

## PRE-EXPONENTIAL FACTOR OF A.C. CONDUCTION IN $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$ (M = Cd, In, Sb) CHALCOGENIDE GLASSES

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In many amorphous and liquid semiconductors and other class of materials, Meyer-Neldel rule is observed in the d.c. conductivity, where the pre-exponential factor ( $\sigma_0$ ) is found to increase exponentially with the activation energy ( $\Delta E$ ). In the present paper, we report on the observation of Meyer- Neldel rule in case of a.c. conductivity near the room temperature in bulk samples of  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  (M = Cd, In, Sb) chalcogenide glasses. The approximate variation of a.c. conductivity with temperature is found to be exponential and the activation energy is found to vary with frequency. The observation of Meyer-Neldel rule in the present study is explained in terms of compensation effect in relaxation time.

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### 1. Introduction

The Meyer-Neldel rule or the compensation law was established [1] empirically in 1937 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

$$\sigma = \sigma_0 \exp\left[\frac{-\Delta E}{k T}\right], \quad (1)$$

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

$$\sigma_0 = \sigma_{00} \exp\left[\frac{\Delta E}{k T_0}\right], \quad (2)$$

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

In disordered materials, this rule has generally been reported for d.c. conduction e.g., in a-Si:H films where  $\Delta E$  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

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[11-20]. However, in case of these glasses this rule is observed by the variation of  $\Delta E$  on changing the composition of the glassy alloys [11-17] in a specific glassy system or by changing  $\Delta E$  by varying electric field across a particular sample in dark or by varying the intensity of light [18-20]. The application of the MN rule in case of a.c. conductivity studies has not been studied in detail. This rule in case of a.c. conductivity has recently been observed by Abdel-Wahab in some chalcogenide glasses [21,22].

In the present work, we have also tried MN rule in the a.c. conductivity measurements in  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Sb}$ ) chalcogenide glasses. For this, we have measured the temperature dependence of a.c. conductivity at different frequencies in audio frequency range.

## 2. Experimental details

Glassy alloys of  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Sb}$ ) chalcogenide glasses were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te, Cd, In 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 materials were then sealed in evacuated ( $\sim 10^{-5}$  Torr) quartz ampoules (length  $\sim 5$ cm and internal diameter  $\sim 8$  mm). Each ampoule containing material was heated to  $600$  °C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of  $3 - 4$  °C / minute. 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 12 hours, the obtained melt was cooled rapidly by removing the ampoule from the furnace and dropping it 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 (XRD) technique. Absence of any sharp peak in XRD pattern confirms the amorphous nature of  $\text{Se}_{80}\text{Te}_{20}$  and  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Sb}$ ) chalcogenide glasses.

The chalcogenide glasses thus prepared were ground to a very fine powder and pellets (diameter  $\sim 6$  mm and thickness  $\sim 1$ mm) were obtained by compressing the powder in a die at a load of 5 Tons. The pellets were coated with vacuum deposited indium films to ensure good electrical contact between sample and the electrodes. The pellets were mounted in between two steel electrodes of a metallic sample holder for electrical conductivity measurements. The temperature measurement was facilitated by a copper-constantan thermocouple mounted very near to the sample. A vacuum of  $\sim 10^{-2}$  Torr was maintained over the entire temperature range.

For calculating a. c. conductivity, conductance and capacitance were measured using a GR 1620 AP capacitance measuring assembly. The parallel conductance was measured and a.c. conductivity was calculated. The experimental results for the temperature dependence of the a.c. conductivity  $\sigma_{ac}(\omega)$  are obtained by subtracting the d.c. conductivity from the total measured conductivity  $\sigma_T$ . Three terminal measurements were performed to avoid the stray capacitances.

## 3. Results and discussion

The temperature dependence (above the room temperature) of a.c. conductivity in  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Sb}$ ) chalcogenide glasses is studied at different audio frequencies. It has been found that above the room temperature,  $\ln \sigma_{ac}$  vs  $1000/T$  curves are almost straight lines at different frequencies as shown in Figs. 1-3 for the present glassy alloys.

