

HIGH FIELD CONDUCTION IN a- $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ THIN FILMS: APPLICABILITY OF MEYER-NELDEL RULE

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In general, in case of semiconductors, conductivity (σ) varies exponentially with temperature (T), i.e., $\sigma = \sigma_0 \exp(-\Delta E / k T)$ where ΔE is the activation energy and σ_0 is called the pre-exponential factor. In most of the semiconducting materials, σ_0 does not depend on ΔE . However, in many organic and amorphous semiconductors, σ_0 is found to increase exponentially with ΔE . This is called Meyer- Neldel rule. In such experiments, changing composition of the glassy sample changes the activation energy. In the present work we have changed ΔE by applying high electric fields. It is shown that Meyer- Neldel rule is obeyed in this case also where composition of the material is not changed. This indicates that this rule is more general in chalcogenide glasses and is not due to changes in certain parameters on changing composition.

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1. Introduction

There has been an increased interest in the properties of Se rich semiconducting glassy alloys due to their current use as photoreceptors in TV vidicon pick-up tubes [1] and particularly in digital x-ray imaging [2]. Recently, it has been pointed out that a- Se-Te alloys have more advantages than a-Se from the technological point of view due to their greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects. Therefore, glassy Se-Te alloys are used to extend the utility of a-Se.

In general, for a semiconducting material, d. c. conductivity increases exponentially with temperature indicating that the conductivity is a thermally activated process. Mathematically it can be expressed as:

$$\sigma = \sigma_0 \exp(-\Delta E / kT) \quad (1)$$

where ΔE is called the activation energy and σ_0 is called the pre-exponential factor.

The above equation is termed as Arrhenius law and is used to determine the activation energy for electrical conduction. Defects or doping in semiconductors can lead to lower effective activation energy and to spread in the values for ΔE for the same property in one material.

In most of the semiconducting materials, σ_0 does not depend on ΔE . However, in many organic and amorphous materials, σ_0 is found to increase exponentially with ΔE [3-18]. It was found empirically, for the first time, by Meyer and Neldel in 1937 [3] that σ_0 satisfies a relation:

$$\sigma_0 = \sigma_{00} \exp(\Delta E / kT_0) \quad (2)$$

where σ_{00} and kT_0 are positive constants within a class of related materials. This expression is termed as Meyer – Neldel rule for d. c. conductivity.

In case of chalcogenide glasses also, MN rule is observed by the variation of ΔE on changing the composition of the glassy alloys [19, 20] in a specific glassy system or by the variation

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of intensity of light [21, 22]. When one changes the ΔE by changing composition in a particular glassy system, there are changes in the density of defect states and its distribution with energy 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, it is interesting to look MN rule in a sample, which is not affected by these complications. Recently, it has been reported that the activation energy of a particular glass composition can also be changed by applying a changing voltage in the high field region [23]. 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.

In the present paper we report on the temperature dependence of d. c. conductivity at different electric fields in amorphous thin films of $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ ($x = 2, 4, 6$). In the present case, changing the electric field applied across the sample of same composition varies activation energy. The results show that the MN rule is obeyed in this case also. This shows that MN rule is more general in chalcogenide glasses and it does not depend on how activation energy is varied.

2. Experimental

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

After rocking for about 10 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water. The quenched samples of Se-Te-Cd system were taken out by breaking the quartz ampoules. The glassy nature of the materials was checked by XRD technique.

Thin films of these glasses were prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the films was ~ 500 nm. The co-planar structure (length ~ 1.0 cm and electrode separation ~ 0.1 mm) was used for the present measurements. A vacuum $\sim 10^{-5}$ Torr was maintained in the entire temperature range (305 K to 343 K). The amorphous nature of thin films was ascertained by x-ray diffraction.

Before measuring the d. c. conductivity, the films were first annealed at 350K for one hour in a vacuum $\sim 10^{-2}$ Torr. I-V characteristics were found to be linear and symmetric up to 100 V. The present measurements were made by applying a voltage from 10 V to 300 V across the films. The resulting current was measured by a digital electrometer (Keithely model: 614). The heating rate was kept quite small (0.5 K / min) for these measurements. Thin film samples were mounted in a specially designed sample holder. A vacuum $\sim 10^{-2}$ Torr was maintained throughout the measurements. The temperature of the films is controlled by mounting a heater inside the sample holder and measured by a calibrated copper- constantan thermocouple mounted very near to the films.

