

## ANALYSIS OF MEYER-NELDEL RULE IN PARTIALLY CRYSTALLINE STATE OF CHALCOGENIDE GLASSES

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We report on the critical analysis of Meyer–Neldel rule, which is generally observed in disordered semiconductors. In the present study, glassy Se-Te system is chosen to see certain situations where MN rule is not obeyed. In the first approach,  $\Delta E$  is varied by partially crystallizing the films to different extent by thermal annealing at different temperatures near crystallization temperature. The second approach is to change  $\Delta E$  by partially crystallizing the sample by light exposure at room temperature for different times. It is observed that MN rule is not followed in both the cases. An explanation of the absence of MN rule, in these two cases, is given in terms of change of mobility by orders of magnitude on crystallization.

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### 1. Introduction

The Meyer-Neldel rule or the compensation law was established empirically in 1937 and subsequently found to apply to various thermally activated phenomena, for example, kinetics and thermodynamics in crystalline, amorphous and liquid semiconductors.

It is well known that pre-exponential factor of electrical conductivity obeys the Meyer-Neldel rule or the compensation law [1]. In the case of a thermally activated electrical conduction, the electrical conductivity ( $\sigma$ ) obeys the Arrhenius equation

$$\sigma_d = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \quad (1)$$

where,  $\Delta E$  is called the activation energy of the thermally activated process under consideration and  $\sigma_0 (= N_c q \mu)$  is called the pre-exponential factor. Here,  $N_c$  is the effective density of states in conduction band,  $q$  is the charge of carrier and  $\mu$  is the mobility of charge carriers.

In most of the amorphous semi-conducting materials,  $\sigma_0$  is found to depend on  $\Delta E$  following the relation:

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

Where,  $\sigma_{00}$  and  $kT_0$  are constants for a given class of materials.  $\sigma_{00}$  is often called as MN pre-exponential factor and  $kT_0$  as MN characteristic energy. Eq. (2) is often referred to as Meyer-Neldel rule (MNR) or the compensation rule.

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This rule is found to be valid in disordered materials when  $\Delta E$  is varied by change in composition or by doping, by surface absorption, light soaking or by preparing films under different conditions [2-8]. This rule has also been observed for liquid semiconductors [9] and in fullerenes [10].

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 semi-conducting devices. The common factor to all these materials is the existence of a large density of localized states.

Chalcogenide glasses are an important class of amorphous semiconductors and, hence, the studies on electrical conductivity of these glasses are important from application point of view as well as to get information about localized states in the mobility gap of these materials.

The validity of MN rule has been reported in the case of chalcogenide glasses also [11-16]. However, in case of these glasses, this rule is observed by the variation of  $\Delta E$  on changing the composition of the glassy alloys in a specific glassy system. Electrical conductivity in dark is measured as a function of temperature for this purpose.

When one changes the  $\Delta E$  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 may be responsible for the observation of MN rule [17], it is desirable to look MN rule in a sample, which is not affected by these complications. Kumar and Kumar [18] and Kushwaha et. al. [19] could change  $\Delta E$  by varying electric field across a particular sample. In this case also, they observed the MN rule in chalcogenide glasses.

In presence of light, Fermi level splits into quasi Fermi levels, the position of which depends on intensity. The activation energy of a particular glass composition can, therefore, be changed in presence of light by varying the intensity of light. In this case also MN rule is found to be valid [20].

In the present work we want to demonstrate that MN rule may not be observed in chalcogenide glasses when  $\Delta E$  is varied in such a way that amorphous state changes to partially crystalline state. This can be done by exposing the sample to white light for different exposure times at room temperature so that photo-crystallization occurs or by thermal annealing near crystallization temperature for different time of annealing so that thermal crystallization occurs. In both these cases sample becomes in partially crystalline state. It may be mentioned here that when  $\Delta E$  is varied by changing composition in a glassy alloy system where samples remains in the amorphous state only, MN rule is followed [11].

