CHAPTER – 6

OPTICAL BAND GAP

CHAPTER - VI

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I. INTRODUCTION :

The theoretical and experimental investigations of the optical behavior of solids deal primarily with optical reflection, transmission and absorption properties, and their relation to the optical constants both of the bulk and thin film forms. 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 selective transmission/absorption are used. Optical properties of a thin film generally differ from those of the bulk. The differences 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, polarimetric 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 Bi_2Te_3 in bulk and thin film forms[5-7]. Black et al [5] have studied the optical absorption of Bi_2Te_3 crystals grown by Bridgman method. Morsy et al[7] have reported optical properties of thermally deposited Bi_2Te_3 thin films in the wavelength range of 2.5 to 10 μm and have used transmittance and reflectance spectra to obtain band gap which was found to be about 0.21 eV.

II. GENERAL DISCUSSION :

It is apparent that a photon with energy $h\nu \geq E_{.g.}$ 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 photo 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 the 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 crystal, 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 are given in Figure - 2.

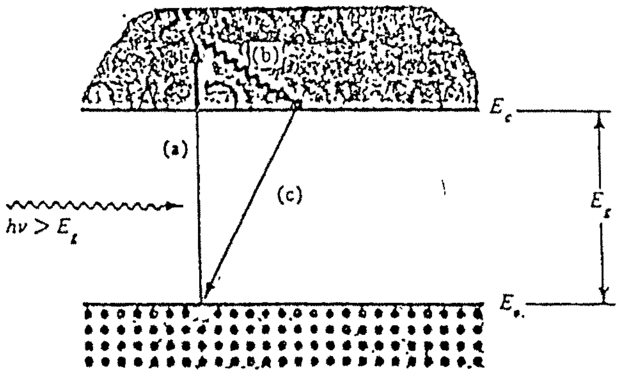

Figure – 1. Optical absorption of a photon with $h\nu > E_g$: (a) an EHP is created during photon absorption; (b) the excited electron gives up energy to the lattice by scattering events; (c) the electron recombines with a hole in the valence band.

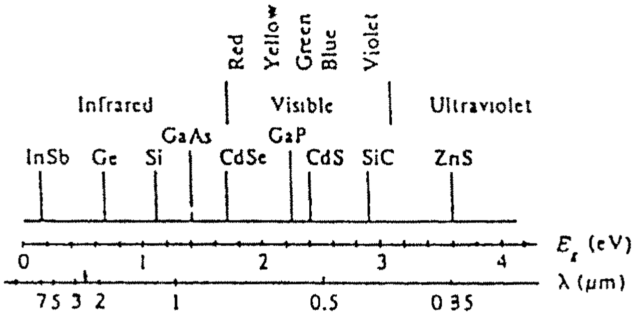

Figure - 2. Band gaps of some common semiconductors relative to the optical spectrum.

If a beam of photons with hν > 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 of thickness ,t, is given by

$$I = I_o e^{-\propto t} \qquad \cdots\cdots 1$$

where ∝ is the absorption coefficient, I_o is the incident photon beam intensity and I is the transmitted intensity.

Near the absorption edge, the absorption coefficient is expressed as[9]

$$\propto \sim (h\nu - Eg)^{\gamma} \qquad \ldots\ldots 2$$

where hν 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 transaction [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

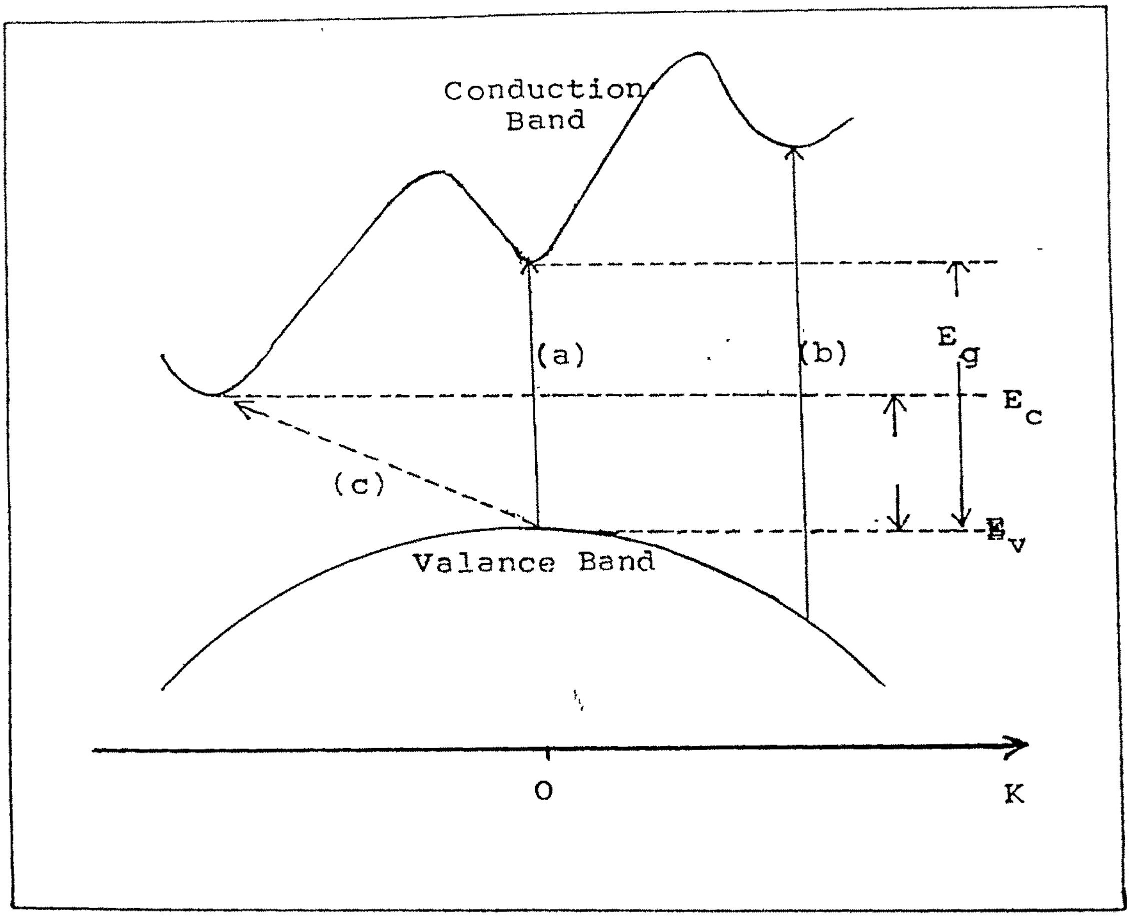

Figure - 3 : Optical transitions.
(a) and (b) Direct transitions.
(c) Indirect transition involving phonons.

