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Thermoelectric and Hall effect in amorphous alloy $As_{0.20}Se_{0.40}Te_{0.40}$

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Measurements of the dc electrical conductivity, thermopower and Hall mobility in the amorphous alloy $As_{0.20}Se_{0.40}Te_{0.40}$, at several temperatures below the glass transition temperature have been performed. Two conduction models, the two-channel model and the small polaron hopping model, capable of explaining satisfactorily the experimental results are presented.

1. Introduction

The electrical, thermoelectric and galvanometric properties of chalcogenide glassy semiconductors have been and still are an important subject in the field of non-crystalline semiconductors, as a consequence of their possible applications as the threshold switching (monostable) and memory switching (bistable) elements [1], as well as microrefrigerators and thermoelectric microheaters [2], sensor cells by the Hall effect [3] and transductor elements [4].

The temperature dependence of the dc electrical conductivity, thermopower, mobility and Hall coefficient in the amorphous As–Se–Te system has been studied by various researchers [5–15]. From the thermopower measurements, two important consequences are deduced that appear to be a common characteristic of the analyzed glass system: a positive value for the Seebeck coefficient, indicating that the majority carriers are the holes, and a difference between the activation energies determined by the dc electric conductivity measurements, E_σ, and the activation energy determined by the thermopower measurements, E_s, being $E_\sigma > E_s$. Such difference varies between 0.12 eV in the $As_{0.40}Se_{0.40}Te_{0.20}$ composition [5] and 0.15 eV in the $As_{0.40}Se_{0.20}Te_{0.40}$ [10]. Moreover, all the experimental results in this system confirm the sign anomaly of the charge carriers (the so-called "n–p anomaly"), namely that the Hall measurements suggest n-type conductivity while the thermoelectric power indicates the p-type. In the As_2Se_3–xAs_2Te_3 ($x=0.5$, 2) compositions, the Hall mobility values determined by Male [14] are of the order of 0.1 $cm^2\ V^{-1}\ s^{-1}$, showing for both compositions a slowly varying function of temperature and apparently without marked changes through the glass to liquid transition. The Hall mobility value found by Roilos [13] for the latter composition, at room temperature, was 0.03 $cm^2\ V^{-1}\ s^{-1}$, showing a much stronger variation with temperature than that indicated by Male. This behaviour was confirmed by Roilos for other compositions belonging to the same glass system ($x=1$, 1.5, 2.5, 3, 7) [12,13]. In the composition $As_{0.40}Se_{0.40}Te_{0.20}$, the mobility value found by Fritzsche [15] was 0.1 $cm^2\ V^{-1}\ s^{-1}$, and this quantity was independent of temperature.

In this paper we report on measurements of the dc electrical conductivity, thermoelectric power and Hall coefficient of the glassy composition $As_{0.20}Se_{0.40}Te_{0.40}$ and discuss the results in terms of the current model of the band structure for amorphous semiconductors.

2. Experimental

The materials were prepared by fusing the mixture of the appropriate amounts of the elements in fused silica ampoules vacuum at about 700°C. After heating for 7 h, the melt material was quenched in water with ice. The cylindrically shaped samples were clamped between two brass plates using graphite paint. For the thermopower measurements, the temperature difference was measured with two thermocouples of chromel–alumel, connected in differential form. The ambient temperature was controlled by an Onrom E5K PID temperature controller and a Pt-100 probe.

For the determination of the Hall constant an N 100 magnetic field generator (Oxford Instruments) was used. The sample of parallelepiped shape was placed at half the polar distance (1 cm). With the coils under tension and connected in series, the magnetic field at half the polar distance was 0.924 T.

The value of the Hall coefficient, R_H, was determined by the following expression:

$$R_H = \frac{S}{BdI} V_H , \tag{1}$$

where V_H is the Hall voltage, B the magnetic induction, d the distance between the electrodes between which the generated Hall voltage is measured, S the area of the electrodes and I the current.

The Hall tension was measured with a Keithley 175 DMM. The offset tension was minimized by placing the contacts, as much as possible, in a symmetrical form, making sure that they were on the same equipotential line.

