

Observation of Meyer–Neldel rule in thermally activated Poole–Frenkel photoconduction in a- $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ thin films

V S KUSHWAHA¹, N MEHTA^{2,*} and A KUMAR³

¹Department of Physics, Kanpur Institute of Technology, Kanpur 208 007, India

²Department of Physics, Banaras Hindu University, Varanasi 221 005, India

³Department of Physics, Harcourt Butler Technological Institute, Kanpur 208 002, India

*Corresponding author. E-mail: dr_neeraj_mehta@yahoo.co.in; nmbhu@rediffmail.com

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Abstract. In the present paper, we report the compensation effect on photoconductivity of thin films of $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ ($x = 2, 4, 6$) alloys for high field conduction. Steady state photoconductivity measurements have been made in thin films for different electric fields. The photoconduction was found to be ohmic at low fields and Poole–Frenkel type at high fields. Meyer–Neldel rule (MN rule) for the pre-exponential factor $(\sigma_{\text{ph}})_0$ and activation energy (ΔE_{ph}) of photoconduction in thin films of $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ is observed in the present study.

Keywords. Chalcogenide glasses; Poole–Frenkel conduction; Meyer–Neldel rule.

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1. Introduction

In general, in the case of semiconductors, DC conductivity (σ_{d}) varies exponentially with temperature (T) , i.e.,

$$\sigma_{\text{d}} = (\sigma_{\text{d}})_0 \exp[-\Delta E_{\text{d}}/kT], \quad (1)$$

where ΔE_{d} is the activation energy and $(\sigma_{\text{d}})_0 (=N_{\text{c}}q\mu)$ is the pre-exponential factor. Here, N_{c} is the effective density of states in the conduction band, q is the charge of the carrier and μ is the mobility of the charge carrier.

In most of the semiconducting materials, $(\sigma_{\text{d}})_0$ does not depend on ΔE_{d} . However, in many organic and amorphous semiconductors, $(\sigma_{\text{d}})_0$ is found to increase exponentially with ΔE_{d} [1–15]. It was found empirically that $(\sigma_{\text{d}})_0$ satisfies the relation

$$(\sigma_{\text{d}})_0 = (\sigma_{\text{d}})_{00} \exp[\Delta E_{\text{d}}/kT_0], \quad (2)$$

where $(\sigma_d)_{00}$ and kT_0 are constants. This is called Meyer–Neldel rule (MN rule) [16]. This rule is applicable in the case of chalcogenide glasses also [17–19] where ΔE_d is varied by changing the composition of the glassy alloys in a specific glass system. When one changes ΔE_d by changing composition in a particular glassy system, the density of defect states and their distribution with energy will change due to compositional disorder. Since the distribution of density of defect states determines the statistical shift which is responsible for the observation of MN rule (see §3), it is desirable to look for MN rule in a sample which is not affected by these complications. Recently, the applicability of MN rule for dark conductivity in chalcogenide glasses for a particular glass composition has been reported by changing the voltage in the high field region [21,22]. This has the advantage that the distribution of the density of defect states in the material remains unchanged with a change in the activation energy.

A study of I – V characteristics is important for properly analysing the conduction mechanism in thin films. I – V characteristics of thin films of $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ ($x = 2, 4, 6$) alloys have been examined at various temperatures in dark and in the presence of light and the presence of Poole–Frenkel conduction is reported. Recently, we have observed that MN rule is satisfied in thermally activated photoconduction in $\text{Se}_{75}\text{Ge}_{20}\text{Ag}_5$ alloy without applying high field [2]. In the present study, we have tried to fit MN rule for photoconductivity in this particular glass composition under high field conduction.

2. Experimental detail

Glassy alloys of $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ ($x = 2, 4, 6$) composition were prepared by the quenching technique. High purity (99.999%) components were weighed according to their atomic percentages and were sealed in a quartz ampoule (length ~ 5 cm and internal dia. ~ 8 mm) in a vacuum of $\sim 10^{-5}$ Torr. The ampoule containing the components was heated to 600°C and held at that temperature for 10–12 h. The temperature of the furnace was raised slowly at a rate of 3 – $4^\circ\text{C}/\text{min}$. During heating, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This was done to obtain homogeneous glassy alloy.

After rocking for about 10 h, the obtained melt was cooled rapidly by removing the ampoule from the furnace and dropping to ice-cooled water. The cooling rate was nearly $500^\circ\text{C}/\text{s}$. The quenched sample was taken out by breaking the quartz ampoules. The glassy nature of the material was checked by XRD technique

Thin films of the alloy were prepared by a standard coating unit (IBP-TORR, type: EPR-002) at a base pressure of 10^{-5} Torr. The vacuum coating unit consists of a deposition chamber inside which proper arrangement was done to deposit the desired material. The material to be deposited is placed in a molybdenum boat inside the chamber from where it is thermally evaporated to the glass substrate, which is held at a height of about 15 cm from the boat. The substrates used in the present work were made of 7059 Corning glass. Before depositing glassy alloy on the substrate, indium was deposited to make electrodes. The thickness of the film was ~ 500 nm. A co-planar structure (length ~ 1.2 cm and electrode separation

