Electrical conductivity and thermoelectric power of the compounds $(Dy_xY_{1-x})_2Mo_2O_7$

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Abstract. The electrical conductivity, σ, and thermoelectric power, S, of the solid solutions $(Dy_xY_{1-x})_2Mo_2O_7$ have been measured in the temperature range 300–10 K. $\log(\sigma T)$ versus $1/T$ and S versus $1/T$ plots were found to be linear down to about 100 K. The activation energies E_σ and E_S obtained from conductivity and thermoelectric power measurements, respectively, differ by one order of magnitude, indicating the presence of a thermally activated mobility. Below 100 K, even though $\log(\sigma\sqrt{T})$ versus $T^{-1/4}$ plots were linear, the Mott parameters were found to be physically unrealistic. The overall conductivity behaviour can, however, be explained in terms of hopping of small polarons.

1. Introduction

The solid solutions $(Dy_xY_{1-x})_2Mo_2O_7$ belong to the family of pyrochlores having the general formula $A_2B_2O_7$ [1]. The preparation, characterisation and magnetic susceptibility data on these solid solutions, with $x = 1.0, 0.8, 0.6, 0.4, 0.2$ and 0 have already been reported [2]. In an earlier study of the pyrochlore compounds $R_2Mo_2O_7$ (R = Nd, Sm, Gd, Tb and Y) Greedan *et al* [3] found that for R = Nd, Sm and Gd the compounds are metallic and ferromagnetic with a Curie temperature of about 90 K while for R = Tb and Y they are semiconducting and not ordered magnetically down to 4.2 K. The magnetic and electrical properties are thus related. In the case of $Y_2Ti_2O_7$ single crystals, Goldschmidt and Tuller [4] observed an activated mobility from electrical conductivity and thermoelectric power measurements and interpreted it in terms of small polaron conduction. An earlier study by Vasudeva Rao *et al* [5] on $R_2Mo_2O_7$ pyrochlores also indicated the existence of an activated mobility. In this paper the electrical conductivity and thermoelectric power results for these solid solutions are reported.

2. Experimental details

Measurements of electrical conductivity, σ, were performed on polycrystalline pellets of dimensions 6 mm × 6 mm × 2 mm, in the temperature range 300–10 K using a continuous flow cryostat (Leybold Heraeus Gmbh, Koln, Federal Republic of Germany) and the Van der Pauw technique as described by Montgomery [6]. A Keithley model 225 current source and a Keithley model 181 nanovoltmeter were used in the conductivity