To demonstrate the above, we have measured the temperature dependence of d. c. conductivity in amorphous  $\text{Se}_{75}\text{Te}_{25}$  films after exposure of white light at different exposure times where  $\Delta E$  is found to decrease on partial crystallization. MN rule is investigated in this case. Temperature dependence of d. c. conductivity is also measured after annealing amorphous  $\text{Se}_{75}\text{Te}_{25}$  films at various annealing times at 385 K. Here also,  $\Delta E$  is found to decrease on partial crystallization. MN rule is investigated in this case also.

## 2. Experimental

Glassy alloys of  $\text{Se}_{100-x}\text{Te}_x$  (5, 10, 15, and 25) were prepared by quenching technique. The exact proportions of high purity (99.999%) 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 materials were then sealed in evacuated ( $\sim 10^{-5}$  Torr) quartz ampoules (length  $\sim 5$  cm and internal diameter  $\sim 8$  mm). The sealed ampoules containing were heated to  $600^\circ\text{C}$  and were held at that temperature for 12 hours inside a furnace. The temperature of the furnace was raised slowly at a rate of  $3 - 4^\circ\text{C} / \text{minute}$ . 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 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 patterns.

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  $\sim 500$  nm. The coplanar structure (length  $\sim 1.2$  cm and electrode separation  $\sim 0.5$  mm) was used for present measurements. The electrical conductivities in dark as well as in presence of light were studied by mounting them in a specially designed sample holder in which illumination could be achieved through a transparent window. A 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 mounted very near to the films. The heating rate was kept quite small (0.5 K/min.) for these measurements. The light source for these measurements was a 200 W tungsten lamp. Intensity of light was measured by a Luxmeter (Testron, model LX - 101) and the current was measured by a digital electrometer (Keithley, model 614).

### 3. Results

#### 3.1 Temperature dependence of D.C. conductivity after annealing at different times at 385 K

In this case, temperature dependence of d. c. conductivity is measured after annealing the amorphous thin films of  $\text{Se}_{75}\text{Te}_{25}$  at different annealing time (0, 30, 75, 135, 225, 375 min) near crystallization temperature (385 K).  $\ln \sigma_d$  vs  $1000 / T$  curves are found to be straight lines for all the cases. Fig.1 shows such plots in this case. From the slope and intercept of these lines, the values of  $\Delta E$  and  $\sigma_0$  are calculated for all the runs. The values of these parameters are given in Table 1. It is clear from this table that pre- exponential factor is not constant for all annealing times. It is also clear from this figure that conductivity increases with a decrease in activation energy after each annealing time. X -ray diffraction analysis shows that the sample starts partially crystallizing after each annealing time. The change of activation energy in this case may be due to a change in band gap in partially crystalline state. We have checked the presence of MN rule in this case by plotting  $\ln \sigma_0$  vs.  $\Delta E$  curve. Fig. 2 shows such a plot, which is not a straight line and hence is not consistent with equation (2). Similar results were obtained in other compositions also. Results are not shown here.

Table 1. Semi-conduction parameters for thin films of  $\text{Se}_{75}\text{Te}_{25}$  after annealing for different times.

Annealing time (min)	$\Delta E$ (eV)	$\ln \sigma_0$
0	0.55	2.85
30	0.30	-6.38
75	0.32	-4.75
135	0.21	-4.46
225	0.15	-4.79
375	0.14	-4.80

