Meyer–Neldel DC conduction in chalcogenide glasses

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Abstract. Meyer–Neldel (MN) formula for DC conductivity (σ_{DC}) of chalcogenide glasses is obtained using extended pair model and random free energy barriers. The integral equations for DC hopping conductivity and external conductance are solved by iterative procedure. It is found that MN energy (ΔE_{MN}) originates from temperature-induced configurational and electronic disorders. Single polaron-correlated barrier hopping model is used to calculate σ_{DC} and the experimental data of Se, As_2S_3, As_2Se_3 and As_2Te_3 are explained. The variation of attempt frequency ν_0 and ΔE_{MN} with parameter (r/a), where r is the intersite separation and a is the radius of localized states, is also studied. It is found that ν_0 and ΔE_{MN} decrease with increase of (r/a), and ΔE_{MN} may not be present for low density of defects.

Keywords. Chalcogenide glasses; DC conductivity; Meyer–Neldel rule.

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1. Introduction

Pollak and Geballe [1] explained that impurity conduction at high temperature in Si is due to single polaron hopping. Emin *et al* [2] have shown that DC conduction, thermoelectric power and Hall mobility in amorphous chalcogenides are due to hopping of hole-like small polarons. Mott and Davis [3] correlated AC and DC conductivities and gap parameter and emphasized that same mechanism was responsible for AC and DC conductions.

Pramanik *et al* [4] simplified the extended pair model of Summerfield and Butcher [5] and used correlated barrier hopping (CBH) for bipolarons to calculate DC conductivity (σ_{DC}) of chalcogenide glasses. The conductance and capacitance are inversely proportional to relaxation time and temperature respectively. The optical band gap and defect density of states, obtained by fitting the experimental results for AC conductivity, and relaxation time 10^{-13} s, were used to calculate σ_{DC} of Se, As_2S_3, As_2Se_3 and As_2Te_3 [6]. The calculated results were found lower by an order of 10^{12}–10^{13} than the experimental values. Hence it was concluded that CBH model was not applicable to DC conduction in chalcogenides.

According to Shimakawa [7] and Goyal and Vohra [8], DC conduction, due to single polaron hopping, dominates in amorphous chalcogenide glasses at higher temperature. In the as-evaporated films, there may be high concentration of intimate valence alternation pairs and at higher temperature large number of neutral defects may be created which may enhance the single polaron hopping.

Shimakawa and Abdel-Wahab [9] fitted the experimental data of σ_{DC} for chalcogenide glasses and found it obeying Meyer–Neldel (MN) rule [10]

$$\sigma_{DC} = \sigma_0 \exp(\Delta E_{DC}/\Delta E_{MN}) \exp(-\Delta E_{DC}/k_B T), \tag{1}$$

where pre-exponential factor $\sigma_0 \exp(\Delta E_{DC}/\Delta E_{MN})$ is temperature-independent and follows exponential law. Here σ_0 is constant, ΔE_{DC} is the hopping barrier height for DC conduction, k_B is the Boltzmann constant, T is the temperature and ΔE_{MN} is the MN energy. Yelon and Movaghar [11] used optical phonon-induced electron hopping and showed multi-excitations to be the origin of MN rule for DC conduction.

Abdel-Wahab [12] analysed DC and AC conduction data for chalcogenide glasses using CBH model. The conductance was augmented by an exponential factor to account for distribution of energy barriers, and capacitance was taken inversely proportional to temperature. The MN rule for AC and DC conduction was obtained. However, pre-exponential factor was temperature-dependent, which was contrary to the experimental observations.

In the light of these facts, we examined extended pair model [5] to calculate DC conductivity of chalcogenide glasses. The CBH model for single polaron hopping, in conjunction with random-free energy barriers [13] was used and MN rule for DC conductivity was obtained. It was found that ΔE_{MN} was due to temperature-induced configurational and electronic disorders. The experimental results of Se, As_2S_3, As_2Se_3 and As_2Te_3 were explained. Variation of attempt frequency ν_0 and ΔE_{MN} with (r/a) where r is the intersite separation and a is the radius of localized states is also studied.