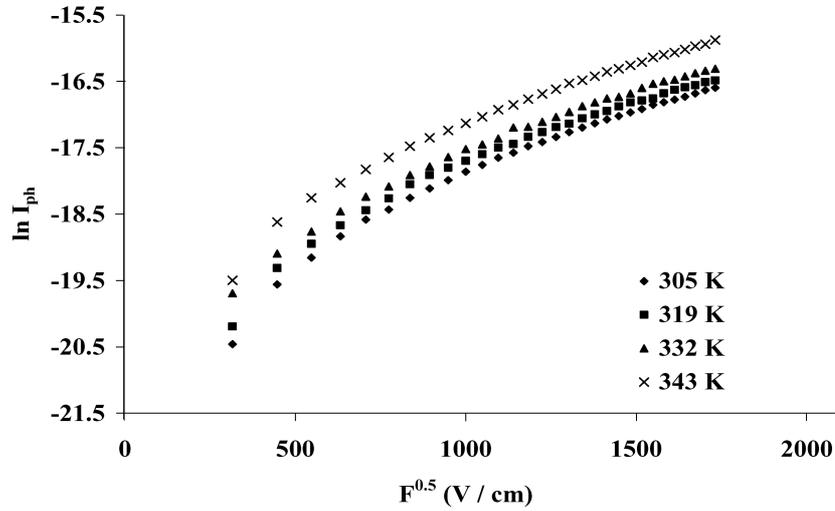


Figure 1. Plots of $\ln I_{\text{ph}}$ vs. $F^{0.5}$ at 293 K for $a\text{-Se}_{70}\text{Te}_{28}\text{Cd}_2$.

~ 0.1 mm) was used for the present measurements. The amorphous nature of thin film was ascertained by X-ray diffraction.

For the measurements of high field conduction, thin film sample was mounted in a specially designed sample holder. A vacuum ($\sim 10^{-2}$ Torr) was maintained throughout the measurements. A DC voltage (0–300 V) was applied across the sample and the resultant current was measured by a digital electrometer (Keithley model: 614). I – V characteristics were measured at various fixed temperatures (290 K–330 K) for these films in the dark and in the presence of light. The temperature of the films was controlled by mounting a heater inside the sample holder, and the temperature measured by a calibrated copper–constantan thermocouple mounted very near to the films. Before measuring I – V characteristics, thin films were annealed in a vacuum of $\sim 10^{-2}$ Torr near the glass transition temperature for 2 h in the same sample holder.

3. Results and discussion

The photocurrent (I_{ph}) was obtained by subtracting the dark current (I_{D}) from the current measured in the presence of light (I_{L}). If we study the $\ln I_{\text{ph}}$ vs. $F^{1/2}$ characteristics at different temperatures, where F is the field corresponding to the applied electric field, the plots are found to be linear in the high field region. Figure 1 shows such plots at different temperatures for $\text{Se}_{70}\text{Te}_{28}\text{Cd}_2$ alloy. This clearly indicates that the conduction mechanism in the high field region is of Poole–Frenkel type [24]. Similar results were obtained for other glassy alloys also.

The Poole–Frenkel photoconductivity in high field region can be expressed by the relation

$$\sigma_{\text{ph}} = (\sigma_0)_{\text{ph}} \exp[-\Delta E_{\text{ph}}/kT]. \quad (3)$$

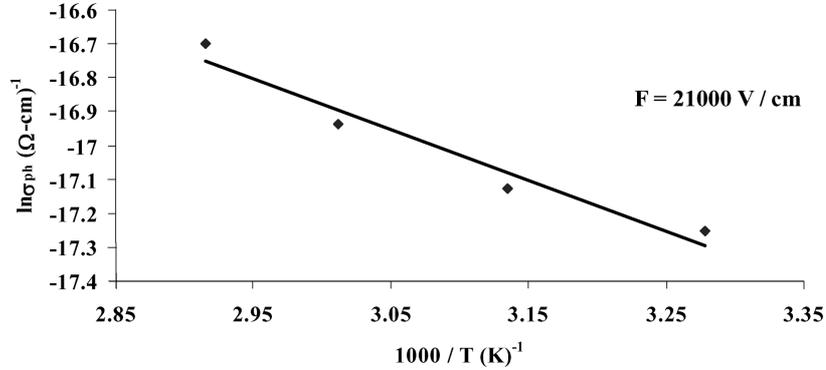


Figure 2. Plot of $\ln \sigma_{ph}$ vs. $1000/T$ at a particular electric field for a-Se₇₀Te₂₈Cd₂.

