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On the DC electrical transport in As₂SeTe glass

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Abstract. Glassy As₂SeTe was prepared by melting the constituent elements in quartz ampoules at 1000 K for 5 h and by cooling in air. The DC electrical conductivity and thermoelectromotive forces at different temperatures were measured. The difference between the activation energies of the DC electrical conductivity and of the thermopower is found to be 0.255 eV. The origin of this difference is discussed using the small-polaron variable-range hopping model, the two-channel model and the single-channel model, respectively. Physically acceptable results were obtained for the single-channel model involving hopping in localized states originating from the tail of the valence band, the hopping process being identified as the nearest-neighbour hopping of self-trapped holes between more or less energy-equivalent sites. The result indicates that the variable-range hopping (percolation) aspects of the electrical transport in this glass are not important. It is pointed out that the results of the analysis of the DC electrical transport in As₂SeTe glass presented in this paper agree both qualitatively and quantitatively with the results of the analysis of the AC electrical transport in the same system presented by El-Den *et al* in 1987.

1. Introduction

Recently the electrical charge transport in As–Se–Te glasses has been investigated using DC and AC conductivity measurements at different temperatures (El-Den *et al* 1987). The important result of their paper was the fact that the DC electrical conductivity activation energy of the glasses studied is the sum of two contributions, the first being the activation energy of charge density, while the second is the activation energy of mobility. As stated by El-Den *et al* (1987), this indicates that electrical charge transport in the glass investigated (As₂SeTe) is probably due to single-channel hopping (the nearest-neighbour hopping distance being $\langle r_{ij} \rangle \simeq 7.5 \text{ \AA}$) involving charges strongly localized through appreciable charge–lattice interaction. In such a case the activation energy E_S of thermopower should be lower than the DC conductivity activation energy E_σ and the difference ΔE between these two quantities given by $\Delta E = E_\sigma - E_S$ should be close to the value of the activation energy E_μ of mobility. The value found by El-Den *et al* (1987) was $E_\mu = 0.253 \text{ eV}$.

It is the aim of this work to study the temperature dependence of both the DC electrical conductivity $\sigma_{\text{DC}}(T)$ and the Seebeck coefficient $S(T)$ in order to verify whether the results of these measurements are compatible with the results of El-Den *et al* (1987). Since the value $\Delta E > 0$ is usually found quite generally in non-crystalline chalcogenide glasses (Van der Plas and Bube 1977) we shall discuss our

results in connection with a number of existing basic theoretical models which attempt to explain the origin of this difference. The following possibilities will be taken into consideration:

- (i) the small-polaron variable-range hopping model;
- (ii) the two-channel model;
- (iii) the single-channel model involving electrical transport in the tail states of the valence band.

2. Experimental details

The glassy As_2SeTe was prepared by direct synthesis from arsenic, tellurium and selenium (99.999% purity). The elements, of total mass 5 g, were placed in a quartz ampoule (inner diameter, 12 mm; wall thickness, 0.8 mm; ampoule length, 80 mm). After synthesis and homogenization (5 h; $T \approx 1000$ K) the ampoule was cooled in air.

X-ray diffraction measurements, optical microscopy (magnification, $100\times$) and differential thermal analysis (DTA) verified the glassy nature of the samples.

The samples for optical measurements were prepared by cutting the bulk and polishing the slices to optical quality (using a suspension of Al_2O_3 powder in isopropyl alcohol). The thickness of samples was typically 0.05–0.1 cm. Optical transmission was measured using a Perkin–Elmer Lambda 9 spectrophotometer.

Samples for the measurements of the electrical properties were prepared from the bulk in the form of thin discs with thicknesses of 0.05, 0.1 and 0.3 cm. Both faces of the discs were roughened by silicon carbide (granularity, 800).