The above results show that, the variation of a.c. conductivity with temperature can approximately be expressed by an exponential relation in the high temperature range:

$$\sigma_{ac} = \sigma_0 \exp\left[\frac{-\Delta E}{kT}\right], \quad (3)$$

where  $\Delta E$  is called the activation energy for a.c. conduction and  $\sigma_0$  is called the pre-exponential factor. As evident from Eqn (3), the pre-exponential factor  $\sigma_0$  and a.c. activation energy  $\Delta E$  can be obtained from the semi-logarithmic plots of the a.c. conductivity versus reciprocal temperature. Hence, the activation energy  $\Delta E$  is determined from the slope of the approximate straight lines in the resulting

plots at different frequencies (see Figs. 1-3). These straight lines are obtained by the best fit to the experimental data using the least squares method. The intercept of line gives the value of  $\ln \sigma_0$ .

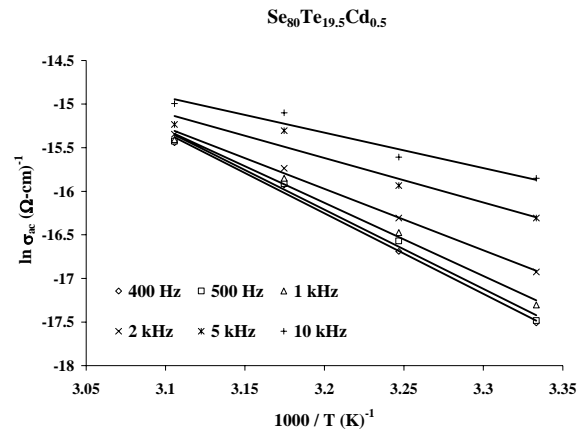


Fig. 1. Linear plots of  $\ln \sigma_{ac}$  vs  $1000/T$  at different audio frequencies for glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{Cd}_{0.5}$  alloy

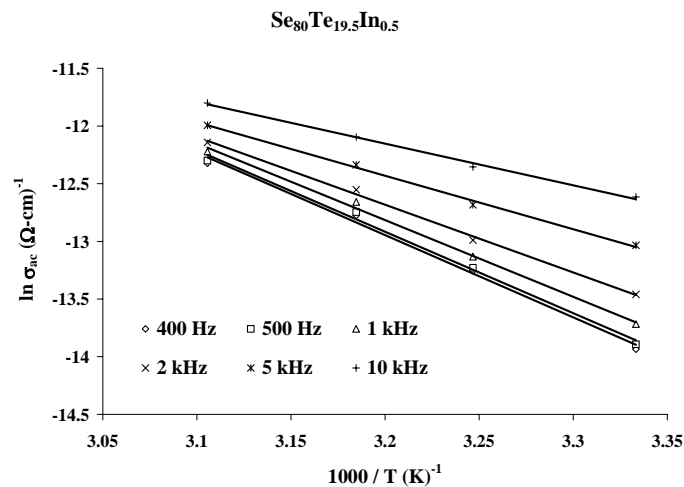


Fig. 2. Linear plots of  $\ln \sigma_{ac}$  vs  $1000/T$  at different audio frequencies for glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{In}_{0.5}$  alloy

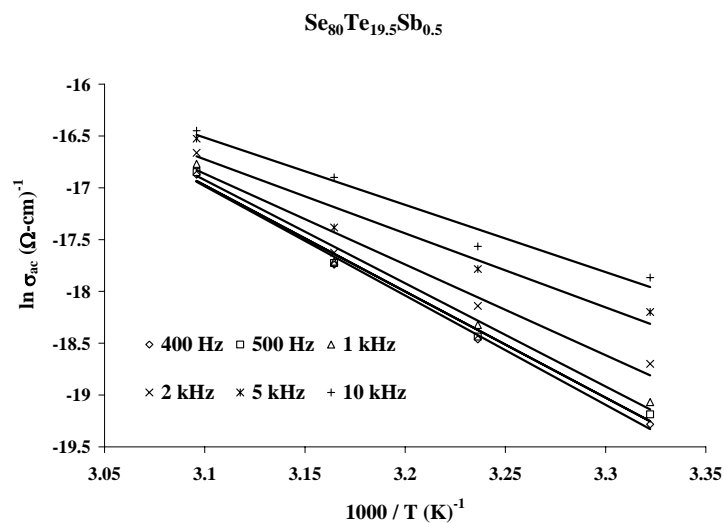


Fig. 3. Linear plots of  $\ln \sigma_{ac}$  vs  $1000/T$  at different audio frequencies for glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{Sb}_{0.5}$  alloy

