The Meyer- Neldel Rule in $Se_{70}Te_{30-x}In_x$

A. Abd-El Mongy

Department of Physics, Faculty of Science, Helwan University,
Ein Helwan, Cairo, Egypt.

The electrical conductivity in Se_{70} Te_{30-x} In_x ($0<x<10$) at. % exhibited an exponential thermally activated behavior with single conduction mechanism for bulk and thin films. Film conductivities were found to be about three orders of magnitude lower than those of their bulk counterparts bulk samples. An obvious decrease in the conductivity on incorporation of indium to the binary $Se_{70}Te_{30-x}$ film was observed. An experimental correlation between the activation energy and the pre-exponential factor was observed indicating the validity of Meyer-Neldel rule in the studied samples. Huge difference in σ_0 values was obtained and hence σ_0 may not directly related to the microscopic conductivity.

Introduction:

In semiconducting materials the dc conductivity (σ) near room temperature is found to obey Armenia's formula:

$$\sigma = \sigma_o \exp(- \Delta E/ KT) \quad (1)$$

Surprisingly, there is a quite often an exponential relation between the activation energy ΔE and the pre-exponential factor σ_o, known as the Meyer-Neldel (MN) rule [1]. The MN rule can be written as:

$$\sigma_o = \sigma_{oo} \exp (\Delta E/KTMN) \quad (2)$$

where σ_{oo} is the pre-pre-exponential and T_{MN} is a characteristic temperature. The relation has been observed experimentally in a wide variety of single crystal and polycrystalline semiconductors [2], in hydrogenated amorphous silicon [3&4], liquid semiconductor [5], and in binary alloys [6]. Although several models have been proposed to explain the MN rule, each explanation is valid only for limited class of solids. In organic semiconductor a model of thermally excited electron tunneling through intermolecular barriers is suggested [7]. In amorphous hydrogenated silicon, Irsingler et al. [8] suggested that whenever the conductivity activation energy is changed the conductivity pre-exponential factor has to be corrected accordingly. In liquid semiconductor, Fortner et al. [5] assumed that multiphonon hopping could explain MN rule of the electrical conductivity. Narasimhan and Arora [6] showed the validity of MN rule in III-V compound semiconductor and reported E_{MN} [$\Delta E/KT_{MN}$] of (25-50 meV). Coutts and Pearsall [2] reported E_{MN} = 40 meV for some chalcogenides. Dwivedi [9] reported E_{MN} (0.2-0.7 eV) for some amorphous chalcogenide systems. Roberts [10] assumed that if the tail states are exponential with energy and Fermi level is controlled by deeper level in the gap, the MN rule is obeyed. Jackson [11] concluded that the energy factor of the MN rule is related to the energy distribution of the traps while the pre-factor is related to the microscopic transport properties.

Evidence for the validity of the MN rule in chalcogenides has not been frequently reported although sufficient data on conductivity are available in the literature. The object of the present work was then to investigate the dc conductivity of the system $Se_{70}Te_{30-x}$ In_x ($0<x<10$) around room temperature. Study was also focused on comparing the conductivity parameters in bulk and film samples. In addition it was aimed to examine whether or not the MN rule is obeyed in such chalcogenides. Theoretical models, proposed for the MN rule, are presented and the results are analyzed with the help of these models.

Experimental procedure:

Glassy alloys of the system Se_{70} Te_{30-x} In_x (x= 0, 2.5, 5, 7.5, 10) were prepared by the normal quenching technique. The raw materials (99.999% pure) were weighted according to their atomic percentages and sealed in an evacuated (10^{-5} Torr) quartz ampoule. The ampoules were heated at a temperature around 850 ^{o}C for 30 hours, under air atmosphere with continuous rotating (using a mechanical system) to make homogeneous melt. The melt was quenched in ice – water and cast into a disc of 30mm in diameter and 2mm thick. Careful grinding and polishing were done before preserving samples in a desicator.

Films were made from the as- prepared alloys by using a vacuum evaporation technique (Edwards coating system E306A) at room temperature and pressure of 10^{-5} Torr. During the film preparation, the thickness was controlled by means of a thickness monitor. After deposition an optical method, by applying multiple-beam Fizeau fringes at reflection, was used to give the accurate film thickness (about 70nm).