The dark-conductivity measurements were carried out over the temperature range 200–400 K in the sandwich geometry. The constant-voltage method was used and the actual values of the current were detected with a Keithley 617 digital electrometer. Aquadac paste was used to make a contact between the sample and two copper electrodes. Prior to the measurements, each sample was heated at 350 K (1 h; $p \approx 10^{-2}$ Pa) to remove traces of moisture. The quality of electrical contacts was controlled

- (i) by measurements of the I – V characteristics which were ohmic up to 75 V,
- (ii) by different geometries of the contacts, and
- (iii) by measurements on samples of three different thicknesses.

In all cases the reproducibility of the measured value of the current was within an error of up to $\pm 7\%$. All measurements were made in a ‘stationary’ state (constant voltage, 10 V), i.e. the temperature was changed in steps and the value of the current was measured after stabilization of the temperature (approximately 30 min).

The thermoelectromotive force was measured in the temperature range 300–400 K on specimens in sandwich geometry, too. Aquadac paste was used to make a contact between the samples of thickness 0.3 cm to two copper electrodes, which were in turn isolated by thin sapphire plates from two copper heaters. The value of the thermoelectric voltage ΔU was measured in both directions of the temperature gradient ΔT . The values of the Seebeck coefficient were taken as the slope of the linear dependence of ΔU versus ΔT . The sign of the Seebeck coefficient was given by the sign of the slope of ΔU versus ΔT .

3. Results

The experimental results are summarized in figure 1. The spectral dependence of the absorption coefficient α (figure 1(a)) follows the usual dependence $\alpha = \alpha_0 \exp(\hbar\omega/\Delta)$, $\Delta \simeq 0.04_5$ eV. The room-temperature value of the 'optical gap' E_{03} estimated as the energy for which $\alpha \simeq 10^3 \text{ cm}^{-1}$ has been found to be 1.18 eV.

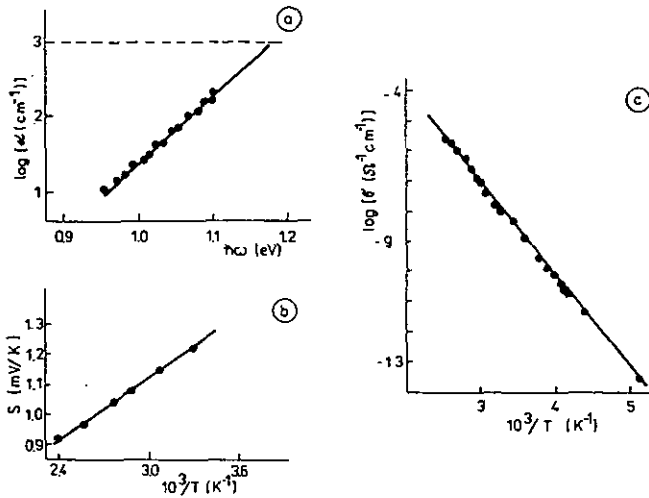


Figure 1. (a) The spectral dependence of the absorption coefficient. (b) The temperature dependence of the DC electrical conductivity. (c) The temperature dependence of the Seebeck coefficient.

The DC electrical conductivity (figure 1(b)) could be approximated by a simple Arrhenius relation $\sigma_{DC} = \sigma_0 \exp(-E_\sigma/kT)$ where $\sigma_0 = 195 \Omega^{-1} \text{ cm}^{-1}$ and $E_\sigma = 0.61$ eV.

The temperature dependence of the p-type Seebeck coefficient (figure 1(c)) was approximated by the relation $S = (k/e)(E_S/kT + A)$, where $E_S = 0.35_5$ eV and $A = 0.73$. The difference $\Delta E = E_\sigma - E_S = 0.255$ eV has been found to be in good agreement with the value of the activation energy of mobility found by El-Den *et al* (1987): $E_\mu = 0.253$ eV.

4. Discussion

As noted in section 1, it is well known (see, e.g., Van der Plas and Bube 1977) that the difference between the activation energies of DC electrical conductivity and of thermopower can be interpreted in terms of a number of possible plausible models for electrical transport. These include

- (i) the small-polaron variable-range hopping model (see, e.g., Tribes and Friedman 1981, 1986),
- (ii) the two-channel model (Nagels *et al* 1973), and
- (iii) the single-channel models (Van der Plas and Bube 1977, Mott and Davis 1979, Seager *et al* 1973).

