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The Normal and Inverted Meyer-Neldel Rule in the ac Conductivity

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Abstract

Recently, a new approach has been proposed for the correlated barrier hopping (CBH) model where the ac relaxation time is thought to obey the Meyer-Neldel (MN) rule. This approach gives quantitative agreement with some reliable published experimental data. We report on an experiment involving the characterization of the ac conductivity of Se-Te thin films over a wide range of frequencies and temperatures, carried out in order to confirm applicability of the MN rule to the ac conductivity. In addition to the normal MN rule, the inverted MN rule was observed.

Key Words: The Meyer-Neldel rule, Correlated barrier hopping, Relaxation time.

1. Introduction

Although the compensation law known as the Meyer-Neldel (MN) rule [1] was established empirically in 1937, it has gained more attention throughout the past two decades due to greater interest in the fabrication of the new materials. This attention comes from the applicability of the MN rule to give us details regarding some of the physical properties of materials under consideration. These properties include the shape of the density of localized states in the mobility gap [2–4], distribution of the traps [5, 6], different types of defects [7, 8], and the number of annihilated phonons during activated processes [9]; and it may also indicate the transport mechanism [5, 10–13]. The MN rule states that, in the case of a thermally-activated processes, the dc electrical conductivity can be related as

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E/kT), \tag{1}$$

where the pre-factor σ_0 correlates with the activation energy ΔE in the form

$$\sigma_0 = \sigma_{00} \exp(\Delta E/kT_0), \tag{2}$$

where σ_{00} is a constant for a set class of materials, and T_0 is the Meyer-Neldel characteristic temperature.

The study of ac conductivity in amorphous solids, particularly chalcogenide glasses, has long been an important tool for the investigation of microscopic motion. The observed ac conductivity has often been interpreted in terms of the bipolaron correlated barrier hopping model (CBH) at low temperatures [14, 15].

Recently, a new approach has been suggested for the CBH model to approximate the calculation of the bipolaron in chalcogenide glasses [16]. It is assumed in this approach that the relaxation time formula is activated, and it includes the Meyer-Neldel rule term rather than its simple activated from. It was shown that the calculation based on the MN rule, gives a good quantitative agreement with the experimental data at high and low temperatures. In the present studies, the starting point is the observation of the MN rule in the ac conductivity. For this purpose we carried out ac conductivity measurements for $Se_{.70}Te_{.30}$ and $Se_{.65}Te_{.35}$ thin films. Next, we shall compare the recent approach of the CBH calculation to the experimental data.

2. Experimental

Bulk composition in the system Se-Te were first prepared by melting together the appropriate amounts of high purity (99.999%) elements in evacuated and sealed quartz ampoules at around 900 °C for about 10 hours. The ampoules were thereafter quenched in ice-cold water. Their resulting bulk alloy samples were used to prepare thin films by using thermal evaporation method in a vacuum 10^{-6} torr. Properly cleaned corning glass slides coated by ITO were used as substrates. The resulting films thickness was around 1 μm. Gold electrodes with about 0.5 cm^2 area were deposited on the Se-Te films. The ac conductivity of the thin film samples was measured in a sandwich structure using Hewlett Packard A284A Capacitance Bridge. The conductance was measured in the frequency range 30 Hz–1 MHz and over the temperature range 100–300 K.

3. Results

The results of ac conductivity as function of reciprocal temperature for evaporated $Se_{.70}Te_{.30}$ and $Se_{.65}Te_{.35}$ thin films are shown as open circles in Figures 1 and 2, respectively. For increased clarity, not all frequency data points are depicted in these figures. The ac conductivity shows strong temperature dependence at high temperature. However, below a certain temperature the ac conductivity is almost temperature independent. The onset of strong temperature dependence increases with frequency until ac conductivity becomes temperature independent. The procedure to obtain the MN plot is described as follows. Generally, the pre-exponential factor parameter $\sigma_0(\omega)$ and ac activation energy ΔE are obtained from the semi-logarithmic plots of the ac conductivity versus reciprocal temperature in the temperature range 260–300 K. The activation energy is then determined as the absolute value of the average slope of the approximate straight line in the resulting plot. However, the pre-exponential can be identified by the intercept of the extrapolation of the conductivity at $1/T = 0$. Let us assume that the slopes (ac activation energy) remains unchanged with temperature and any apparent decrease is due to the change in frequency. Then this behavior can be described by the equivalent representation shown in Figures 3 and 4 for $Se_{.70}Te_{.30}$ and $Se_{.65}Te_{.35}$, respectively, where the logarithm of pre-factor of the ac conductivity is plotted against the ac activation energy. In these figures (Figures 3, 4), the open circles represent the experimental data. The solid lines show the best fit to the experimental data using the least squares method.

