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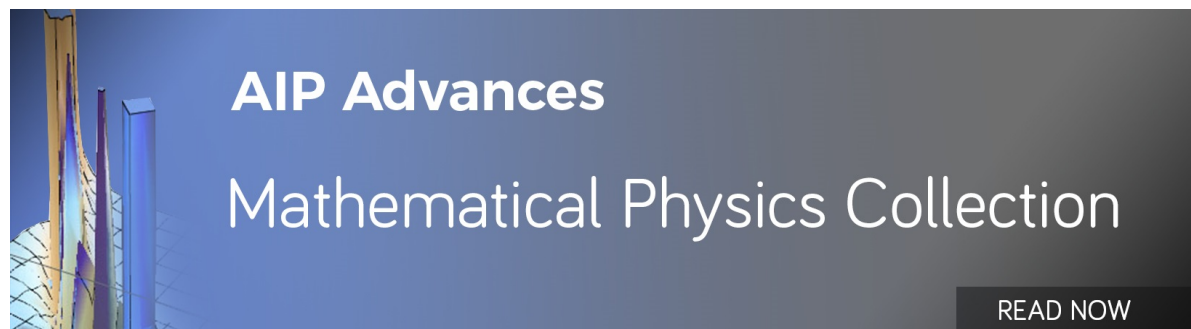
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Random free energy barrier hopping model for ac conduction in chalcogenide glasses

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The random free energy barrier hopping model is proposed to explain the ac conductivity (σ_{ac}) of chalcogenide glasses. The Coulomb correlation is consistently accounted for in the polarizability and defect distribution functions and the relaxation time is augmented to include the overlapping of hopping particle wave functions. It is observed that ac and dc conduction in chalcogenides are due to same mechanism and Meyer-Neldel (MN) rule is the consequence of temperature dependence of hopping barriers. The exponential parameter s is calculated and it is found that s is subjected to sample preparation and measurement conditions and its value can be less than or greater than one. The calculated results for $a - Se$, As_2S_3 , As_2Se_3 and As_2Te_3 are found in close agreement with the experimental data. The bipolaron and single polaron hopping contributions dominates at lower and higher temperatures respectively and in addition to high energy optical phonons, low energy optical and high energy acoustic phonons also contribute to the hopping process. The variations of hopping distance with temperature is also studied. The estimated defect number density and static barrier heights are compared with other existing calculations. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4944497>]

I. INTRODUCTION

Observation of the low frequency ac conductivity $\sigma(\omega)$ at low temperature being proportional to the applied field frequency ω to the power $1 - s'$ i.e $\sigma(\omega) = A\omega^s$ where A is complex constant and s and s' are less than one.^{1,2} This is ubiquitous feature of hopping conduction.³ It is well known that this feature simply results from having a broad distribution of relaxation rates surrounding the low (e.g. KHz) observation frequency.⁴

Polaron hopping has been reported in a wide variety of low mobility solids. In particular reports of polaron hopping in chalcogenides glasses began in 1972 with study of the dc transport of As-Te based glasses.⁵ Subsequent dc measurements indicated polaron hopping in simple binary chalcogenide glasses.⁶

Elliot⁷ extended the Pike³ formalism, based on microscopic model of Pollak and Geballe¹ and Pollak,² to explain the defect induced conductivity of chalcogenides glasses. It is assumed that electron wave functions are well localized within the potential wells of specific defect sites D^+ and D^- and ac conduction is due to bipolaron hopping between these defect sites.⁸⁻¹⁰ The hopping barrier height between these defect sites is correlated with intersite separation. This proposed correlated barrier hopping (CBH) model is used to explain the salient features of temperature dependence of ac conductivity of chalcogenide glasses. The estimated defect number density is found comparable with the experimental data.

Street¹¹ and Elliot¹² modified the CBH model by including Coulomb interaction in the defect distribution function and it is used by Hirata et. al.¹³ to explain the ac conductivity of Ag doped

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As_2Se_3 . However Shimakwa¹⁴ suggested that in addition to bipolaron hopping, neutral defects D^0 produced by reverse reaction $2D^0 \rightarrow D^+ + D^-$ also contribute to ac conduction through single polaron hopping. The CBH model is extended by including single polaron hopping and the results for undoped and doped chalcogenides are explained.

Takano *et. al.*¹⁵ added the contribution of simple pairs in the CBH model to explain the pronounced peaks in the temperature dependent ac conductivity of transition metal atom doped As_2Se_3 . Since then, the above variances of CBH model are extensively used to explain the temperature dependence of ac conductivity in chalcogenide glasses.¹⁶⁻²²

Shimakawa and Abdel- Wahab²³ showed that dc conductivity of chalcogenides glasses follows the Meyer-Neldel[MN] rule.²⁴ Abdel - Wahab *et. al.*²⁵ introduced temperature dependent exponential factor in the relaxation time to account for MN rule in the ac conductivity. The CBH results were rederived with an additional temperature dependent multiplying factor $1/\eta$, where $\eta = 1 - T/T_0$, and T_0 is denoted as characteristic temperature. The results for $\sigma_{ac}(\omega)$ for doped and undoped As and Se based chalcogenides were unevenly explained and T_0 is assigned the values between 500 K⁰ to 900 K⁰. Mehta *et. al.*²⁶ and Sharma *et. al.*²⁷ also used the similar expressions to explain the ac and dc conductivities of $Se_{80}Te_{19.5}M_{0.5}$ (M = Cd, In, Sb, Ag). However the above formulation leads to an expression for dc conductivity where the pre-exponential factor is temperature dependent which is contrary to the experimental observations.

Dyre²⁸ proposed the random free energy barrier hopping model for ac conduction in disordered solids. The conduction is through hopping process and charge carriers are subjected to spatially randomly varying energy barriers. Assuming that these energy barriers are free energy barriers, the ac and dc conductivities and dielectric losses are explained. Prakash *et. al.*²⁹ used extended pair model and random free energy barriers to obtain the Meyer -Neldel formula for dc conduction in chalcogenide glasses. It is found that Meyer -Neldel energy originates from temperature induced configurational and electronic disorders and it depends upon intersite separation and radius of localized states.

We found it interesting to extend random free energy barrier hopping [RFBH] model to calculate ac conductivity of chalcogenide glasses. The nearest neighbor Coulomb correlation is included in both polarizability and defect distribution functions. The carrier wave functions overlap between the sites is accounted for in the relaxation time by multiplying with the function $\exp(2\alpha r)$ where α is the inverse of polaron radius. The explicit expressions for σ_{ac} and s are obtained. It is found that temperature dependence of free energy barrier leads to MN signature in σ_{ac} . The experimental data for ac conductivities of a-Se, As_2Se_3 , As_2S_3 , As_2Te_3 are explained. It is found that in addition to high energy optical phonons, the low energy optical and high energy acoustic phonons also contribute to the hopping process.

The plan of the paper is as follows: The necessary formalism is presented in Sec. II, calculations and results are given in Sec. III, and these are discussed in Sec. IV.