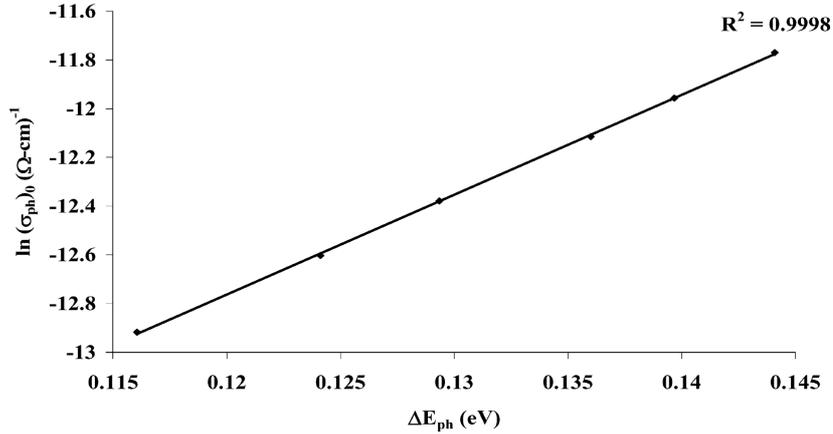


Figure 3. Plot of $\ln(\sigma_{ph})_0$ vs. ΔE_{ph} for a-Se₇₀Te₂₈Cd₂.

The temperature dependence of σ_{ph} is studied at different electric fields in amorphous thin films of Se₇₀Te₂₈Cd₂ in the temperature range 290 K to 330 K. Such a plot is shown in figure 2 at a particular electric field. Similar plots are obtained at other electric fields. From the slope and the intercepts of $\ln \sigma_{ph}$ vs. $1000/T$ curves, the values of ΔE_{ph} and $(\sigma_{ph})_0$ have been calculated for all the three glassy alloys.

It is interesting to note that ΔE_{ph} decreases with the increase in the applied electric field. The values of pre-exponential factor $(\sigma_{ph})_0$ are also found to be dependent on electric fields. Figure 3 shows the plot of $\ln(\sigma_{ph})_0$ vs. ΔE_{ph} for the glassy Se₇₀Te₂₈Cd₂ alloy, which is a straight line indicating that pre-exponential factor of Poole–Frenkel photoconductivity varies exponentially with ΔE_{ph} as follows:

$$(\sigma_{ph})_0 = (\sigma_{ph})_{00} \exp[\Delta E_{ph}/kT_0]. \quad (4)$$

The values of kT_0 and $(\sigma_{\text{ph}})_{00}$ for a-Se₇₀Te_{30-x}Cd_x thin films have been determined by the slope of $\ln(\sigma_{\text{ph}})_0$ vs. ΔE_{ph} curves. It has been found that under high electric field, the activation energy of photoconduction is less than that of the dark conduction under the same electric field [22]. This indicates that photo-induced carrier generation is field-dependent and hence less activation energy is required for thermally activated photoconduction under electric field.

Given below are the theoretical considerations to observe MN rule in chalcogenide glasses by changing the activation energy with the applied electric field.

For convenience, we are considering electron transport mechanism but similar arguments are valid for holes also. The temperature dependence of the mobility edges of the conduction band and that of Fermi level can be approximated as

$$E_c(T) = E_{c0} - \gamma_c T \quad (5)$$

$$E_f(T) = E_{f0} - \gamma_f T. \quad (6)$$

The suffix c and f refer to the mobility edges of the conduction band and the Fermi level respectively. Here we assume that the conduction and valence band edges contribute equally to the temperature dependence of the band gap. From eqs (5) and (6) we get the experimentally measured activation energy to be

$$\Delta E = E_{c0} - E_{f0}, \quad (7)$$

where E_{c0} is the value of E_c at $T = 0$ K. The pre-factor σ_0 can now be written as

$$\sigma_0 = N_c q \mu \exp[(\gamma_c - \gamma_f)/k]. \quad (8)$$

We now qualitatively explain how γ_f can account for the MN rule.

In the case of semiconductors the charge neutrality determines the position of the Fermi level. Normally, only states within a couple of kT above E_f have any significant occupancy and control the temperature dependence of E_f . However, If the ratio of conduction band tail states (CBT) to the midgap density of states is large, then states $\gg kT$ from E_f have significant occupancy and can influence the motion of E_f and in turn will obey MN rule [25]. This happens when the DOS increases at least as fast as the Fermi function falls off the energy. The wings of the Fermi function will then contribute to the occupancy. Since the DOS for the CBT in the case of amorphous system have exponential distribution with energy [26], the above condition gets satisfied and MN rule is applicable in chalcogenide glasses [17–19].

The position of E_f depends on the density of states and is a function of both the applied voltage and temperature [26,27]. Therefore, the considerations that determine the temperature dependence of E_f at a constant voltage are qualitatively similar to those that determine the temperature dependence of E_f . Temperature dependence of E_f is responsible for the observation of MN rule in the case of high field conduction experiment reported in the present paper.

4. Conclusion

Temperature dependence of Poole–Frenkel photoconductivity in thin films of a- $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ ($x = 2, 4, 6$) is studied at different electric fields in the temperature range of 290 K to 330 K. We find that σ_{ph} is thermally activated and the activation energy depends on the electric field applied. In the present case, the activation energy is varied by changing the electric field applied across the samples instead of changing the composition of the glassy alloys. The MN rule is observed in the present case also thereby indicating that MN rule is more general in these materials and it is applicable for photoconduction also under high fields.

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