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Electrical transport properties of thallium-doped p-type $Pb_{0.8}Sn_{0.2}Te$ thin films

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Hall coefficient and d.c. conductivity studies were made on p-type $Pb_{0.8}Sn_{0.2}Te$ thin films doped with different concentrations of thallium in the temperature range 77 to 500 K. The Hall coefficient and Hall mobility are found to decrease with an increase in the doping concentration of thallium. Hall coefficient data have been analysed in the light of a double valence-band model. Various band parameters such as valence band separation, population ratio, mobility ratio and effective mass ratio have been calculated. Hall mobility data have been analysed in the light of lattice- and defect-limited scattering mechanisms.

1. Introduction

Lead chalcogenide systems are of considerable interest due to their wide use in infrared detectors [1–4] and lasers [5–7]. Ternary systems with a band gap sensitive to composition and temperature are desirable to achieve maximum response at a given wavelength. In addition to the band gap variation, the contribution of ionized impurity scattering in lead chalcogenide systems is negligible [8] due to their high dielectric constant [9]. As a result, their carrier mobility is high even for carrier concentrations as high as $10^{18}\,cm^{-3}$, resulting in a high photoconductive response. $Pb_{1-x}Sn_xTe$ with a composition in the range $x = 0.18$ to 0.25 has received considerable attention due to its use in the fabrication of infrared detectors operating at and above 77 K, that are sensitive in the 8 to 14 μm atmospheric window region of the infrared spectrum [10]. It is well known that besides impurities, deviations from stoichiometry introduce acceptors and donors in these alloys. It is found that excess metal yields donor levels whereas excess non-metal yields acceptor levels [11].

The ionization energy of a hydrogen-like donor or acceptor, which usually represents the model for shallow lattice defects, is expected to be very small in lead salts. Parada and Pratt [12–14], however, pointed out that a vacancy potential differs significantly from a hydrogen-like impurity. They assume that a vacancy or an interstitial represents a much stronger perturbation of the periodicity of the lattice than is the case for a chemical impurity. According to this model, the vacancy states are resonant with the band states. It has been found that at high impurity doping the carrier concentration in $Pb_{1-x}Sn_xTe$ saturates to a constant value independent of the impurity concentration due to the stabilization of the Fermi level [15]. In such a case most of the impurity atoms are incorporated into the crystal lattice as electrically neutral impurities which, however, may act as scattering centres thereby reducing the mobility of the charge carriers. The effects of various impurities such as thallium, indium, gallium and aluminium on PbTe have been studied extensively [16–19]. Very little work has been done on the effect of impurities on the electrical properties of $Pb_{1-x}Sn_xTe$ films [15, 20].

In the present work, the effect of thallium on the electrical properties of $Pb_{0.8}Sn_{0.2}Te$ thin films has been studied. Various band parameters such as energy band separation between light and heavy hole valence bands, ratio of effective mass of light to heavy holes, mobility ratio and population ratio have been calculated from the Hall coefficient data. Hall mobility data have been analysed in the light of lattice- and defect-scattering mechanisms. Defect mobility as a function of doping concentration has been estimated.

2. Experimental details

Rectangular films of $Pb_{0.8}Sn_{0.2}Te$ (5 × 20 mm) doped with thallium were grown using the flash evaporation technique under a vacuum of $\sim 5 \times 10^{-6}$ torr on to mica substrates kept at 400° C. The films grown from a stoichiometric charge are found to be p-type. In order to dope the films with different concentrations of thallium, a polycrystalline $Pb_{0.8}Sn_{0.2}Te$ charge doped with different amounts of thallium was grown using a vertical furnace [21]. This charge containing thallium was then used to grow doped films by flash evaporation. The rates of evaporation and thickness of the films was monitored using a quartz crystal monitor. The growth rate was maintained at $1.0 \pm 0.1\,nm\,sec^{-1}$ in all cases. Ohmic contacts were grown on to the films by evaporating gold using a tantalum mask. The current contacts were spread over the entire width of the sample whereas the Hall contacts were about 0.8 mm in diameter. The ohmic nature of the contacts was verified throughout the temperature