The plan of the paper is as follows: The necessary formalism is presented in §2, calculations and results are given in §3 and discussions are given in §4.

2. Formalism

Summerfield and Butcher [5] solved Kirchhoff's equations for equivalent RC network of localized states in amorphous solids in the extended pair model. These authors used mean-field theory which is essentially a two-site approximation. The external network where each pair of sites is embedded, is accounted for, by averaging the external network parameters over the pair site coordinates. The DC hopping conductivity for three-dimensional solids is given by the integral equation

$$\sigma_{DC} = (4\pi n_s^2/6) \int_{r_{min}}^{r_{max}} dr\, r^4 \left[\frac{1}{g(E,r)} + \frac{2}{Y(E)}\right]^{-1}, \tag{2}$$

where r_{min} and r_{max} are the lower and upper limits of integration, n_s is the density of defect sites and $g(E,r)$ is the internal conductance between the states of energy E of the defect sites at separation r. $g(E,r)$ is determined by equilibrium occupation probabilities of these sites and transition rate between them.

The external conductance $Y(E)$ for energy E is given as

$$Y(E) = \left(4\pi n_s/B_p\right) \int_{r_{\min}}^{r_{\max}} \mathrm{d}r r^2 \left[\frac{1}{g(E,r)} + \frac{1}{Y(E)}\right]^{-1}. \tag{3}$$

Here $(1/B_p)$ is the proportionality constant. In the limits $Y(E)/g(E,r) \approx 0$, $r_{\min} \approx 0$ and $r_{\max} \approx r_p$, we get percolation radius r_p from eq. (3) as

$$r_p = \left(3B_p/4\pi n_s\right)^{(1/3)}. \tag{4}$$

$(1/B_p)$ is determined with the prediction of percolation theory [14] and for three-dimensional solids, $B_p = 2.7$. If e is the electronic charge, $eY(E)$ is the mean current which enters the site due to voltage generators.

The exact solutions of eqs (2) and (3) are non-trivial. Therefore, we solved these equations by iterative procedure. Equation (3) is rewritten as

$$Y(E) = \left(4\pi n_s/B_p\right) \int_{r_{\min}}^{r_{\max}} \mathrm{d}r r^2 \left[\frac{Y(E)}{1 + Y(E)/g(E,r)}\right]. \tag{5}$$

In the first iteration, we assume that external conductance is equal to internal conductance at percolation radius, i.e.

$$Y(E) = g\left(E, r_p\right) = g_0 \exp(-\Delta E(r_p)/k_B T), \tag{6}$$

where, in general

$$g(E,r) = g_0 \exp\left(-\Delta E(r)/k_B T\right). \tag{7}$$

Here g_0 is the proportionality constant and barrier height $\Delta E(r)$ in the CBH model is given as

$$\Delta E(r) = E_M - (4ze^2/\varepsilon r), \tag{8}$$

where E_M is the maximum barrier height, ε is the dielectric constant and $z = 1$ and 2 for single polaron and bipolarons, respectively. The possibility of negative barrier height between two defect centres is eliminated by defining

$$r_{\min} = (4ze^2/\varepsilon E_M). \tag{9}$$

Using eqs (6) and (7) in eq. (5) gives

$$Y(E) = \left(4\pi n_s/B_p\right)g(E, r_p) \int_{r_{\min}}^{r_{\max}} \mathrm{d}r r^2 \left[\frac{1}{1 + g(E, r_p)/g(E,r)}\right], \tag{10}$$

where

$$g(E, r_p)/g(E, r) = \exp(a(1/r_p - 1/r)) \tag{11}$$

and

$$a = 4(ze^2/k_B T). \tag{12}$$

To simplify the integral in eq. (10), it is assumed that $r_{max} \approx r_p$, as for large values of r, the factor in square brackets in eq. (10) nearly vanishes. For smaller values of r, $(g(E, r_p)/g(E, r))$ is too small. Therefore, the factor in the square brackets is represented by a step function [4]. This may be an overestimation of the integral, but, the results may not change qualitatively. This simplifies eq. (10) as

