

## OBSERVATION OF MEYER-NELDEL RULE IN a- Se<sub>60</sub>Te<sub>20</sub>Ge<sub>20</sub> THIN FILMS IN PRESENCE OF LIGHT

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In general, in case of semiconductors, conductivity ( $\sigma$ ) varies exponentially with temperature (T), i.e.,  $\sigma = \sigma_0 \exp [-\Delta E/k T]$ . In most of the materials,  $\sigma_0$  does not depend on  $\Delta E$ . However, in many amorphous and liquid semiconductors and many other class of materials,  $\sigma_0$  is found to increase exponentially with  $\Delta E$ . This is called Meyer- Neldel rule. This rule is generally verified by selecting different compositions of different  $\Delta E$  in a given class of materials. This opens a possibility of change in various other physical properties apart from  $\Delta E$ . In the present paper, we report on the observation of Meyer- Neldel rule where  $\Delta E$  is varied by varying the intensity of light while measuring the photoconductivity in amorphous thin films of Se<sub>60</sub>Te<sub>20</sub>Ge<sub>20</sub> instead of changing composition of the glassy system. The observation of Meyer-Neldel rule in the present case indicates that this rule is more general and does not fail due to change in density or distribution of defect states or any other physical property due to change in composition.

### 1. Introduction

The Meyer-Neldel rule or the compensation law was established empirically in 1937 [1] and subsequently found to apply to various thermally activated phenomena, for example, kinetics and thermodynamics in crystalline, amorphous and liquid semiconductors.

In the case of a thermally activated electrical conduction, the rule states that the conductivity ( $\sigma$ ) obeys the equation

$$\sigma = \sigma_0 \exp [-\Delta E/k T] \quad (1)$$

where  $\Delta E$  is called the activation energy and  $\sigma_0$  is called the pre-exponential factor. In most of the semiconducting materials,  $\sigma_0$  does not depend on  $\Delta E$ . However in some cases  $\sigma_0$  correlates with the activation energy  $\Delta E$  as

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

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. Equation 2 is often refereed to as MN rule or the compensation rule.

This rule is generally observed in disordered materials. In the class of amorphous semiconductors, the MN rule has been reported for a-Si:H films in which  $\Delta E$  is varied 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 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. Dark conductivity is measured as a function of temperature for this purpose.

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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 [17] for the observation of MN rule, it is desirable to look MN rule in a sample, which is not affected by these complications. In our earlier communication [18], we could change  $\Delta E$  by varying electric field across a particular sample and verify MN rule.

In presence of light, Fermi level splits into quasi Fermi levels, the position of which depends on intensity [19]. The activation energy of a particular glass composition can, therefore, be changed in presence of light by varying the intensity of light. 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.

With the above point of view, we have measured the temperature dependence of conductivity at different intensities in amorphous thin films of  $\text{Se}_{60}\text{Te}_{20}\text{Ge}_{20}$ . This particular composition is selected due to good photosensitivity so that the appreciable shift of the Fermi level could be observed at different intensities of light.

Section 2 describes the experimental details of sample preparation and measurements. The results are presented and discussed in section 3. The last section deals with the conclusions drawn from the present work.

## 2. Experimental

Glassy alloy of  $\text{Se}_{60}\text{Te}_{20}\text{Ge}_{20}$  was prepared by quenching technique. High purity (99.999 %) materials were weighed according to their atomic percentages and are sealed in quartz ampoules (length  $\sim 5$  cm and internal dia  $\sim 8$  mm) with a vacuum  $\sim 10^{-5}$  Torr. The ampoules containing the materials were heated to 1000 °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, 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 homogenous glassy alloy.

After rocking for about 10 hours, the obtained melt was cooled rapidly by removing the ampoule from the furnace and dropping to ice-cooled water. The quenched sample of  $\text{Se}_{60}\text{Te}_{20}\text{Ge}_{20}$  was taken out by breaking the quartz ampoule.

Thin films of this glass 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 is  $\sim 500$  nm. The co-planar structure (length  $\sim 1.4$  cm and electrode separation  $\sim 0.5$  mm) are used for the present measurements. Before measuring the conductivity, the films are first annealed at 340K for one hour in a vacuum  $\sim 10^{-2}$  Torr.

Thin films samples were mounted in a specially designed sample holder, which has a transparent window to shine light. A vacuum  $\sim 10^{-2}$  Torr was maintained throughout the measurements. The temperature of the films was controlled by mounting a heater inside the sample holder, and measured by a calibrated copper- constantan thermocouple mounted very near to the films. The source of light is a 200 W tungsten lamp. Interference filters were used to get a desired wavelength. The present measurements have been made at a wavelength of 620 nm. The intensity of light was varied by changing the voltage across the lamp and measured by a lux - meter.

I-V characteristics were found to be linear and symmetric up to 100 V. The present measurements were, however, made by applying only 50 V across the films. The resulting current was measured by a digital Pico-Ammeter. The heating rate was kept quite small (0.5 K/min) for these measurements.

## 3. Results and discussion

The temperature dependence of conductivity was studied in dark as well as in presence of light at different intensities in a-  $\text{Se}_{60}\text{Te}_{20}\text{Ge}_{20}$ . Fig. 1 shows such results between 305 K to 335 K. The conductivity ( $\sigma$ ) varies exponentially with temperature as  $\ln \sigma$  vs  $1000/T$  curves are straight lines (see Fig. 1). Such a behaviour is consistent with equation 1.

From the slope and the intercepts of Fig. 1, the values of  $\Delta E$  and  $\sigma_0$  have been calculated and these values are given in Table 1 for different intensities. Fig. 2 shows a plot of  $\ln \sigma_0$  vs  $\Delta E$  which is a straight line indicating that  $\sigma_0$  varies exponentially with  $\Delta E$  following the relation (2).