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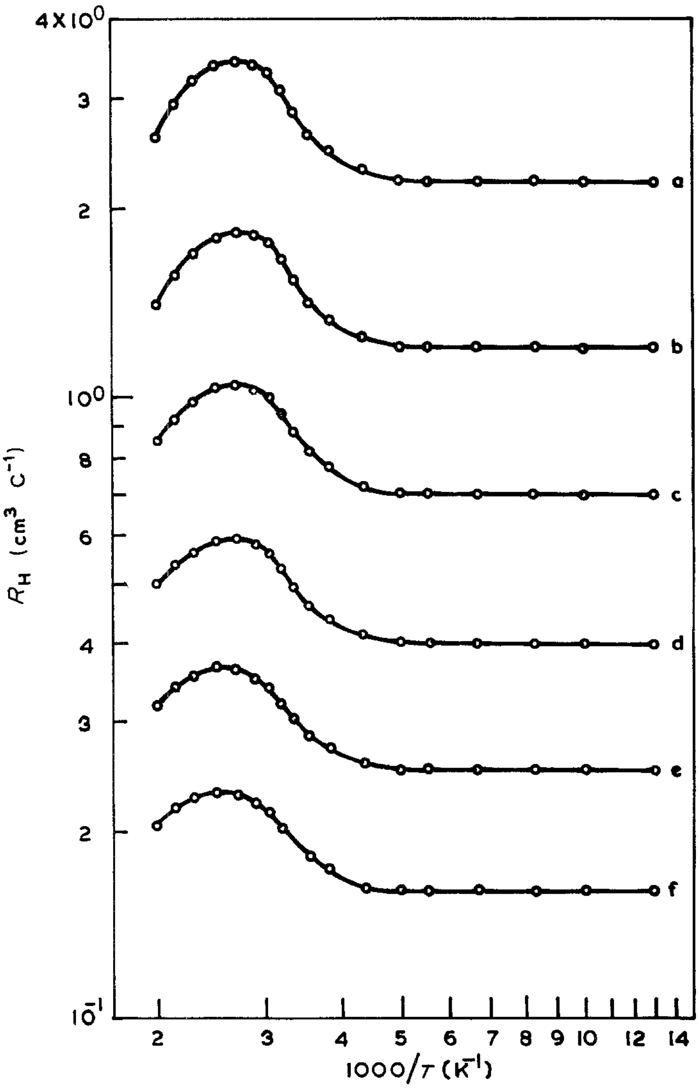

Figure 1 Variation of Hall coefficient with temperature, log R_H against log (1000/T), for thallium-doped $Pb_{0.8}Sn_{0.2}Te$ films. (a) As-grown; (b) 0.3, (c) 0.7, (d) 1.0, (e) 1.5, (f) 2.0 at %.

range by linearity of the I–V characteristics. The five-probe technique [22] was used to measure the Hall coefficient and d.c. conductivity. A vacuum cryostat was used to carry out the measurements from 77 to 500 K. The heater arrangement available in the cryostat was used to make measurements above room temperature. A copper–constantan thermocouple soldered to the copper block on which the sample was mounted was used to measure the temperature. The Hall coefficient data were found to be independent of magnetic field (up to 5 kG) and the sample current. The current through the films and the magnetic field directions were reversed in order to eliminate errors due to thermomagnetic and thermoelectric effects. The influence of geometry on the Hall measurements was avoided as the length to breadth ratio was four in the films. The overall error in the Hall mobility was estimated to be about 5%. The sign of the Hall voltage showed that as-grown as well as thallium-doped samples were p-type.