The potential difference between hot and cold contacts was used to test the conductivity type. The planar geometry configuration was used for the conductivity measurement. The electrode geometry was measured using a travelling microscope. Aluminum electrodes were deposited at vacuum of about 10^{-3} Torr and a thin layer of silver paste was used to ensure good ohmic contacts. The ohmic nature of the contacts was investigated by applying the voltage in both directions and measuring the corresponding current. A constant voltage (in the ohmic region) was applied and a Keithley electrometer was used to detect the current passing through the samples. The temperature was measured in the range 300 K< T< 360 K by means of an Oxford temperature controller (DTC2). Using the dimensions of the specimens, the distance between electrodes L, the electrode width b, the dc conductivity was calculated according to the relation $\sigma = l/(Rdb)$, where R and d are the resistance and the thickness of the sample respectively.

Results:

The amorphous nature of both bulk and film samples was proved by XRD, using Diano diffractometer (Ni filtered Co-Kα radiation at 50 kV and 30 mA).

The hot-point probe method showed that the investigated samples are p-type. In fact a weak response was observed for film specimens, which was attributed to their high resistivities.

Figures (1 & 2) show the temperature dependence of the dc conductivity in bulk and film samples respectively for different indium concentration. For all samples and in the measured temperature range the plot of lnσ-1/T showed an activated behaviour with one mode of conduction. The straight lines indicated the validity of Arrhenius equation. From the slope and the intercept (extrapolation of the line to 1/T = 0), the activation energy ΔE and the conductivity pre-exponential σ_o values are calculated subsequently. Inspection of results reveals the increase of conductivity (decrease of ΔE) as indium content is increased in bulk and film forms. However in film samples the conductivity of the specimen without indium showed anomalous behavior. Figures (3 & 4) depict a linear dependence of ln σ_0 when plotted versus ΔE. The slope of these lines yield $(KT_{MN})^{-1}$ = 21.36 $(eV)^{-1}$ and intercept at σ_{00} (line extrapolated to ΔE=0) =3.75 x10^{-3} S cm^{-1} in bulk while in film specimens the respective values are 26.76 $(eV)^{-1}$ & 2.9x10^{-6} S cm^{-1}. As can be seen the magnitude of σ_0 in film samples of different In concentration is very much different.

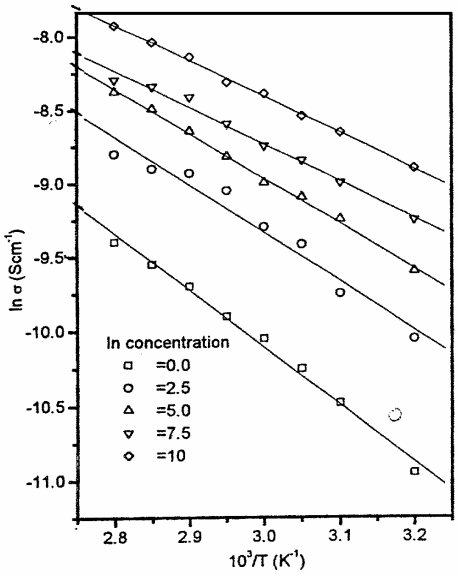

Fig. (1): The plot of ln σ and 1/T for bulk samples at different ln concentration.

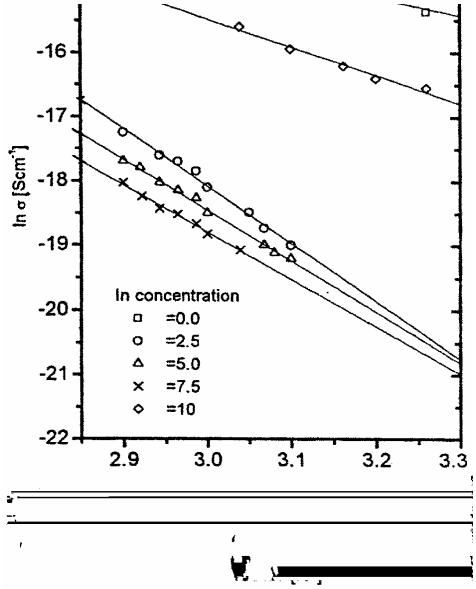

Fig. (2): ln σ - 1/T plot for thin film specimens at different ln concentration.