II. FORMALISM

A. General expression for σ_{ac}

The real part of ac conductivity for the field frequency ω is given as¹

$$\sigma_{ac}(\omega) = N_P \int_{\tau_{min}}^{\tau_{max}} \alpha(\tau, \Delta E) \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} n(\tau) d\tau, \quad (1)$$

where N_P is the number density of acceptor sites, τ is the relaxation time, $n(\tau)d\tau$ is the probability of a given pair of sites having relaxation time between τ and $\tau + d\tau$, τ_{min} and τ_{max} are the allowed minimum and maximum values of τ for the carrier hopping to take place. $N_P = N/2$, if N is the number density of localized sites.

The pair polarizability function

$$\alpha(r, \Delta E) = \frac{(ne)^2 r^2}{12k_B T \cosh^2\left(\frac{\Delta E(r)}{2k_B T}\right)}, \quad (2)$$

where $n=1$ for one electron hopping and $n=2$ for two electron hopping, r is the separation between two hopping sites, k_B is the Boltzman constant, T is the temperature and $\Delta E(r)$ is the difference in the energy levels between the pair of sites. In the CBH model the hopping barrier height W is temperature independent and it is related to the intersite separation r as

$$W = W_m - \frac{4ne^2}{\epsilon r}, \quad (3)$$

where W_m is the binding energy of carriers and ϵ is the effective dielectric constant. The experiments are at the finite temperature and there does exist a temperature gradient in the sample due to applied field, therefore to account for temperature induced configurational and electronic disorders barrier height W is replaced by free energy F and Eq. (3) is rewritten as

$$F = W_m - \frac{4ne^2}{\epsilon r}, \quad (4)$$

where

$$F = W - TS. \quad (5)$$

Here we assume that TS is maximum entropy barrier. Evidently from Eq. (4)

$$r = \frac{4ne^2}{\epsilon(W_m - F)}, \quad (6)$$

and

$$dr = \frac{\epsilon r^2}{4ne^2} dF. \quad (7)$$

Kastner *et. al.*³⁸ pointed out that the energy of charged defects is lowered by Coulomb interaction. Therefore Street¹¹ and Elliot¹² included the Coulomb interaction between the defect pairs (D^+ , D^-) in the defect distribution function at glass transition temperature T_g to estimate ac conductivity of chalcogenides. These authors presumed that below T_g defects may annihilate. However this presumption is not necessary as at any given temperature T , σ_{ac} is measurable. Therefore there does exist the finite defect number density. The Coulomb interaction is also included in the free energy barrier heights, therefore for consistency we write spatial distribution of these defects at a given temperature T as

$$p(r)dr = 4\pi r^2 N \exp\left(\frac{z^2 e^2}{\epsilon r k_B T}\right) dr. \quad (8)$$

Here the Coulomb interaction between the defect pairs (D^+ , D^-) is $-z^2 e^2 / \epsilon r$, where $z^2 = z_1 z_2$, z_1 and z_2 are charge units on defects D^+ and D^- respectively.

Using Eqs. (6) and (7) in Eq. (8) and equating the probability distribution $p(r)$ to distribution in r and F we get

$$p(r)dr = \frac{\pi \epsilon N}{ne^2} \left(\frac{4ne^2}{\epsilon(W_m - F)}\right)^4 \exp\left(\frac{z^2(W_m - F)}{4nk_B T}\right) dF = p(F)dF. \quad (9)$$

In the quantum hopping model Pike³ suggested the relation between the relaxation time and activation energy W as

$$\tau = \tau_0 \phi(r/a) \exp(W/k_B T), \quad (10)$$

where τ_0 is of the order of atomic vibrational period, a is the radius of localized orbital wavefunction and $\phi(r/a)$ depends upon carrier wavefunction overlap between the sites. For large (r/a) , $\phi(r/a)$ goes as $\exp(2r/a)$ and as (r/a) goes to unity, $\phi(r/a)$ becomes weak function of its argument and its value becomes of the order of unity. Pike³ used $\tau_1 = \tau_0 \phi(r/a)$, the effective vibrational period in the analysis of $\sigma(\omega)$ for ScO films.

In chalcogenides, the carrier hopping is phonon induced and these carriers are dressed with lattice distortion field. Thus the ac conduction in chalcogenides is effectively due to polaron hopping between defects sites D^+ and D^- and for polaron hopping process Emin and Holesien and Emin³⁰ suggested that $\tau = \tau_0 \exp(2\alpha r) \exp(W_\mu/k_B T)$ where α is the inverse of polaron radius and W_μ is the half of polaron binding energy. The continuous alternation of carrier wave function with atomic movements and long range interaction among the carrier does alter the atomic vibrational frequency, hopping distance and hopping activation energy. In this sprit in the present random free energy model, we rewrite Eq. (10) as

$$\tau = \tau_1 \exp(F/k_B T), \quad (11)$$

where

$$\tau_1 = \tau_0 \exp(2\alpha r). \quad (12)$$

It is non-trivial to determine parameter α and further the defect sites in the very narrow range of intersite separation contribute in the hopping process. Therefore we write $\alpha r = \zeta\omega$, a parameter for a given applied field frequency ω . Long³¹ has pointed out that parameter $2\alpha r$ is varied in the range of 2.5 to 16 to explain the ac conductivity of amorphous semiconductors.

Evidently we find from Eq. (11)

$$\frac{d\tau}{\tau} = \frac{dF}{k_B T}. \quad (13)$$

Substituting polarizability function given in Eq. (2) in Eq. (1) we get

$$\sigma_{ac}(\omega) = \frac{N}{2} \int_{\tau_{min}}^{\tau_{max}} \frac{(ne)^2 r^2}{12k_B T \cosh^2(\frac{\Delta E(r)}{2k_B T})} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} n(\tau) d\tau. \quad (14)$$

Further use of the relation $n(\tau)d\tau = p(r)dr = p(F)dF$, as given in Eq. (9), Eq. (14) simplifies as

$$\sigma_{ac}(\omega) = \frac{\pi \epsilon n N^2 \omega}{24} \int_{\tau_{min}}^{\tau_{max}} \frac{1}{\cosh^2(\frac{\Delta E(r)}{2k_B T})} r^6 \frac{\omega \tau}{1 + \omega^2 \tau^2} \exp(\frac{z^2 e^2}{k_B T \epsilon r}) \frac{d\tau}{\tau}. \quad (15)$$

Here $\tau_{min} = \tau_1$ and $\tau_{max} = \tau_1 \exp(\frac{W_m}{k_B T})$, are the extreme values of relaxation time for hopping carriers. As the contributions to the integral in the limits 0 to τ_{min} and τ_{max} to ∞ are negligible, the integration limits are extended from 0 to ∞ for further calculations.