and temperature measurements. The experimental error in measuring electrical conductivity was found to be less than 2%. For thermoelectric power measurements, the specimen was sandwiched firmly between two copper blocks using a spring loaded plunger arrangement. A calibrated Au–0.07%Fe versus chromel differential thermocouple with its two junctions embedded in the two copper blocks (electrically insulated from the copper blocks using delta bond) served to measure the temperature difference, ΔT, between the ends of the sample. The thermo-EMF, ΔE, was measured across the copper blocks. The absolute thermoelectric power, S, of the sample was calculated by correcting it for the thermoelectric power of the copper leads. The overall experimental error in measuring absolute thermoelectric power was about 5%. The same specimens were used in the measurements of σ and S.
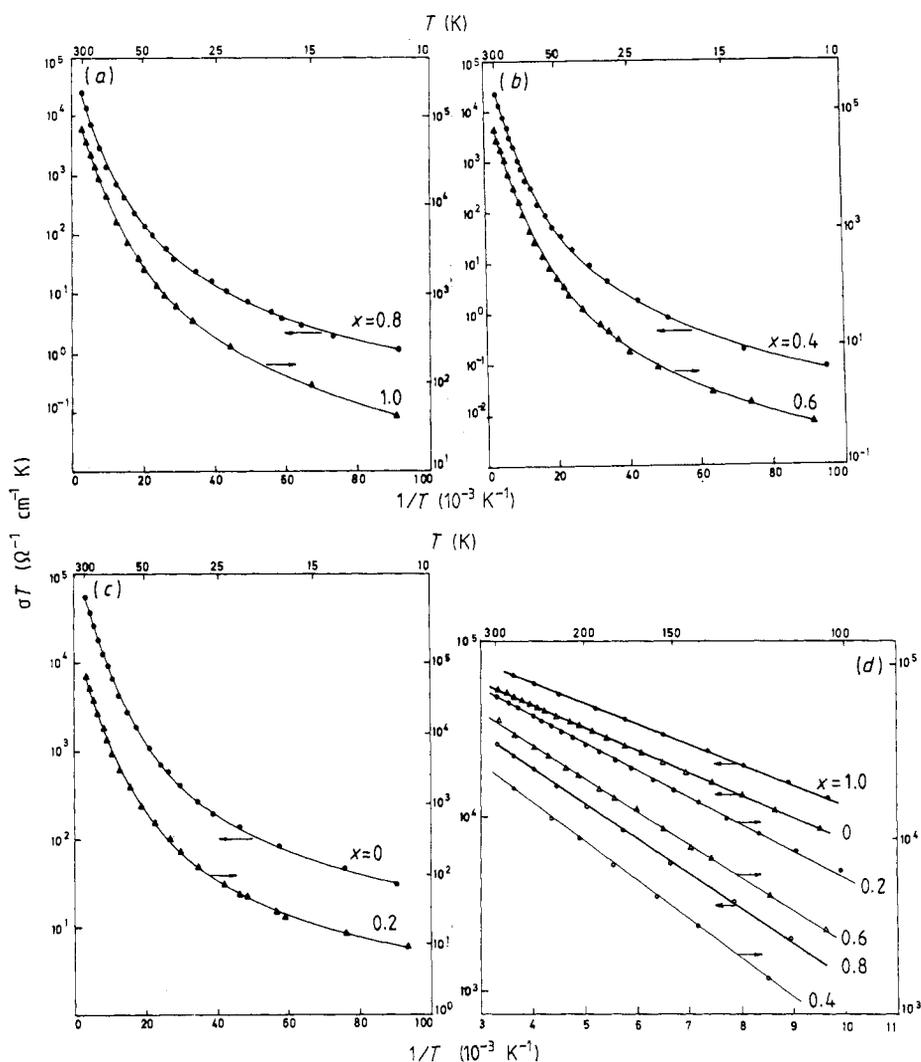
Figure 1. Plots of $\log(\sigma T)$ versus reciprocal temperature for $(Dy_x Y_{1-x})_2 Mo_2 O_7$.

Table 1. Activation energies E_σ and pre-exponential factors A obtained from expression (1) for different values of x for $(Dy_xY_{1-x})_2Mo_2O_7$ in the temperature range 300–100 K.

Sample No	x	E_σ (10^{-3} eV)	A ($10^5\ \Omega^{-1}\ cm^{-1}\ K$)
1	1.0	23 ± 1.0	1.7 ± 0.1
2	0.8	34 ± 1.0	1.0 ± 0.1
3	0.6	37 ± 1.0	1.9 ± 0.1
4	0.4	40 ± 1.0	1.0 ± 0.1
5	0.2	30 ± 1.0	2.0 ± 0.1
6	0	25 ± 1.0	1.4 ± 0.1

3. Results and discussion

3.1. Electrical conductivity data

In figure 1 the conductivity results for all the solid solutions are plotted. The room temperature conductivity value was found to agree closely with the values reported by Subramanian *et al* [7] and Greedan *et al* [3] in the case of $Y_2Mo_2O_7$ and in the case of $Dy_2Mo_2O_7$ with the value reported by the former. The plots of log σ versus $1/T$ were found to be linear for all the solid solutions in the limited temperature range 200–100 K. However $\log(\sigma T)$ versus $1000/T$ graphs were linear from 300 K down to about 100 K. This shows that the conductivity data from 300–100 K obey the following expression:

$$\sigma T = A \exp(-E_\sigma/kT) \tag{1}$$

and probably indicates that the temperature dependence of the pre-exponential factor due to the mobility has to be taken into account. A plot of $\log(\sigma\sqrt{T})$ versus $1/T$ gave a less satisfactory fit to the data in all the cases. Below about 100 K deviation from linear behaviour was found and the slope of the curve decreases continuously down to 10 K.

An expanded version of these plots in the temperature range 300–100 K is shown in figure 1(*d*). They are straight lines with different slopes. The activation energies, E_σ, for electrical conductivity and the pre-exponential factors, A, for all the compounds were calculated from the slopes of these straight lines and there are tabulated against the composition x in table 1. Figure 2 shows the variation of E_σ against composition x. From this figure it can be seen that the values of E_σ are almost the same for the end compounds with $x = 1.0$ and 0 and the maximum value corresponds to $x \simeq 0.5$. Thus there appears to be a correlation between E_σ and the disorder at the A site (in $A_2B_2O_7$). The pre-exponential factor A remains more or less the same for all values of x.