The values of  $\Delta E$  and  $\sigma_0$  are given in Tables 1-3 for  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Sb}$ ) alloys. Figs. 5-6 show the plots of  $\ln \sigma_0$  vs  $\Delta E$  for different glassy alloys, which are straight lines indicating that  $\sigma_0$  varies exponentially with  $\Delta E$  following the relation given by Eq. 2.

Table 1. Semi-conduction parameters for  $\text{Se}_{80}\text{Te}_{19.5}\text{Cd}_{0.5}$  alloy.

Frequency (Hz)	$\Delta E$ (eV)	$\sigma_0$ ( $\Omega\text{-cm}$ ) <sup>-1</sup>	$\sigma_0 = \sigma_{00} \exp [\Delta E / k T_0]$ ( $\Omega\text{-cm}$ ) <sup>-1</sup>
400	0.79	$1.7 \times 10^{-6}$	$2.0 \times 10^{-6}$
500	0.78	$2.6 \times 10^{-6}$	$2.7 \times 10^{-6}$
1000	0.72	$2.2 \times 10^{-6}$	$2.2 \times 10^{-6}$
2000	0.60	$1.4 \times 10^{-3}$	$1.3 \times 10^{-3}$
5000	0.44	0.48	0.46
10000	0.35	10.1	10.8

Table 2. Semi-conduction parameters for  $\text{Se}_{80}\text{Te}_{19.5}\text{In}_{0.5}$  alloy.

Frequency (Hz)	$\Delta E$ (eV)	$\sigma_0$ ( $\Omega\text{-cm}$ ) <sup>-1</sup>	$\sigma_0 = \sigma_{00} \exp [\Delta E / k T_0]$ ( $\Omega\text{-cm}$ ) <sup>-1</sup>
400	0.61	$5.2 \times 10^{-5}$	$5.0 \times 10^{-5}$
500	0.60	$6.3 \times 10^{-6}$	$6.0 \times 10^{-6}$
1000	0.57	$2.1 \times 10^{-4}$	$2.0 \times 10^{-4}$
2000	0.50	$2.2 \times 10^{-3}$	$2.0 \times 10^{-3}$
5000	0.39	$8.9 \times 10^{-2}$	$8.7 \times 10^{-2}$
10000	0.31	1.81	1.86

Table 3. Semi-conduction parameters for  $\text{Se}_{80}\text{Te}_{19.5}\text{Sb}_{0.5}$  alloy.

Frequency (Hz)	$\Delta E$ (eV)	$\sigma_0$ ( $\Omega\text{-cm}$ ) <sup>-1</sup>	$\sigma_0 = \sigma_{00} \exp [\Delta E / k T_0]$ ( $\Omega\text{-cm}$ ) <sup>-1</sup>
400	0.91	$1.5 \times 10^{-7}$	$2.0 \times 10^{-7}$
500	0.88	$3.7 \times 10^{-7}$	$4.0 \times 10^{-7}$
1000	0.86	$8.8 \times 10^{-7}$	$9.0 \times 10^{-7}$
2000	0.75	$3.5 \times 10^{-5}$	$3.0 \times 10^{-5}$
5000	0.61	$4.4 \times 10^{-3}$	$4.0 \times 10^{-3}$
10000	0.56	$2.6 \times 10^{-2}$	$2.9 \times 10^{-2}$

The slope of  $\ln \sigma_0$  vs  $\Delta E$  curve yields the values of  $(kT_0)^{-1}$  and  $\ln \sigma_{00}$  for the present glasses. Using these values of  $(kT_0)^{-1}$  and  $\ln \sigma_{00}$ , the expected  $\ln \sigma_0$  values have been calculated for the glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Sb}$ ) alloys and compared with the reported values (see Tables 1-4). An overall good agreement confirms the validity of Meyer-Neldel rule.