3. Theoretical considerations

In order to interpret the electrical, thermoelectric and galvanometric data, two models seem to be applicable: the two-channel model proposed by Nagels [16] and the small polaron model proposed by Emin [17].

In the first model we shall assume that the density of electron states in amorphous semiconductors suggested by Mott and Davis [18] is applicable. The essential feature of this model is the existence of narrow tails of localized states at the extremes of valence and conduction bands. This leads to two conduction processes:

(a) The conduction due to holes excited beyond the mobility edge into extended states. The expression for the conductivity corresponding to this process is

$$\sigma_1 = \sigma_{10} \exp[-(E_F - E_V)/K_B T] , \tag{2}$$

where $E_F - E_V$ (see fig. 1) is the difference between the Fermi level and the mobility edge, K_B is the Boltzmann constant and σ_{10} a pre-exponential factor.

In the same process the thermopower is given by

$$S_1 = \frac{K}{e}\left(\frac{E_F - E_V}{K_B T} + A_1\right), \tag{3}$$

with $A_1 \approx 1$ [19,15].

If the difference $E_F - E_V$ varies linearly with temperature,

$$E_f = E_F - E_V = E_f^0 - \gamma_1 T , \tag{4}$$

E_f^0 being its extrapolation at 0 K, and assuming that γ_1 is constant, then

$$\sigma_1 = C_1 \exp(-E_f^0/K_B T) , \tag{5}$$

$$S_1 = \frac{K}{e}\left(1 - \frac{\gamma_1}{K_B} + \frac{E_f^0}{K_B T}\right), \tag{6}$$

where

$$C_1 = \sigma_{10} \exp(\gamma_1/K_B) .$$

(b) The conduction due to the holes excited in the states localized in the tail below the edge (fig. 1). If E_B is the maximum energy of the localized states joined to the valence band, a hopping energy, W, should be added to the difference $E_F - E_B$, energy difference between the energy level and the top valence band tail.

The expression for the conductivity is now

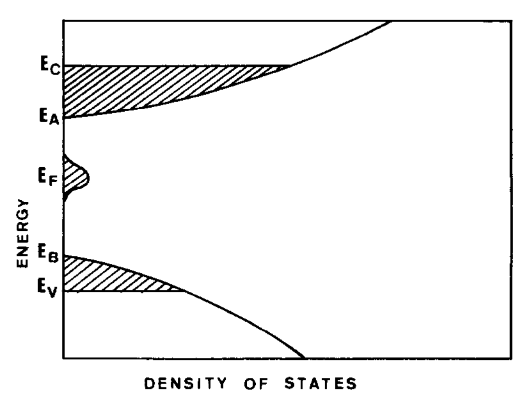

Fig. 1. Density of electron states according to the model proposed by Mott and Davis [18].

$$\sigma_2 = \sigma_{20} \exp\left(-\frac{E_F - E_B + W}{K_B T}\right), \tag{7}$$

and that for the thermopower is

$$S_2 = \frac{K}{e}\left(\frac{E_F - E_B}{K_B T} + A_2\right), \tag{8}$$

σ_{20} being a pre-exponential factor and $A_2 \approx 0$ [20] for a hopping movement.

If the difference $E_F - E_B$ varies linearly with temperature,

$$E_b = E_F - E_B = E_b^0 - \gamma_2 T, \tag{9}$$

E_b^0 being its extrapolation at 0 K, and assuming that γ_2 is constant, then

$$\sigma_2 = C_2 \exp\left(-\frac{E_b^0 + W}{K_B T}\right), \tag{10}$$

$$S_2 = \frac{K}{e}\left(\frac{E_b^0}{K_B T} - \frac{\gamma_2}{K_B}\right). \tag{11}$$