In the next section we shall discuss our results within these models.

4.1. Small-polaron variable-range hopping model

Based on the generalized molecular crystal model for a small polaron and using the percolation theory to treat the possible variable-range hopping aspects of small-polaron motion it was shown (Triberis and Friedman 1981, 1986) that the DC conductivity and 'macroscopic' thermopower can be given by the following relations, respectively†:

$$\sigma_{\text{DC}} = \exp[-(T'_0/T)^{2/5}] / Z_0 \quad (1)$$

$$S = (k/e)[(T_0^*/T)^{2/5} + A] \quad (2)$$

$$T'_0 = 8.5 N_S^{1/2} \alpha^{2/3} / k N_0 \quad (3)$$

$$T_0^* = 0.75 N_S^{1/2} \alpha^{2/3} / k N_0. \quad (4)$$

The quantity Z_0 is defined by Triberis and Friedman (1981, equation (3.15)), N_S is the concentration of localized sites randomly distributed in energy and position which are available for electronic motion, α is the spatial extent of the wavefunction localized at a given site and N_0 is the density of states.

Our DC electrical conductivity data are shown in figure 2 where $\ln \sigma_{\text{DC}}$ is plotted versus $T^{-2/5}$. From the value‡ $T'_0/T_0^* = 11.33$ the theoretical temperature dependence $S(T)$ can be easily calculated using equation (2). The full line in the inset of figure 2 shows the $S(T)$ dependence as predicted by the model (equation (2)) with the constant A set to zero ($A = 0$). The full circles are the experimental values and the broken line is the fit to our experimental data. Reasonable agreement between the experimental data and the small-polaron variable-range hopping model would require $A < 0$ (more specifically $A = -10.29$). Such a value of A has of course no physical meaning since the constant A ('heat-of-transport' constant) can hardly be negative (Emin 1975, 1977). We are therefore forced to conclude that the interpretation of our DC conductivity and thermopower data in terms of the small-polaron variable-range hopping model of Triberis and Friedman is not possible.

It should be noted at this point that the same conclusion, namely the absence of the variable-range hopping (percolation) aspects in the electrical transport of As_2SeTe has also been deduced by El-Den *et al* (1987) on the basis of an analysis of the electrical field and temperature dependences of the DC electrical conductivity in this system.

4.2. Two-channel model

In the two-channel model the electrical transport is assumed to consist of two contributions of which one contribution σ_1 is due to transport in delocalized states (below the valence band mobility edge E_V) and the other contribution σ_2 is due to the finite conductivity in localized states above the valence band mobility edge (at

† We do not discuss the $\sigma(T)$ and $S(T)$ relations derived assuming a correlation due to the energy of the common site because in this case $\log \sigma \sim T^{-1/4}$ and $S \sim T^{-1/4}$ (in the high-temperature limit) which is incompatible with our experimental data.

‡ T'_0 has been found to be 9.76×10^6 K.