The slope of  $\ln \sigma_0$  vs  $\Delta E$  curve yields the values of  $(kT_0)^{-1} \sim 28 \text{ (eV)}^{-1}$  and  $\sigma_{00} \sim 6.51 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$  for a- $\text{Se}_{60}\text{Te}_{20}\text{Ge}_{20}$  thin films. Using these values of  $(kT_0)^{-1}$  and  $\sigma_{00}$ , the expected  $\sigma_0$  values have been calculated for the above glassy alloy and compared with the reported values (see Table 1). An overall good agreement confirms the validity of Meyer- Neldel rule.

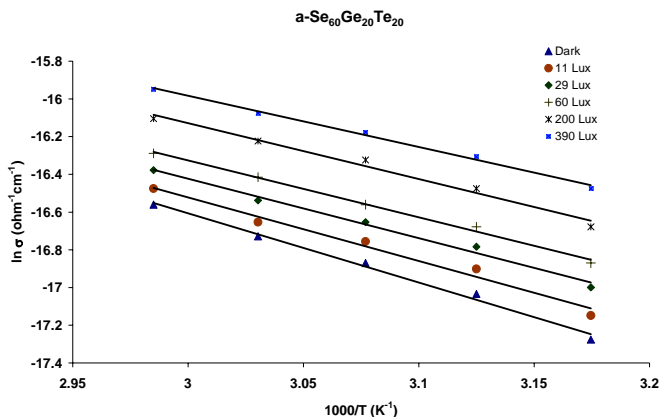


Fig. 1. Plot of the conductivity as a function of reciprocal temperature at different light intensities in a- $\text{Se}_{60}\text{Te}_{20}\text{Ge}_{20}$ .

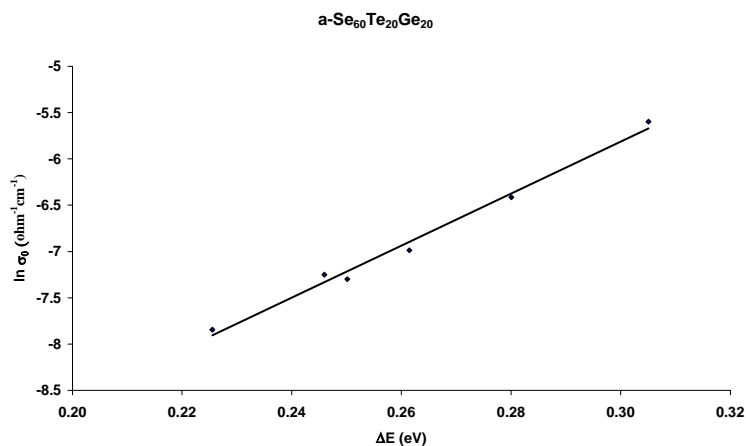


Fig. 2. Plot of pre-exponential factor  $\sigma_0$  vs activation energy  $\Delta E$  in a- $\text{Se}_{60}\text{Te}_{20}\text{Ge}_{20}$ .

In case of dark conductivity, 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. Based on the above model the MN rule can be understood as follows:

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. The conditions which prevail in dark, might also prevail in presence of light which may cause MN rule in the present case.

While the above approach is appealing, Fortner et al. [9,20] have shown that it can not explain the MN rule for liquid semiconductors. Others [13,21,22] speculate that MN rule arises because of the entropy of multiple excitations. This approach is very general and can not be an universal explanation for this rule [23]. Fortner et. al. [9] propose that MN rule arises from hopping conductivity.

The above reports show that, till now, there is no universal explanation for MN rule. In the present work also, we can not identify the exact origin but we have shown that MN rule is more general in chalcogenide glasses and does not depend on the way how  $\Delta E$  is changed. Also, the change in physical properties due to change in composition can be ruled out in the present case.

#### 4. Conclusion

Amorphous thin films of  $\text{Se}_{60}\text{Te}_{20}\text{Ge}_{20}$  have been prepared by vacuum evaporation technique. The temperature dependence of conductivity was studied in dark as well as in presence of light at different intensities between 305 K- 335 K. We find that conductivity in dark as well as in presence of light is thermally activated. The activation energy depends on the intensity of light. The activation energy and pre-exponential factor in presence of light satisfies the Meyer-Neldel rule. In the present case, activation energy is varied by changing the intensity of light instead of changing the composition of the glassy alloy. This shows that Meyer-Neldel rule is more general in these materials as it does not depend on the way how the activation energy is changed.

Table 1. Semiconduction parameters for a-  $\text{Se}_{60}\text{Te}_{20}\text{Ge}_{20}$ .

Intensity (Lux)	$\Delta E$ (eV)	$\sigma_0$ ( $\Omega^{-1} \text{cm}^{-1}$ )	$\sigma_0 = \sigma_{00} \exp [\Delta E/k T_0]$ ( $\Omega^{-1} \text{cm}^{-1}$ )
0	0.305	$3.71 \times 10^{-3}$	$3.34 \times 10^{-3}$
11	0.280	$1.64 \times 10^{-3}$	$1.66 \times 10^{-3}$
29	0.261	$9.23 \times 10^{-4}$	$9.84 \times 10^{-4}$
60	0.250	$6.76 \times 10^{-4}$	$7.17 \times 10^{-4}$
200	0.246	$7.09 \times 10^{-4}$	$6.38 \times 10^{-4}$
390	0.226	$3.92 \times 10^{-4}$	$3.60 \times 10^{-4}$

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