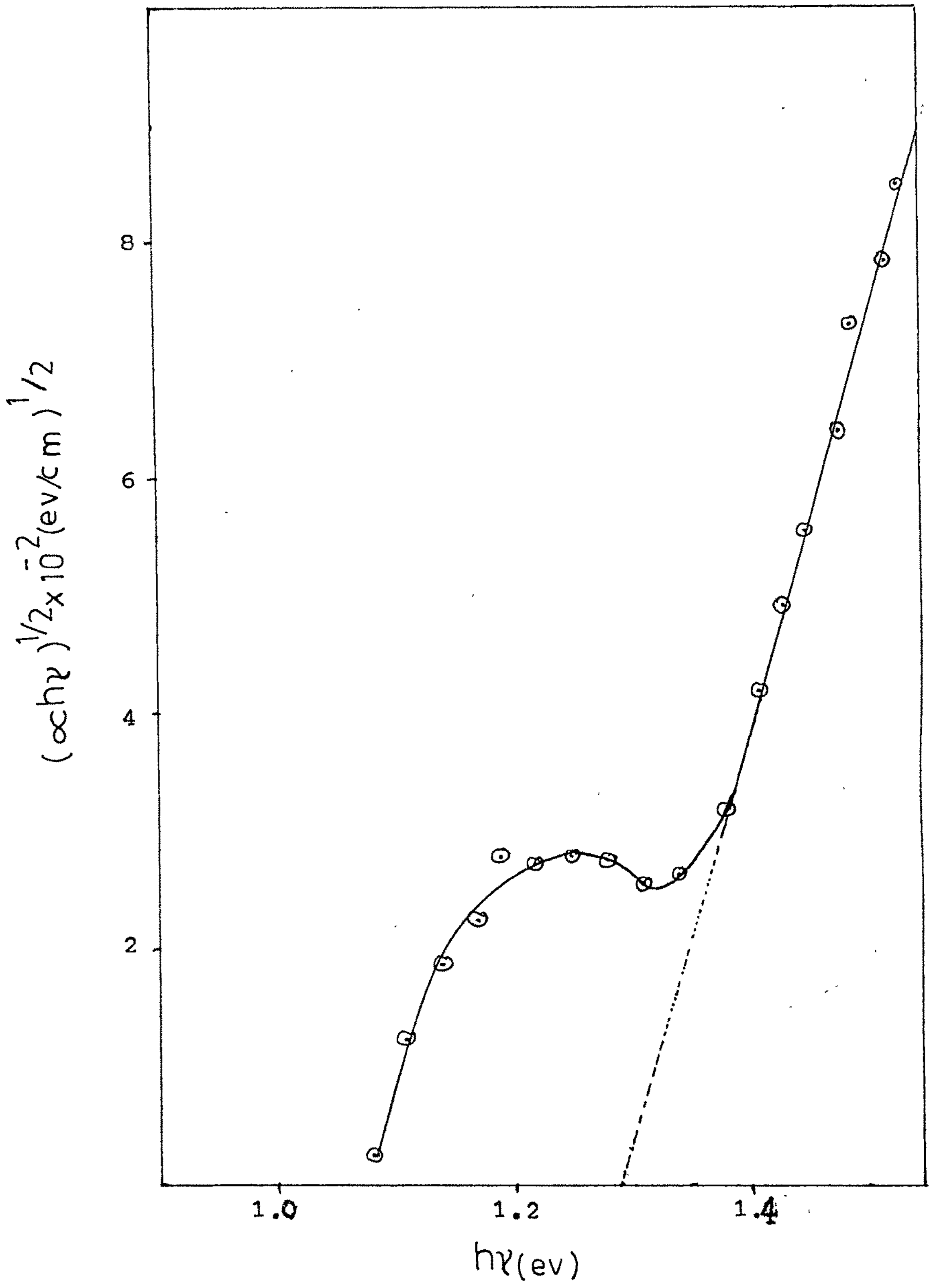

Figure - 10 : Plot of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$: $SnSe_2$ film.
(t ~ 2000Å)