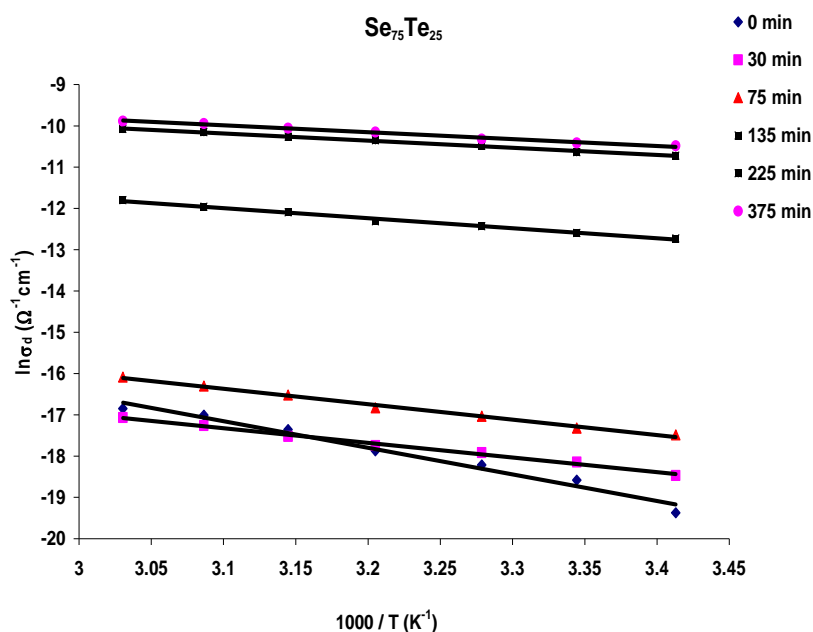


Fig.1. Temperature dependence of d. c. conductivity after annealing the films at different annealing times at 385 K..

### 3.2 Temperature dependence of D.C. conductivity after exposure of white light for different exposure times.

In this approach, d. c. conductivity is studied before and after exposure of white light at different illumination times in amorphous  $\text{Se}_{75}\text{Te}_{25}$  thin films. Results are shown in Fig. 3. It is clear from this figure that conductivity increases with a decrease in activation energy after each exposure. X – ray diffraction analysis shows that the sample starts crystallizing after exposure of light. The change of activation energy in this case may be due to change in band gap in partially crystalline state. From the slope and intercept of  $\ln \sigma_d$  vs.  $1000 / T$  curves,  $\Delta E$  and  $\ln \sigma_0$  for different exposure times have been evaluated. These values are given in Table.4. Plot of  $\ln \sigma_0$  as a function  $\Delta E$  has been made to check the validity of MN rule in this case also. Such a plot is shown in Fig. 4, which shows that MN rule is not valid in this case as  $\ln \sigma_0$  and  $\Delta E$  do not follow a linear relation. Similar results were obtained in other compositions also. Results are not shown here.

Table 2. Semi-conduction parameters for thin films of  $\text{Se}_{75}\text{Te}_{25}$  after exposure to white light for different illumination times

Exposure time(min)	$\Delta E$	$\ln \sigma_0$
0	0.39	-5.78
30	0.33	-7.82
90	0.38	-6.09
180	0.44	-4.19
300	0.21	-10.60
540	0.23	-6.74
1020	0.20	-4.70

#### 4. Discussion

Theoretical considerations have been given below to observe MN rule in chalcogenied glasses by changing the activation energy. For convenience, we have considered 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 given as follows:

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

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

where suffix c and f refer to the mobility edges of the conduction band and the Fermi level respectively. Here we assume that the conduction band and valence band edges contribute equally to the temperature dependence of the band gap. From equation 1, 2 and 3 we get measured activation energy as:

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

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

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

To explain MN rule, Roberts [17] has given a model, which considers the exponential tailing of localized states with energy and distance near valence and conduction bands which is, in general, accepted in case of glassy semiconductors also. Based on the above model, the MN rule is generally explained as follows:

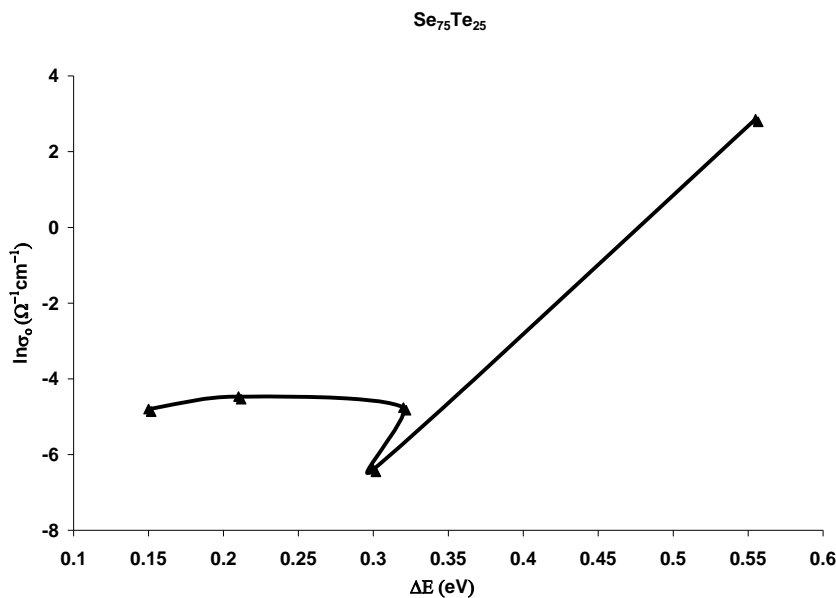


Fig.2. Plot of  $\ln \sigma_0$  versus  $\Delta E$  for  $a\text{-Se}_{75}\text{Te}_{25}$  thin films after annealing at different annealing times at 385K.

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 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 in turn gives rise to the MN rule. This happens because the DOS increases at least as fast as the Fermi function falls off the energy due to exponential distribution of density of states with energy. The wings of the Fermi function contribute to occupancy.

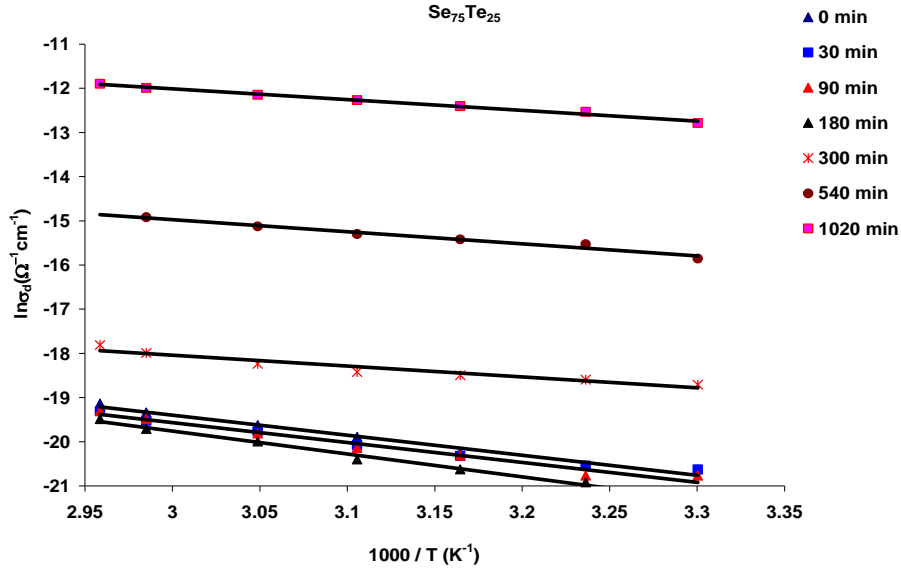


Fig. 3. Temperature dependence of d. c. conductivity for  $a\text{-Se}_{75}\text{Te}_{25}$  thin films after exposure of light for different exposure times.

In the present work, we find that when  $\Delta E$  is varied by partial crystallization either by thermal crystallization or by photo crystallization, MN rule is not valid. This indicates that MN rule is not followed if the amorphous state is not maintained. The absence of MN rule in these two cases may be due to large mobility change in crystalline state as compared to amorphous state. When samples are in amorphous state only, mobility of charge carriers may not be drastically different even if the atomic percentage of one component is changed in a glassy system. On the other hand, when sample starts crystallizing, the partially crystalline state may have quite different mobility as mobility may be many orders of magnitude in crystalline state as compared to amorphous state. Since the mobility appears in the expression of  $\sigma_0$  (see equation 6), exponential dependence on energy will be dominant only when  $\mu$  increases slightly or remain unchanged. In the present case, i.e., during photo crystallization or thermal crystallization, mobility change by orders of magnitude may affect the exponential decrease of  $\sigma_0$  with decrease of activation energy  $\Delta E$  on crystallization.