3. Results and discussion

Films of different doping concentrations (0.3, 0.7, 1.0, 1.5 and 2.0 at %) of thallium were grown. X-ray diffraction studies revealed that the as-grown films are crystalline with (2 0 0) preferred orientation of the cubic phase. Films doped with thallium showed broader diffraction peaks, and the intensities of the peaks were less when compared to the diffraction spectra of as-grown films. This reduction in peak height may be due to the defects in the doped films. Electron diffraction studies revealed that the films were oriented in the (2 0 0) direction of the cubic phase. As-grown films showed sharp diffraction spots whereas doped films showed blurred diffraction spots in selected-area diffraction patterns recorded using a Philips transmission electron microscope. This may be due to the point defects created by the impurity atoms in the films. Large number of films of various thicknesses (0.5 to 0.9 μm) were grown and measurements of Hall coefficient and d.c. conductivity were made on these films. No significant effect of thickness on these properties was observed in the thickness range studied. Typical results on films of 0.8 μm thick are given here.

3.1. Hall coefficient

The observed variation of Hall coefficient as a function of temperature (log R_H against log (1000/T)) for films doped with thallium is shown in Fig. 1. It can be observed from this figure at any given temperature, the value of R_H decreases with an increase in the doping concentration of thallium. There is no saturation effect in the value of R_H at higher doping concentrations (2 at %). Films doped with higher amounts of thallium (2.5 at %) showed a separate phase of thallium and no electrical studies were made on these films. It is found that in all the films, there is a similarity in the behaviour of R_H with temperature. In the low-temperature region (77 to 180 K) the value of R_H is practically independent of temperature, which is a typical characteristic of a nearly extrinsic degenerate IV–VI compound semiconductor. This temperature-independent behaviour of R_H in these films suggests that mainly one type of carrier (light holes) is contributing to the conduction process in this temperature range (77 to 180 K). At temperatures above 180 K, R_H starts increasing with the increase in temperature till it reaches a maximum value of $R_{H\max}$ at $T_{\max}$, and with further increase of temperature the value of R_H decrease in the as-grown as well as thallium-doped films. This behaviour of R_H can be explained on the basis of a double valence-band structure, which was first suggested by Aukerman and Willardson [23] for non-degenerate semiconductors and later extended to degenerate semiconductors by Allgaier [24]. The increase in the value of R_H above 180 K can be attributed to the redistribution of carriers between the main valence band V_1 and the extrema of the secondary valence band V_2 where the transport properties are different. The carriers in the second valence band have high effective mass and low mobility. If the carriers are transferred to the band having high effective mass and low mobility, qualitatively the result of such carrier transfer is to deplete the conducting holes thereby increasing the Hall coefficient value.

The Hall coefficient will reach a maximum value $R_{H\max}$ at a temperature $T_{\max}$, where the edges of light- and heavy-hole bands are approximately at the same level and the contribution of the two types of carrier to the conductivity are equal, i.e. $p_1 e \mu_l = p_2 e \mu_h$ where p_1 and p_2 are the concentrations of holes in the light- and heavy-hole valence bands, respectively, and μ_l and μ_h are their respective mobilities. The fall in the value of R_H after attaining a peak value beyond the temperature $T_{\max}$ is on account of the contribution of carriers of opposite sign, i.e. the intrinsic electrons, to the conduction process. This contribution of intrinsic electrons to the conduction process can be explained by the fact that the mobility of electrons is higher than that of holes ($\mu_n > \mu_p$); the decrease in the average hole mobility due to the contribution of heavy holes resulting from the redistribution of holes in sub-bands is more when compared to the decrease in electron mobility with the increase of temperature. At higher temperatures (above $T_{\max}$) the ratio of electron to hole mobility (μ_n/μ_p) becomes so large that for even a small contribution of intrinsic carriers their relative contribution to the Hall coefficient becomes appreciable. It is further observed that the rate of fall of the Hall coefficient with temperature above $T_{\max}$, is faster in the films having lower carrier concentrations, which further supports the contribution of intrinsic carriers at higher temperatures.