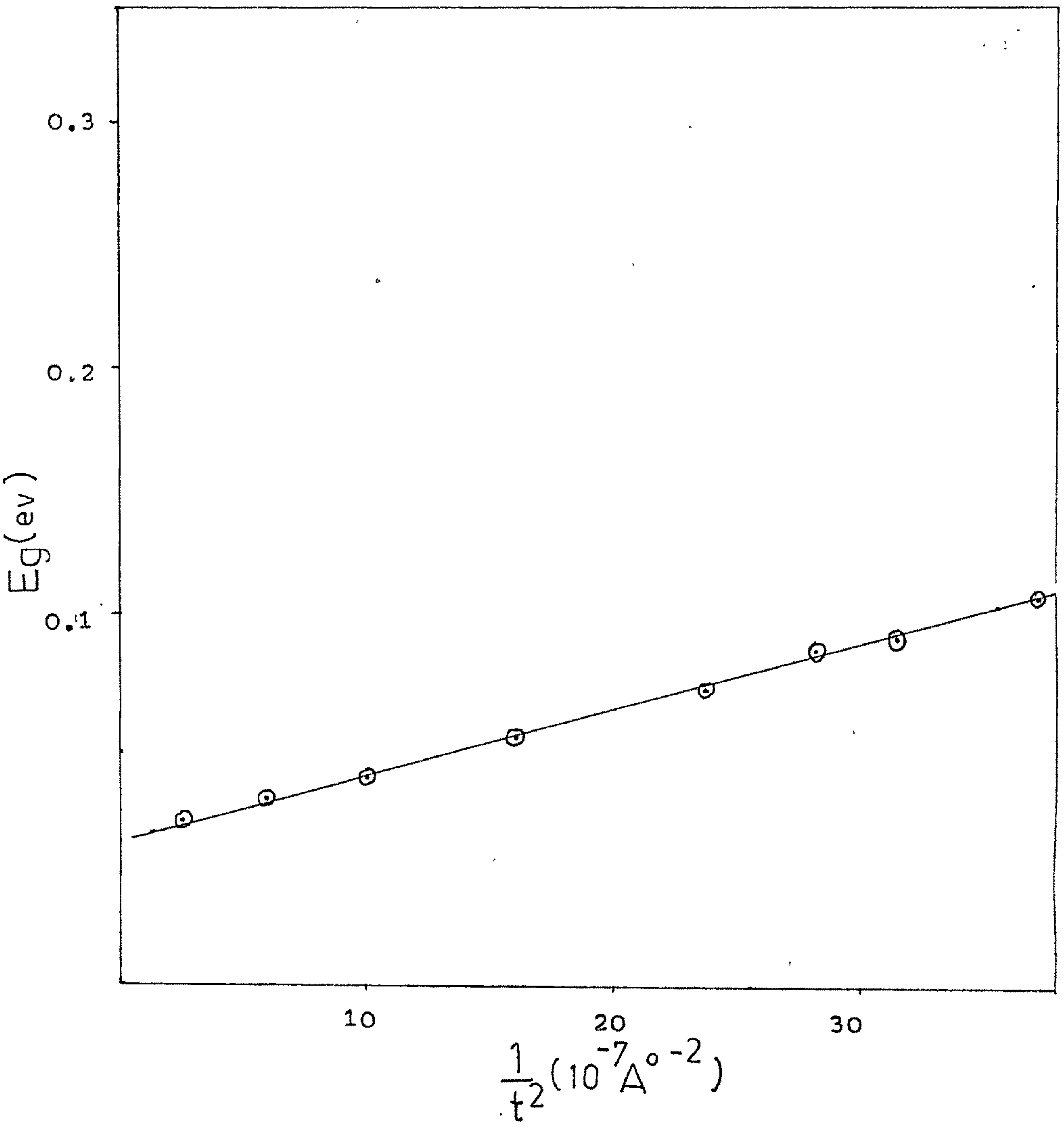

Figure - 11 : Plot of E_g vs $1/t^2$; SnSe films directly evp. from the compound.