$$Y(E) = (4\pi n_s/B_p)g(E, r_p)(r_p^3 - r_{min}^3). \tag{13}$$

For $z = 1$ and assuming that $E_M \cong B$, the optical band gap as given in table 1, the calculated values of r_{min} are 4.5, 3.2, 2.57 and 5.76 Å for Se, As$_2$S$_3$, As$_2$Se$_3$ and As$_2$Te$_3$, respectively. It is noted from table 1 that r_{min} is less than r_p by an order of magnitude except for As$_2$Te$_3$. Thus r_{min}^3 becomes negligible compared to r_p^3 and even for As$_2$Te$_3$, r_{min}^3 is about 30% of r_p^3. Thus we write

$$Y(E) \approx (4\pi n_s/B_p)g(E, r_p) r_p^3. \tag{14}$$

Using eq. (14) in eq. (2) gives

$$\sigma_{DC} = (4\pi n_s^2/6)Y(E) \int_{r_{min}}^{r_p} dr r^4 \left[\frac{1}{2 + Y(E)/g(E, r)} \right], \tag{15}$$

where eqs (7), (8) and (14) gives

$$Y(E)/g(E, r) = (4\pi n_s r_p^3/3B) \exp(a(1/r_p - 1/r)). \tag{16}$$

The r dependence in eqs (16) and (11) is the same. For small values of r, $(Y(E)/g(E, r))$ is negligible, therefore the factor in the square brackets in eq. (15) is replaced by (1/2). This simplifies eq. (15) as

$$\sigma_{DC} = (4\pi n_s^2/6) (Y(E)/10) (r_p^5 - r_{min}^5). \tag{17}$$

Table 1. Physical parameters of Se, As$_2$S$_3$, As$_2$Se$_3$ and As$_2$Te$_3$.

Material	ε	B (eV)	n_s (cm^{-3})	r_p (cm)	T (K)	σ_{DC}(exp) (Ω^{-1} cm^{-1})
Se	6.4	2.00	2.0×10^{19}	3.2×10^{-7}	300	2.8×10^{-14}
As$_2$S$_3$	7.8	2.30	3.6×10^{19}	2.6×10^{-7}	300	5.0×10^{-15}
As$_2$Se$_3$	11.2	2.00	2.0×10^{20}	1.5×10^{-7}	300	1.0×10^{-12}
As$_2$Te$_3$	10.0	1.00	1.2×10^{21}	8.1×10^{-8}	100	1.0×10^{-12}

Note: The values are taken from [4] and references therein. Here ε is the dielectric constant, B is the optical band gap, n_s is the defect density, r_p is the percolation radius, T is the temperature and σ_{DC}(exp) is the experimental value of DC conductivity.

As r_{min}^5 is not significant when compared to r_{p}^5, substituting eq. (14) in eq. (17) gives

$$\sigma_{\text{DC}} = (\pi n_{\text{s}}^2 r_{\text{p}}^5 / 15) g(E, r_{\text{p}}). \tag{18}$$

In thermally activated DC conduction in amorphous solids, σ_{DC} is proportional to $\exp(-\Delta E / k_{\text{B}} T)$ where activation energy ΔE is the maximum potential barrier height which is independent of temperature [3]. However, if temperature-induced configurational and electronic disorders are accounted for, ΔE involves thermal fluctuations and hence a range of activation energies contribute to the conduction process. Thus, ΔE represents a distribution of free energy barriers which is given as

$$\Delta E = \Delta E_{\text{DC}} - T \Delta S, \tag{19}$$

where ΔE_{DC} is the constant part of the barrier height and entropy barrier $T \Delta S$ accounts for thermal fluctuations. Evidently, ΔE_{DC} is compensated by $T \Delta S$. It is referred as random free energy barrier model.

