

INVESTIGATION OF MEYER-NELDEL RULE IN THIN FILMS OF $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ FOR DIFFERENT STATES

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In the present paper, we report on the temperature dependence of conductivity in thin films of $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ in three different cases. In the first case, the films are in amorphous state. In the second case, the films are in partially crystalline state and in the third case; the films are in crystalline state. We have observed Meyer–Neldel (MN) rule between pre-exponential factor and activation energy in the first case, where $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films are in amorphous state. However, in the second and third cases, it has been found that the plot of $\ln \sigma_0$ vs. ΔE departs from MN rule. This indicates that MN rule is observed in chalcogenide glasses due to their short-range order structure.

Key words: chalcogenide glasses; Meyer–Neldel rule; pre-exponential factor.

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I. INTRODUCTION

Studies of the chalcogenide glasses in Se–Te–Sb system have received great attention because of their important applications as photoreceptor in xerography and in switching devices [1]. The addition of Sb in Se–Te system modifies considerably the structure of the system. Se–Te–Sb shows memory type switching [2].

The nature of electron transport in amorphous materials has been a subject of curiosity among scientists as well as engineers due to their potential use in semiconducting devices. Chalcogenide glasses are an important class of amorphous semiconductors and, therefore, the studies on electrical conductivity of these glasses are important from application point of view as well as from the point of investigation of localized states in the mobility gap of these materials.

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]. It was found empirically, for the first time; by Meyer and Neldel in 1937 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 dc conductivity.

This rule is generally observed in disordered materials. In the class of amorphous semiconductors, the MN rule has been reported in *a*-Si:H films in which ΔE is varied by doping, by surface absorption, light soaking or by preparing films under different conditions [4–6].

In case of chalcogenide glasses, MN rule is observed by the variation of ΔE on changing the composition of the glassy alloys [7–11] in a specific glassy system or by the variation of intensity of light [12,13]. It is interesting to see whether MN rule is observed only in glassy state in these materials or it is observed in crystalline state also. With this point of view, we have tried to fit MN rule in the glassy samples in different phases, i.e., amorphous, partially crystalline and crystalline state. We have investigated the $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films for this purpose. Our results show that observation of the MN rule in chalcogenide glasses is probably due to some fundamental characteristics arising due to their short-range order structure.

II. MATERIAL PREPARATION

Glassy alloys of $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ ($x = 0, 5, 10, 15$) were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te and Sb elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm). The ampoules containing material were heated to 800°C and were held at that temperature for 12 hours. The temperature of the furnace was raised slowly at the rate of $3\text{--}4^\circ\text{C}$ / minute. During heating, 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 homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by X-ray diffraction.

Thin films of $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ were prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at the bottom were used for the electrical contact. The thickness of the films was ~ 500 nm. The coplanar structure (length ~ 1.2 cm and electrode separation ~ 0.5 mm) was used for present measurements. The amorphous nature of the films was verified by X-ray diffraction and the composition was checked by Electron Probe Micro Analyzer (EPMA).

III. EXPERIMENTAL

The electrical conductivities of $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films in dark were studied by mounting them in a specially designed sample holder. The vacuum of about 10^{-2} Torr was maintained throughout these measurements. The temperature of the films was controlled by mounting the heater inside the sample holder and measured by a

calibrated copper constantan thermocouple.

It has already been reported by us that photocrystallization occurs in $\text{Se}_{65}\text{Te}_{20}\text{Sb}_{15}$ amorphous films on exposure of white light for long durations [14]. The conductivity as well as the activation energy changes on increasing exposure time. However, after a certain exposure time, no further change is observed in these parameters. The initial state is amorphous state and the final state may be called fully crystallized state and the intermediate state is called partially crystalline state. It is also reported [14] that X-ray diffraction experiment confirms that initially films are in amorphous state and crystallization peaks occurs in light exposed samples. In the present study, we have done similar experiments on four glassy alloys of Se-Te-Sb system and found that 18 hrs exposure saturates the crystallization process. We have chosen state A as amorphous state, state B as partially crystalline state (exposure time 8 hrs) and state C as fully crystalline state (exposure time 18 hrs).

IV. RESULTS

The temperature dependence of conductivity is studied in $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films. Fig. 1 shows such results between 300 K and 335 K in the three states (states A, B and C). The conductivity (σ) varies exponentially with temperature as $\ln \sigma$ vs. $1000/T$ curves are straight lines (see Fig. 1). Such behaviour is consistent with Eq. (1).