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(hν)along its propagation :

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

where L(hv) is incident light intensity. $\propto$ is the absorption coefficient [8,9].

The basic theory of direct and indirect transitions in semiconductors was formulated by Bardeen et al[10]. The direct transitions are generally supposed to be taking place from valence band to conduction band under the selection rule :

$$K - K^1 + \frac{2\pi i}{\lambda} = 0 \qquad \ldots\ldots 4$$

where K and K^1 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 $K^1 = K$, since $2\pi / \lambda$ is small compared to either K or K^1. 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 probable 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

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

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 the indirect transition,

$$(\propto h\nu) = A\ (h\nu - E_g \pm Ep)^{x} \qquad \ldots\ldots 6$$

where x = 2 for indirect allowed transitions and x = 3 for forbidden transitions, E_g is the band gap and E_g is the absorbed or emitted phonon energy [11,12,13]. At room temperature, transitions, both with phonon emission and phonon absorption, will contribute to the absorption.

III. EXPERIMENTAL RESULTS :

The I.R.Spectrophotometer (BOMEM, Canada, MB104) was used for measurement of optical absorption of the samples. In the case of crystals, fine crystalline powder was throughly mixed with spectroscopic grade dry KBr powder at about less than 5% concentration and the mixture was formed into a palette of about 1cm diameter, using vaccum palettizer. The absorption data was used to study the band gap.

3.1 $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Tc_3$ and $Bi_2Te_{2.8}Se_{0.2}$ crystals :

The optical absorption was measured in the wave number range 500 cm^{-1} to 4000 cm^{-1} and the absorption spectrum was recorded. By analysing the spectrum, absorption coefficient was calculated as a function of photon energy. Since in the paletted samples ,the material thickness is undetermined ,an arbitrary thickness was assumed. This would of course not give absolute absorption coefficient. However, the relative variations only are significant for the purpose of evaluating band gap .The plots of $(\alpha h\nu)^2$ vs $h\nu$ were used to evaluate the optical band gaps. These plots for $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ are given in Figure 4,5,6 respectively. The plots are observed to be linear in the region of strong absorption near the fundamental absorption edge. Hence by extrapolating the linear portion to $h\nu = 0$ the band gap was evaluated. The values of the band gaps obtained are given Table-1.