Pollak² has shown that $\Delta E(r)$ is the sum of energy difference between the ground state energy of defect sites ΔE^0 and the Coulomb correlation between other occupied sites in the vicinity of the defect sites. However if we consider the Coulomb correlation only between the two participating defect sites and neglect the correlation between other sites, we get²

$$\Delta E(r) = \Delta E^0 + \frac{z^2 e^2}{\epsilon r}, \quad (16)$$

Assuming that ΔE^0 is negligible as compared to Coulomb interaction, we write

$$\Delta E(r) = \frac{z^2 e^2}{\epsilon r} = E_c(r), \quad (17)$$

and simplify Eq. (15) as

$$\sigma_{ac}(\omega) = \frac{\pi \epsilon n N^2 \omega}{24} \int_0^\infty \frac{r^6}{\cosh^2(\frac{E_c(r)}{2k_B T})} \frac{\omega \tau}{1 + \omega^2 \tau^2} \exp(\frac{E_c(r)}{k_B T}) \frac{d\tau}{\tau}. \quad (18)$$

As argued by Elliot⁷ the factor $\frac{\omega \tau}{1 + \omega^2 \tau^2}$ is sharply peaked at $\omega \tau \approx 1$, it is also extremely sharply peaked in the domain F or r, therefore it can be treated as delta function and integrand can be taken at constant F or r. Thus $r = r_\omega$, or $F = F_\omega$ for the those sites for which $\omega \tau \approx 1$ and using the relation

$$\int_0^\infty \frac{\omega \tau}{1 + \omega^2 \tau^2} = \frac{\pi}{2} - \tan^{-1}(\omega \tau) \approx \frac{\pi}{2}, \quad (19)$$

Eq. (18) simplifies as

$$\sigma_{ac}(\omega) = \frac{\pi^2 \epsilon n N^2 \omega r_\omega^6}{48 \cosh^2(\frac{E_c(r_\omega)}{2k_B T})} \exp(\frac{E_c(r_\omega)}{k_B T}). \quad (20)$$

Here

$$r_\omega = \frac{4ne^2}{\epsilon(W_m - F_\omega)}. \quad (21)$$

These are the basic equations to calculate $\sigma_{ac}(\omega)$ in the random free energy barrier hopping model. If we take $n=2$ for bipolaron hopping, $E_c(r_\omega) \approx 0$ and $F_\omega = W_\omega$, we get the results due to Elliot.⁷ Further if we assume that T is very large such that $\cosh^2(\frac{E_c(r)}{2k_B T}) \approx 1$ and $\exp(\frac{E_c(r)}{k_B T}) \approx \exp(\frac{z^2 e^2}{k_B T_g \epsilon r})$, where T_g is glass transition temperature, we get the another result due to Elliot.¹² However Eq. (20) is more general than those obtained by earlier authors.

It is interesting to note that the ratio of exponential and hyperbolic functions in Eq. (20) partially cancel the temperature dependence of $\sigma_{ac}(\omega)$. If the Coulomb correlation is weak and temperature is high, the ratio of exponential and hyperbolic function becomes unity and CBH model results are retrieved. However for higher defects density (r_ω is small) and low temperature, the above ratio will be nearly 4 and hence in this limit σ_{ac} will be nearly four times larger than that achieved in the CBH model. Thus the magnitude as well as temperature dependence of σ_{ac} get altered by considering free energy barriers and Coulomb correlations in both the polarizability and defect distribution functions.

B. Evaluation of r

Taking the sixth power of r_ω in Eq. (21), we get

$$r_\omega^6 = \left(\frac{4ne^2}{\epsilon}\right)^6 \frac{1}{(W_t - W_\omega)^6}, \quad (22)$$

where

$$W_\omega = F_\omega + TS \quad (23)$$

and

$$W_t = W_m + TS. \quad (24)$$

Here W_t is the effective binding energy of polarons at temperature T . Assuming that $W_t \gg W_\omega$ and expanding $(1 - W_\omega/W_t)$ in power series of (W_ω/W_t) . Eq. (22) simplifies as

$$r_\omega^6 = \left(\frac{4ne^2}{\epsilon W_t}\right)^6 \exp\left(\frac{6W_\omega}{W_t}\right). \quad (25)$$

As F and r explicitly depend on ω , we write $\tau = \tau_\omega$ in Eq. (11) as

$$\tau_\omega = \tau_{1\omega} \exp\left(\frac{F_\omega}{k_B T}\right), \quad (26)$$

where $\tau_{1\omega} = \tau_0 \exp(2\zeta_\omega)$. Further use of Eq. (23) in Eq. (26) gives

$$\tau_\omega = \tau_{1s} \exp\left(\frac{W_\omega}{k_B T}\right), \quad (27)$$

where

$$\tau_{1s} = \tau_{1\omega} \exp\left(\frac{-S}{k_B}\right). \quad (28)$$

Defining $\beta = \frac{6k_B T}{W_t}$ and using Eqs. (26)-(28), the hopping distance is expressed as

$$r_\omega^6 = \left(\frac{4ne^2}{\epsilon W_t}\right)^6 \left(\frac{\omega \tau_\omega}{\omega \tau_{1s}}\right)^\beta, \quad (29)$$

and further use of relations $\omega \tau_\omega = 1$, $(\omega \tau_{1s})^{\frac{\beta}{6}} = \exp(\frac{\beta}{6} \ln(\omega \tau_{1s}))$ one finds

$$r_\omega = \frac{4ne^2}{\epsilon W_t} \frac{1}{\left[1 + \frac{k_B T}{W_t} \ln(\omega \tau_{1s}) - \frac{T S}{W_t}\right]}. \quad (30)$$

This is the end result to calculate r_ω for the evaluation of $\sigma_{ac}(\omega)$ given in Eq. (20). If the entropy $S=0$, and $\tau_{1\omega} = \tau_0$, Elliot⁷ result of r_ω is retrieved. The entropy enhances r_ω and hence ac conductivity.

C. Meyer- Neldel Rule

Multiplying and dividing by W_ω in the argument of exponential function of Eq. (28) one gets

$$\tau_{1s} = \tau_{1\omega} \exp\left(\frac{-W_\omega}{E_{MN}}\right), \quad (31)$$

where the Meyer-Neldel energy,²⁹

$$E_{MN} = \frac{k_B W_\omega}{S} = k_B T_c. \quad (32)$$

Here the characteristic temperature T_c , the ratio of barrier height W_ω and entropy S , will depend upon the material properties and the experimental procedure followed to measure ac conductivity. The use of Eqs. (32) and (29) in Eq. (20) gives

$$\sigma_{ac}(\omega) = \frac{\pi^2 \epsilon n N^2}{48 \cosh^2\left(\frac{E_c(r_\omega)}{2k_B T}\right)} \left(\frac{4ne^2}{\epsilon W_t}\right)^6 \left(\frac{\omega^{1-\beta}}{(\tau_{1\omega})^\beta}\right) \exp\left(\frac{\beta W_\omega}{E_{MN}}\right) \exp\left(\frac{E_c(r_\omega)}{k_B T}\right). \quad (33)$$

However to be more specific, let $E_c(r_\omega) = 0$, as approximated in the earlier calculations,⁷ we get

$$\sigma_{ac}(\omega) = \frac{\pi^2 \epsilon n N^2}{48} \left(\frac{4ne^2}{\epsilon W_t}\right)^6 \frac{\omega^{1-\beta}}{(\tau_{1\omega})^\beta} \exp\left(\frac{\beta W_\omega}{E_{MN}}\right). \quad (34)$$

Thus Mayer- Neldel signature is achieved in σ_{ac} of chalcogenides. If the entropy is not accounted for, the exponential function will be unity and MN signature will vanish.