From the temperature dependence of the Hall coefficient R_H, various band parameters were calculated for all the films. The values of $b = \mu_l/\mu_h$ were calculated from the observed peak value of R_H using the relation

$$\alpha_{\text{extremum}} = \frac{R_{H\max} - R_L}{R_L} = \frac{(1-b)^2}{4b} \quad (1)$$

where R_L is the value of R_H at 77 K. These values of b for various doping concentrations of thallium are given in Table I. It is observed that the mobility ratio b decreases with an increase of carrier concentration in the films doped with thallium. This decrease in the value of b with an increase of hole concentration can be attributed to the decrease in light-hole mobility. Such a decrease of μ_l/μ_h with an increase of hole concentration has also been reported by Gruzinov *et al.* [25] and Dawar *et al.* [26] for thallium-doped p-type PbTe. A decrease of μ_l with p can be explained on the basis that at higher carrier concentrations the contribution of ionized impurity scattering may be significant for light holes [25], thereby reducing light-hole mobility.

In order to estimate the values of ΔE_v, m_2^*/m_1^* and p_2/p_1 (Table I) the values of log α_T, where $\alpha_T = (R_T - R_L)/R_L$, as a function of temperature have been plotted in Fig. 2 for as-grown and thallium-doped films. The values of ΔE_v have been estimated from the slope of these curves in accordance with the relation [23]

$$\alpha_T = \frac{R_T - R_L}{R_L} = \left(\frac{b-1}{b}\right)^2 \left(\frac{m_2^*}{m_1^*}\right)^{3/2} \exp\left(-\frac{\Delta E_v}{kT}\right) \quad (2)$$

These values of ΔE_v correspond to 0 K and it has been assumed that m_2^*/m_1^* is temperature-independent. It is found that ΔE_v does not change with the carrier concentration. Similar results have also been reported for p-type PbTe. Using the Equation 2 the values of m_2^*/m_1^* have also been calculated and these values for a temperature of 300 K are listed in Table I. It is observed that the value of m_2^*/m_1^* decreases with an increase of carrier concentration in the film. This decrease is due

TABLE I Calculated parameters of thallium-doped $Pb_{0.8}Sn_{0.2}Te$ thin films

Dopant concentration (at %)	Hole concentration at 77 K (cm^{-3})	Mobility ratio, b ($= \mu_l/\mu_h$)	Energy separation between valence band edges, ΔE_v (eV)	Effective mass ratio, m_2^*/m_1^*, at 300 K	Population ratio, p^* ($= p_2/p_1$), at 300 K
As-grown	2.84×10^{18}	3.95	0.153	34.76	0.720
0.3	5.20×10^{18}	3.86	0.154	33.08	0.697
0.7	8.93×10^{18}	3.76	0.154	31.80	0.648
1.0	1.56×10^{19}	3.65	0.155	30.54	0.602
1.5	2.50×10^{19}	3.57	0.155	29.22	0.554
2.0	3.91×10^{19}	3.50	0.154	28.10	0.516