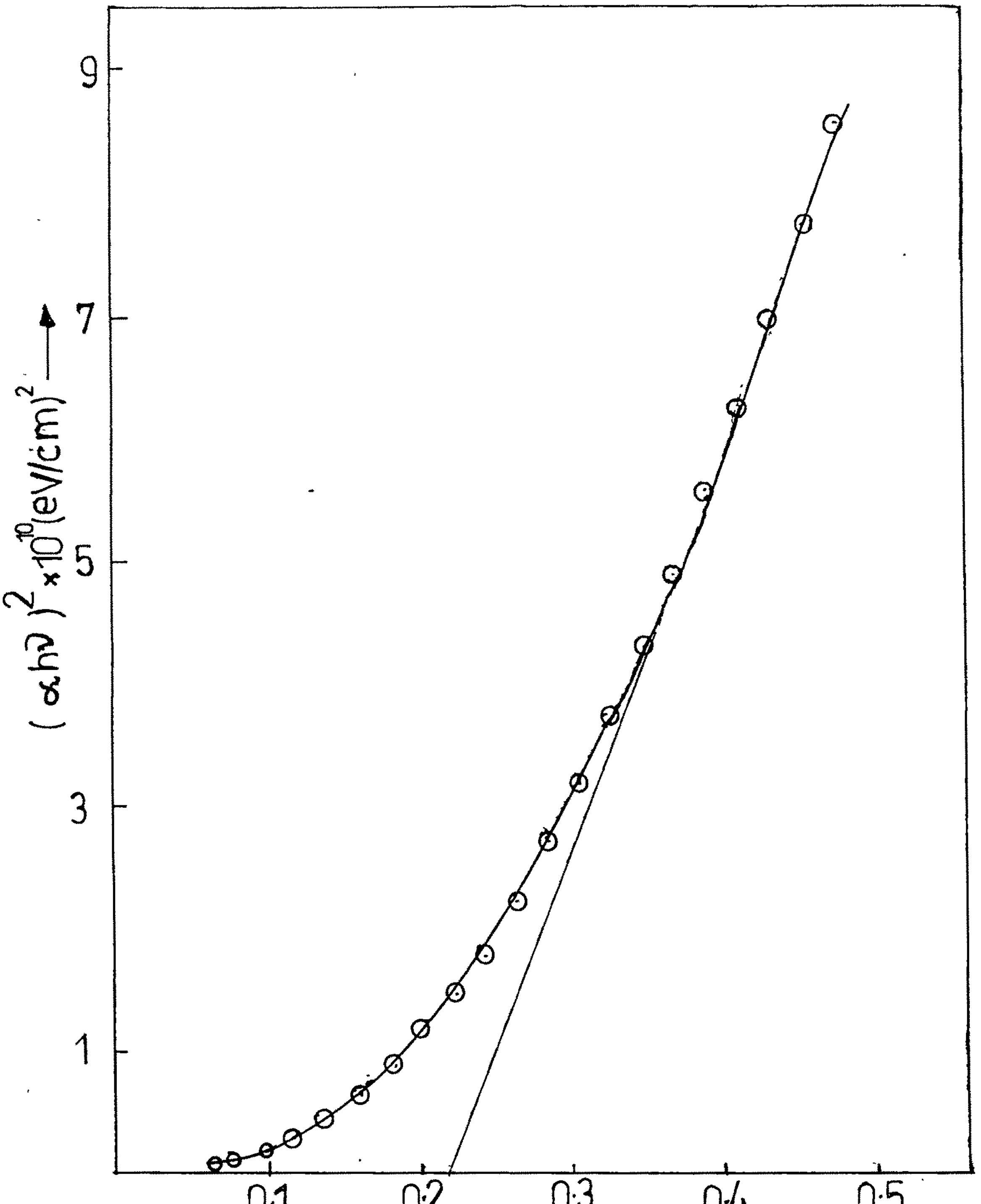

Fig. 4

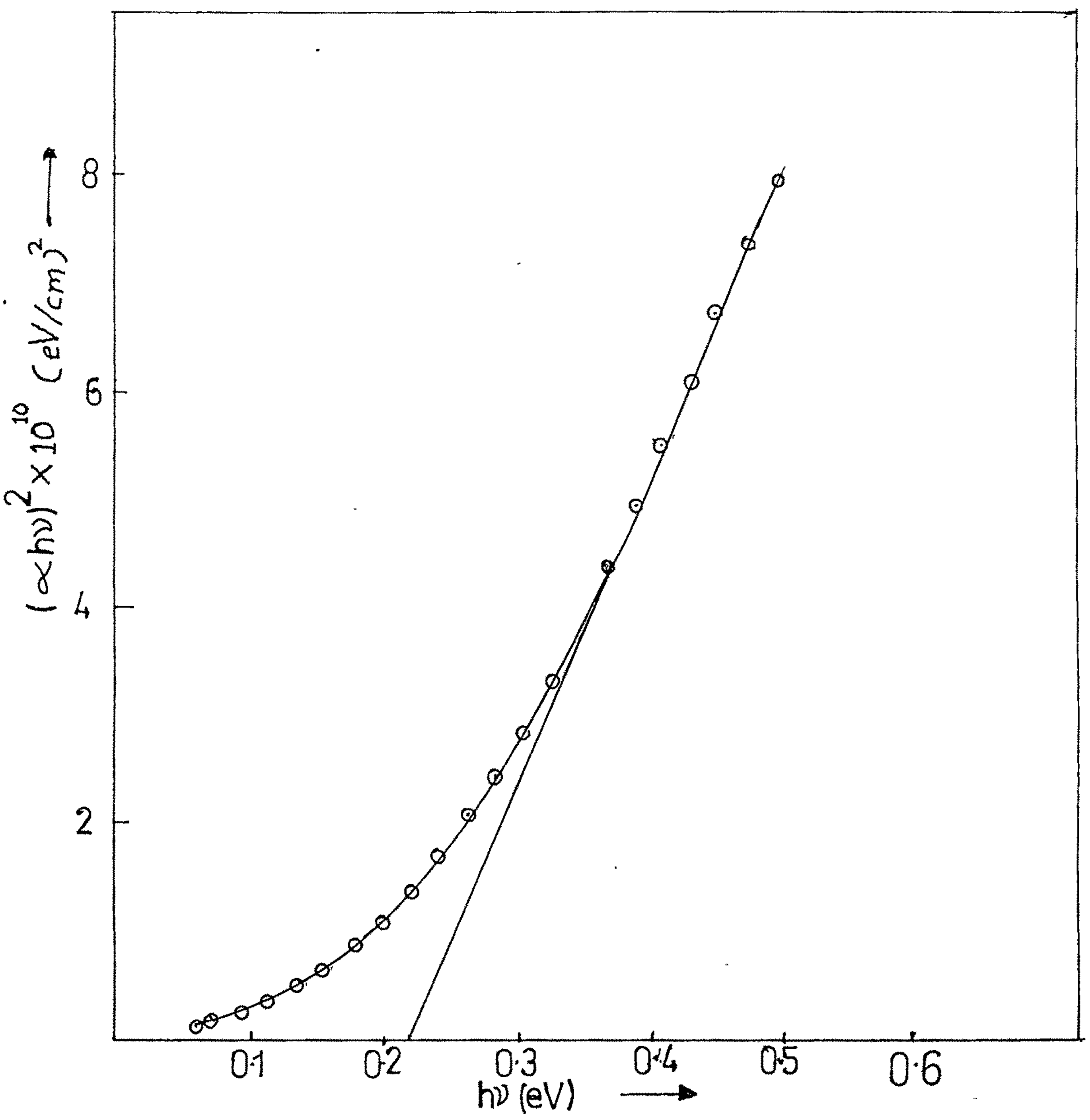

Fig. 5

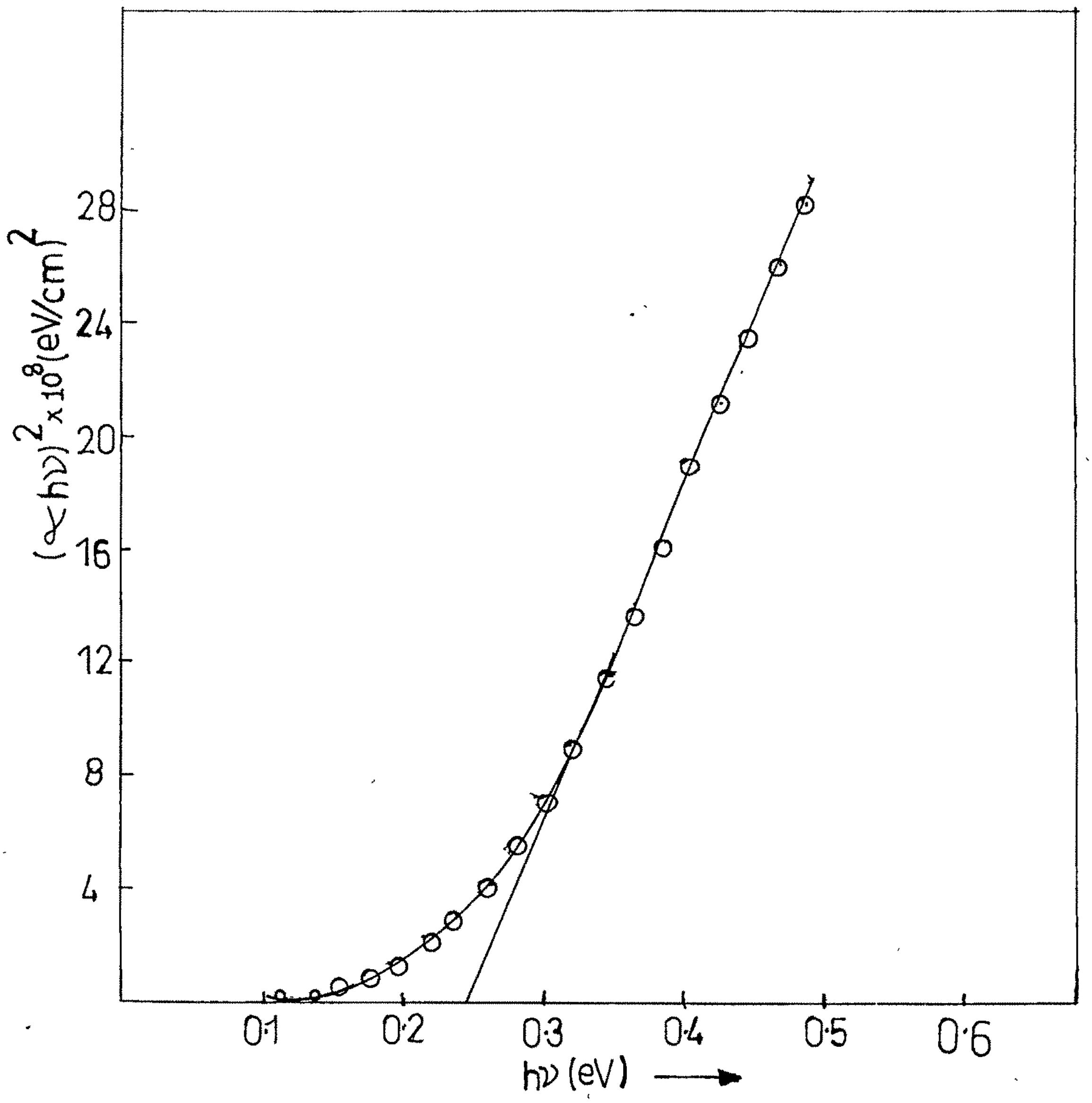
$(\alpha h\nu)^2 \times 10^8 (eV/cm)^2$
28
24
20
16
12
8
4
0·1
0·2
0·3
0·4
0·5
0·6
hν (eV)

Fig. 6

Table.1

Measured Bandgaps

Crystal	**Direct gap (eV)**
$Sb_{0.2}Bi_{1.8}Te_3$	0.22
$Sn_{0.2}Bi_{1.8}Te_3$	0.22
$Bi_2Te_{2.8}Se_{0.2}$	0.24

3.2 $Sb_{0.2}\,Bi_{1.8}\,Te_3$ $Sn_{0.2}\,Bi_{1.8}\,Te_3$ and $Bi_2\,Te_{2.8}\,Se_{0.2}$ films :

The plot of $(\propto h\nu)^2$ versus $h\nu$ obtained for $Sb_{0.2}\,Bi_{1.8}\,Te_3$ $Sn_{0.2}\,Bi_{1.8}\,Te_3$ and $Bi_2\,Te_{2.8},\,Se_{0.2}$ films of thicknesses around 550 Å are given in Figure 7,8 and 9, respectively. Similar plots for the films of other thicknesses were plotted and the band gaps obtained. The band gap is found to vary as the inverse square of the film thickness as shown in Figures 10, 11 and 12 for $Sb_{0.2}\,Bi_{1.8}\,Te_3$ $Sn_{0.2}\,Bi_{1.8}\,Te_3$ and $Bi_2\,Te_{2.8}$ $Se_{0.2}$, respectively.

It is seen that with increasing film thickness the band gap decreases. Such thickness dependence of band gap can be explained in terms of quantum size effect and dislocation density [14,15].

The band gap variation with film thickness follows the relation[15]

$$E_z = \frac{\hbar^2 \pi^2}{2m^*} \frac{1}{t^2} \qquad \ldots\ldots 7$$

Here m^* is the effective mass of the charge carrier, t is the thickness of the film and E_z is the kinetic energy contribution due to motion normal to the film plane. Accordingly, the plot of E_g Vs $1/t^2$ is found to be linear. Such variation can be explained in terms of quantum size effect. This is usually defined as the dependence of certain physical properties of a solid on its characteristic