Obviously, those figures can be represented by the following formula

$$\ln \sigma_0(\omega) = \sigma_{00}^{\pm} \pm \frac{\Delta E}{kT_0^{\pm}}, \tag{3}$$

where $\sigma_{00}^{\pm}$ and $T_0^{\pm}$ are constants. The positive and negative superscript sign of T_0 indicates on the normal and inverted MN rule, respectively. These values are given in Table 1. It should be noted that the experimental data at low frequencies is found to obey the normal MN rule; however the high frequency data are found to obey the inverted MN rule.

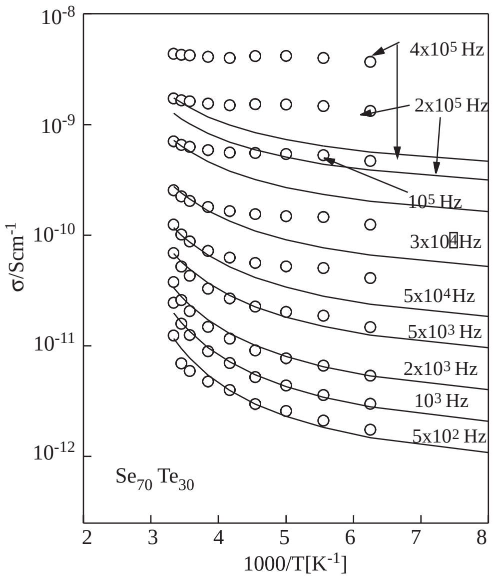

Figure 1. The temperature dependences of the measured AC conductivity at various frequencies for $Se_{.70}Te_{.30}$ thin film. The solid curves are calculated results using Eq. (7).

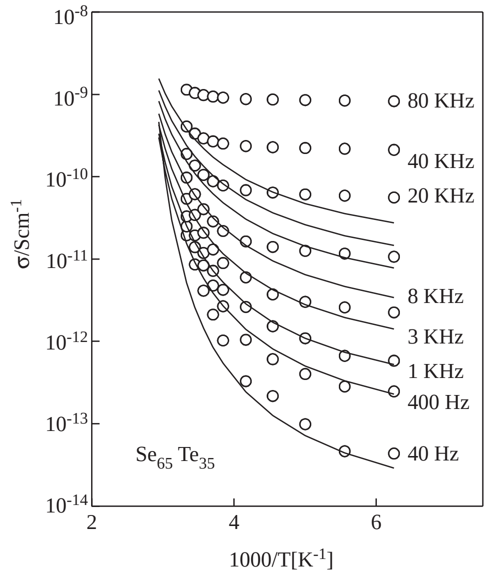

Figure 2. AC conductivity of $Se_{.65}Te_{.35}$ as function of reciprocal temperature for various frequencies.

Table 1. The Meyer-Neldel rule parameters using a least squares and the values of parameters used in the fitting of the CBH model based on the MN rule.

	Se $_{70}$Te$_{30}$	Se $_{65}$Te$_{35}$
σ_{00}^{+}/ Scm^{-1}	3 x 10^{-7}	1.5 x 10^{-7}
σ_{00}^{-}/ Scm^{-1}	3.7 x 10^{-6}	8 x 10^{-4}
T_0^{+}/K	545	383
T_0^{-}/K	193	35
W$_m$/eV	1.67	1.45
NN_p/ cm^{-6}	4 x 10^{34}	2.5 x 10^{35}

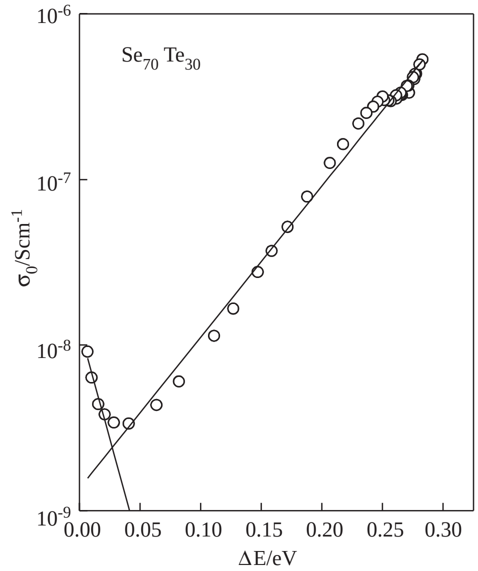

Figure 3. The Meyer-Neldel plots for $Se_{.70}Te_{.30}$. The open circles are computed from the experimental data. The solid lines are least-squares fits.