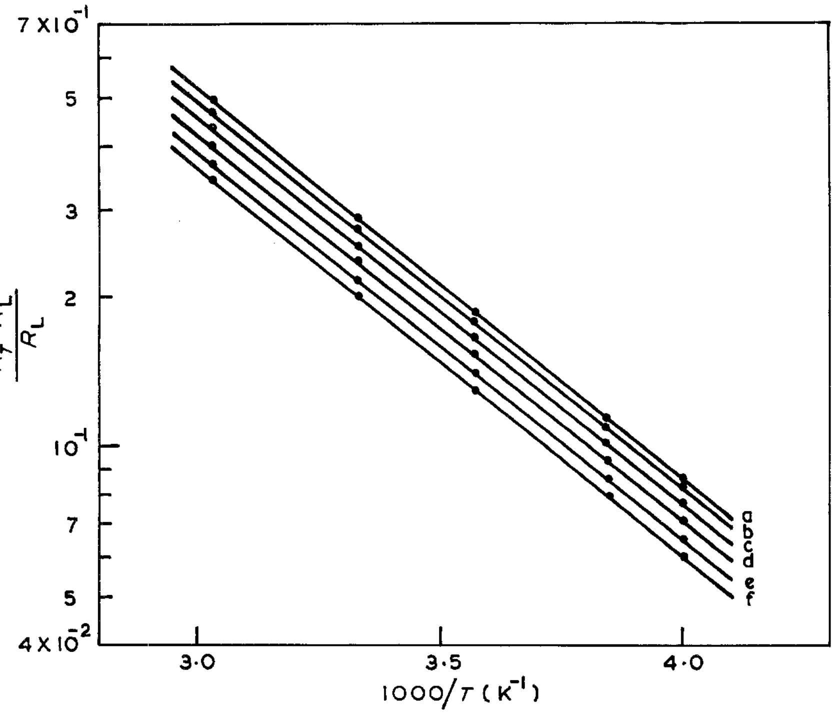

Figure 2 Variation of $(R_T - R_L)/R_L$ with temperature, $\log[(R_T - R_L)/R_L]$ against $(1000/T)$, for thallium-doped $Pb_{0.8}Sn_{0.2}Te$ films. (a) As-grown; (b) 0.3, (c) 0.7, (d) 1.0, (e) 1.5, (f) 2.0 at %.

to the increase of m_1^*, the effective mass of light holes, which is expected in heavily doped materials on the basis of Kane's band model.

The population ratio $p^* = p_2/p_1$ has been calculated using the relation

$$\alpha_T = R_T - R_L = \frac{(b-1)^2 p^*}{(b+p^*)^2} \quad (3)$$

The calculated values of p^* as a function of temperature for all the films are shown in Fig. 3. It is observed from this figure that for any given film the value of p^* increases with an increase of temperature. However, at any given temperature the value of p^* decreases with an increase of carrier concentration. This decrease in p^* can be attributed to an increase of p_1 with an increase of carrier concentration, which has also been observed by other workers [27].