3. Theoretical consideration

Given below are the theoretical considerations to observe MN rule in chalcogenide glasses by changing the activation energy:

For convenience, we are considering the 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:

$$E_c(T) = E_{c0} - \gamma_c T \quad (3)$$

$$E_f(T) = E_{f0} - \gamma_f T \quad (4)$$

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 equations (1), (3) and (4) we get the experimentally measured activation energy to be

$$\Delta E = E_{c0} - E_{f0} \quad (5)$$

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

$$\sigma_0 = N_c q \mu \exp [(\gamma_c - \gamma_f) / k] \quad (6)$$

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

In 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 gives rise to the MN rule [24]. 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 case of amorphous system have exponential distribution with energy [25], the above condition gets satisfied and MN rule is observed in chalcogenide glasses [19,20].

The position of E_{fn} 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_{fn} at a constant voltage are qualitatively similar to those that determine the temperature dependence of E_f . Temperature dependence of E_{fn} is responsible for the occurrence of MN rule in case of high field conduction experiment reported in the present paper.

4. Results and discussions

The temperature dependence of d. c. conductivity is studied at different electric fields in amorphous thin films of $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$ in temperature range 305 K to 343 K. From the slope and the intercepts of $\ln \sigma$ vs. $1000/T$ curves, the values of ΔE and σ_0 have been calculated. The activation energy decreases with the increase in applied electric field. The values of σ_0 are also found to be dependent on electric fields [given in Tables 1-3]. Figs. 1-3 show the plots of $\ln \sigma_0$ vs. ΔE for all the glassy alloys, which are the straight lines indicating that σ_0 varies exponentially with ΔE as expected from equation (2).

Table 1. Semiconduction parameters for a- $\text{Se}_{70}\text{Te}_{28}\text{Cd}_2$.

Electric Field V/cm	ΔE (eV)	σ_0 ($\Omega^{-1} \text{cm}^{-1}$)	$\sigma_0 = \sigma_{00} \exp [\Delta E / k T_0]$
1.0×10^3	0.77	1.43×10^4	1.42×10^4
1.0×10^4	0.69	8.04×10^2	8.21×10^2
1.5×10^4	0.67	4.25×10^2	4.27×10^2
2.0×10^4	0.66	3.13×10^2	3.17×10^2
3.0×10^4	0.65	2.73×10^2	2.65×10^2

Table 2. Semiconduction parameters for a- $\text{Se}_{70}\text{Te}_{26}\text{Cd}_4$.

Electric Field V/cm	ΔE (eV)	σ_0 ($\Omega^{-1} \text{cm}^{-1}$)	$\sigma_0 = \sigma_{00} \exp [\Delta E / k T_0]$
1.0×10^3	0.83	1.29×10^5	1.28×10^5
5.0×10^3	0.66	3.61×10^2	3.67×10^2
1.0×10^4	0.64	1.90×10^2	1.89×10^2
1.5×10^4	0.61	7.90×10^1	8.0×10^1
2.5×10^4	0.59	4.20×10^1	4.10×10^1

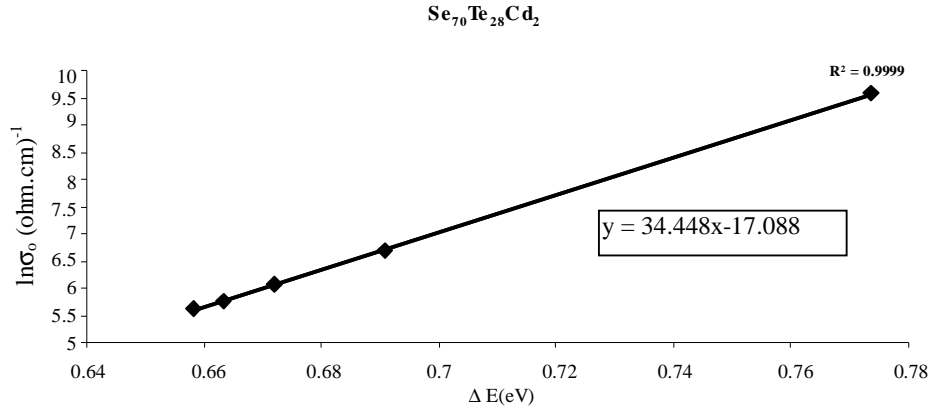


Fig. 1. Plot of $\ln \sigma_0$ vs. ΔE at different electric fields for a- Se₇₀Te₂₈Cd₂.