The experimental thermopower, S, is the sum weighed by the thermopower conductivity associated with the individual channels,

$$S = \frac{S_1\sigma_1 + S_2\sigma_2}{\sigma_1 + \sigma_2}. \tag{12}$$

From eqs. (5), (6), (10), (11) and (12), it results

$$S(\sigma_1 + \sigma_2) = \frac{K}{e}\left[\left(\frac{E_f^0}{K_B T} + 1 - \frac{\gamma_1}{K_B}\right) C_1 \exp\left(-\frac{E_f^0}{K_B T}\right) + \left(\frac{E_b^0}{K_B T} - \frac{\gamma_2}{K_B}\right) C_2 \exp\left(-\frac{E_b^0 + W}{K_B T}\right)\right]. \tag{13}$$

In addition, the Hall mobility increases with temperature. Nagels et al. [15] have used the two-channel model to interpret this behaviour. For the conduction processes in the localized and extended states, the Hall experimental mobility, μ_H, like the thermopower, is given by

$$\mu_H = \frac{\mu_{H1}\sigma_1 + \mu_{H2}\sigma_2}{\sigma_1 + \sigma_2}. \tag{14}$$

If the mobility in the hopping regime, μ_{H2}, is much smaller than that in the extended states, μ_{H1}, substituting eqs. (5) and (10) in (14), the following equation is obtained:

$$\mu_H = \mu_{H1}\left[1 + \frac{C_2}{C_1}\exp\left(\frac{E_f^0 - E_b^0 - W}{K_B T}\right)\right]^{-1}. \tag{15}$$

On the other hand, the formation of small polarons in non-crystalline materials has been studied by Emin [17]. If the carrier, due to its low mobility, is situated far enough in the proximity of an atom to produce displacements in the neighbouring atoms, a potential well is created that causes the barrier to be trapped whereby the carrier and the deformed region form a polaron.

According to the small polaron theory [17], the electrical conductivity would be basically thermally activated with the expression

$$\sigma_2 = C_2 \exp\left(-\frac{H}{K_B T}\right), \tag{16}$$

where $C_2 = \sigma_{20}\exp(\gamma_2/K_B)$, and H is the sum of the extrapolated difference at 0K of the Fermi energy, E_F, the polaron binding energy, E_B, and the polaron hopping energy, W.

For the same type of carrier, the thermopower is given by the expression

$$S_2 = \frac{E_b^0 - \gamma_2 T}{K_B T}. \tag{17}$$

For three-site interference in the non-adiabatic regime proposed by Friedman and Holstein [19],

$$\mu_H = \frac{ea^2}{\eta} J\left(\frac{\pi}{12 K_B T W}\right)^{1/2} \exp\left(-\frac{W}{3K_B T}\right), \tag{18}$$

i.e. the activation energy for the Hall mobility is about 1/3 of that corresponding to the electrical conductivity mobility.

4. Results and discussion

The conductivity data for the sample $As_{0.20}Se_{0.40}Te_{0.40}$ are shown in fig. 2, where the dc electrical conductivity has been plotted as a function of the inverse of the temperature. The experimental values can be fitted to a single exponential function,

$$\sigma = \sigma_0 \exp\left(\frac{-E_\sigma}{K_B T}\right), \tag{19}$$

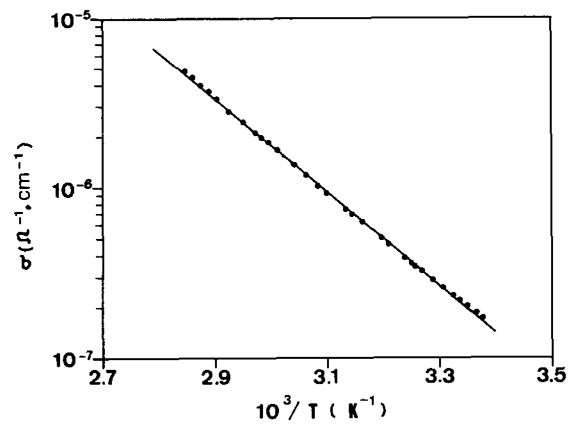

Fig. 2. Dark electrical conductivity as a function of the reciprocal of the temperature for the glass composition $As_{0.20}Se_{0.40}Te_{0.40}$.