3.2. Hall mobility

The variation of Hall mobility with temperature (log

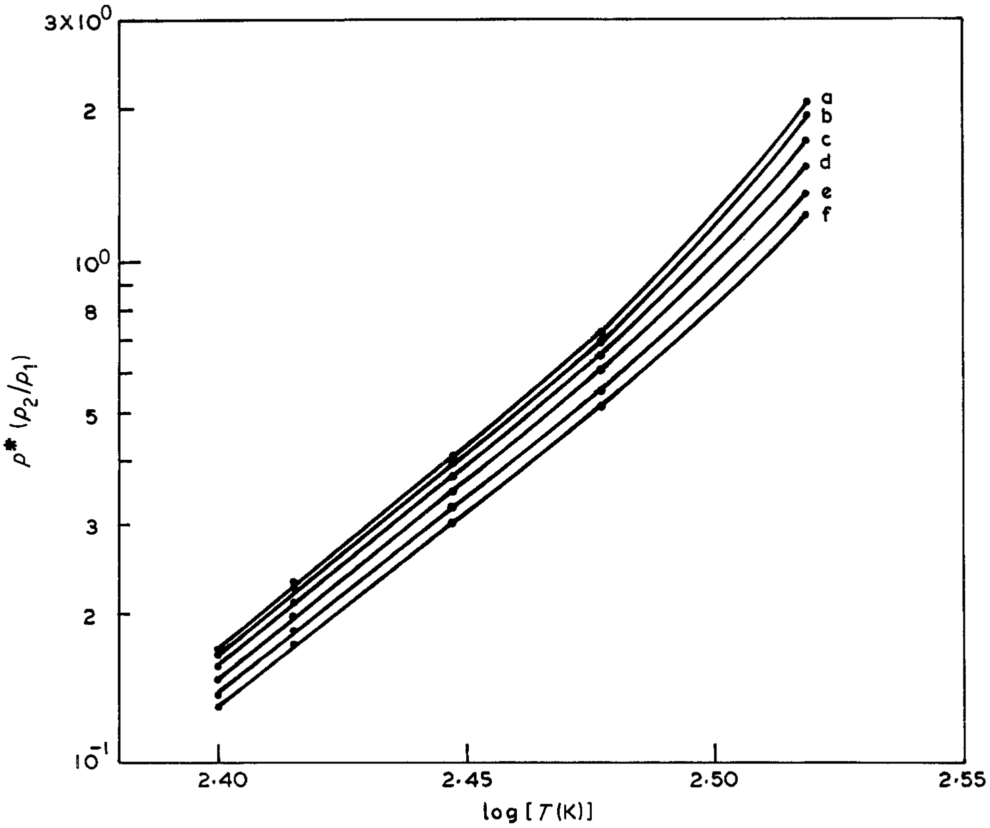

Figure 3 Variation of population ratio $p^* (= p_2/p_1)$ with temperature, $\log p^*$ against $\log T$, for thallium-doped $Pb_{0.8}Sn_{0.2}Te$ films. (a) As-grown; (b) 0.3, (c) 0.7, (d) 1.0, (e) 1.5, (f) 2.0 at %.