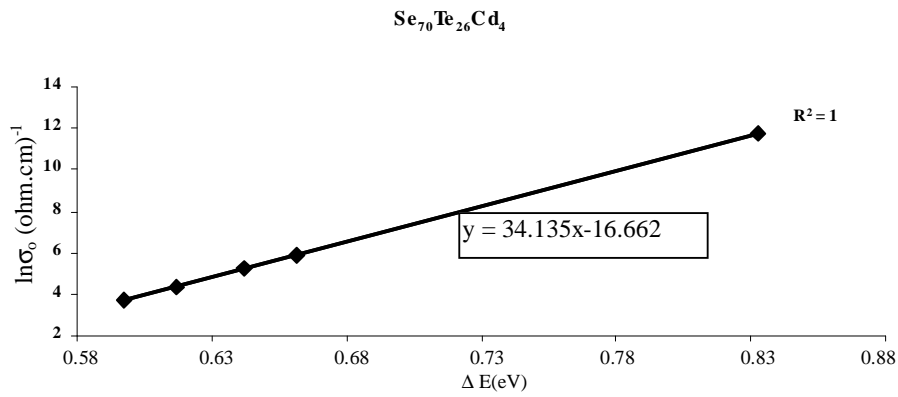


Fig. 2. Plot of $\ln \sigma_0$ vs. ΔE at different electric fields for a- Se₇₀Te₂₆Cd₄.

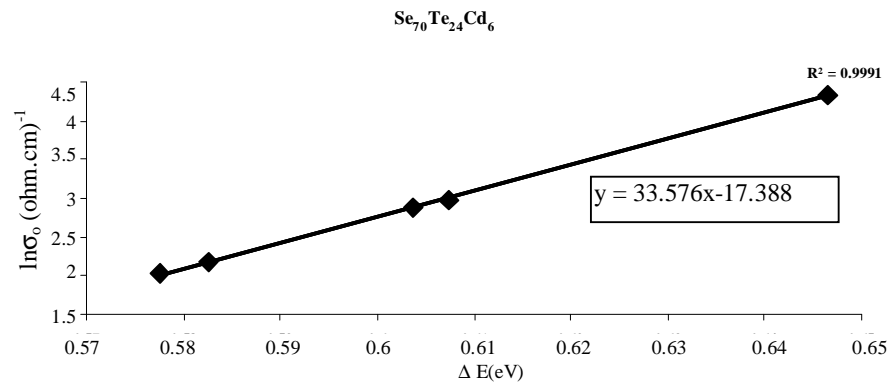


Fig. 3. Plot of $\ln \sigma_0$ vs. ΔE at different electric fields for a- Se₇₀Te₂₄Cd₆.

The values of kT_0 and σ_{00} for a- Se₇₀Te_{30-x}Cd_x thin films have been determined by the slope of $\ln \sigma_0$ vs. ΔE curves and are given in Table 4. Using these values of kT_0 and σ_{00} , the expected σ_0 values have been calculated for the above glassy alloys and compared with the reported values (see Tables 1-3). An overall good agreement confirms the validity of Meyer- Neldel rule.

Table 3. Semi-conduction Parameters for a- $\text{Se}_{70}\text{Te}_{24}\text{Cd}_6$.

Electric Field V/cm	ΔE (eV)	σ_0 ($\Omega^{-1} \text{cm}^{-1}$)	$\sigma_0 = \sigma_{00} \exp [\Delta E / k T_0]$
5.0×10^3	0.65	7.65×10^1	7.5×10^1
1.0×10^4	0.61	1.94×10^1	2.0×10^1
1.5×10^4	0.60	1.78×10^1	1.7×10^1
2.0×10^4	0.58	8.7×10^0	8.8×10^0
2.5×10^4	0.56	7.6×10^0	7.4×10^0

Table 4. Semi-conduction Parameters (σ_{00} and kT_0) for a- $\text{Se}_{70}\text{Te}_{30-x}\text{Cd}_x$.