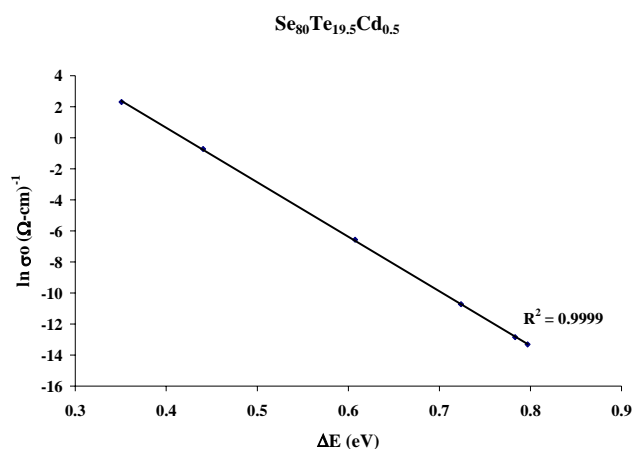


Fig. 4. Plots of pre-exponential factor  $\sigma_0$  vs activation energy  $\Delta E$  for glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{Cd}_{0.5}$  alloy

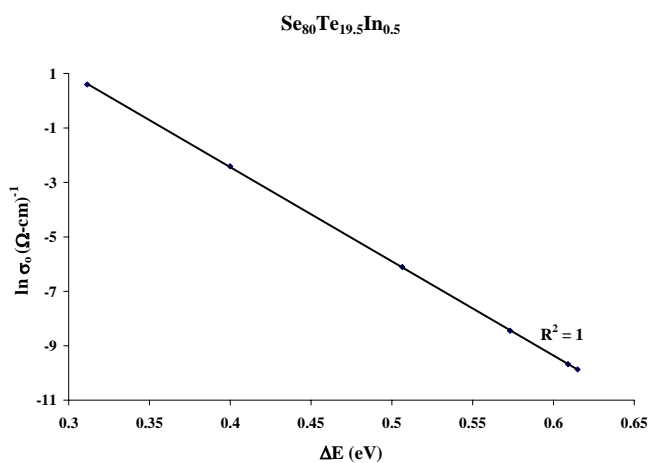


Fig. 5. Plots of pre-exponential factor  $\sigma_0$  vs activation energy  $\Delta E$  for glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{In}_{0.5}$  alloy

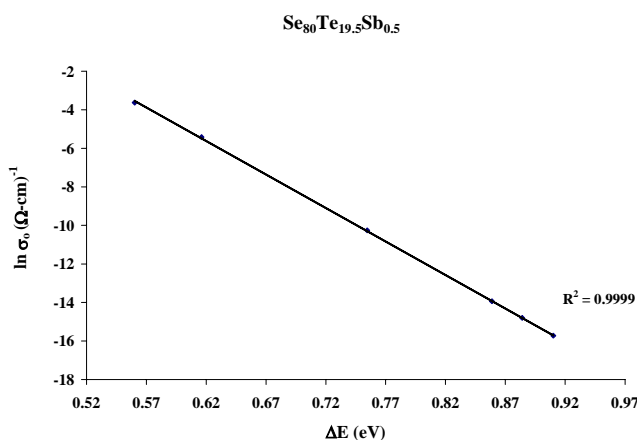


Fig. 6. Plots of pre-exponential factor  $\sigma_0$  vs activation energy  $\Delta E$  for glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{Sb}_{0.5}$  alloys

A.C. conductivity measurements have been widely used to investigate the nature of defect centers in disordered systems since it is assumed that they are responsible for this type of conduction. The correlated barrier-hopping (CBH) model [23] has been extensively applied to the chalcogenide glassy semiconductors.

In the CBH model [23, 24], the electrons in charged defect states hop over the Coulombic barrier whose height,  $W$ , is given as

$$W = W_m - \left( \frac{ne^2}{\pi \varepsilon \varepsilon_0 r} \right), \quad (4)$$

where  $W_m$  is the maximum barrier height,  $\varepsilon$  is the bulk dielectric constant,  $\varepsilon_0$  is the permittivity of free space,  $r$  is the distance between hopping sites and  $n$  is the number of electrons involved in a hop ( $n = 1$  and  $n = 2$  for the single polaron and bipolaron processes, respectively).