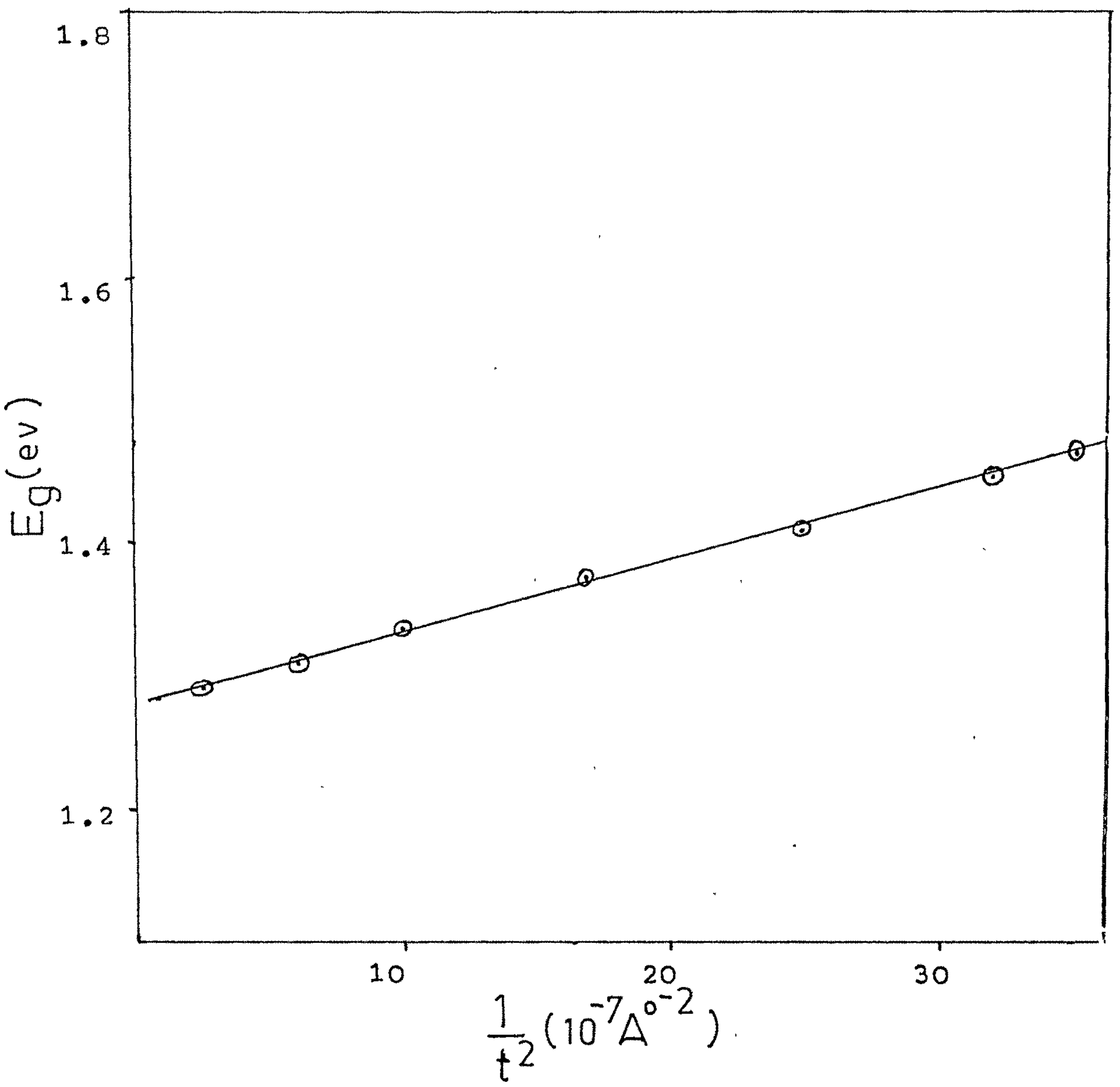

Figure - 12 : Plot of E_g vs $1/t^2$; $SnSe_2$ films.

TABLE - 1

Measured band gaps

Crystal	Direct gap (eV)	Indirect gap (eV)
SnSe	0.95	0.89
$SnSe_2$	1.03	0.99
$SnSe\text{-}SnSe_2$	-	0.93

TABLE - 2

Band-gap of SnSe and $SnSe_2$ films of various thicknesses

	Band - gap (eV)	
Thickness (Å)	SnSe film	$SnSe_2$ film
500	0.98	1.50
1000	0.93	1.35
1200	0.92	1.31
2000	0.91	1.29

where t is the thickness and m^* is the effective carrier mass(19). The straight line plots of Eg vs $1/t^2$ in Figures 11 and 12 are in agreement with the above relation and imply the quantum size effect operative in the present case.

It is also known that a fairly large number of dislocations are created during the formation of the films and their density increases as the thickness increases up to a particular value beyond which the density is practically constant. However, the dependence of dislocation density on thickness has not been quantified and in any case the dependence is complex. There are considerable lattice disturbances due to dislocations, the disrupted or danging bonds with their specific charge and the space charge domain that form immediately in the vicinity of the dislocations bearing their effects on the band gap.

With increasing film thickness, the effect of the initial granular structure on the optical properties decreases but is not eliminated completely. Therefore, thickness dependence is still observed although the general behaviour of the optical parameters follows that of the bulk, at least qualitatively. In an infinite thick crystal, the electron energy is a multivalued continuous function of the quasi-momentum. In a thin film specimen, the quasi-momentum assumes discrete values along the thickness dimension. The energy spectrum represents a system of discrete levels with the separation between them given by the uncertainity principle. The effect of the discrete energy levels on the forbidden gap of a semiconductor has been considered by Sandomiskii(20). According to him, all levels of the energy spectrum of a semiconductor will be shifted by ΔE. In the thin film specimen, provided smearing of energy levels by temperature and diffuse scattering of the carriers at the film surfaces are not significant, this shift will increase the band gap and thus affect the optical behaviour of semiconducting films. The absorption is reduced in thinner films as compared with the bulk. The variation of band gap with the crystallite size has been explained by the modified form of Stellar's formula(21). According to him, the increased barrier height is given by

$$E = Eo + C\ (X-fD)^2 \qquad \ldots.\ 8$$

where Eo is the original barrier height, C is a term depending on the density of charge carriers, electronic charge and dielectric constant of the material. X is the barrier width, D is the dimension of the grain and f is a factor depending upon the charge accumulation and carrier concentration.