However, the conductivity data from about 100 K down to 20 K were found to follow the relation

$$\sigma\sqrt{T} = B \exp(-T_0/T)^{1/4}. \tag{2}$$

$\text{Log}(\sigma\sqrt{T})$ versus $T^{-1/4}$ graphs are shown in figure 3. This type of conductivity variation with temperature is generally ascribed to variable-range hopping processes among the localised states in the band gap. From these straight lines we calculated the Mott parameters following the procedure described by Paul and Mitra [8]. For the calculation of the Mott parameters information on the phonon frequency, ν_{ph}, is needed. Blacklock *et al* [9] reported specific heat studies on $Y_2Mo_2O_7$. From these we calculated the Debye
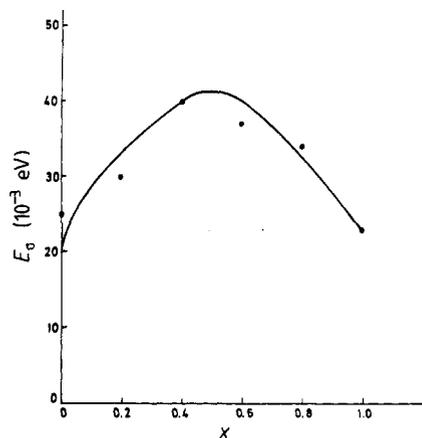
Figure 2. The variation of the activation energy, E_σ, obtained from the conductivity results with composition x for $(Dy_xY_{1-x})_2Mo_2O_7$.
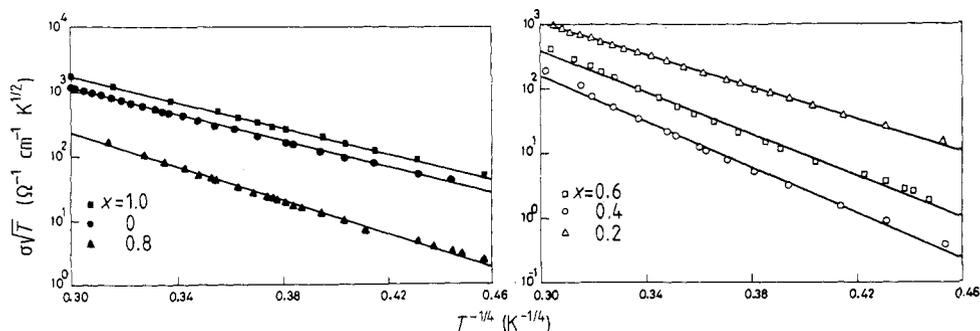
Figure 3. Plots of $\log(\sigma\sqrt{T})$ versus $T^{-1/4}$ for $(Dy_xY_{1-x})_2Mo_2O_7$.

temperature θ_D and it was found to be 280 K, which in turn gives a value of ν_{ph} of 4×10^{12} Hz. From specific heat measurements of one of these solid solutions $(Dy_{0.8}Y_{0.2})_2Mo_2O_7$ (the sample used in the present measurements) the Debye temperature θ_D was found to be 220 K [10]. Since the θ_D-values of $Y_2Mo_2O_7$ and $(Dy_{0.8}Y_{0.2})_2Mo_2O_7$ are not very different from each other we used the same value of 4×10^{12} Hz for all the compounds to calculate the Mott parameters and they are tabulated in table 2. It can be seen that for all the samples the values of $N(E_F)$ are greater than 10^{32} cm^{-3} eV^{-1} and the hopping distances, R, are smaller than 10^{-10} cm. These numbers are physically unreasonable and might suggest that the assumption of variable-range hopping processes in these compounds is not valid. In order to throw more light on the transport process in these compounds, thermopower studies were carried out and the results are described below.

3.2. Thermoelectric power data

In figure 4 the thermoelectric power variation of all the samples with temperature is shown. It can be seen from this figure that the sign of the thermoelectric power is negative and indicates that the majority charge carriers are electrons. The variation of

Table 2. Mott's parameters obtained from expression (2) in the temperature range 100–20 K for $(Dy_xY_{1-x})_2Mo_2O_7$.