D. Exponential parameter s

The exponent s is defined as

$$s = \frac{d \ln \sigma_{ac}(\omega)}{d \ln \omega}. \quad (35)$$

In the CBH model $s = 1 - \beta$, and if the third order term in the expansion of $(W_m - W_\omega)^{-6}$ is also added one gets $s = 1 - \beta + \gamma$, where $\gamma = 6\left(\frac{k_B T}{W_\omega}\right)^2 \ln(\omega \tau_0)$. Using random free energy barrier hopping results for σ_{ac} and r_ω in Eq. (35), we get

$$s = 1 - \beta + \frac{z^2}{4n} (\omega \tau_{1s})^{\frac{\beta}{6}} \left[1 - \tanh\left(\frac{z^2 e^2}{2\epsilon k_B T r_\omega}\right)\right]. \quad (36)$$

The third term in Eq. (36) arise due to Coulomb correlation in the defect distribution and polarizability functions. If the ratio of the Coulomb correlation and thermal field is such that $\tanh(x)$ is nearly one, then $s = 1 - \beta$ as obtained in CBH model. If we take $z^2 = 1$, $n=2$, $(\omega \tau_{1s}) \approx 1$, replace

T by T_g in Eq. (8) and neglect the Coulomb correlation between the defect sites, it can be readily shown that

$$s = 1 - \beta + \frac{1}{8} \frac{T}{T_g}. \quad (37)$$

This was the result obtained by Elliot.¹² If the temperature is higher and inter defect site separation r_ω is also large such that $\tanh(x) \rightarrow 0$, one gets

$$s = 1 - \beta + \frac{z^2}{4n} (\omega\tau_{1s})^{\frac{\beta}{6}}. \quad (38)$$

As the third term in Eqs. (36) and (38) explicitly depends on frequency of applied field, polaron radii, inter defect site separation and entropy of the system and if it exceeds β , s may be greater than one. Thus the value of s will depend on the material characteristics and the conditions of the measurements. Even for the same material if the conditions of preparing the samples and measurements change, s will change.

III. CALCULATIONS AND RESULTS

Here it is pertinent to discuss the parameters involved in Eq. (20) and Eq. (30) to calculate σ_{ac} and r_ω . To calculate r_ω , the parameters W_t , $\tau_{1\omega}$ and S are needed. The effective binding energy W_t is the sum of maximum barrier height W_m and thermal energy TS . The following arguments are put forward by various authors to estimate W_m ^{7,14,31} with the help of energy level diagram for the chalcogenide defect states given in Fig. 1. If W_2 , is the energy to take the first electron from defect center D^+ to conduction band and $(B - W_1)$ is the energy to take second electron from defect center D^0 to conduction band, then the maximum energy to take pair of electrons in the conduction band is

$$W_m = W_2 + (B - W_1), \quad (39)$$

where B is the band gap obtained from optical data. As suggested by Mott⁸ and used by Elliot⁷ that $W_2 \approx W_1$ and hence $W_m = B$. This approximation has been invoked later³² and W_m is taken simply twice the energy difference between Fermi energy E_f and optical band gap i.e

$$W_m = 2(B - E_f). \quad (40)$$

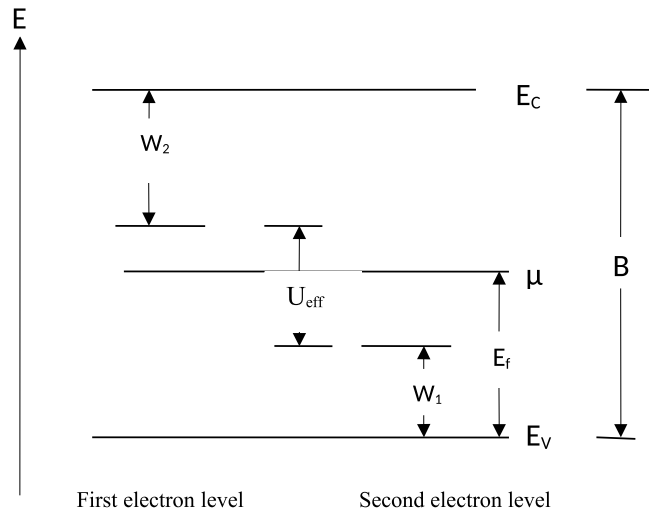


FIG. 1. The schematic energy levels diagram for the chalcogenide defect states,¹⁴ B is the band gap obtained from optical data, E_v and E_c are the highest valence band and lowest conduction band edge energies, μ is Fermi energy level and W_1 and W_2 are the same as described in Table I.

Here E_f is indetermined and amorphous chalcogenides exhibit dc conductivity with activation energy E_{dc} , therefore E_f is replaced by E_{dc} and W_m is estimated with known parameters B and E_{dc} as

$$W_m = 2(B - E_{dc}). \quad (41)$$

If $E_{dc} \approx B/2$, $W_m = B$, is retrieved. Further assuming that $W_w \approx E_{dc}$ in Eq. (33) and using the parameters B, E_{dc} and E_{MN} given in Ref. 29 W_m , S and W_t are determined with the help of Eqs. (41), (32), and (24). The other two critical parameters are the dielectric function ϵ and characteristic relaxation time $\tau_{1\omega} = \tau_0 \exp(2\zeta_\omega)$ and both are frequency dependent. Various authors have used different values of ϵ , and $\tau_{1\omega}$. Shimakawa¹⁴ used just the half of the static value of ϵ and $\tau = \tau_0 = 10^{-13} \text{sec}$. presuming that single high energy optical phonon mode contribute to hopping process. However to be consistent with earlier calculations^{7,29,31} we use $\epsilon = \epsilon_\infty$ and assign the positive values to ζ_ω for each ω to get the best explanation of $\sigma_{ac}(\omega)$. This amount to increase the relaxation time and hence the jump frequencies will decrease and may be of the order of low energy optical and high energy acoustic phonon frequencies and a band of phonon modes contribute to the hopping process.³⁰

An attempt is made to explain the temperature dependence of experimental data for ac conductivity of Se, As_2S_3 , As_2Se_3 and As_2Te_3 . The results of $\sigma_{ac}(\omega)$ were satisfactorily explained for $2\zeta_\omega$ in the range of 1 to 11 and N in the range of 10^{18}cm^{-3} for a-Se, As_2S_3 , As_2Se_3 and in the order of 10^{20}cm^{-3} for As_2Te_3 in the low temperature range. However the deviations of the experimental data from linearity at higher temperatures could not be explained for any acceptable values of ζ_ω and N.