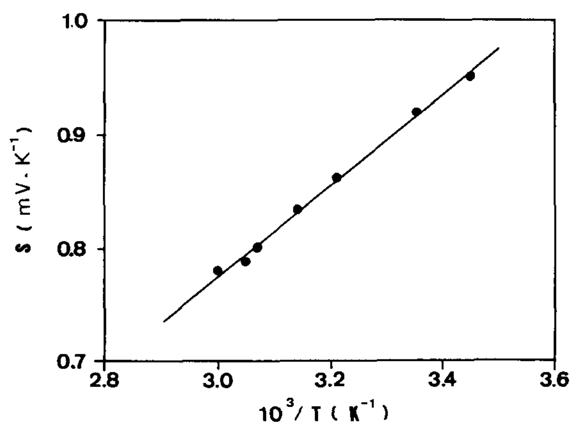

Fig. 3. Thermoelectric power as a function of the reciprocal of the temperature for the glass composition $As_{0.20}Se_{0.40}Te_{0.40}$.

the exponential factor being 294 Ω^{-1} cm^{-1} and the activation energy 0.54 eV.

On the other hand, the thermopower measurements indicate p-type conduction for the glass composition studied. Fig. 3 shows the Seebeck coefficient as a function of $1/T$, so that the activation energy E_s can be calculated using the relation

$$S=\frac{K}{e}\left(\frac{E_s}{K_B T}+A'\right). \tag{20}$$

The values obtained were $E_s=0.41$ eV and $A'=-5.3$.

The measured thermopower, S, is expressed by eq. (13), while the measured electrical conductivity is the sum of conductivities of the individual channels. Seven parameters, C_1, C_2, E_f^0, E_b^0, W, γ_1, γ_2, were adjusted in order to obtain a fairly good theoretical fit to both the thermopower and electrical conductivity data. The results were: $C_1=515\ \Omega^{-1}\ cm^{-1}$, $C_2=0.7\ \Omega^{-1}\ cm^{-1}$, $E_f^0=0.56$ eV, $E_b^0=0.28$ eV, $W=0.15$ eV, $\gamma_1=8.64\times10^{-4}$ eV K^{-1}, $\gamma_2=88.24\times10^{-4}$ eV K^{-1}. The maximum relative error between the experimental values and those deduced by means of the two-channel conduction model was 2.6% for the conductivity measurements and 2.8% for the thermopower.

In fig. 4 are given the experimental Hall mobility values μ_H, whereas fig. 5 shows the Hall coefficients

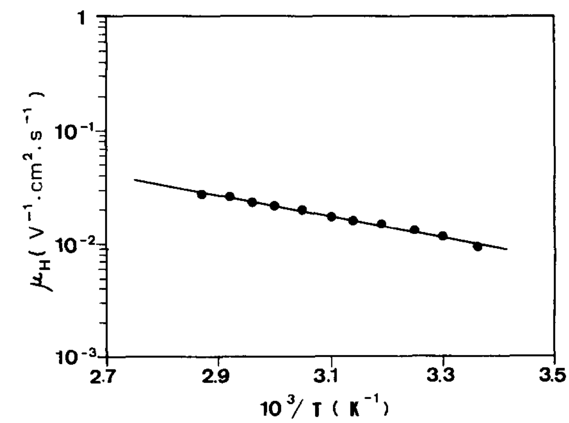

Fig. 4. Hall mobility versus the reciprocal of the temperature for the chalcogenide glass $As_{0.20}Se_{0.40}Te_{0.40}$.

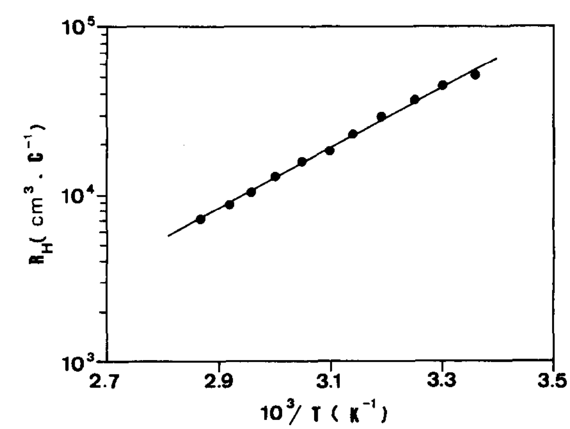

Fig. 5. Hall coefficient versus the reciprocal of the temperature for the chalcogenide glass $As_{0.20}Se_{0.40}Te_{0.40}$.