It is known from the literature(22) that the grain size is approximately proportional to thickness and hence increases as thickness increases. Hence if we replace D, the grain size in the above exression by the film thickness t, we find that E in the above expression should be proportional to

$$(X-ft)^2 \qquad \ldots . \; 9$$

However, in the present observations, we find that the band gap varies inversely as the square of the thickness of the film and hence it can be concluded that the observed band gap variation with thickness cannot be attributed to the above effect.

3.2.2 SnSe Solid State reacted film :

Films having thickness in the range 500 Å to 2500 Å were studied. The plot of $(\alpha h\nu)^{\frac{1}{2}}$ as a function of $h\nu$ (shown in Figure - 13) is linear in the strong absorption region obeying equation 6. This indicates that the absorption takesplace through indirect interband transition. Also the absorption edge is probably due to transition between the impurity level and the well defined edge of the band. According to Pankov[23], the absorption coefficient for transitions involving the impurity level covers a smaller range than the transition between the valence and the conduction bands because the density of states in the impurity level is lower than the density of states in the bands. In practice the shallow impurities are seldom resolved in the background absorption due to transitions involving tails of states. In the case of deep levels, the ionization energy for impurity level can contribute to a definite step on absorption edge.

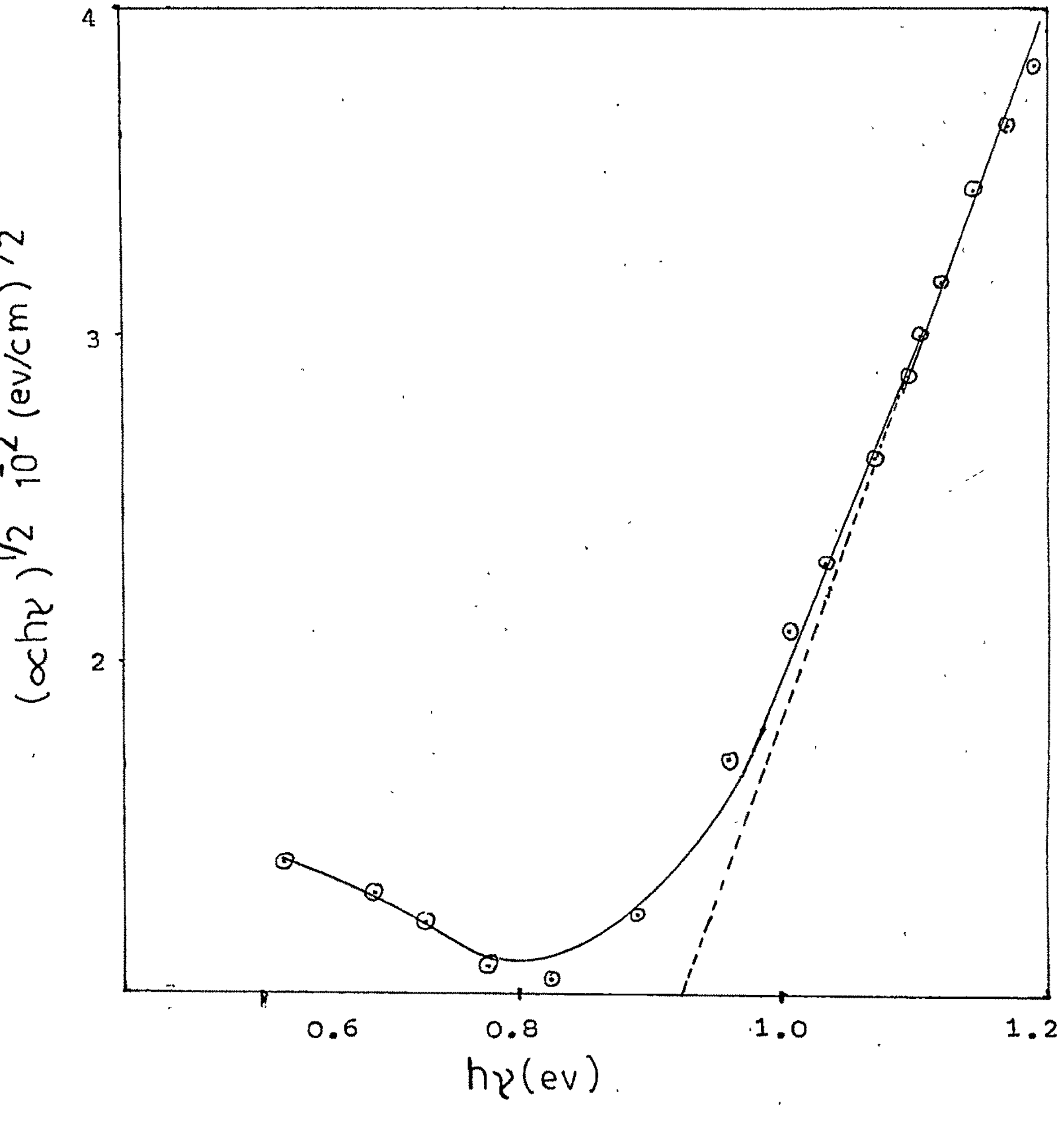

Figure - 13 : Plot of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$; SnSe solid state reacted film.