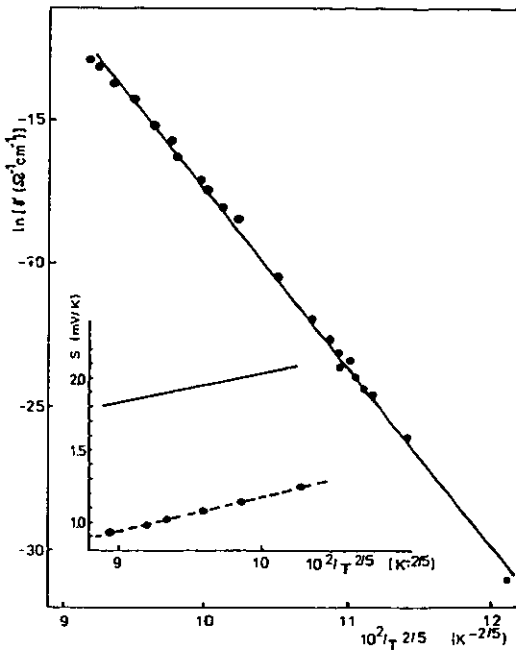


Figure 2. The temperature dependence of the DC electrical conductivity plotted as $\ln \sigma$ versus $T^{-2/5}$: ●, experimental values; —, fit to equation (1). The inset shows the temperature dependence of the Seebeck coefficient plotted as S versus $T^{-2/5}$: ●, experimental values; —, calculated according to equation (2) assuming $A = 0$; ---, fit to equation (2) using $T_0^* = T_0^*/11.33$; see text.

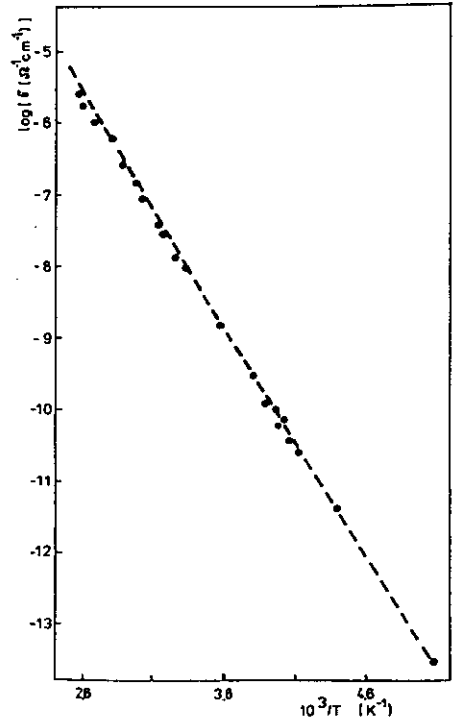


Figure 3. The temperature dependence of the DC electrical conductivity: ●, experimental values; ---, fit to experimental points by a curve with small curvature.

E_B). The relations for DC electrical conductivity and thermopower then take the following form:

$$\sigma_{DC} = \sigma_{01} \exp(-E_1^\sigma/kT) + \sigma_{02} \exp(-E_2^\sigma/kT)$$

$$E_1^\sigma = E_F - E_V \quad E_2^\sigma = E_F - E_B + E_\mu \tag{5}$$

$$S = (\sigma_1/\sigma)(k/e)(E_1^\sigma/kT + A_1) + (\sigma_2/\sigma)(k/e)(E_2^\sigma/kT + A_2)$$

$$E_2' = E_2^\sigma - E_\mu \tag{6}$$

Here E_F is the Fermi level and E_μ is the activation energy of mobility. The other symbols in equations (5) and (6) have their usual meanings. Our experimental data can be fitted by equation (5) only if the $\log \sigma$ versus $10^3/T$ dependence can be approximated by a curve with very small curvature. The best fit is shown in figure 3 (broken curve). The following parameters were obtained: $E_1^\sigma = 0.69$ eV, $\sigma_{01} = 3192 \Omega^{-1} \text{ cm}^{-1}$, $E_2^\sigma = 0.57$ eV and $\sigma_{02} = 12.26 \Omega^{-1} \text{ cm}^{-1}$. Since $E_1^\sigma - E_2^\sigma = E_B - E_V - E_\mu$, it is clear that for $E_\mu > 0$ the width of localized states

($\Delta = E_B - E_V$) should be higher than 0.12 eV. Although the values of E_1^σ , E_2^σ , σ_{01} and σ_{02} seem to be reasonable, the fitting of our experimental $S(T)$ data using equation (6) with calculated σ_{01} , σ_{02} and E_1^σ values again gives unphysical values for the 'heat-of-transport' terms, namely $A_1 = -5.87$ and $A_2 = -55.29$, and of the activation energy of electrical transport in localized states above the valence mobility edge, namely $E_2' = 1.4$ eV. It should also be noted that, even for $A_1 = A_2 = 0$, the calculated values of $S(T)$ exceed by at least 100% the experimental $S(T)$ -values for any value for $E_2' > 0$. Hence we conclude that the two-channel model also cannot be used for the interpretation of our experimental results.