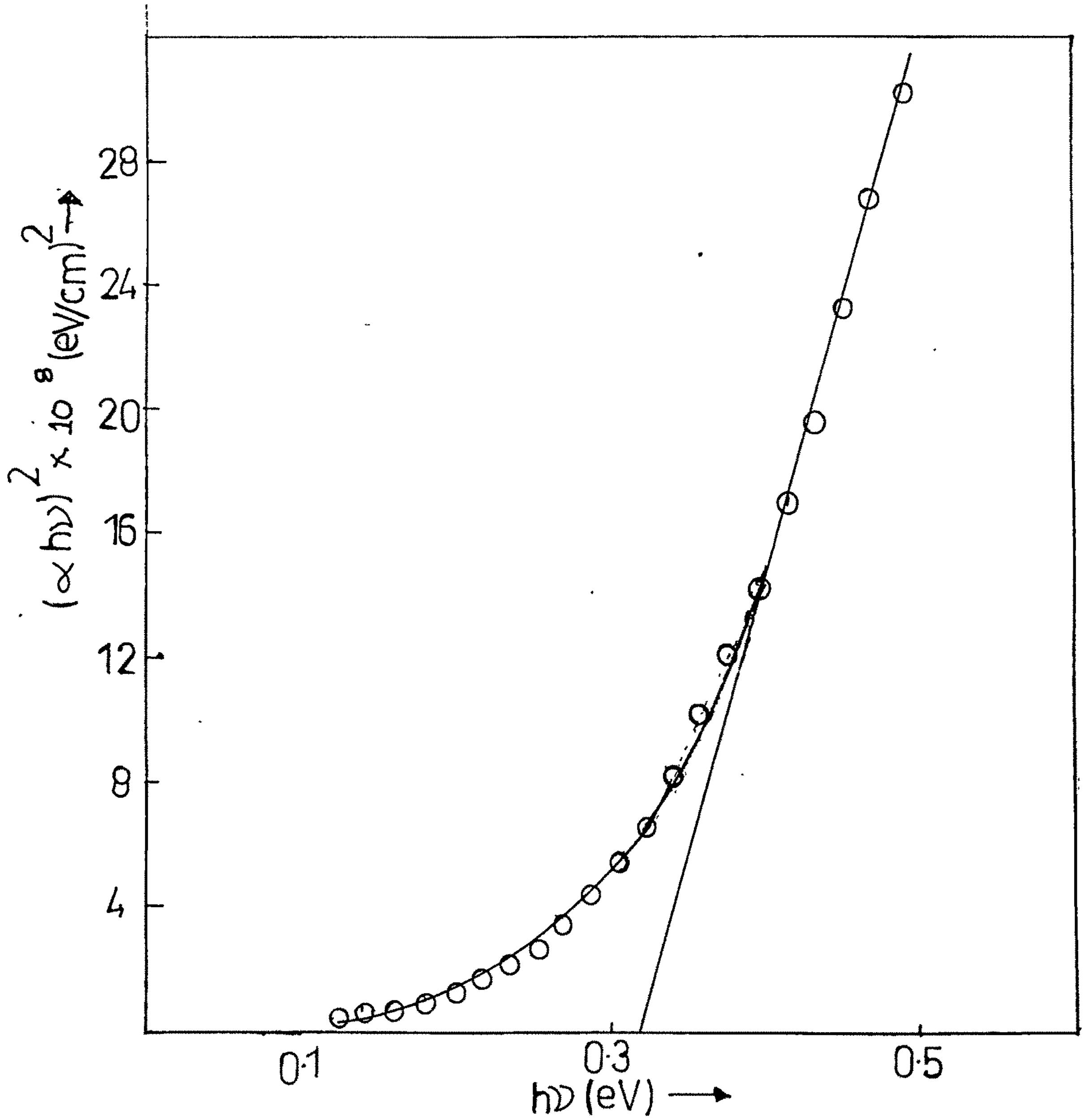
28
24
20
16
12
8
4
$(\alpha h\nu)^2 \times 10^8\ (\mathrm{eV/cm})^2 \rightarrow$
0·1
0·3
0·5
hν (eV) →