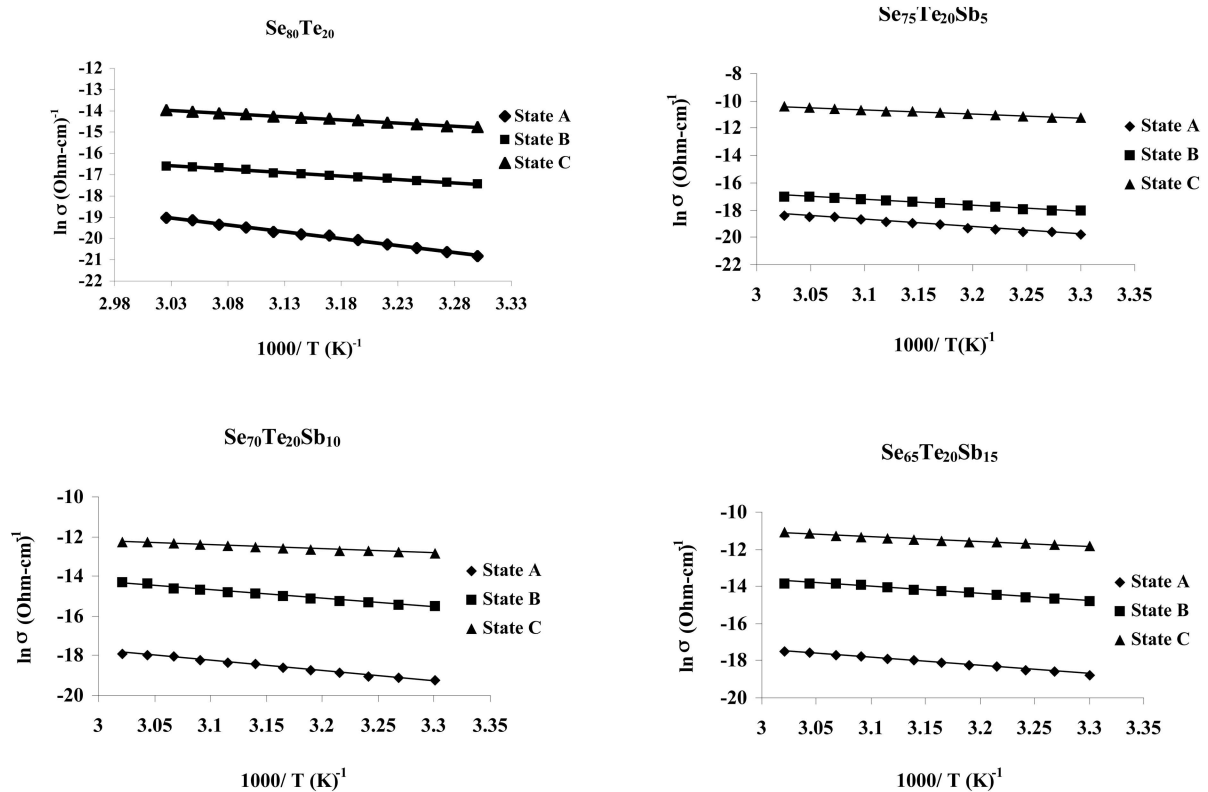


Fig. 1. $\ln \sigma$ versus $1000/T$ plots for $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films in states A, B and C.