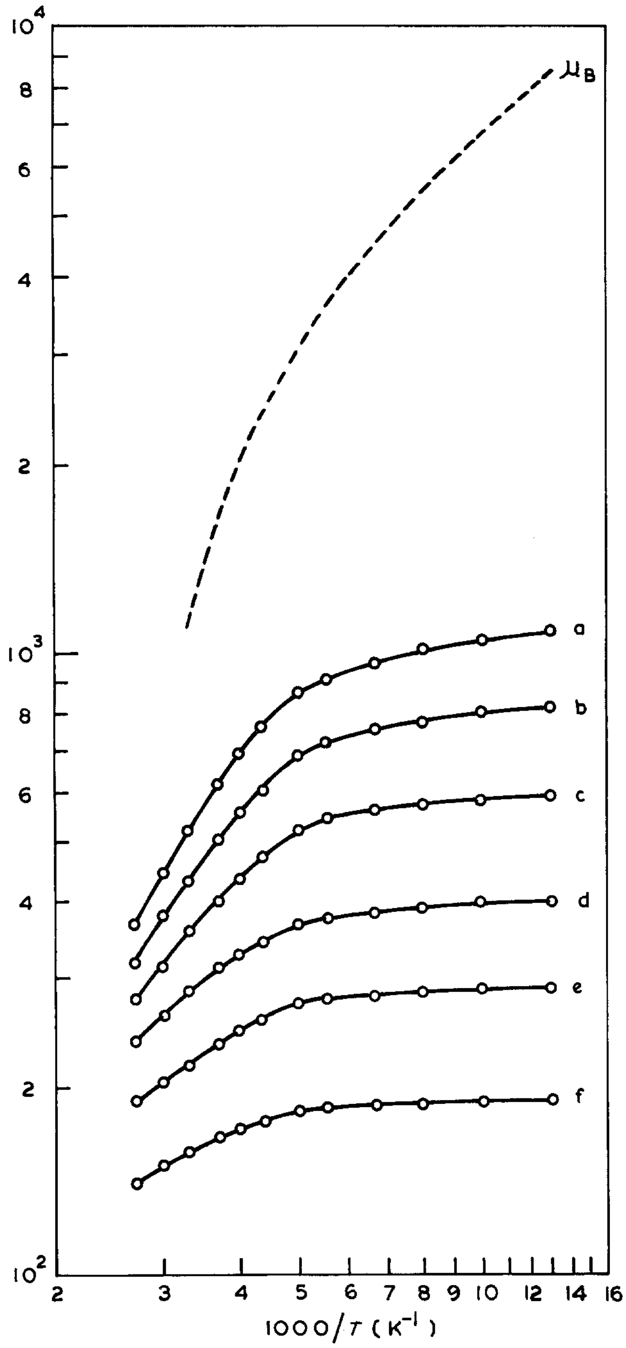

Figure 4 Variation of Hall mobility with temperature, log μ_H against log (1000/T), for thallium-doped $Pb_{0.8}Sn_{0.2}Te$ films. (a) As-grown; (b) 0.3, (c) 0.7, (d) 1.0, (e) 1.5, (f) 2.0 at %. (---) From Ocio [28] for carrier concentration $2.85 \times 10^{18}\,cm^{-3}$.

μ_H against log (1000/T)) for films doped with different concentrations of thallium is shown in Fig. 4. It can be observed from this figure that at any given temperature the value of μ_H is decreased with an increase in the doping concentration of thallium. This decrease in mobility with increase of doping density can be attributed to the increase in defects and scattering due to neutral impurity centres created by the unionized impurity atoms. It can be seen from Fig. 4 that the mobility decreases with an increase in temperature for all the films. However, the rate of decrease of mobility is slow in the low temperature region (77 to 180 K) and it becomes faster at higher temperatures (above 180 K). The linearity of the curves in the low-temperature range suggests that only one type of carrier (light holes) is contributing to the conduction process, and the mobility corresponds to that of the light holes, μ_l which is mainly limited by lattice scattering. This is also supported by the R_H data in this temperature range, which remains almost constant, showing the presence of only one type of carrier. A sharp fall in mobility above 180 K is the consequence of the onset of multi-band conduction due to an increased contribution of heavy holes, which have a smaller mobility.

The nature of the curves in Fig. 4 indicates that the mobility varies with temperature in accordance with the relation $\mu_H \propto T^{-y}$, suggesting the predominance of lattice scattering. The values of the exponent have been estimated from the slope of log μ_H against log (1000/T) curves for all the films, and is found to decrease with an increase of doping concentration. It has been observed that the value of y in the low-temperature region (77 to 180 K) also decreases with an increase of doping concentration. The higher values of y in the high-temperature region can be attributed to the increased contribution of heavy holes to the conduction process. The calculated values of y in the present case are much smaller than the values reported for bulk samples [28] of $Pb_{0.8}Sn_{0.2}Te$ in both temperature regions. The possible cause of this discrepancy