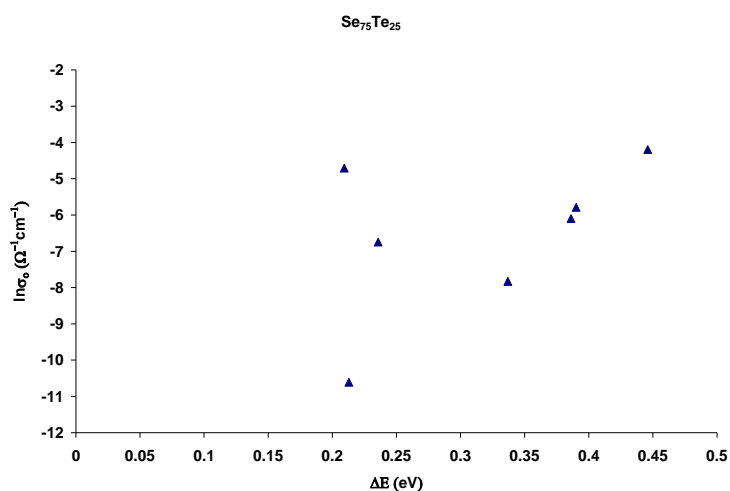


Fig.4. Plot of  $\ln \sigma_0$  versus  $\Delta E$  for  $a\text{-Se}_{75}\text{Te}_{25}$  thin films after light exposure for different times.

The present study thus indicate that to observe MN rule, the process by which  $\Delta E$  is changed should be such that the mobility is not changed drastically, i.e., by orders of magnitude. The model of statistical shift of Fermi level may explain the occurrence of MN rule only when mobility changes are not drastic during the process of  $\Delta E$  change

## 5. Conclusions

A critical analysis of Meyer–Neldel rule is made to see certain situations where MN rule is not obeyed. For this study,  $\Delta E$  is varied by partially crystallizing the films to different extent by thermal annealing at different temperatures near crystallization temperature. The other approach is to change  $\Delta E$  by partially crystallizing the sample by light exposure at room temperature for different times. It is observed that MN rule is not followed in both the cases. An explanation of the absence of MN rule, in these cases, is given in terms of change of mobility by orders of magnitude on crystallization.

## References

- [1] W. Meyer, H. Neldel, Z. Tech. Phys., **12**, 588 (1937)
- [2] D. E. Carlson, C. R. Wronski, "Amorphous Semiconductors" (Ed. By M. H. Brodsky, Springer Berlin, Heidelberg, New York (1979).
- [3] W. E. Spear, D. Allan, P. Lecomber, A. Gaith, Phil. Mag. B, **41**, 419 (1980).
- [4] D. L. Staebler, C. R. Wronski, Appl. Phys. Lett., **21**, 292 (1977).
- [5] M. Tanielian, Phil. Mag. B, **45**, 435 (1982).
- [6] R. S. Crandall, Phys. Rev. B, **43**, 4057 (1991).
- [7] D. A. Anderson, W. Paul, Phil. Mag. B, **45**, 1 (1982).
- [8] T. Drusedau, R. Bindemann, Phys. Stat. Sol.(b), **136**, K 61 (1986).
- [9] J. Fortner, V. G. Karpov, Marie-Louise Saboungi, Appl. Phys. Lett., **66**, 997 (1995).
- [10] J. C. Wang, Y. F. Chen, Appl. Phys. Lett., **73**, 948 (1998).
- [11] R. Arora, A. Kumar, Phys. Stat. Sol. (a), **125**, 273 (1991).
- [12] S. K. Dwivedi, M. Dixit, A. Kumar, J. Mater. Sci. Lett., **17**, 233 (1998).
- [13] A. Yelon, B. Movaghar, Appl. Phys. Lett., **71**, 3549 (1997).
- [14] K. Shimakawa, F. Abdel-Wahab, Appl. Phys. Lett., **70**, 652 (1997).

- [15] A. Abd-El Mongy, Egypt. J. Sol., **24**, 1 (2001).
- [16] Y. L. A. El-Kady, Physica B: Condensed Matter, **305**, 259 (2001).
- [17] G. G. Roberts, J. Phys. C, **4**, 3167 (1971).
- [18] D. Kumar, S. Kumar, Jap. J. Appl. Phys. **43**, 901 (2004).
- [19] V. S. Kushwaha, N. Mehta, N. Kushwaha, A. Kumar, J. Optoelectron. Adv. Mater. **7**, 2035 (2005).
- [20] D. Kumar, S. Kumar, J. Optoelectron. Adv. Mater. **6**, 777 (2004)