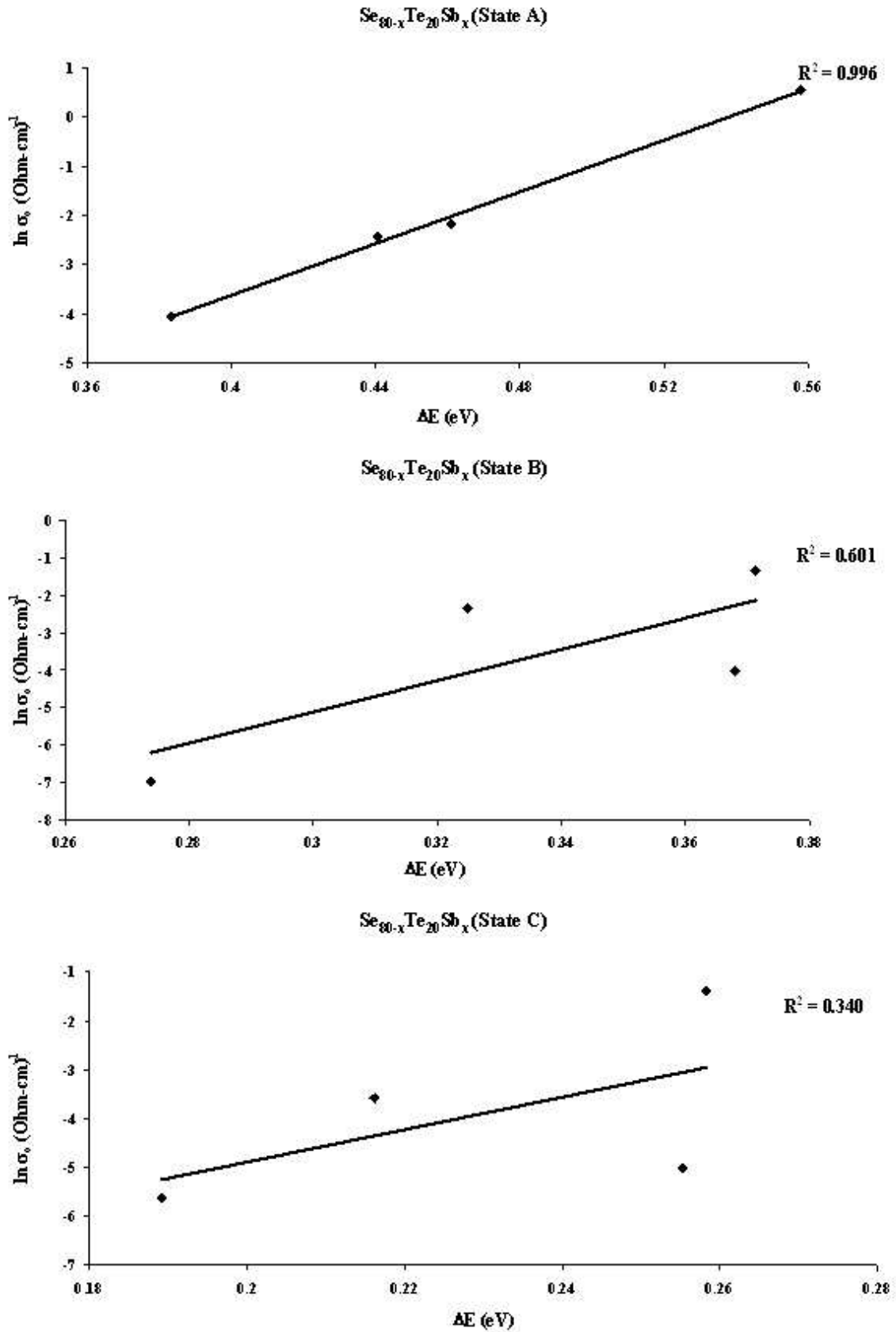


Fig. 2. $\ln \sigma_0$ versus ΔE plots for $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films in state A. $\ln \sigma_0$ versus ΔE plots for $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films in state B. $\ln \sigma_0$ versus ΔE plots for $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films in state C.

From the slopes and the intercepts of the plots in Fig. 1, the values of ΔE and σ_0 have been calculated for the three states in all the glassy alloys used in the present study. These values are given in table 1. It is clear from this table that ΔE and σ_0 are composition dependent and σ_0 is not a constant but depends on ΔE . Fig. 2 shows the plots of $\ln \sigma_0$ vs. ΔE for $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films in the three states (states A, B and C). Curve fitting is done by least square method and the correlation coefficients (R^2) of the $\ln \sigma_0$ vs. ΔE plots are indicated in Fig. 2. It is clear from this figure that $\ln \sigma_0$ vs. ΔE plot is a straight line of good correlation coefficient for state A only indicating that σ_0 varies exponentially with ΔE following the relation:

$$\ln \sigma_0 = \ln \sigma_{00} + \Delta E/kT_0. \quad (3)$$

Composition	State A		State B		State C	
	ΔE (eV)	$\ln \sigma_0$ (Ohm cm) ⁻¹	ΔE (eV)	$\ln \sigma_0$ (Ohm cm) ⁻¹	ΔE (eV)	$\ln \sigma_0$ (Ohm cm) ⁻¹
$\text{Se}_{80}\text{Te}_{20}$	0.560	0.55	0.273	-6.96	0.255	-5.02
$\text{Se}_{75}\text{Te}_{20}\text{Sb}_5$	0.461	-2.18	0.368	-4.02	0.258	-1.38
$\text{Se}_{70}\text{Te}_{20}\text{Sb}_{10}$	0.440	-2.42	0.371	-1.35	0.190	-5.63
$\text{Se}_{65}\text{Te}_{20}\text{Sb}_{15}$	0.383	-4.06	0.325	-1.32	0.220	-3.33

Table 1. Semi-conduction parameters for $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films in states A, B and C.