Sample No	x	T_0 $(10^5 K)$	B $(10^6 \Omega^{-1} cm^{-1} K^{1/2})$	$N(E_F)$ $(eV^{-1} cm^{-3})$	α (cm^{-1})	R at 60 K (cm)	W at 60 K $(10^{-3} eV)$
1	1.0	3.28	2.34	1.61×10^{32}	6.33×10^{10}	5.10×10^{-11}	11.15
2	0.8	7.86	3.17	6.18×10^{32}	1.33×10^{11}	3.03×10^{-11}	13.88
3	0.6	20.75	38.02	1.73×10^{36}	2.59×10^{12}	1.98×10^{-12}	17.72
4	0.4	31.50	56.23	6.91×10^{36}	4.71×10^{12}	1.21×10^{-12}	19.63
5	0.2	6.54	3.72	9.12×10^{32}	1.42×10^{11}	2.70×10^{-11}	13.25
6	0.0	2.93	1.20	2.04×10^{31}	3.07×10^{10}	1.03×10^{-10}	10.86
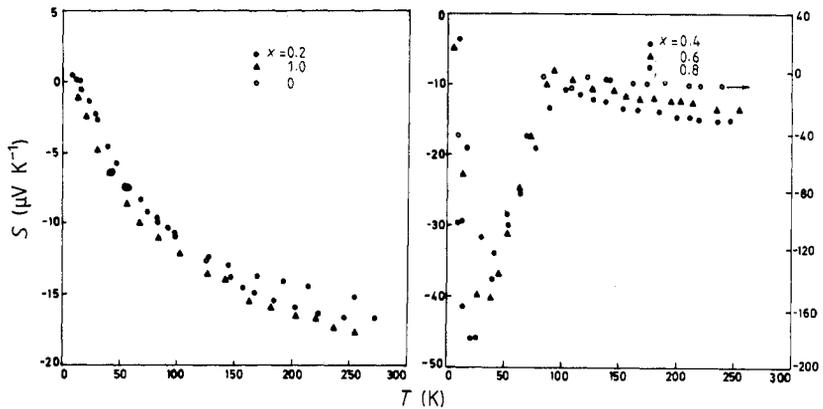
Figure 4. The variation of the thermoelectric power, S, with temperature for $(Dy_xY_{1-x})_2Mo_2O_7$.

thermopower is qualitatively the same for all the samples down to about 100 K below which some of the samples show thermopower anomalies. The origin of these anomalies is not clearly understood. Possible sources such as ferromagnetic impurities, valence fluctuations and phonon drag were considered but did not correspond to the observed temperature variations and concentration dependence. In the high temperature region the plots of thermopower S versus $1000/T$ showed a straight line behaviour down to about 100 K. These plots are shown in figure 5 and the activation energies, E_S, obtained from them are tabulated in table 3. The values of E_S are around 10^{-3} eV, i.e. one order less than those of E_σ.

In the case of thermoelectric power analysis of $R_2Mo_2O_7$, Vasudeva Rao *et al* [5] assumed the presence of donor impurities with concentration N_d in the impurity conduction region and fitted their thermoelectric power data to an equation of the type

$$S = B \log(T) + C/T. \tag{3}$$

In the present case also this procedure is applicable and the ST versus $T \log(T)$ plots for all the samples were drawn and are shown in figure 6. As can be seen from these graphs the straight lines are much better than the ones in figure 6: the region of linearity extends down to about 60 K in specimens for which no anomalies occur. The intercepts on the
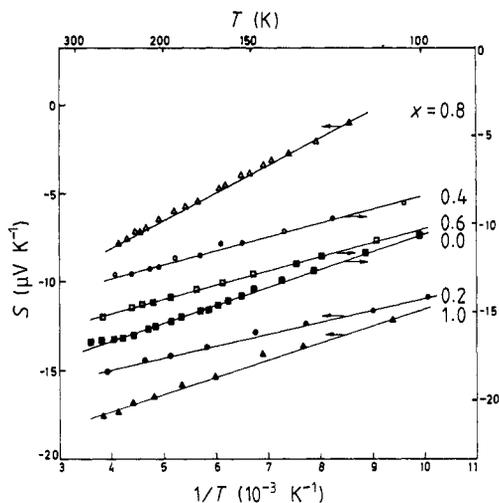
Figure 5. Plots of the thermoelectric power, S, versus reciprocal temperature for $(Dy_xY_{1-x})_2Mo_2O_7$.

Table 3. Activation energies, E_S, obtained from thermoelectric power for different values of x for $(Dy_xY_{1-x})_2Mo_2O_7$.