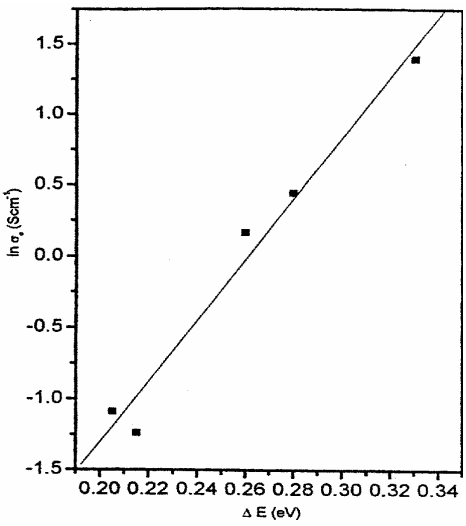

Fig. (3): The plot of in σ_o versus activation energy for bulk samples.

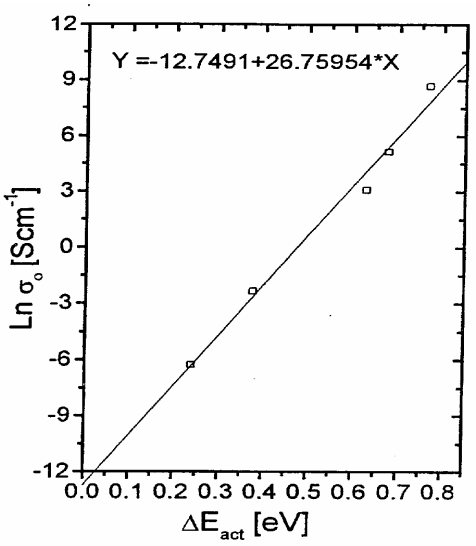

Fig. (4): ln σ_o - ΔE plot for thin films.

Table (1): Conducting parameters for the system $Se_{70}Te_{30-x}In_x$, bulk samples: σ_{00} =3.75x10^{-3} S cm^{-1} , $(KT_{MN})^{-1}$ = 21.36 (e V)$^{-1}$

In Con. (at %)	*ΔE (e V) ±0.01*	*σ_o (S cm^{-1})*
0.0	0.33	4.05
2.5	0.28	1.57
5.0	0.26	1.18
7.5	0.22	0.29
10	0.21	0.34

Table (2): Conducting parameters for the system $Se_{70}Te_{30-x}In_x$, film samples: σ_{00} =2.9x10^{-6} S cm $^{-1}$, $(KT_{MN})^{-1}$ =26.76 (e V)$^{-1}$

In Con. (at %)	*ΔE (e V) ±0.03*	*σ_o (S cm^{-1})*
0	0.24	1.92 x10^{-3}
2.5	0.77	5.94 x10^{3}
5	0.68	1.72 x10^{2}
7.5	0.63	2.15 x10
10	0.38	9.55 x10^{-2}

Discussion:

The increase of the dc conductivity with temperature, Figures (1 & 2), is believed to be due to an increase in the free carrier concentration (holes) due to the statistical shift of the Fermi level. Comparing Figures (1 & 2) and Tables (1 & 2) one can say that conductivities of film samples are about three orders of magnitude lower than those of the bulk samples. The main reason is the difference in the electronic density of states for films (two-dimensional system) and that of bulk samples. The considerable decrease in conductivity on incorporation of In to the binary $Se_{70}Te_{30-x}$ film could be due to a change in the cross-linking of Se-Te chains which enhances the disorder in the system in agreement with Dixit and Kumer [12]. The linear increase in σ_0 values with increasing ΔE, Figures (2 & 4), proved the validity of MN rule in the investigated samples.

In chalcogenides the interesting phenomena concerning the electrical conductivity near room temperature could be considered through two schools, the Mott-Davis [13] and the Emin one [14]. On the basis of Mott's model and at room temperature the carriers are excited across the mobility edge into extended states. Mott estimated a constant value of σ_0 in chalcogenides = 100 Scm^{-1}. In Emin's model a small polaron formation is suggested. The electrical conductivity associated with around room temperature small polaron motion is essentially thermally activated; σ_0 will vary little between specimens and predicted to be (10^2 –10^3 S cm^{-1}).