4.3. Single-channel model

The last transport mechanism to be discussed is single-channel electrical transport by positive charges in the energy band tail states below the chemical potential of As_2SeTe . Two fundamentally different situations for the electrical transport have to be considered and will be discussed. They differ in whether the electronic energy states responsible for the electrical transport are 'rigid' (the site energies do not change when occupied by a diffusing charge) or 'deformable' (the site energies do depend on the occupancy).

4.3.1. 'Rigid'-site-energies situation. The difference $\Delta E = E_\sigma - E_S$ between the activation energy of the DC electrical conductivity σ_{DC} and the activation energy of the thermopower S , together with the values for pre-factor σ_0 ($\sigma_{\text{DC}} = \sigma_0 \exp(-E_\sigma/kT)$) and A (heat-of-transport constant) are usually discussed in terms of a number of possible specific transport models. As we have found the two-channel model (hopping above the mobility edge and extended electrical transport below the mobility edge; both transport channels situated well below the chemical potential) to be incompatible with the present experimental data, the following remaining models have to be considered.

(a) First is the 'long-range potential fluctuations' model of Beyer and Overhof (1984) and Overhof and Beyer (1984) (extended-state transport below the mobility edge affected by long-range potential fluctuations).

The electrical transport takes place in the extended states of the valence band and the apparent difference $\Delta E = E_\sigma - E_S$ is caused by postulated long-range potential fluctuations of the order of $\Delta E = E_\sigma - E_S = 1.2\delta$.

The present experimental data indicate that the value of δ would be approximately 0.2 eV, a value for the magnitude of potential fluctuations that is in our opinion unrealistically high. Also there does not seem to exist any independent supportive evidence for such a high value of δ from other experiments (it has to be borne in mind that any real bare potential fluctuations due to some possible localized charges will be screened by the appropriate dielectric constant of the material). Moreover within the model of Overhof and Beyer (1984) the combination

$$Q = \ln \sigma_{\text{DC}} + (e/k)S \quad (7)$$

which cancels the Fermi level shift gives as the Q versus T^{-1} coordinates the linear dependence

$$Q(T) = Q_0 - E_Q/kT \quad E_Q = E_\sigma - E_S$$

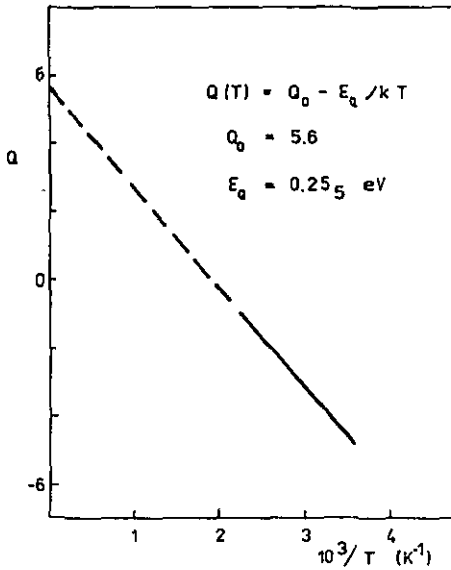


Figure 4. The temperature dependence of Q for the glass studied.

showing (Overhof and Beyer 1984) for a variety of chalcogenide glasses and a-Si films an almost constant ('universal') value $Q_0 = 10.5 \pm 1$. In figure 4 our data ($\sigma_{DC}(T)$ and $S(T)$) are plotted as $Q(T)$ versus T^{-1} . The extrapolated ($1/T \rightarrow 0$) value $Q_0 = 5.6$ is far below the value observed by Overhof and Beyer (1984).

More important than the tentative arguments mentioned above is, however, the fact that the analysis of the electrical transport in As_2SeTe (El-Den *et al* 1987) showed that the mobility in the relevant transport channel is activated with the pre-exponential factor $\mu_0 \simeq 0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a value clearly incompatible with any form of extended-state transport.