Fig. 7

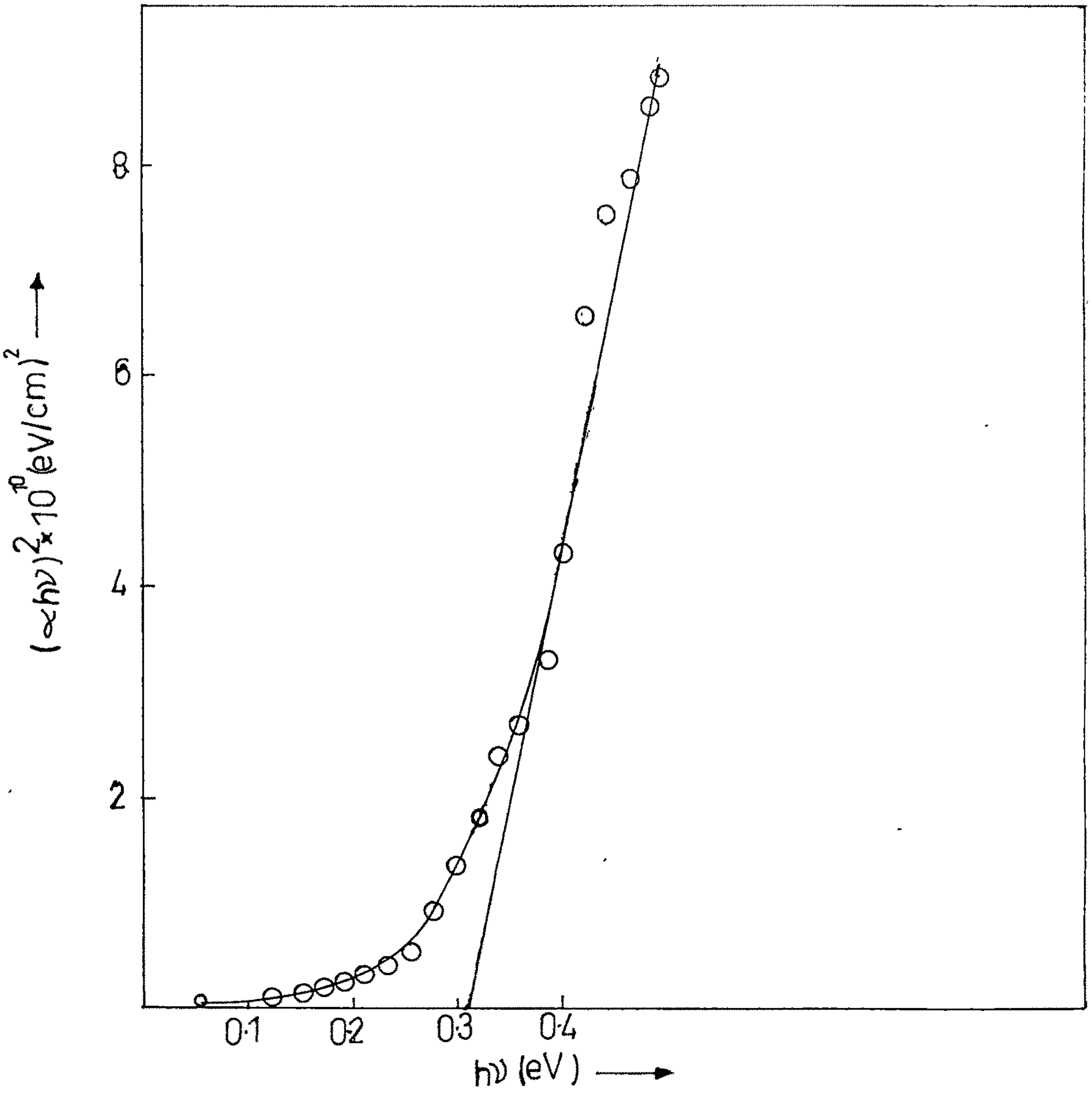

Fig. 8

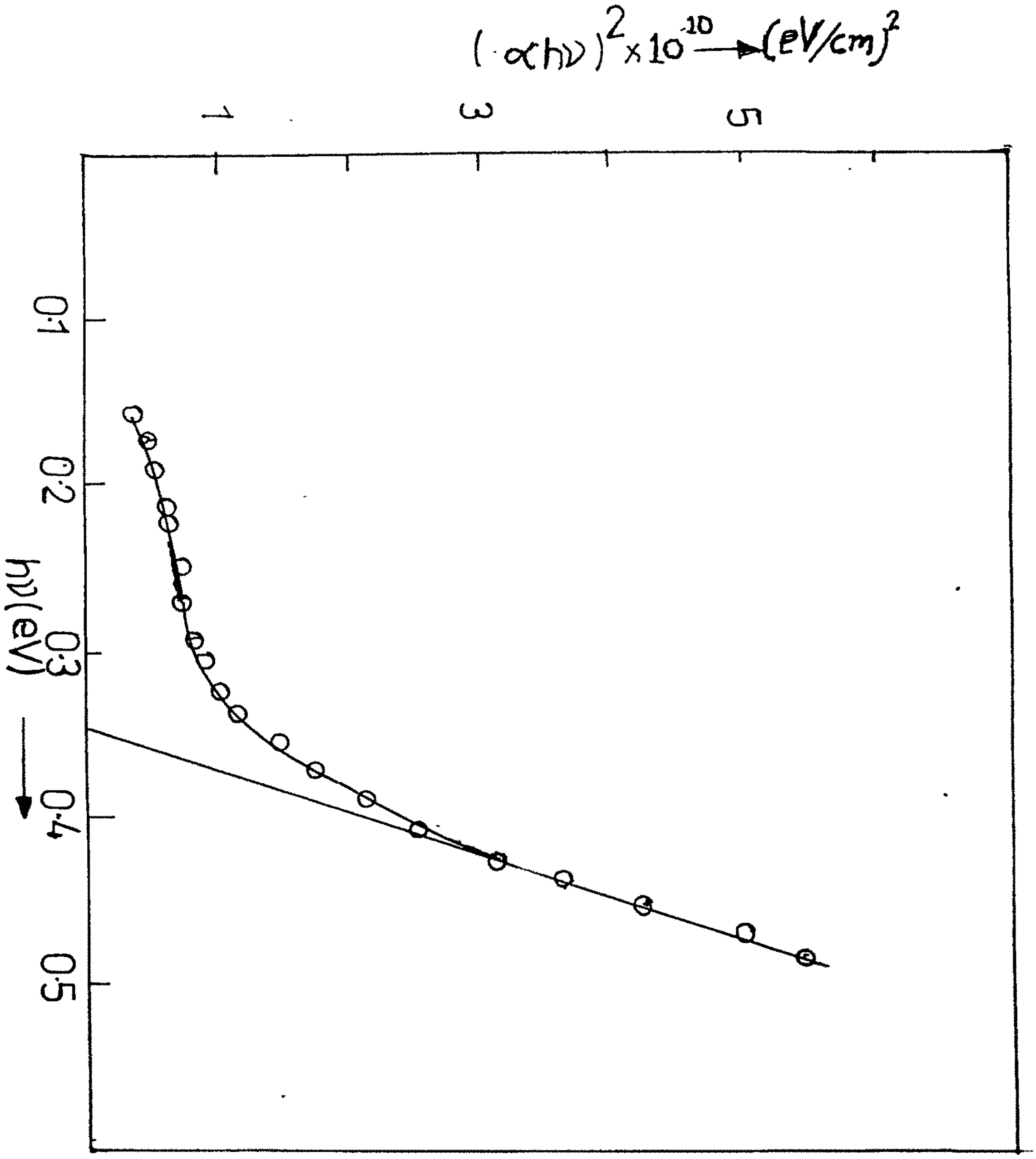

Fig.9

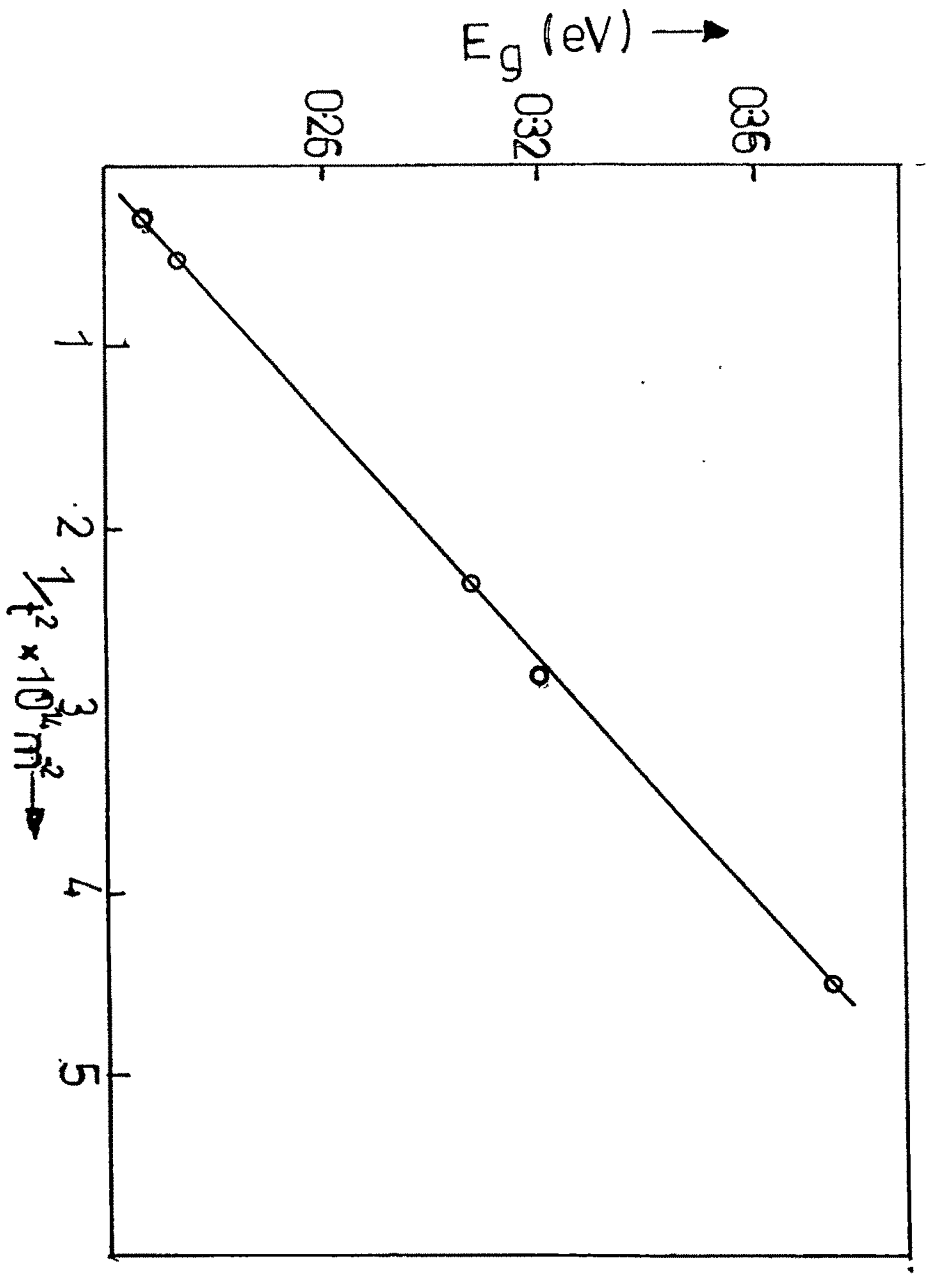

Fig. 10

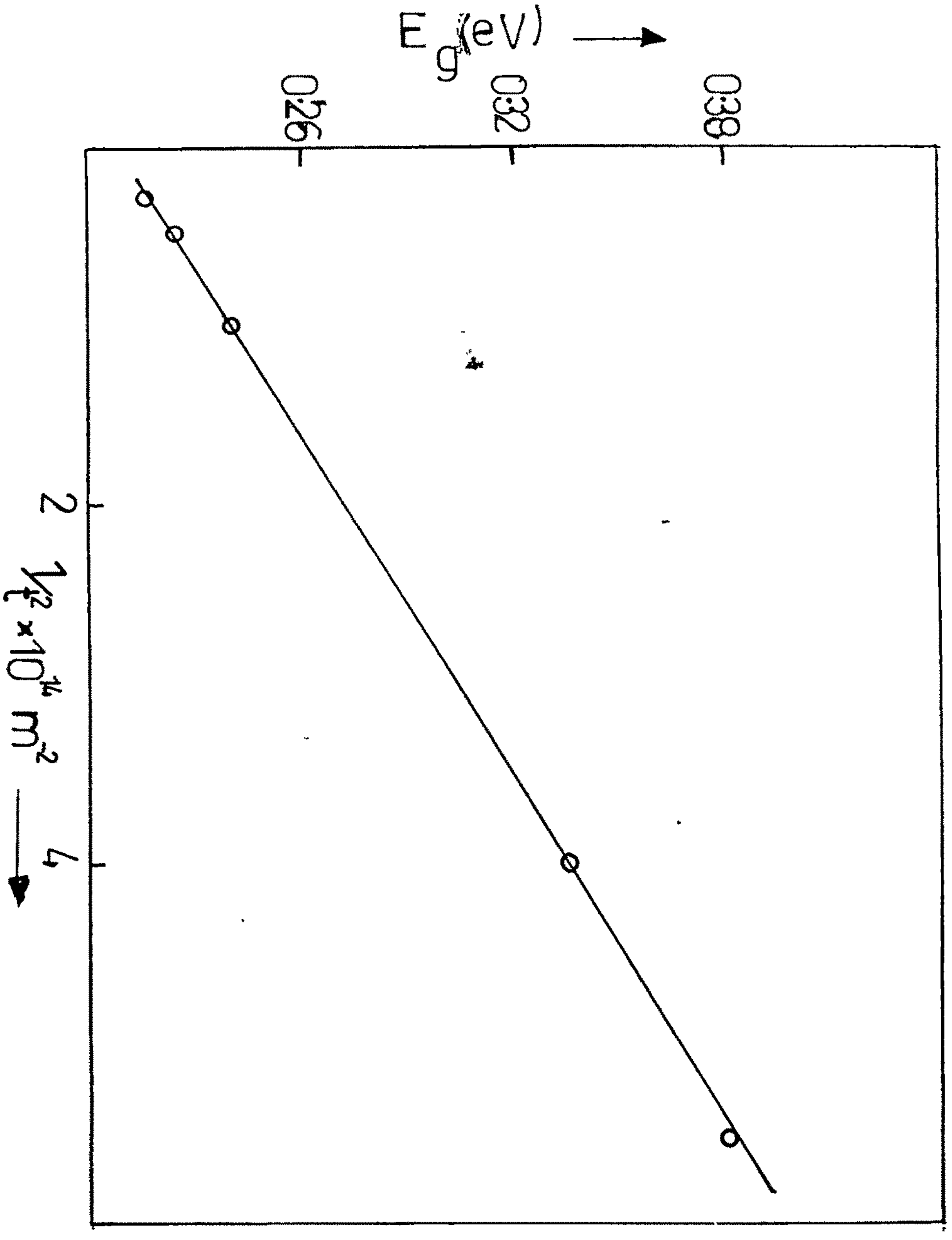

Fig. 11

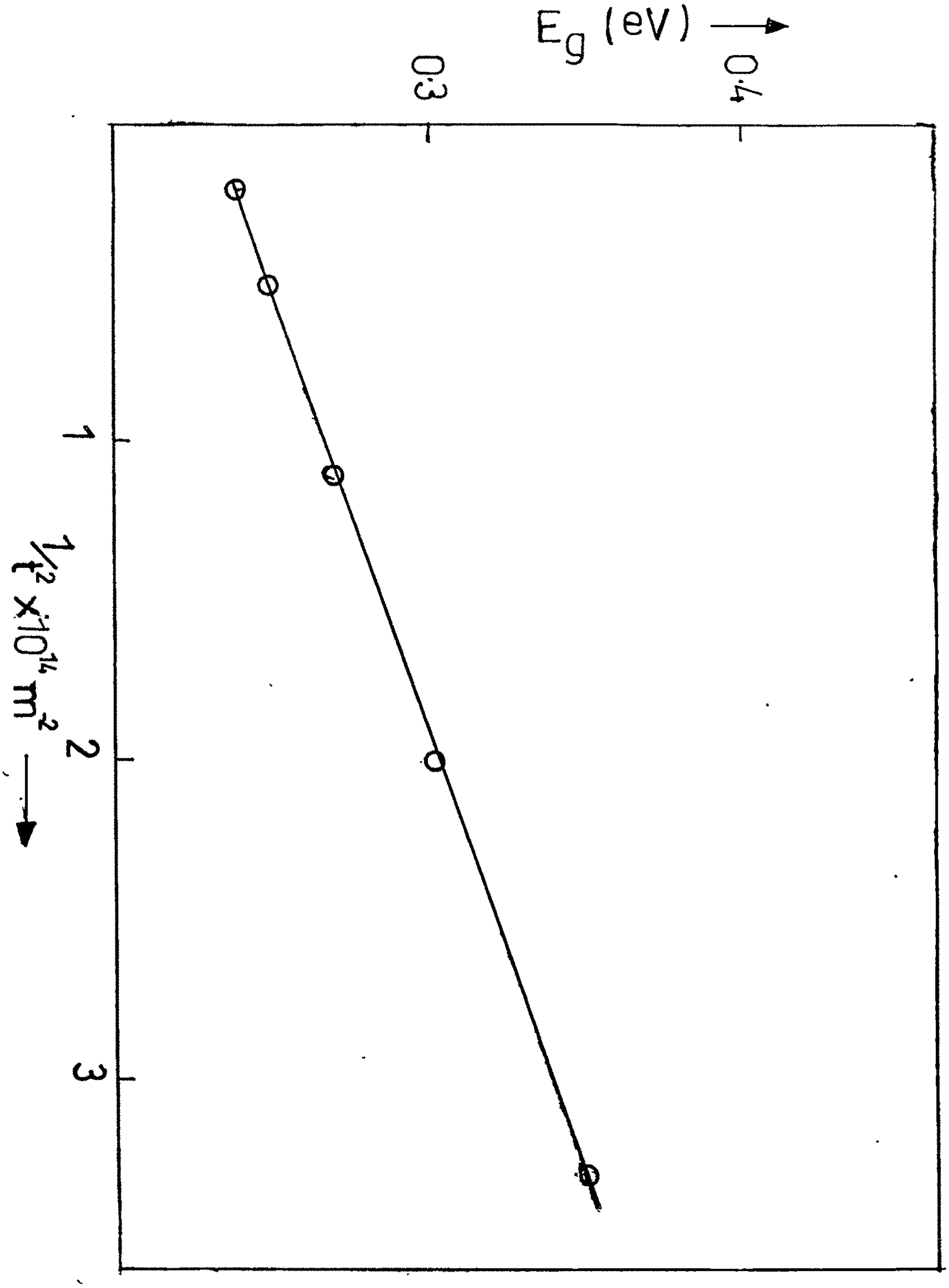

Fig. 12

geometric dimensions, when these dimensions become comparable with the de Broglie wave length of the charge carriers[18,19]. Because of the finite thickness of the film, the transverse component of quasi-momentum is quantized. Therefore the electron-hole states assume quasi-discrete energy values in a thin film.As a consequence, the separation of valence and conduction bands increases by an amount ΔE given by the above relation. The effective mass of holes calculated from the slope of the E_g Vs $1/t^2$ plot (assuming electrons to be heavy) is found to be 8.01×10^{-4} m_0, 0.104×10^{-4} m_0 and 0.1193×10^{-4} m_0 in $Sb_{0.2}Bi_{1.8}Te_3$, $Bi_2Te_{2.8}Se_{0.2}$ and $Sn_{0.2}$ $Bi_{1.8}$ Te_3, respectively, where m_0 is the electron rest mass. The estimates of de Broglie wavelength