The dependence of the band gap with film thickness is shown in Figure - 14 as a plot of E_g vs $1/t^2$. This variation can be explained in terms of quantum size effect or dislocation density as explained earlier.

In the solid state reaction method to obtain the films, the number of layers reacted was also varied. With increasing number of layers, the thickness of the individual component layers was decreased so as to keep the total thickness of the film constant, viz 1200 Å. The number of layers thus varied was between 3 to 9. The values of the band gap of the films with different numbers of reacted layers were obtained from the absorbance spectra again and are listed in Table - 3. It is seen that Eg increases with the number of layers. With the number increasing, the thickness of the individual elemental layer decreases. This causes a more effective and uniform reaction to take place. Hence such films ought to be of the structural and chemical perfection better than that of the films of less number of reacted layers which are thicker. This behaviour of band gap also corresponds to the increased band gap of annealed films of SnSe(24).

3.2.3 $SnSe-SnSe_2$ eutectic films :

The absorption coefficients of these films were also obtained in the photon energy range 0.5 eV to 1.2 eV for various

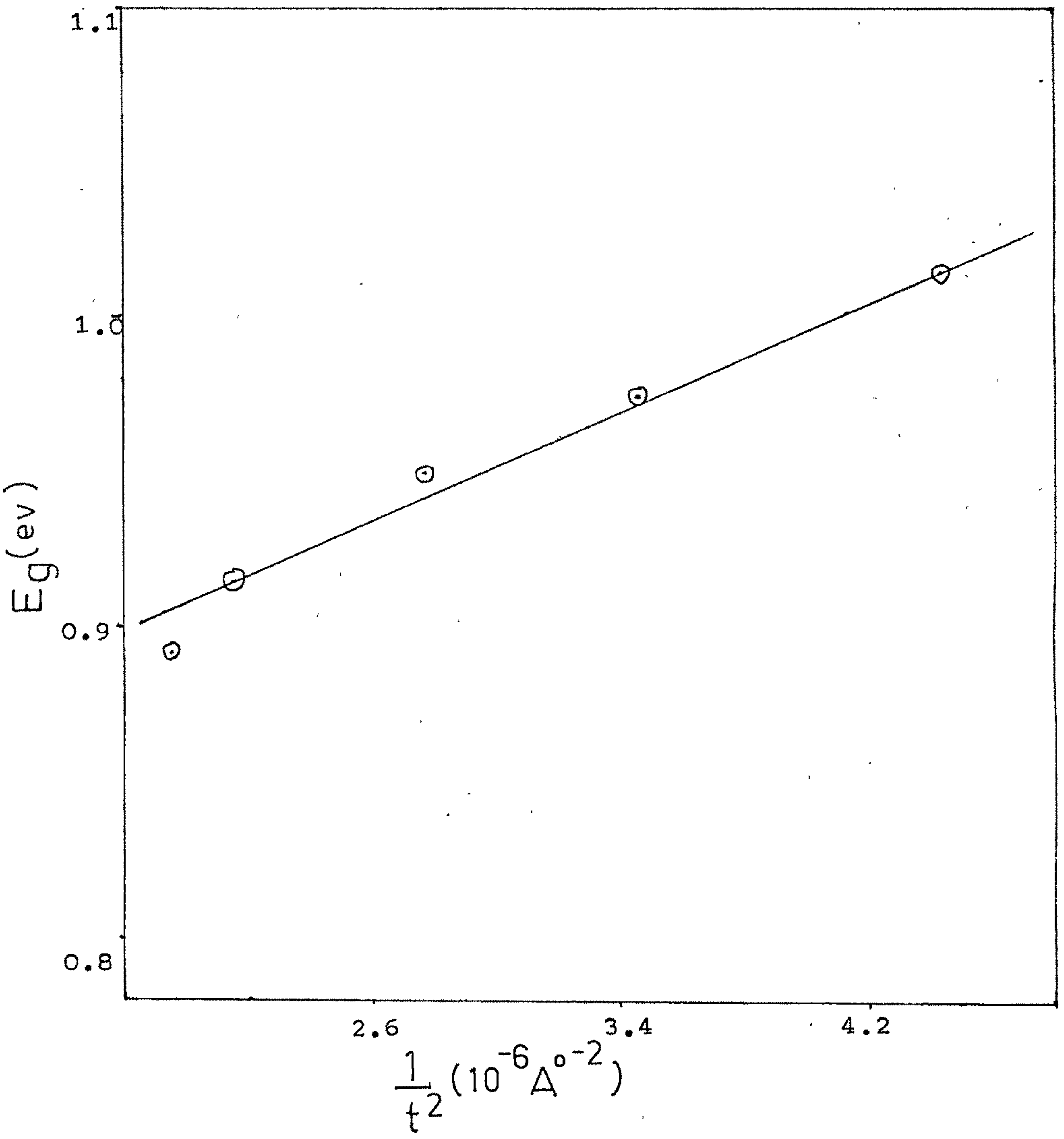

Figure - 14 : Plot of E_g vs $1/t^2$; SnSe solid state reacted film.

film thicknesses. A typical plot of $(\alpha h\nu)^{\frac{1}{2}}$ versus $h\nu$ obtained for a film of thickness 1000 Å deposited at substrate temperature 150°C is shown in Figure - 15. The indirect band gap obtained is about 1.02 eV. However, thereare probably no direct transitions allowed in these films since no similar graph is obtainable for $(\alpha h\nu)^2$ versus $h\nu$. This fact is in agreement with the results for the single crystals.

The band gap of the films has been found to vary as the inverse square of film thickness as shown in Figure - 16. Thus QSE in optical transitions is manifest in these films also within the thickness range used.

Effect of substrate temperature on band gap : Films with thickness 500 Å were deposited on glass substrates at various temperatures ranging from room temperature to 150°C. The band gaps of films obtained at various substrate temperatures are given in Table - 4. There is no systematic change in the band gap with substrate temperature but the band gap is found to increase in general with the substrate temperature. This may be due to increase in grain size with the substrate temperature, which is a general empirical fact. With increase in grain size, the grain by itself would tend to exhibit its intrinsic property like a bulk crystal. The band gap of a bulk crystal is less than that of a thin film. Thus the decrease in band-gap with substrate temperature can be attributed to the increased grain size in a qualitative way.