In view of this we adopted Shimakawa¹⁴ suggestion that at higher temperature, where dc conduction dominates, single polaron hopping may also contribute substantially to the ac conduction process. Following Shimakawa¹⁴ we write

$$\sigma_{ac} = \sigma_b + \sigma_{sh} + \sigma_{se}, = \sigma_b + \sigma_s \quad (42)$$

where σ_b , σ_{sh} and σ_{se} are the ac conductivities due to bipolaron, single hole polaron and single electron polaron hopping respectively.

Shimakawa¹⁴ proposed that at higher temperature the defects D^+ and D^- get annihilated and produce neutral defects D^0 following the reverse reaction $2D^0 \rightarrow D^+ + D^-$. Using the law of mass action the number density of excited D^0 centers is obtained as

$$N_D = N \exp\left(-\frac{U_{eff}}{2k_B T}\right), \quad (43)$$

where U_{eff} is the energy released in the annihilation process of charged defects D^+ and D^- as shown in Fig. 1. The hole and electron polaron hoppings are in between $D^0 \leftrightarrow D^-$ and $D^0 \leftrightarrow D^+$ defects respectively and it is assumed that half of D^0 contribute to hole hopping and remaining half to electron hopping processes. To calculate σ_{sh} and σ_{se} we take $n=1$, replace $N^2/2 \rightarrow (N^2/4) \exp(-U_{eff}/2k_B T)$, in Eq. (20), and subsequent relations.

The other critical quantity to evaluate single polaron hopping process is W_m . Evidently from Fig. 1

$$B = W_1 + W_2 + U_{eff}. \quad (44)$$

As W_1 is the energy required to take a hole from D^0 center to the valence band, consequently Mott et. al.³² suggested that W_1 is equivalent to the activation energy in the drift mobility and in the photocurrent in the region when photocurrent is less than the dark current. However the next suggestion of Mott et. al.³² that $W_2 = (B - E_{dc})$ and $E_{dc} \approx W_1 + (1/2)U_{eff} \approx E_f$ does not satisfy the sum rule given in Eq. (44). In view of this we take $W_m = W_1$, for hole hopping and estimate W_1 with the help of activation energy for the drift mobility. For electron hopping process we take $W_m = W_2$, as hole mobility is larger than the electron mobility, we keep $W_1 < W_2$.

First we calculate σ_b to get the best fit at low temperature and lowest frequency data by choosing suitable values of ζ_ω and N. Assuming that N may not change with frequency of applied field, ζ_ω is suitably changed to get the best fit of σ_b for different frequencies for low temperature data. To account for deviation at higher temperature σ_{sh} and σ_{se} are calculated as discussed above using

TABLE I. The physical parameters used in the calculations : B is band gap obtained from optical data, ϵ is dielectric constant, W_m , W_1 and W_2 are maximum barrier heights for bipolaron, single hole polaron and single electron polaron hopping respectively. E_{dc} is activation energy for dc conduction, E_{MN} is Meyer -Neldel energy. and N is the number density of charged defects.

Material	B (eV)	ϵ	W_m (eV)	W_1 (eV)	W_2 (eV)	U_{eff} (eV)	E_{dc} (eV)	E_{MN} (meV)	N (cm^{-3})
$a-Se$	2.00	6.4	1.46	0.67	1.09	0.25	1.27	74	2.0×10^{18}
As_2S_3	2.30	7.8	1.72	0.73	1.32	0.25	1.439	67	3.3×10^{18}
As_2Se_3	2.00	11.2	1.56	0.61	0.84	0.55	1.219	70	7.6×10^{18}
As_2Te_3	1.00	10.0	1.00	0.30	0.49	0.21	0.43	22	1.03×10^{20}

the same values for ζ_ω and N as for bipolaron hopping and varying W_1 and W_2 and estimating U_{eff} as given in Eq. (44). The best fit values of W_1 , W_2 , U_{eff} and N are given in Table I and $2\zeta_\omega$ is tabulated in Table II. Further results for each chalcogenide are given as follows.

A. a-Se

The calculated σ_{ac} for a-Se is compared with the experimental data due to Lakatos and Abkowitz³³ in Fig. 2. The calculated results are close to the experimental data particularly at higher temperature and at higher frequencies as compared to earlier calculations.¹⁴ The low and intermediate temperature range data is explained considering only bipolaron hopping with $N = 2.0 \times 10^{18} cm^{-3}$ and $2\zeta_\omega = 4, 2.2$ and 1.1 for 0.1, 1.0, 10 KHz data respectively and single polaron contribution is added to explain the high temperature data. The best explanation is obtained for $W_1 = 0.67$ eV and $W_2 = 1.08$ eV. We found that σ_{se} is negligible as compared to σ_{sh} and major contribution to single polaron hopping is due to hole polaron hopping. The contribution of single polaron hopping increases rapidly with increase of temperature.

Elliot⁷ and Shimakawa¹⁴ also used the same experimental data of Lakatos and Abkowitz to estimate N and their values are $3.3 \times 10^{18} cm^{-3}$ and $4.2 \times 10^{18} cm^{-3}$ respectively. Our estimated $N = 2.0 \times 10^{18} cm^{-3}$ is lower than these values but the order of magnitude is the same. The predicted defects number density through dc conductivity is $20 \times 10^{18} cm^{-3}$.²⁹ This is reasonable as the density deduced from σ_{ac} is an average over entire temperature range while from σ_{dc} it is only at the higher temperature.

Using the values of $2\zeta_\omega$, the values of effective relaxation time $\tau_{1\omega}$ are, 5.5×10^{-12} , 9×10^{-13} and 2.7×10^{-13} sec. which correspond to hopping frequencies 1.8×10^{11} , 1.1×10^{12} , 3.7×10^{12} Hz and thus we find that optical and acoustic phonons in the range of 10^{11} to 10^{12} Hz contribute in the hopping process of ac conductivity.

B. As_2S_3

The calculated results for As_2S_3 for σ_b , $\sigma_s (= \sigma_{sh} + \sigma_{se})$ and σ_{ac} along with the experimental data due to Goyal and Vohra³⁴ are shown in Fig. 3. The low and intermediate temperature range data is explained with $N = 3.3 \times 10^{18} cm^{-3}$ and $2\zeta_\omega = 5.5, 4.5, 4.0$ for 2KHz, 10KHz, 50KHz

TABLE II. The parameter $2\zeta_\omega$ for applied field frequencies ω for a-Se, As_2S_3 , As_2Se_3 and As_2Te_3 .