The relaxation time,  $\tau$ , for the electrons to hop over a barrier of height,  $W$ , is given by

$$\tau = \tau_0 \exp\left(\frac{W}{kT}\right), \quad (5)$$

where  $\tau_0$  is a characteristic relaxation time which is of the order of an atomic vibrational period and  $k$  is the Boltzmann constant. The ac conductivity,  $\sigma_{ac}(\omega)$ , for bipolaron hopping originating from intimate  $D^+$  and  $D^-$  pairs having a non-random distribution can be written as

$$\sigma_{ac} = \frac{1}{6} n \pi^3 \varepsilon \varepsilon_0 N N_p \omega (R_\omega)^6 \exp\left(\frac{e^2}{4\pi \varepsilon \varepsilon_0 k T_g R_\omega}\right), \quad (6)$$

where the hopping distance,  $R_\omega$ , is given by

$$R_\omega = \left( \frac{2e^2}{\pi \varepsilon \varepsilon_0 W_m} \right) \left[ 1 + \frac{kT}{W_m \ln(\tau_0 \omega)} \right]^{-1} \quad (7)$$

Here  $N$  is the density of localized states at which carriers exist,  $N_p$  is the density of localized states to which the carriers hop,  $T_g$  is the glass transition temperature and  $n = 2$  and  $n = 1$  for bipolaron and single polaron hopping, respectively. The maximum height  $W_m$  is regarded as the band gap.

Recently, a new approach has been suggested for the CBH model in the chalcogenide glasses [21, 22]. It is reported in this approach that the relaxation time formula is activated, and it includes the Meyer-Neldel rule term rather than its simple activated form.

The chalcogenide glassy material during a.c. conduction can be considered as a medium consisting of network of resistors and capacitors [25]. If the local conductivity is thermally activated, and all capacitors are assumed to be equal, then the resistance and capacitance between pairs of sites are given by:

$$R = R_0 \exp\left(\frac{W}{kT}\right), \quad (8)$$

and

$$C = C_0, \quad (9)$$

where  $R_0$  and  $C_0$  are constant. For the whole system, a broad distribution of energy barriers<sup>25</sup>  $P(W)$  can be anticipated, and the resistance of the sample is given by:

$$R = R_0 P(W) \exp\left(\frac{W}{kT}\right), \quad (10)$$

The time constant of the circuit is:

$$\tau = RC = R_0 C_0 P(W) \exp\left(\frac{W}{kT}\right) = \tau_0 P(W) \exp\left(\frac{W}{kT}\right), \quad (11)$$

where

$$\tau = R_0 C_0 \quad (12)$$

For  $P(W) = \text{constant}$ , the relaxation time has an Arrhenius form (Eqn. 5).  
If the distribution of the energy barriers has an exponential form [25-29]:

$$P(W) \approx \exp\left(\frac{-W}{kT_0}\right) \quad (13)$$

where  $T_0$  is the characteristic temperature, then Eqn. (5) yields:

$$\tau = \tau_0 \exp\left(\frac{W}{kT}\right) \exp\left(\frac{-W}{kT_0}\right) \quad (14)$$

This is exactly the same as MN rule formula.

In the present case, the activation energy of a.c. conduction varies with increase in frequency and it satisfies MN relation with pre-exponential factor. This may be due to compensation effect in relaxation time as suggested by Abdel-Wahab for some chalcogenide glasses [21,22].

#### 4. Conclusion

In the present study, it has been found that a.c. conductivity shows strong temperature dependence and can be considered to be thermally activated with single activation energy for the glassy  $\text{Se}_{80}\text{Te}_{19.5}\text{M}_{0.5}$  ( $M = \text{Cd, In, Sb}$ ) alloys. The activation energy, however, depends on the applied frequency. The activation energy and pre-exponential factor for a.c. conduction satisfies the Meyer-Neldel rule. The reason for the observation of MN rule in a.c. conductivity may be due to fact that the relaxation time itself follows the MN rule.

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