R_H as a function of inverse temperature. The values for the mobility activation energy and the Hall coefficients are $E_\mu = 0.19$ eV and $E_R = 0.36$ eV respectively.

In the experimental temperature interval 25–75°C, the values of Hall mobility of holes in extended states deduced with the help of eq. (15) are $\mu_1 = \mu_{ext} = 0.017$ cm^2 V^{-1} s^{-1}, in agreement with Friedman's theory.

The experimental data for the conductivity as well as those for the thermopower can be satisfactorily adjusted to expressions (16) and (17) which are characteristic of a small polaron conduction process. The values obtained from the parameters were: $E_b^0 = 0.40$ eV, $W = 0.15$ eV, $C_2 = 333$ Ω^{-1} cm^{-1}, $\gamma_2 = 4.30 \times 10^{-4}$ eV K^{-1}.

5. Conclusions

The thermoelectric power measurements indicate p-type while the Hall measurements indicate n-type conduction. The experimental results are consistent with two transport models: two-channel model and small polaron model. The chaotic band model does not seem applicable even though $E_\mu = E_\sigma - E_s = 0.15$ eV is a reasonable estimate of the average height of the potential fluctuations of the energy level within the material. This model predicts that the mobility should be temperature independent, while the experimental results indicate a mobility which is thermally activated. The information from other experimental techniques would help to find the proper description.

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References

[1] S.R. Ovshinsky, Phys. Rev. Letters 21 (1968) 1450.
[2] A.F. Ioffe, Semiconductor thermoelements and thermoelectric cooling (Inforsearh Ltd., London, 1957).
[3] G. Steinbauth, Electronics 53 (1980) 112.
[4] A. Madan and M.P. Shaw, The physics and applications of amorphous semiconductors (Academic Press, New York, 1988).
[5] S. Mahadevan and K.J. Rao, J. Non-Cryst. Solids 34 (1979) 54.
[6] H.L. Uphoff and J.S. Healy, J. Appl. Phys. 32 (1961) 950.
[7] I. Esme, J. Skarlatos and D. Tu, J. Phys. Astrophys. 12 (1978) 77.
[8] H. Overhof and W. Beyer, Phil. Mag. B 49 (1984) L9.
[9] M.J. Zope and J.K. Zope, J. Non-Cryst. Solids 74 (1985) 47.
[10] T.C. Arnoldussen, C.A. Menezes, Y. Nakagava and R.H. Bube, Phys. Rev. B 9 (1974) 3377.
[11] H.A. van der Plas and R.H. Bube, J. Non-Cryst. Solids 24 (1977) 382.
[12] M. Roilos, D. Meimaris and K. Zigiris, J. Non-Cryst. Solids 7 (1972) 275.
[13] M. Roilos, J. Non-Cryst. Solids 6 (1971) 9.
[14] J.C. Male, Brit. J. Appl. Phys. 18 (1967) 1548.
[15] H. Fritzsche, Amorphous and liquid semiconductors (Plenum Press, New York, 1974) p. 341.
[16] P. Nagels, R. Callaerts and M. Denayer, Proceedings of the 5th International Conference on Amorphous and Liquid Semiconductors, ed. J. Stuke (Taylor and Francis, London, 1974).
[17] D. Emin, in: Electronic and structural properties of amorphous semiconductors, eds. P.G. Le Comber and J. Mort (Academic Press, New York, 1973) p. 261.
[18] N.F. Mott and E.A. Davis, Electronic and structural properties of amorphous semiconductors (Clarendon Press, Oxford, 1971).
[19] L. Friedman and T. Holstein, Ann. Phys. (NY) 21 (1963) 494.
[20] M. Cuttler and N.F. Mott, Phys. Rev. 181 (1969) 1336.