Material	ω (KHz)	$2\zeta_\omega$	Material	ω (KHz)	$2\zeta_\omega$
$a-Se$	0.1	4	As_2Se_3	1.0	11
	1.0	2.2		10	9.5
	10	1.0		100	8.0
As_2S_3	2.0	5.5	As_2Te_3	10	6.5
	10	4.5		100	5.4
	50	4.0			

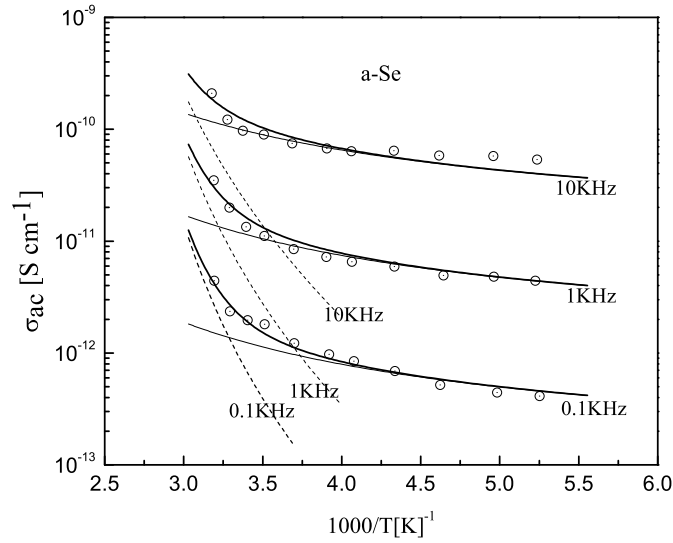


FIG. 2. Temperature dependence of ac conductivity of a-Se for different frequencies of applied field. The dotted lines represent single polaron hopping conductivity, thin continuous lines represent bipolaron hopping conductivity and total ac conductivity is represented by thick solid lines. The dots represent the experimental data due to Lakatos and Abkowitz.³³

frequencies data respectively. The addition of single polaron hopping contribution gives the best explanation of experimental data for $W_1 = 0.73$ eV and $W_2 = 1.32$ eV. The relative contribution of σ_b and σ_s in the different temperature ranges is the same as for a-Se.

Elliot⁷ estimated $N = 1.8 \times 10^{18} \text{cm}^{-3}$ while fitting the experimental data due to Owen and Robertson³⁵ for σ_{ac} , Goyal and Vohra³⁴ estimated $N = 8 \times 10^{18} \text{cm}^{-3}$ using CBH model and Prakash²⁹ estimated $N = 3.6 \times 10^{19} \text{cm}^{-3}$ to explain σ_{dc} due to Lakatos and Abkowitz.³³ However the values obtained for W_1 , W_2 and U_{eff} in Ref. 34 do not satisfy the sum rule given in Eq. (44). Our estimated N is lower than obtained in Ref. 34 and larger than that due to Elliot,⁷ and lower by an order of magnitude than that obtained by dc conduction. The values of effective relaxation time $\tau_{1\omega}$ are 2.4×10^{-11} , 9.0×10^{-12} and 5.45×10^{-12} sec. and corresponding hopping frequencies are 4.1×10^{10} , 1.1×10^{11} and 1.8×10^{11} Hz which contribute to hopping process.

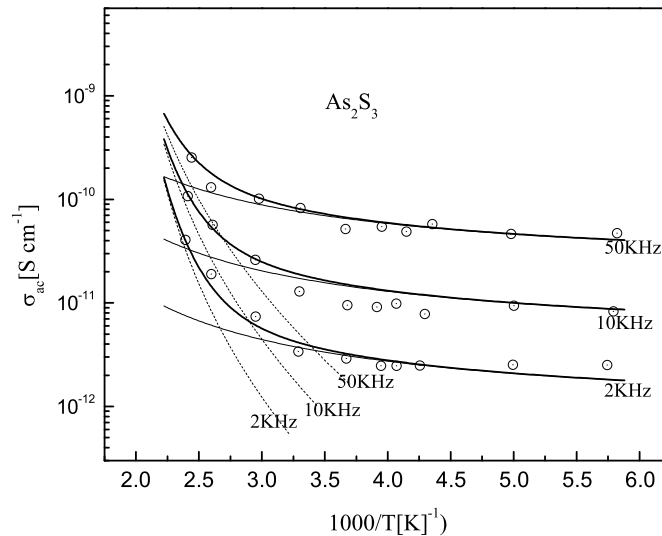


FIG. 3. The temperature dependence of ac conductivity of glassy As_2S_3 for different frequencies of applied field. The description is same as for Fig. 2. Here the dots represent the experimental data due to Goyal and Vohra.³⁴

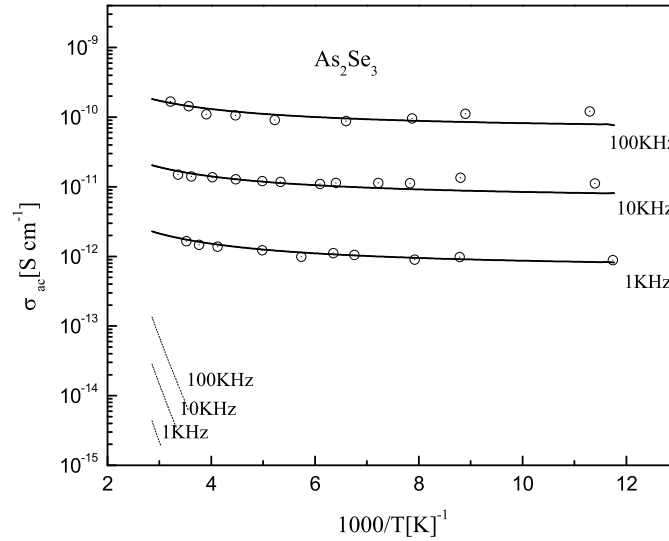


FIG. 4. The temperature dependence of ac conductivity of glassy As_2Se_3 for different frequencies of applied field. The description is same as for Fig. 2. Here the dots represent the experimental data due to Hirata et. al.¹³

C. As_2Se_3

As discussed earlier the low and intermediate temperature data for σ_{ac} was explained by taking $N = 7.6 \times 10^{18} cm^{-3}$ and $\zeta_{\omega} = 11, 9.5$ and 8 for $1, 10$ and 100 KHz frequencies data respectively. The single polaron contribution is added by varying W_1 and W_2 and keeping $W_2 > W_1$ and the best explanation is achieved for $W_1 = 0.61$ eV and $W_2 = 0.84$ eV. These calculated results for temperature variation of σ_{ac} for As_2Se_3 are compared with experimental data due to Hirata et. al.¹³ in Fig. 4. The bipolaron and single polaron hopping contribution are also shown there separately. Our results are closer to the experimental data than those obtained in earlier calculations.^{13,14,25} It is evident from Fig. 4 that single polaron hopping contribution is negligible and most of σ_{ac} is due to bipolaron hopping process.

Shimakawa¹⁴ explained the experimental results of As_2Se_3 for σ_{ac} due to Kitao³⁶ for 100 KHz frequency and estimated $N = 4.2 \times 10^{18} cm^{-3}$ with $W_1 = 0.55$ eV, $W_2 = 0.75$ eV and $\zeta_{\omega} = 0$. Elliot estimated $N = 1.3 \times 10^{18} cm^{-3}$ with the help of experimental data due to Owen and Robertson³⁵ accounting only the bipolaron hopping. Hirata et. al.¹³ estimated $N = 6.48 \times 10^{17} cm^{-3}$ in the CBH model and Abdel- Wahab²⁵ estimated $N = 1.21 \times 10^{18}$. The best fit for σ_{dc} for As_2Se_3 gives $N = 2.0 \times 10^{20} cm^{-3}$.²⁹

The effective relaxation time $\tau_{1\omega}$ are 5.98×10^{-9} , 1.34×10^{-9} and 2.98×10^{-10} sec. which correspond to optical and acoustical phonons in the range 1.67×10^8 to 3.4×10^9 Hz.