Considering the data in the present work it can be seen that σ_0 does not have a constant value as predicted by Mott. Rather a huge difference was observed in bulk and film samples. Even in the bulk specimens, the obtained values are very much lower than the σ_0 predicted by the model. Therefore the model can not be applied in such chalcogenides. Besides the observed difference in σ_0 values suggests that σ_0 can not be regarded as a microscopic conductivity. Instead σ_{00} may have the physical meaning in terms of a microscopic conductivity. On the other hand the magnitude of predicted σ_0 for small polaron hopping is very much larger than the estimated values in bulk samples and most films. Also as shown in Table II σ_0 changes too much when indium concentration changes. Hence the polaron model is also unable to explain the dc transport in the system $Se_{70}Te_{30-x}$ In_x.

On the other side the E_{MN} values estimated in the present study (4-21 meV) were found in a good agreement with the published data [15]. Besides very low values of σ_{00} (10^{-5} – 10^{-15} S cm^{-1}) for organic semiconductors were reported [16]. In such materials the electrical transport is assumed to be dominated by electron tunneling through intermolecular barriers which leads to

small tunneling factor and thereby small σ_{00} . A similar situation may occur in some chalcogenides and thereby σ_{00} becomes very small. However the high activation energy values and the big difference between σ_{00} in the present work and those predicted by this model put restrictions on the conduction process in the present system to be due to tunneling.

How then can this discrepancy be explained?. The validity of the MN rule and the obtained activation energy values speculates that Se_{70} Te_{30-x} In_x ($0<x<10$) system gives a wide band gap semiconductor with exponential localized tail states as proposed by Roberts [10]. Accordingly the argument is that the major contribution of the conduction processes does not come from the region of Fermi level but more likely from these tail states which extend exponentially towards a finite energy value near the midgap. Hence σ_0 could not have the same value for all samples, since the energetic positions of these tail states are strongly influenced by addition of In content. The big difference in σ_0 values observed in the films indicated that σ_o can not have the physical meaning in terms of a microscopic conductivity. In addition and instead of the tunneling model, a hopping model is proposed. In fact a hop over about 0.27 e V and 0.5 e V obtained for bulk and film samples, respectively, needs more than one phonon suggesting a multiphonon effect to play the major role for transport in these compounds. The localized density of state distribution suggests the existence of different values for Meyer-Neldel energy. The values reported in the present study (4-21meV), depending on indium concentration, support this idea.

Conclusions:

The resistivity of film samples in the system Se_{70} Te_{30-x} In_x ($0<x<10$) at. % were found three orders higher than the bulk ones. Addition of In to the binary chalcogenide $Se_{70}Te_{3-x}$ led to a marked decrease in the conductivity. An experimental evidence for the correlation between σ_0 and ΔE in both bulk and film samples was obtained. The estimated σ_{00} ($3.75x10^{-3}$ &$2.9x10^{-6}$ S cm^{-1} for bulk and film forms respectively) can be regarded as a microscopic conductivity, instead of σ_0 .

References:

1. Shimakawa K and Abdel-Wahab, Appl.Phys.Lett., **70**, 652 (1977).
2. Coutts T.J and Pearsall N.M, Appl. Phys. Lett., **44**, 134 (1984).
3. Wanger D. Irsingler P and Dunstant D.J,J.Non.Cryst. Solids, **59**&**60,** 413 (1983).
4. Djamdji F and LeComber P.G, Phil. Mag., B **56**,31 (1987).
5. Fortner J, Karpov V.G, and Saboung I, Appl. Phys. Lett., **66**, 977(1994).

6. Narasimhan K.L, and Arora B.M, Solid State Commum., **55**, 615 (1985).
7. Kemeny G, and Rosenberg B, J.Chem. Phys., **52**, 4151 (1970).
8. Irsingler P, Wanger D, and Dunstant D.J, Phys. C, **16**, 6605. (1983).
9. Dwivedi S.K, Dixit M, Kumar A, J. of Mat. Sci. Lett., **17** 233 (1998).
10. Roberts G.G, J. Phys.C, **4**, 3167 (1971).
11. Jackson W.B, Phys. Rev. B, **38**, 3595 (1988).
12. Dixit M, Kumar A, Physica B, **252,** 286-294 (1989).
13. Mott N.F, Davis E.A and Street R.A, Phil. Mag., **32**,961 (1975).
14. Emin D, Seager C.H, Quinn R.K, Phys. Rev.Lett., **28**, 813 (1972).
15. Abd el-Wahab F, Ph. D. Thesis, Gifu Univ., Japan (1998).
16. Rosenberg B, Bhowmik B.B, Harder H.C and Postrow J.Chem Phys. **49**, 4108 (1968).