of the holes estimated by taking the Fermi energy to be half of the average bandgap, turns out to be about 1306Å, 1090Å and 1070 Å.. Thus quantum size effect is expected to be exhibited by the films.

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 dangling 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. Whereas, in a thin film specimen, the quasi-momentum assumes discrete values along the thickness dimension. The energy spectrum represents a system of discreate levels with the separation between them given by the uncertainty principle. The effect of the discrete energy levels on the forbidden gap of a semiconductor has been considered by Sandomiskii[16]. According to him, all levels of the energy spectrum of a semiconductor will be shifted by an amount 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[17]. According to him, the increased barrier height is given by

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

where Eo is the original barrier height, C is a term depending on the density ofcharge 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[18] 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

$$(X - ft)^2 \qquad \text{.......9}$$

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.

IV. CONCLUSIONS :

1. The band gap of $Sb_{0.2}$ $Bi_{1.8}$ Te_3, $Sn_{0.2}$ $Bi_{1.8}$, Te_3 and Bi_2 $Te_{2.8}$ $Se_{0.2}$ crystals are about 0.22eV, 0.22eV, 0.24eV (all direct), respectively. There are no observable indirect transitions in the crystals.

2. The band gaps of $Sb_{0.2}$ $Bi_{1.8}$ Te_3, $Sn_{0.2}$ $Bi_{1.8}$, Te_3 and Bi_2 $Te_{2.8}$ $Se_{0.2}$ thin films are on an average 0.21eV, 0.22eV and 0.24eV (direct), respectively, for film thicknesses around 2000 Å or more. At smaller thicknesses the band gaps are larger than the bulk values.

3. The film thickness dependence of the band gap of $Sb_{0.2}$ $Bi_{1.8}$ Te_3, $Sn_{0.2}$ $Bi_{1.8}$, Te_3 and Bi_2 $Te_{2.8}$ $Se_{0.2}$ indicate the optical transitions to be governed by quantum size effect within the thickness range studied.

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