D. As_2Te_3

Following the same procedure as described above we calculated $\sigma_{ac}(\omega)$ for As_2Te_3 . These results along with the experimental data due to Rockstad³⁷ are shown in Fig. 5. The calculated results are quite close to the experimental data. It is noted that σ_{ac} is nearly due to bipolaron hopping up to $T = 180^0K$, however at higher temperature single polaron hopping contribution starts increasing and it become significant above $T = 300^0K$. The estimated parameters are $W_1 = 0.30$ eV, $W_2 = 0.49$ eV, $N = 1.03 \times 10^{20} cm^{-3}$ and $2\zeta_{\omega} = 6.5$ and 5.4 for 10 and 100 KHz frequencies respectively. Shimakawa estimated $W_1 = 0.30$ eV, $W_2 = 0.33$ eV and $N = 1.8 \times 10^{19} cm^{-3}$ from the same data, However Elliot⁷ estimated $N = 2.2 \times 10^{19} cm^{-3}$ accounting for bipolaron hopping and Abdel- Wahab suggested $N = 1.2 \times 10^{18} cm^{-3}$ for $T_0 = 500^0K$. The estimated defect density of states from σ_{dc} is $1.2 \times 10^{21} cm^{-3}$.²⁹

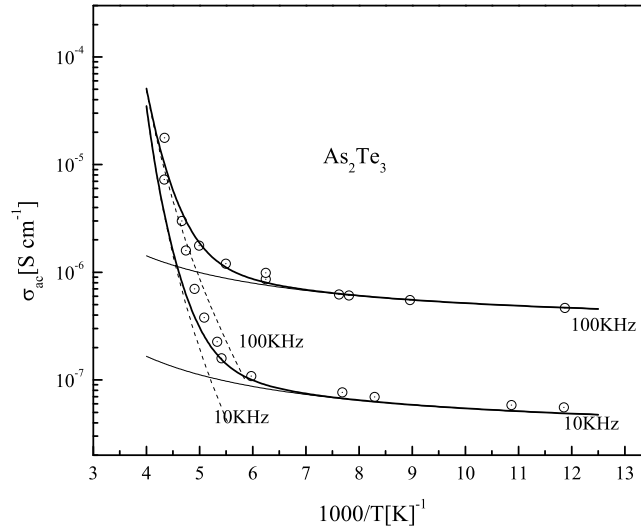


FIG. 5. The temperature dependence of ac conductivity of glassy As_2Te_3 for different frequencies of applied field. The description is same as for Fig. 2. The dots represent the experimental data due to Rockstad.³⁷

The effective relaxation times are 6.65×10^{-11} and 2.2×10^{-11} sec. for field frequencies 10 and 100KHz respectively and this suggests that the narrow band of optical and acoustic phonons of 4.5 to 1.5×10^{10} Hz contribute to the hopping process.

IV. DISCUSSION

It is pertinent to discuss the non adiabatic and adiabatic hopping process as the barrier height is temperature dependent and we have used the relaxation time given in Eq. (11) obtained for the adiabatic hopping instead of that given in Eq. (10) obtained for non adiabatic hopping process.

As described in Landau-Zener charge transfer theory there are two distinct types of hopping (phonon-assisted charge transfer):non adiabatic and adiabatic.

In non- adiabatic limit the separation between sites involved in hopping is large enough for its electron -transfer energy to be orders of magnitude smaller than the relevant phonon energy.Then the hopping rate is proportional to the absolute square of the electron -transfer energy . This factor may be approximated as $\exp(-2ar)$ as given in Eq. (12).The non-adiabatic limits have been applied to non-polaronic hopping between impurity states in very lightly doped crystalline semiconductors,where the typical inter-site separation is of the order of 100 nm as in Ref. 1. These authors used the explicit expression of transition rate given by Millar and Abrahams³⁹ to explain the ac conductivity of As and Sb doped with Si.The extreme slowness of the low temperature non-adiabatic relaxation rates results from the long distances that non-polaronic carriers hop.

By contrast polaron hops are relatively short ,<1nm, and therefore adiabatic.Then the hopping rate is nearly independent of the electron -transfer energy.The theory of the low temperature low frequency ac conductivity of adiabatic polaron hopping was developed by Emin.⁴⁰ The extreme slowness of the low-temperature adiabatic relaxation rates results from the sluggish atomic movements that must accompany low-temperature hops.

As we are discussing here the ac conductivity of binary chalcogenide glasses in terms of polaron hopping.Therefore, it can be said that it is assumed here that the polarons hop in the extreme non adiabatic limit as polaron hopping is usually adiabatic as discussed above.

Here the random free energy barrier hopping model is formulated for both the bipolaron and single polaron hopping contributions for the ac conductivity of chalcogenides. The different sets of defect number densities, charge carrier units and barrier heights are used to evaluate σ_b and σ_s which dominate at lower and higher temperatures respectively. In the initial formulation of Pike and Geballe¹ for ac conduction the relaxation was for the single electron and later it was successfully

extended for the hopping of pair of electrons and holes,³⁰ assuming that their localization and relaxation process is the same as for single electron. In view of this it is assumed here that the Eqs. (20) and (30) are equally applicable to bipolaron and single polaron hopping although the number density of single polaron is augmented by temperature dependent exponential function. In the hole hopping process $D^0 \longleftrightarrow D^-$ an electron has to be localized on the D^0 state before D^- state can relax.³¹

In Eq. (18) the integral over space coordinate r is for $r = r_\omega$ i.e. a narrow band of defect distribution participate in the hopping process. This approximation is reasonable, however at higher temperature this may not equally valid. In the present model r_ω is temperature and frequency dependent as given in Eq. (30). As an illustration the variation of r_ω with T for As_2Te_3 is shown in Fig. 6. The variation in r_ω is rather negligible for bipolarons, but for single electron polaron its value increase about 1.5 times and for hole polaron hopping it increases about 3.5 times at higher temperature than its value at lower temperature. In lower temperature range magnitude of r_ω for hole polaron is nearly three times than that for bipolaron and electron polaron.

Here it is noted that the barrier height for bipolaron hopping W_m is more than two times than that for hole hopping W_1 , while W_m is comparable to the barrier height for electron hopping process W_2 . The hole hopping is more pronounced than electron hopping as $W_2 > W_1$.

It is found that σ_s is smaller by order of magnitude than σ_b at low temperature for all these materials. However as the temperature increases σ_s become comparable to σ_b and it increases exponentially due to the temperature dependent factor $\exp(\frac{-U_{eff}}{2k_B T})$ which is nearly the characteristic of σ_{dc} in the conduction process.