Composition	ΔE (eV)	$\ln \sigma_0$ (Ohm cm) ⁻¹	$\ln \sigma_0 = \ln \sigma_{00} +$ $[\Delta E/kT_0]$
$\text{Se}_{80}\text{Te}_{20}$	0.560	0.55	0.52
$\text{Se}_{75}\text{Te}_{20}\text{Sb}_5$	0.461	-2.18	-2.02
$\text{Se}_{70}\text{Te}_{20}\text{Sb}_{10}$	0.440	-2.42	-2.56
$\text{Se}_{65}\text{Te}_{20}\text{Sb}_{15}$	0.383	-4.06	-4.06

Table 2. Semi-conduction parameters for amorphous $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films.

V. DISCUSSION

In case of dark conductivity, a model has been given [15] which considers the exponential tailing of localized states with energy and distance near valence and conduction bands, which is, in general, accepted in the case of glassy semiconductors. The increase of the d. c. conductivity with temperature is believed to be due to an increase in the free carrier concentration (holes) due to the statistical shift of the Fermi level (E_F).

In case of semiconductors, the Fermi level (E_F) is temperature dependent and the position of E_F is determined by the charge neutrality. Normally, only the states within a couple of kT above E_F have any significant occupancy and control the temperature dependence of E_F . If the ratio of conduction band tail states 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

From the slope and intercept of the line, we have calculated the values of $(kT_0)^{-1} = 26.3 \text{ eV}$ and $\sigma_{00} = 7.3 \times 10^{-7} (\Omega\text{-cm})^{-1}$ for state A. Using these values, the expected σ_0 values have been calculated for the amorphous $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films and compared with the reported values (see Table 2). An overall good agreement between these two values confirms the validity of MN Rule in amorphous $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ thin films.

However, in the second and third states, i. e., for partially crystalline (state B) and crystalline (state C) state, the plot of $\ln \sigma_0$ vs ΔE departs from the MN rule (see Fig. 2). This shows that MN rule follows in chalcogenide glasses if they remain in amorphous phase and when the structure of the alloy transforms from short-range order to long-range order structure, the deviation from MN rule is observed.

in turn give rise to the MN rule. This happens because the density of localized states increases at least as fast as the Fermi function falls off the energy due to exponential distribution of density of states with energy. The view that the position of the Fermi level is controlled by the midgap localized states has been supported by a.c. conductivity measurements in chalcogenide glasses [16, 17].

While the above approach is appealing, it has been reported [18, 19] that MN rule arises because of the entropy of multiple excitations. Some other authors [20] proposed that MN rule arises from hopping conductivity. In the present case, the pre-exponential factor satisfies the MN rule in amorphous state but it departs from MN rule in the partially crystalline and completely crystalline states. These results are consistent with the above models. The absence of MN rule in states B and C may be due to the decrease in entropy in these states as compared to state A. The hopping conductivity is also a characteristic property of amorphous state hence, if hopping conduction is responsible for MN rule, this should not occur in states B and C, as observed in the present case.

VI. CONCLUSION

Amorphous thin films of $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ ($x = 0, 5, 10, 15$) have been prepared by vacuum evaporation technique. Temperature dependence of dc conductivity is

studied in amorphous, partially crystalline and completely crystalline states between the temperature ranges 300–335 K. We find that conductivity is thermally activated in all the three states. The activation energy, however, depends on the composition.

The activation energy and pre-exponential factor

satisfies the MN rule for amorphous thin films of $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ but this rule does not obey in partially crystallized and completely crystallized thin films of $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$. This shows that the MN rule is due to some characteristic properties of a disordered material.

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ДОСЛІДЖЕННЯ ПРАВИЛА МАЄРА–НЕЛЬДЕЛЯ В ТОНКИХ ПЛІВКАХ $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ ДЛЯ РІЗНИХ СТАНІВ

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Розглянуто температурну залежність провідності в тонких плівках $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ для трьох різних випадків. У першому випадку плівки перебувають в аморфному стані. Для другого — вони частково кристалізовані, а в третьому випадку плівки перебувають у кристалічному стані. Ми спостерігали виконання правила Маєра–Нельделя між передекспонентним множником й активаційною енергією в першому випадку, де тонкі плівки $\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x$ перебувають в аморфному стані. Проте в другому та третьому випадках спостерігалось відхилення графіка $\ln \sigma_0 - \Delta E$ від правила Маєра–Нельделя. Це вказує на те, що правило Маєра–Нельделя виконується в халькогенідних стеклах завдяки наявності структури ближнього порядку.