Substituting eq. (19) in (7), one gets

$$g(E, r_{\text{p}}) = g_0 \exp(\Delta S / k_{\text{B}}) \exp(-\Delta E_{\text{DC}}(r_{\text{p}}) / k_{\text{B}} T). \tag{20}$$

The pre-exponential factor can also be expressed as

$$g_0 \exp(\Delta S / k_{\text{B}}) = C \omega_0 \exp(\Delta E_{\text{DC}} / \Delta E_{\text{MN}}), \tag{21}$$

where

$$\Delta E_{\text{MN}} = k_{\text{B}} \Delta E_{\text{DC}} / \Delta S = k_{\text{B}} T_0. \tag{22}$$

Here C and ω_0 have the dimensions of capacitance and frequency, respectively, and T_0 is the characteristic temperature. Thus, we get MN rule for DC conduction in chalcogenide glasses as a consequence of free energy barriers which account for temperature-induced configurational and electronic disorders. Abdel-Wahab [12] used brute force method to augment $g(E, r_{\text{p}})$ by an exponential factor to account for distribution of energy barriers, whereas Pramanik *et al* [4] ignored this factor.

Evidently, ΔE_{MN} is directly proportional to ΔE_{DC} and inversely proportional to ΔS. For a given ΔE_{DC}, ΔE_{MN} will increase with decrease of entropy. However, for very large and small values of ΔS, ΔE_{MN} will lose its significance.

Pramanik *et al* [4] and Abdel-Wahab [12] used $C = (e^2 / 4 k_{\text{B}} T)$. This inverse temperature dependence of capacitance is rather incorrect. In fact, capacitance increases with increase in temperature [15] and ω_0 also changes with temperature. The exact temperature dependence of $C \omega_0$ is not known [16], and therefore, $C \omega_0$ is taken as temperature-independent and to represent the results in the same units as given in refs [4] and [6], we write

$$C \omega_0 = (e^2 / \pi k_{\text{B}} \theta_{\text{D}}) \nu_0, \tag{23}$$

where θ_{D} is the Debye temperature and ν_0 is the effective jump frequency. Here θ_{D} and ν_0 depend on material properties.

Substituting eqs (21) and (23) in eq. (18), we get eq. (1) where

$$\sigma_0 = (e^2 n_s^2 r_p^5 / 15 k_B \theta_D) \nu_0. \tag{24}$$

Here DC conduction is due to the phonon-assisted single polaron hopping. In eq. (1), as $T \to 0$, $\Delta S \to 0$, phonon assistance vanishes and hence $\sigma_{DC} = 0$. If T decreases, σ_{DC} also decreases due to decrease in ΔS and T. Thus entropy barrier plays a significant role in the conduction process.

3. Calculations and results

Calculations are carried out for Se, As$_2$S$_3$, As$_2$Se$_3$ and As$_2$Te$_3$ using the values of ε, B, n_s, r_p, T as given in ref. [4] and for ready reference these are tabulated in table 1. ΔE_{DC} is calculated replacing r by r_p in eq. (8) and using the relation $E_M = 2(B - \Delta E_{DC})$ [4]. This gives

$$\Delta E_{DC} = (1/3)(2B - 4ze^2/\varepsilon r_p). \tag{25}$$

The neutron scattering measurements on crystalline and amorphous Ge and As show that θ_D decreases from 374 to 315 K for Ge and from 278 to 169 K for As [3]. This is due to phonon softening in the amorphous phase. Due to the non-availability of θ_D for the materials in question, θ_D is estimated by reducing the data of crystalline Se and Te [15] in the same ratio as for As, θ_D for binary compounds is calculated using weighted average of these reduced values which are given in table 2.