Sample	kT_0 (meV)	σ_{00} ($\Omega^{-1} \text{cm}^{-1}$)
$\text{Se}_{70}\text{Te}_{28}\text{Cd}_2$	336	3.79×10^{-8}
$\text{Se}_{70}\text{Te}_{26}\text{Cd}_4$	339	5.80×10^{-8}
$\text{Se}_{70}\text{Te}_{24}\text{Cd}_6$	345	2.80×10^{-8}

5. Conclusion

Temperature dependence of d. c. conductivity is studied at different electric fields in temperature range 305 K to 343 K. We find that electrical conductivity is thermally activated and the activation energy depends on the electric field applied.

In the present case, though the activation energy is varied by changing the electric field applied across the samples instead of changing the composition of the glassy system or by changing the intensity of light, the MN rule is observed. This shows that MN rule is more general in these materials and it does not depend on how activation energy is varied.

References

- [1] E. Maruyama, Jpn. J. Appl. Phys. **21**, 231 (1982).
- [2] D. C. Hunt, S. S. Kirby, J. A. Rowlands, Med. Phys. **29**, 2464 (2002).
- [3] W. Meyer, H. Neldel, Z. Tech. Phys. (Leipzig) **12**, 588 (1937).
- [4] K. Shimakawa, Abdel -Wahab, Appl. Phys. Lett. **70**, 652 (1997).
- [5] Y. L. A. El-Kady, Physica B, **305**, 259 (2001).
- [6] Y. Lubianiker, I. Balberg, Phys. Rev. Lett. **78**, 2433 (1997).
- [7] Y. F. Chen, S. F. Huang, Phys. Rev. B. **44**, 13775 (1991).
- [8] A. Yelon, B. Movaghar, Appl. Phys. Lett. **17**, 3549 (1997).
- [9] H. Overhof, P. Thomas, Electronic Transport in Hydrogenated Amorphous Semiconductors (Springer, Berlin), (1989).
- [10] D. L. Staebler, C. R. Wronski, Appl. Phys. Lett. **21**, 292 (1977).
- [11] B. Rogenberg, B. B. Bhowmic, H. C. Harder, E. Postow, J. Chem. Phys. **49**, 4108 (1968).
- [12] A. Many, E. Harnik, D. Gerlick, J. Chem. Phys. **23**, 1733 (1955).
- [13] S. W. Johanston, R. S. Crandall, A. Yelon, App. Phys. Lett. **83**, 908 (2003).
- [14] Minoru Kikuchi, J. Appl. Phys. **64**, 4997 (1988).
- [15] K. Moril, T. Matsui, H. Tsuda, H. Mabuchi Appl. Phys. Lett. **77**, 2361 (2000).
- [16] J. Fortner, V. G. Karpov, Marie- Louise Saboungi, Appl. Phys. Lett. **66**, 997 (1995).
- [17] K. L. Narashimhan, B. M. Arora, Sol. Stat. Commun. **55**, 615 (1985).
- [18] G. Kemeny, B. Rosenberg, J. Chem. Phys. **52**, 4151 (1970).
- [19] R. Arora, A. Kumar, Phys. Stat. Sol. (a) **125**, 273 (1991).
- [20] S. K. Dwivedi, M. Dixit, A. Kumar, J. Mat. Sci. Lett. **17**, 233 (1998).
- [21] D. Kumar, S. Kumar, Vacuum **74**, 113 (2004).

- [22] D. Kumar, S. Kumar, *J. Optoelectron. Adv. Mater.* **6**, 777 (2004).
- [23] D. Kumar and S. Kumar, *Japanese J. of Appl. Phys.* **43**(3), 901, (2004).
- [24] H. Overhof, Beyer, *Phil. Mag. B*, **43**, 4376 (1981).
- [25] G. G. Roberts, *J. Phys. C*, **4** 3167 (1971).
- [26] M. A. Lampert, P. Mark "Current Injection in Solids", (Academic Press, NY) 1970.
- [27] A. Rose, "Concepts in Photoconductivity and Allied Problems" (New York: John Wiley- Inter-Science- Publisher) 1963.