We have taken $2\zeta_\omega$ as parameter to account for material characteristics and measurement procedure. This parameter is found between the limits 1 to 11 and these limits are well within those as found by Long.³¹ Thus contrary to earlier belief that only single high energy optical phonon assist the hopping process, we found that a finite band of optical and high energy acoustic phonons also assist to the hopping process.

We have earlier used the extended pair model and random free energy barriers to explain σ_{dc} of chalcogenides and MN rule was achieved.²⁹ The same model is extended here to explain the ac conductivity of chalcogenides and MN rule is achieved for σ_{ac} also. The effect of other sites in hopping process is included through Coulomb correlation in polarizability and defect distribution function. Thus it is concluded that dc and ac conductivities in chalcogenides are due to same mechanism and MN rule is the consequence of temperature dependence of hopping barriers.

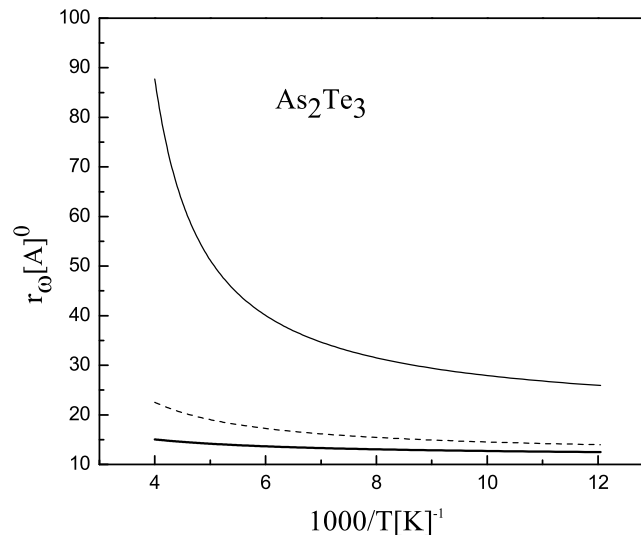


FIG. 6. Temperature dependence of r_ω for As_2Te_3 . Thick continuous line represents hopping length for bipolaron, dashed line for electron and thin continuous line for hole polaron respectively. Here $\omega = 10^5$ Hz and $2\zeta_\omega = 5.7$ and other parameter are taken from Table I.

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- ¹ M. Pollak and T. H. Geballe, *Phys. Rev.* **122**, 1742 (1961).
- ² M. Pollak, *Phil.Mag.* **23**, 519 (1971).
- ³ G.E. Pike, *Phys.Rev.B* **6**, 1572 (1972).
- ⁴ M. Pollak and G.E. Pike, *Phy.Rev.Lett.* **28**, 1449 (1972).
- ⁵ D. Emin, C.H. Seager, and R.K. Quinn, *Phy.Rev.Lett.* **28**, 813 (1972).
- ⁶ C.H. Seager and R.K. Quinn, *J.Non-Cryst.Solids* **17**, 386 (1975).
- ⁷ S.R. Elliot, *Phil.Mag.* **36**, 1291 (1977).
- ⁸ N.F. Mott, *Adv.Phys.* **16**, 49 (1967).
- ⁹ P.W. Anderson, *Phys.Rev.Lett.* **34**, 953 (1975).
- ¹⁰ W.A. Philips, *Phil.Mag.* **34**, 983 (1976).
- ¹¹ R.A. Street, *Phys.Rev.B* **17**, 3984 (1978).
- ¹² S.R. Elliot, *Phil.Mag.B* **40**, 507 (1979).
- ¹³ K. Hirata, M. Kitao, and S. Yamada, *J.Phys.Soc.Jpn.* **52**, 1317 (1983).
- ¹⁴ K Shimakwa, *Phil.Mag.B* **46**, 123 (1982).
- ¹⁵ Y. Takano, M. Kitao, and S Yamada, *Philos.Mag.B* **55**, 515 (1987).
- ¹⁶ J.J. Hauser, *Phy.Rev.Lett.* **44**, 1534 (1980).
- ¹⁷ Fathy Salman, *Turk J.Phys.* **28**, 41 (2004).
- ¹⁸ S.D. Savransky, *J.Ovonic Res.* **1**, 25 (2005).
- ¹⁹ R. Shukla, P. Khurana, and K.K. Srivastava, *Phil.Mag.B* **64**, 389 (1991).
- ²⁰ N. Goyal, R. Shukla, and Manohar Lal, *Parmana* **40**, 377 (1993).
- ²¹ F.I. Mustafa, Shikha Gupta, N. Goyal, and S.K. Tripathi, *Physica B* **405**, 4087 (2010).
- ²² A. Thakur, V. Sharma, G.S.S. Saini, N. Goyal, and S.K. Tripathi, *J.Phys.D.Appl. Physics* **38**, 1 (2005).
- ²³ K. Shimakwa and F. Abdel-Wahab, *Appl.Phys.Lett.* **70**, 652 (1997).
- ²⁴ W. Meyer and H. Neldel, *Z.Tech.Phys.(Leipzig)* **12**, 588 (1937).
- ²⁵ F. Abdel-Wahab, *J.Appl.Phys.* **91**, 265 (2002); *Phil.Mag.B* **82**, 1327 (2002).
- ²⁶ N. Mehta, A.S. Mann, and A. Kumar, *Chalcogenide Letters.* **4**, 139 (2007).
- ²⁷ R.S. Sharma, N. Mehta, and A. Kumar, *Chem.Phys.Letters* **25**, 4079 (2008).
- ²⁸ J C Dyre, *J.Appl.Phys.* **64**, 2456 (1988).
- ²⁹ S. Prakash, Kulbir Kaur, Navdeep Goyal, and S.K. Tripathi, *Pramana J.Phys.* **76**, 629 (2011).
- ³⁰ D. Emin and T. Holstein, *Ann. Phys.* **53**, 439 (1969); D. Emin, *Phys.Rev.Letteres* **100**, 166602 (2008).
- ³¹ A.R Long, *Adv. Phys.* **31**, 553 (1982).
- ³² N.F. Mott and E.A. Davis, in *Electronic Processes in Non-crystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979), Chap. 9.
- ³³ A.I. Lakatos and M. Abkowitz, *Phys.Rev.B* **3**, 1791 (1971).
- ³⁴ N. Goyal and A. Vohra, *Phys.Status Solidi (b)* **171**, 477 (1992).
- ³⁵ A.E. Owen and J.M. Robertson, *J.Non Crystalline Solids* **2**, 40 (1970).
- ³⁶ M. Kitao, *Jap.J.Appl.Phys.* **11**, 1472 (1972).
- ³⁷ H.K. Rockstad, *J.Non-Crystalline Solids* **8-10**, 621 (1972).
- ³⁸ M. Kastner, D. Adler, and H. Fritzsche, *Phys. Rev.Lett.* **37**, 1504 (1976).
- ³⁹ A. Millar and E. Abrahams, *Phys.Rev.* **120**, 745 (1960).
- ⁴⁰ D. Emin, *Phys.Rev.B* **46**, 9419 (1992).