(b) Second we consider localized-state hopping transport. This transport mechanism involves the hopping of hole-like charges between the one-particle electronic localized states in the valence band tail (the electronic states in question lie above the valence band mobility edge but well below the position of the chemical potential). Distinguishing between the variable-range hopping process and the nearest-neighbour hopping process in this model is complicated by the fact that the transport channel is situated well below the position of the chemical potential. This means that both the $\sigma(T)$ and the $S(T)$ dependences are dominated by the activation energy of the charge density, making straightforward analysis difficult.

The variable-range hopping aspects of the electrical transport in As_2SeTe within this model can be dismissed, however, as unimportant on the grounds that they would demonstrate themselves in the DC electrical field (E) dependence of the conductivity $\sigma_{DC}(T, E)$. As can be seen from the results of El-Den *et al* (1987) the expected electrical field dependence of σ_{DC} (Apsley and Huges 1974, 1975) has not been found. On the contrary it was possible to identify the transport mechanism as nearest-neighbour hopping (the average hopping distance was about 7.5 \AA) of localized charges between more or less equivalent energy sites (site disorder energy small compared with hopping energy).

Having identified the transport mechanism as the nearest-neighbour hopping process, there are two cases that have to be distinguished.

(i) The first case deals with nearest-neighbour hopping in a band of localized states (of band width B and with a slowly varying density of states), situated somewhere below the position of the chemical potential of the material studied. The hopping activation energy $E_\mu = E_\sigma - E_S$ is identified in this case with the average difference between nearest neighbours ($\Delta E = \frac{1}{2}B$) and in the present case it gives a band width B of the localized band of the order of 0.5 eV. One would therefore expect an appreciable optical absorption in the gap but this is not borne out by the experiment. Alternatively, if one identified the measured exponential band tail absorption with the localized band in question, the deduced width B would only be about 0.2 eV, a value too small to explain the experimental value of ΔE .

It is also important to stress that with the chemical potential lying somewhere near the midgap (Anderson 1975, Mott and Davis 1979) the band of localized states of band width $B \simeq 0.5$ eV would overlap with one-particle extended states below the mobility edge and the effect of the latter states should be felt in the electrical transport (two-channel transport). Since this is not the case, the electrical transport model involving the hopping of hole-like charges in a flat (and relatively wide) band of one-particle localized states situated below the position of the chemical potential has to be considered as inapplicable also.

(ii) The second case deals with the nearest-neighbour hopping between the valence band tail states assuming a strong exponential variation in the density of states. Here Grünewald and Thomas (1973) showed that in such a case the average hopping energy $\Delta E = E_\sigma - E_S$ is related to the quantity ϵ that characterizes the exponential density of states $N \simeq N_0 \exp(E/\epsilon)$ by a relation $\Delta E = E_\sigma - E_S = 3.5\epsilon$. The present data on the optical absorption (figure 1) show that in the case of As_2SeTe the ϵ -value is approximately 0.045 eV, giving the difference $\Delta E \simeq 0.16$ eV, in contrast with the observed value of $\Delta E = 0.255$ eV.

Summarizing so far we can therefore conclude that none of the specific 'rigid'-site-energies electrical transport models accounts satisfactorily and self-consistently for the experimental data of the present work and those of El-Den *et al* (1987).

4.3.2. Deformable-site-energies scenario. In what follows we suppose that the 'deformable'-site-energies scenario is more appropriate for the case of As_2SeTe —and most probably for other disordered materials also (see, e.g., Anderson 1975)—and that the electrical transport mechanism in As_2SeTe involves the movement of self-trapped hole-like charges in states that (before occupation by holes) formed a part of the top of the valence band.

When the site energies responsible for the electrical transport do depend on the occupancy of the site by a charge, a phenomenon of self-trapping (polaron formation) can take place, whereby the energy of a given site is lowered by corresponding deformation of the surrounding lattice. The electrical transport is then by hopping of self-trapped charges. In the case of nearest-neighbour hopping (as opposed to the variable-range hopping of polarons; see the previous section) and at sufficiently high temperatures the energy difference $\Delta E = E_\sigma - E_S$ is directly related to the activation energy of the electrical mobility (high-temperature limit of multiphonon hopping), even with zero site energy disorder.