First we calculated σ_{DC} in the bipolaron hopping model using $\nu_0 = 10^{13}$ cps as in ref. [4]. The measured values of σ_{DC} for Se, As$_2$S$_3$ and As$_2$Se$_3$ could be explained. However, estimated values of ΔE_{MN} were found to be nearly twice the values suggested by Shimakawa and Abdel-Wahab [9] and ΔE_{MN} was found to be negative for As$_2$Te$_3$. The same trend continued even after replacing $\nu_0 = \nu_D (= k_B \theta_D / h)$. In view of these facts we gave up bipolaron hopping model and calculated σ_{DC} in the single polaron hopping model using $\nu_0 = \nu_D$. The experimental results were closely reproduced for $\Delta E_{MN} = 74$, 67, 70 and 22 meV for Se, As$_2$S$_3$, As$_2$Se$_3$ and As$_2$Te$_3$, respectively. These results along with ν_D are given in table 2. The values of ΔE_{MN} are well within the predictions of Shimakawa *et al* [9]. The calculations were further repeated for $\nu_0 = 10^{13}$cps, and

Table 2. Estimated values of Debye temperature θ_D, Debye frequency ν_D, barrier height ΔE_{DC} and Meyer–Neldel energy ΔE_{MN}.

Material	θ_D (K)	$\nu_D \times 10^{12}$ (cps)	ΔE_{MN} (meV)	ΔE_{DC} (eV)	σ_{DC}(calc.) (Ω^{-1} cm^{-1})
Se	54.7	1.14	74	1.27	2.82×10^{-14}
As$_2$S$_3$	169	3.5	67	1.439	5.0×10^{-15}
As$_2$Se$_3$	100	2.1	70	1.219	1.0×10^{-12}
As$_2$Te$_3$	121	2.5	22	0.43	1.0×10^{-12}

the results agreed with the experimental data for $\Delta E_{MN} = 84, 71, 77$ and 24 meV for Se, As_2S_3, As_2Se_3 and As_2Te_3, respectively. Thus ΔE_{MN} increased with increase in ν_0 as evident from eqs (1) and (24).

In tables 1 and 2, B and ΔE_{DC} for As_2S_3, Se, As_2Se_3 and As_2Te_3 are in decreasing order. Although ε is large and r_p is small for As_2Se_3 and As_2Te_3, larger n_s and smaller ΔE_{DC} may be responsible for large conductivities of these compounds.

Miller and Abrahams [17] calculated relaxation time for transition rate between localized states of radius a and intersite separation r which was used by Pollak and Geballe [1] to establish correlation between AC and DC conductivities. The effective jump frequency, suggested by these authors, at higher temperature is given as

$$\nu_0 \approx 2 \times 10^{12}(r/a)^{3/2}\exp(-2r/a). \tag{26}$$

The parameter (r/a) represents material characteristics. For example, if thin films are prepared by depositing thin layers along z-axis, atomic configuration along z-direction may not be the same as along x and y directions. If the samples are prepared by different heating and quenching rates, it is likely that atomic configurations in different samples will be different and the measurements of the same physical quantity on different samples may not be identical [18]. Therefore, we further explained experimental data of DC conductivity of these materials by varying (r/a).

Assuming that the radius of localized state will not exceed the intersite separation, ν_0 is calculated for $(r/a) \geq 1$ using eq. (26) and the results are shown in figure 1. As (r/a) increases, ν_0 decreases nearly by an order of magnitude for unit increase in (r/a) and it goes to the order of acoustic phonon frequencies for larger (r/a). Evidently σ_{DC} will decrease either with increase in r or with decrease in a. Thus σ_{DC} may be absent for too large interparticle separation or for too localized defect states.
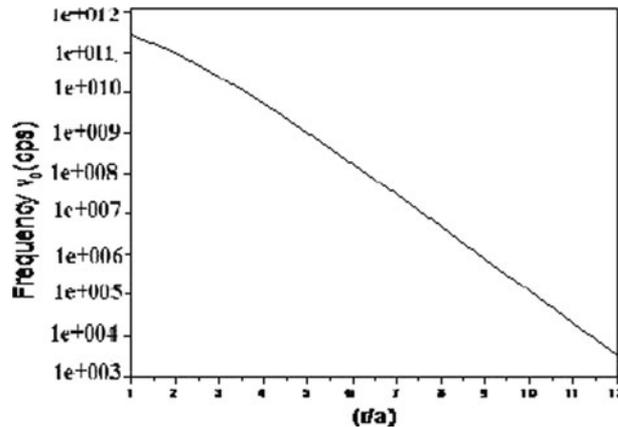