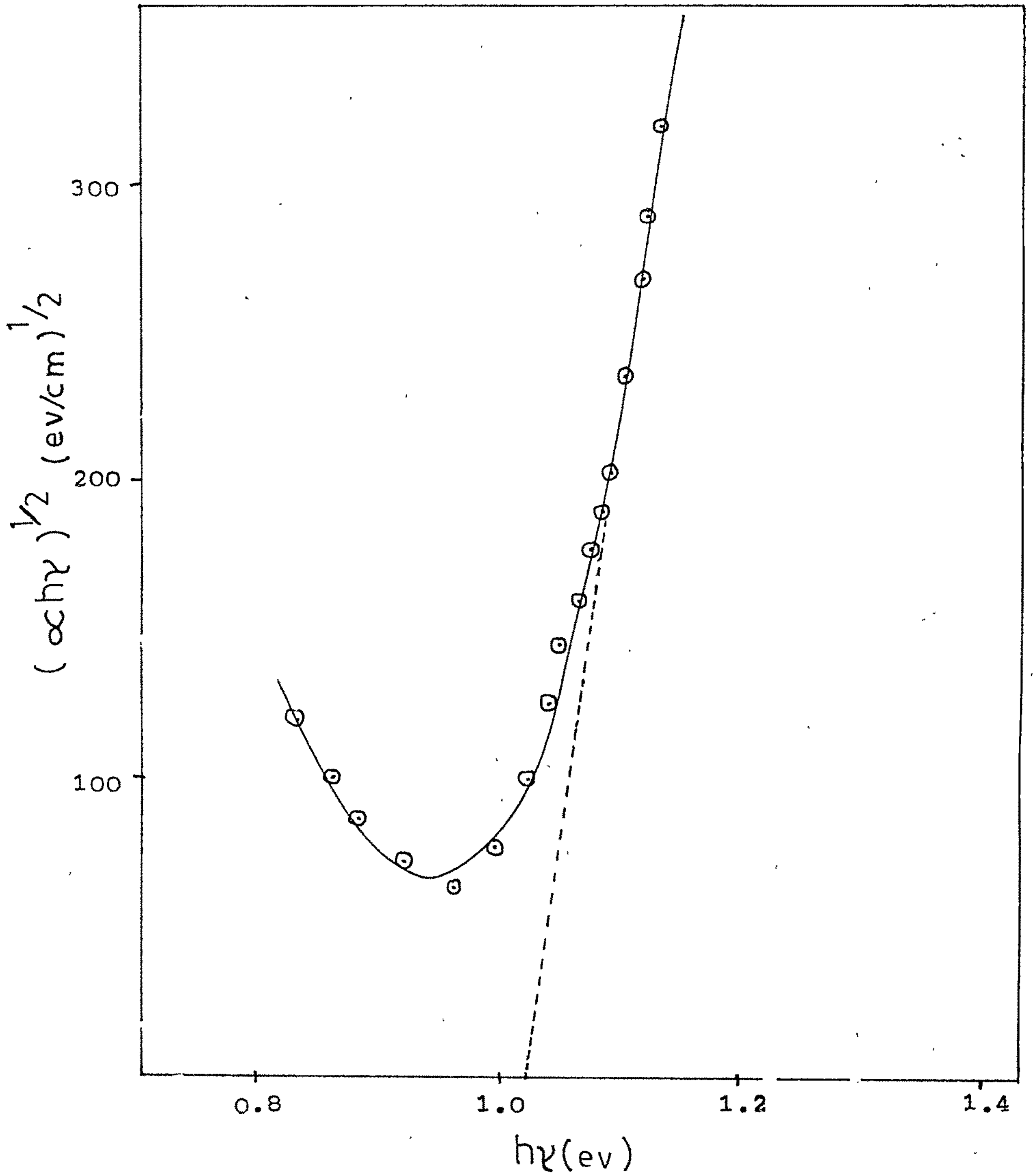

Figure - 15 : Plot of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$; $SnSe-SnSe_2$ eutectic films. (t ~ 1000 A)

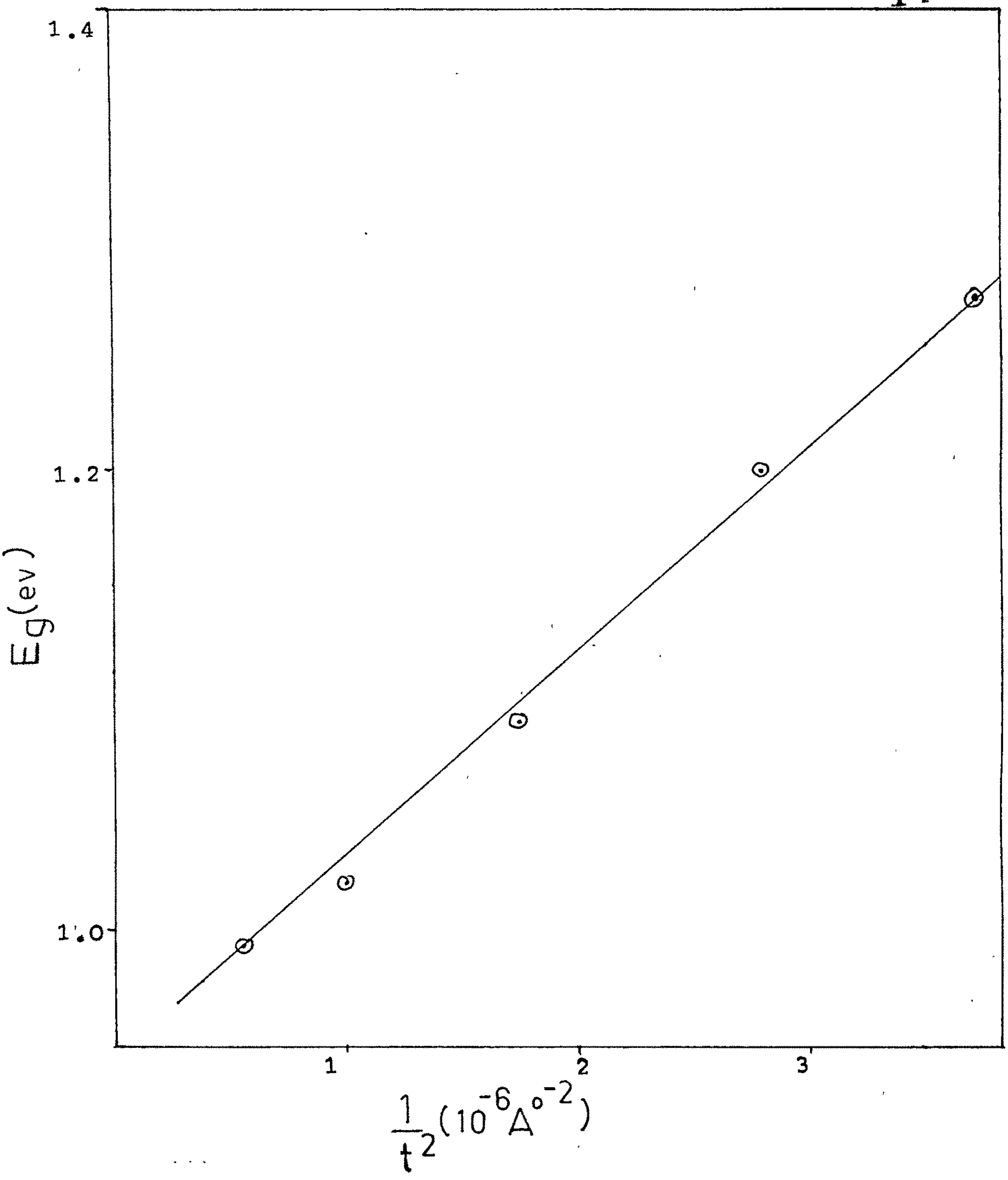

Figure - 16 : Plot of E_g vs $1/t^2$; SnSe-SnSe$_2$ eutectic film.