It is worthwhile to summarize at this point the main results of the present investigation and those of El-Den *et al* (1987).

(i) The DC electrical transport measurements gave the following results: the activation energy E_σ of the DC electrical conductivity σ_{DC} , 0.61 eV; the slope E_S of the temperature dependence of the thermopower $S(T)$, 0.355 eV; $\Delta E = E_\sigma - E_S = 0.255$ eV; heat-of-transport constant $A = 0.73$; 'nearest-neighbour' hopping distance $\langle r_{ij} \rangle \simeq 7.5 \text{ \AA}$.

(ii) From the AC electrical impedance analysis, electrical transport was identified as the nearest-neighbour hopping of strongly localized charges with the electrical mobility and charge density given by

$$\mu = \mu_0 \exp(-0.253 \text{ eV}/kT)$$

$$N = N_0 \exp(-0.267 \text{ eV}/kT)$$

$$\mu_0 = 0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \quad N_0 = 1.34 \times 10^{21} \text{ cm}^{-3}.$$

All the data presented seem to indicate in a self-consistent manner that electrical transport in As_2SeTe could be nearest-neighbour hopping of self-trapped holes in states that originate most probably from the top of the valence band. The high value of the hopping energy ($\Delta E = E_\sigma - E_S$) implies that the jump processes are of a multiphonon variety. In such a case according to Emin (1975, 1977) the magnitude of A measures the disorder energy relative to kT which in our case ($A \simeq 0.73$) should be of the order of kT .

Although speculative, we assume the following one-particle model for electrical transport in As_2SeTe glass. The valence band of As_2SeTe is approximated by a single parabolic band (one-particle approximation; extended states with two electrons with opposite spins per energy state). The parabolic density of states is broadened at the edge into an exponential tail, the disorder being structural and/or thermal. The site energies will decrease through finite deformation of the surrounding lattice when a site is occupied by a single particle (hole self-trapping). At finite temperatures the concentration N of self-trapped charges will be finite and the electrical transport takes place by nearest-neighbour multiphonon hopping of the self-trapped charges between the potential self-trapping sites frozen within the valence band tail (concentration N_0 , where $N_0 > N$).

The experimentally deduced values of the average hopping distance $\langle r_{ij} \rangle \simeq 7.5 \text{ \AA}$ and the potential self-trapping site concentration $N_0 \simeq 1.64 \times 10^{21} \text{ cm}^{-3}$ suggest that not all lattice sites are potential self-trapping sites. If this turns out to be correct, a natural candidate for potential self-trapping sites could be the 'soft modes' suggested by Klinger (1988) that are predicted to exist in glasses in a typical concentration of 1–10 at.%, the actual value depending on the glass transition temperature and the quenching rate. In such a case it would also be easier to understand the relatively very large values of self-trapping binding energies (which equal the polaron binding energy of about $2(E_\sigma - E_S)$) deduced from the present experiment.

5. Summary

Glassy As_2SeTe was prepared by standard synthesis. The temperature dependences of the DC electrical conductivity and thermopower were studied. The results were

discussed within the small-polaron variable-range hopping model, the two-channel model and the single-channel model involving hopping of holes in localized states at the valence band edge. It was found that a physically acceptable interpretation of experimental data can be made using the single-channel nearest-neighbour hopping of self-trapped holes between more or less energy-equivalent sites originating probably from the top of the valence band. The activation energy of mobile charge density was found to be 0.35₅ eV, the mobility activation energy was found to be 0.25₅ eV and the disorder-induced average spread in hopping site energies should be of the order of $\langle E_{ij} \rangle \simeq kT$. These results are in good agreement with recent results obtained from electrical impedance spectroscopy (El-Den *et al* 1987) on the same material.

Acknowledgments

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