Figure 1. Variation of effective jump frequency ν_0 with parameter (r/a) as described in the text. Here $1e + 003 = 10^3$ and so on.
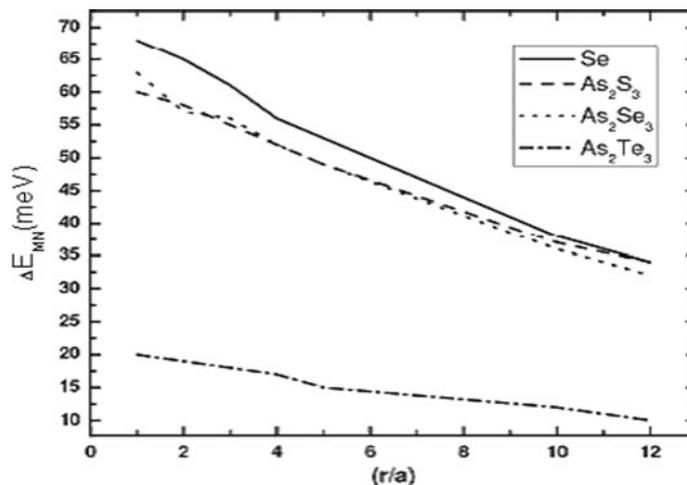
Figure 2. Variation of ΔE_{MN} with parameter (r/a).

The calculated values of ν_0 are used to predict ΔE_{MN} by comparing the calculated and experimental results of σ_{DC}. As shown in figure 2, ΔE_{MN} for Se, As_2S_3, As_2Se_3 are within the range of 15% and these tend to converge for larger values of (r/a), whereas ΔE_{MN} of As_2Te_3 is nearly one-third of ΔE_{MN} for As_2S_3. This may be because atomic radii of S and Se are almost equal and less than the atomic radius of As, but atomic radius of Te is larger almost by 20% than those of Se and S in the same order as of As [15]. Thus, configurational disorder created by Te in As may be more than that created by S and Se. Again the overlap interaction between $4p^3$ orbital of As and $5p^4$ orbital of Te is larger than that of $3p^4$ and $4p^4$ orbitals of S and Se, respectively. Thus entropy due to distortion field and electronic interaction created by Te in As is larger than that created by Se and S.

4. Discussions

Butcher and Summerfield [5] established equivalence between DC hopping conduction and percolation theory. The internal conductance $g = g_0 \exp(-\lambda)$ vanishes if λ is sufficiently large and g_0 is constant. Let this critical value of λ is λ_p. As external conductance Y is also a factor of σ_{DC}, DC conduction will vanish if $Y = 0$. Assuming that external conductance $Y = g_0 \exp(-\lambda')$, Y vanishes beyond a critical value of λ', say λ'_p. If $\lambda_p = \lambda'_p$, hopping conduction is equivalent to percolation theory for the right choice of percolation radius r_p. In view of these facts, we solved eqs (2) and (3) by iterative procedure. The factor $g(E, r_p)/g(E, r)$ was approximated to zero for $r < r_p$ in eqs (11) and (16). But, for r in the vicinity of r_p, this approximation may not be valid and this factor should be accounted for in the integration.

It is evident from eq. (22) that ΔE_{DC}, ΔE_{MN} and ΔS are correlated and ΔE_{MN} is inversely proportional to ΔS for a given ΔE_{DC}. Therefore, it is expected that the origin of ΔE_{MN} lies in the temperature-induced configurational and electronic disorders. If $\Delta S \approx k_B$, $\Delta E_{MN} \cong \Delta E_{DC}$, thus ΔE_{MN} will be a fraction of ΔE_{DC} for all values of $\Delta S > k_B$. In the limit $\Delta S \to 0$, MN factor in eq. (1) becomes unity.

In conclusion, it is shown that DC conduction in chalcogenide glasses is due to single polaron hopping and temperature-induced disorder is the origin of MN rule.

Acknowledgements

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