TABLE - 3

Band-gap of SnSe films obtained for different number of layers reacted (t ~ 1200 Å)

No. of layers	E_g (eV)
3	0.60
5	0.86
7	0.93
9	0.99

TABLE - 4

Band-gap of $SnSe-SnSe_2$ eutectic films deposited at various substrate temp. (t ~ 500 Å)

Sub. temp (°C)	E_g (eV)
28	1.20
70	1.25
100	1.25
150	1.29

IV CONCLUSION :

1. The band gaps of SnSe, $SnSe_2$ and SnSe-$SnSe_2$ eutectic crystals are about 0.89 eV, 0.99 eV and 0.93 eV (all indirect), respectively. Whereas direct transition in SnSe and $SnSe_2$ do occur, with respective band gaps about 0.95eV and 1.03eV, there are no observable direct transitions in the eutectic crystals.

2. On an average the band gap of SnSe films, directly evaporated from the compound, is 0.94 eV (indirect).

3. The band gap of $SnSe_2$ films is on an average 1.36 eV (indirect).

4. SnSe Solid State reacted films have an indirect band gap of about 0.94 eV.

5. With increase in the number of layers in the SnSe Solid State reacted films (for constant total thicknes of the films), the band gap increases which may be due to improved structural and chemical perfection.

6. The indirect band gap of the films obtained from SnSe-$SnSe_2$ eutectic is about 1.12 eV.

7. In all the cases, the annealing treatment does not induce any noticeable change in the band gap.

8. The film thickness dependence of the band-gap of SnSe, $SnSe_2$ and SnSe-$SnSe_2$ eutectic indicate the optical transitions to be governed by quantum size effect within the thickness ranges studied.

REFERENCES :

1. O.S. Heavens : Optical properties of thin solid films , Butter Worths, London, (1955).

2. O.S. Heavens : Rept. Progr. Physics 23 (1960) 1.

3. P.H. Bering : Physics of thin films, Academic press, New York (1964) 69.

4. H.E. Bennett and J.M. Bennettin : Physics of thin films, Academic press, New York 4 (1967) 1.

5. A.K. Garg, A.K. Jain and O.P Agnithotri : Indian J. of Pure and Applied Phys. 21 (1983) 276.

6. J.G.Yu., A.S. Yue and O.M. Statsadd Jr. : J of Cryst Growth 54 (1981) 248.

7. Dang Tran Quan : Phy. Stat Sol (a) 86 (1984) 421.

8. W. Albers and J.Verberkt : J. of Mat. Science 5 (1970) 24.

9. V.P. Bhatt, K.Gireesan, G.R. Pandya : J. of Cryst growth 96 (189) 649.

10. G.Valiukonis, F.M. Gashimzade, D.A. Gusinoa, G.Karivaite, M.M. Mamedav and A.Sileika : Phys. Stat. Sol (b) 122 (1984) 623.

11. Ben G. Streetman : Solid State Electronic devices, Prentic - Hall of Indian Pvt. New Delhi. (1982).

12. J. Barden, H. Hall and F.J. Balatt : preceeding of the conference on photoconductivity, New York (1956) 146.

13. R. Tovar Barradas, C.Rincon, J. Genzalez and G. Sancher Pertez : J. Phys. Chem. Solids 45 (1984) 1185.

14. Eva C. Freeman and Willam Paul : Physical Review B 20 (1979) 716.

15. J.Mendolia and D.Lemone : Phys State Sol. (a) 97 (1986) 601.

16. V.P. Bhatt, K. Gireesan and C.F. Desai : Cryst. Res. Technol 25 (1990) 209.

17. Dang Tran Quan : Thin Solid films 149 (1987) 197.

18. A.K. Stasenko : Sov. Phys. Solid State 10 (1968) 186.

19. V. Damodara Das and D.Karunkaran : J. App. Phys 54 (1983) 5252.

20. V.B. Sandomirskii : Sov. Phys. JEPT 10 (1963) 1630.

21. J.C. Staller : Physics Rev. 103 (1956) 1631.

22. K.L. Chopra : Thin film phenomena McGraw-Hill, New York (1969).

23. J.I. Pankove : Optical process in semiconductors preventic-Hall. Inc. N.J. (1971) 103.

24. V.P. Bhatt, K. Gireesan, C.F. Desai : Cryst. Res. Technol 24 (1989) 187.

25 S.M. Sze : Physics of Semiconductor devices : Wiley eastern limited New Delhi. (1979).