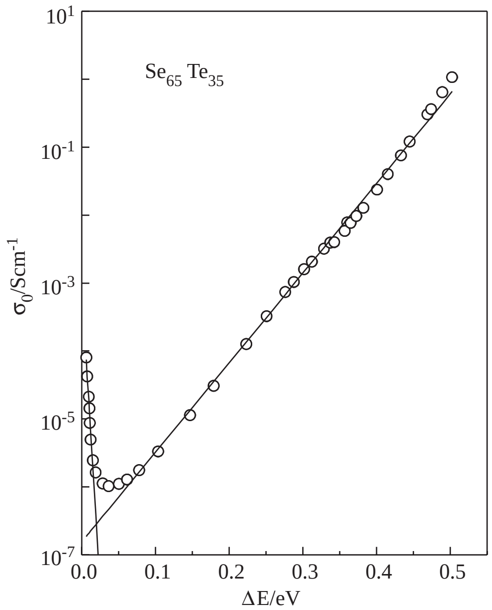

Figure 4. The Meyer-Neldel plots for $Se_{.65}Te_{.35}$.

4. Theory

Before proceeding with the discussion of the normal and inverted MN rule, we are going to review the recent approach of the CBH model. It is well known that the CBH model based on barrier height W should correlate with the separating distance between pairs (R) by the expression

$$W = W_m - \left(\frac{2e^2}{\varepsilon_0 \varepsilon_1 R}\right), \tag{4}$$

where W_m is the height of the energy barrier corresponding to $R = \infty$. The ε_0 is the permitivity of the free space and ε is the dielectric constant. It is assumed that the inhomogeneity in disordered materials produces a distribution in the energy barrier, and for that reason we proposed a new formula for the relaxation time that can be expressed as

$$\tau = \tau_0 \exp\left(\frac{W(r)}{kT}\right) \exp\left(-\frac{W(r)}{kT_0}\right) \tag{5}$$

The expression of ac conductivity of the correlated barrier-hopping (CBH) model based on the MN rule can be given as [16]

$$\sigma_{ac} = \frac{1}{24\xi} n\pi^2 N N_P \varepsilon_0 \varepsilon \omega R_\omega^6, \tag{6}$$

where N, N_P is the number of sites and carriers, respectively, $\xi = \frac{T_0 - T}{T_0}$, and

$$R_\omega = \frac{2e^2}{\pi\varepsilon\varepsilon_0} \frac{1}{W_M + (kT/\xi)\ln(\omega\tau_0)}. \tag{7}$$

5. Discussion

In order to check the validity of the CBH based on the MN rule, the calculated results (solid curves) are compared with experimental data of $Se_{.70}Te_{.30}$ and $Se_{.65}Te_{.35}$, as shown in Figures. 1 and 2, respectively. As can be seen from the figures at low frequencies, the experimental values of ac conductivity fall on the values predicted by the CBH model. However, at high frequencies the measured values of $\sigma(\omega)$ are higher than the theoretical values. The difference between experimental and theoretical prediction shows a continuous increase with increasing frequency. The fitting parameters are given in Table 1. From Figures 1–4, one can conclude that the MN rule comes from the hopping of the carrier over energy barrier. On the other hand, the inverted MN rule shown in Fig. 3 and 4 is a puzzling phenomenon. In fact, there are a number of theories which have been proposed in order to explain the MN rule of the dc transport [3, 17, 18]. Among those models, only the statistical shift of the Fermi-level [3] predicted the inverse MN rule. According to this model the inverse MN rule is due to moving the Fermi level deeply in the band tails. More recently, Widenhorn et al [19] demonstrated that the MN rule occurs due to of two process intrinsic process and impurity process. The inverted MN rule is also obtained in this model, and its origin is regarded to heavy impurity concentration. On the other hand the inverted MN rule of the dc conductivity was confirmed experimentally for hydrogenated microcrystalline Si [20], heavily doped microcrystalline Si [21] and nanocrystalline Si [22]. In the present study the inverted MN rule is observed in the high frequency region. However its origin is not yet clear, and more experimental data using different types of electrodes is needed.

6. Conclusion

In conclusion, the normal and inverted Meyer-Neldel rule of ac conductivity is observed for the first time in Se-Te thin films. We demonstrated that the MN rule is a result of bipolaron hopping over a barrier. However, the origin of the inverted MN rule is not clear.

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