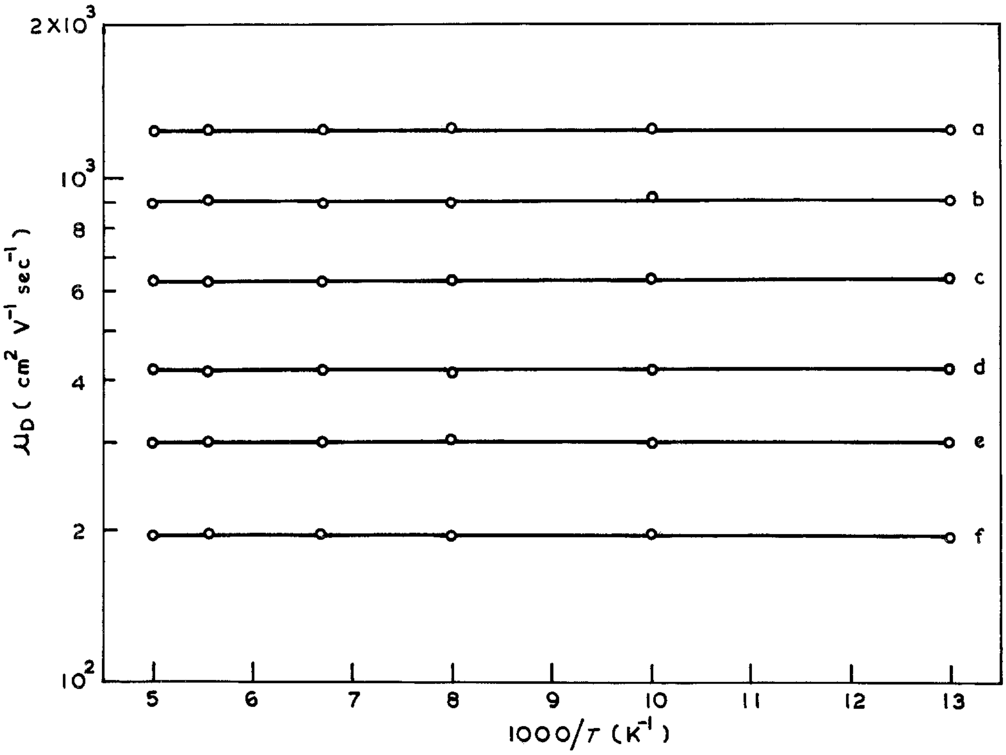

Figure 5 Variation of defect mobility with temperature, log μ_D against (1000/T), for thallium-doped $Pb_{0.8}Sn_{0.2}Te$ films. (a) As-grown; (b) 0.3, (c) 0.7, (d) 1.0, (e) 1.5, (f) 2.0 at %.

is the presence of inherent defects, such as surface asperities, dislocations and neutral impurities, as a result of the doping of the films. The observed values of mobility in the films are found to be lower than the corresponding bulk mobilities for similar carrier concentrations.

The observed mobility can be expressed [29] as

$$\frac{1}{\mu_H} = \frac{1}{\mu_d} + \frac{1}{\mu_D} \qquad (4)$$

where μ_d is the average mobility corrected for diffuse scattering, related to μ_B by the relation [30]

$$\mu_d = \frac{\mu_B}{1 + (3/8)k_r} \qquad (5)$$

where μ_B is the mobility of the bulk and k_r is the ratio of film thickness t to the mean free path λ of the carriers. In the present case $\lambda \ll t$, therefore $\mu_d \simeq \mu_B$. μ_D is the mobility limited by defects which include grain boundaries, dislocations, surface asperities, and neutral and ionized impurities. The use of Matheissen's rule for the additivity of the inverse mobility is justified because the Hall scattering parameter is close to unity for this material [31], in the temperature range studied and at concentrations greater than $10^{17}\,cm^{-3}$.

The values of μ_D for all the films have been calculated using the Equation 4 and using the values of μ_B reported by Ocio [28]. The values of μ_B should be taken for bulk samples of similar carrier concentration for these calculations, but since not many data on p-type $Pb_{0.8}Sn_{0.2}Te$ bulk crystals are available in the higher concentration range, only data corresponding to the carrier concentration $2.85 \times 10^{18}\,cm^{-3}$ have been plotted in Fig. 4 (dotted line). The calculated values of μ_D as a function of temperature on the range 77 to 200 K have been plotted in Fig. 5 for thallium-doped films. It is found that in this temperature range the defect-limited mobility is independent of temperature. Such a temperature-independent behaviour of mobility limited by defects is also observed by other workers in IV–VI compounds [32, 33]. It is found that the value of μ_D decreases with increasing carrier concentration in the films. This decrease in μ_D with an increase of carrier concentration can be explained by using the relation [27]

$$\mu_D = \left(\frac{\pi}{3}\right)^{1/3}\left(\frac{2e}{h}\right)\left(\frac{1}{Qp^{4/3}}\right) \qquad (6)$$

where Q is the scattering cross-section per scatterer, which is assumed to be independent of carrier density.

4. Conclusions

Thallium is found to give acceptors in these films. The separation between valence bands ΔE_v is independent of carrier concentration. The mobility ratio, effective mass ratio and population ratio are found to decrease with an increase in the doping concentration of thallium in these films. The Hall mobility is found to decrease with an increase in doping concentration due to a decrease in the value of the defect-limited mobility.

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