Sample No	x	E_S $(10^{-3}$ eV$)$†	E_S $(10^{-3}$ eV$)$‡
1	1.0	1.0 ± 0.02	0.4 ± 0.02
2	0.8	1.5 ± 0.02	1.1 ± 0.02
3	0.6	0.8 ± 0.02	0.3 ± 0.02
4	0.4	0.8 ± 0.02	0.3 ± 0.02
5	0.2	0.6 ± 0.02	0.2 ± 0.02
6	0	1.0 ± 0.02	0.4 ± 0.02

† Obtained from S versus $1/T$ plots.
‡ Obtained from ST versus $T \log(T)$ plots.

Y axis give the activation energies and their values are also shown in table 3. These are somewhat smaller than those obtained from S versus $1/T$ graphs.

Now we are in a position to compare E_σ and E_S values. The large difference between the values of E_σ and E_S in all the cases indicates that the mobility is thermally activated and electrical conduction takes place in these compounds by hopping. The conductivity variation with temperature and the activated mobility reveals that the mobility u is proportional to $T^{-1}\exp(-E_h/kT)$ where E_h is the hopping energy. This type of mobility is expected for small polaron hopping conduction [11].

In a series of papers Emin [12] has dealt with the small polaron hopping conduction mechanism. He calculated the jump rate, r, for small polarons which is related to the DC conductivity as follows:

$$\sigma = ne^2a^2r/kT \tag{4}$$

where n is the carrier concentration, a is the lattice constant and the other symbols have their usual meanings. Since the hopping energy E_h is much larger than the energy
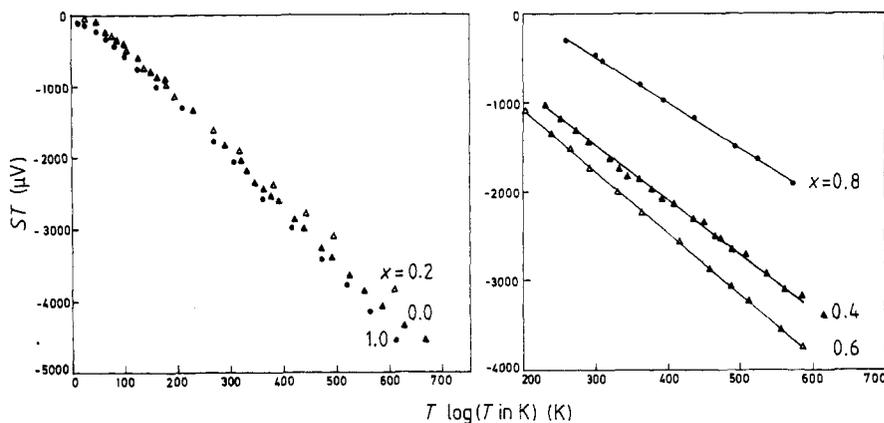
Figure 6. Plots ST versus $T\log(T)$ for $(Dy_xY_{1-x})_2Mo_2O_7$.
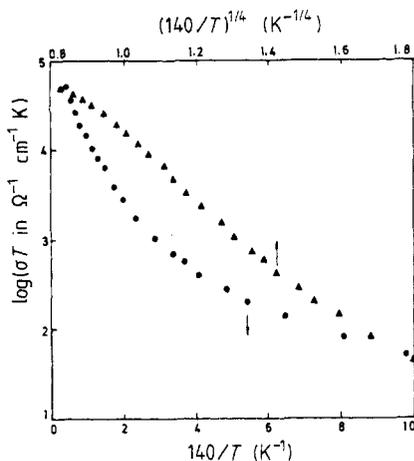
Figure 7. The variation of $\log(\sigma T)$ with $(140/T)$ and $(140/T)^{-1/4}$ for $Y_2Mo_2O_7$.

required for carrier generation, i.e., E_S, the temperature dependence of the conductivity in these compounds is essentially that of the mobility.

The theoretically calculated jump rate of small polarons was found to be characterised by a non-Arrhenius behaviour at low temperatures and an activation energy at high temperatures. The experimental variation of $\log(\sigma T)$ with θ_m/T and $(\theta_m/T)^{1/4}$, where θ_m is the optical mode temperature and is approximately equivalent to half of the Debye temperature θ_D, is shown for the case of $Y_2Mo_2O_7$ (θ_m has been taken to be 140 K as $\theta_D = 280$ K from the data of Blacklock *et al*) in figure 7. The overall variation is found to be similar to the calculated variation of the jump rate with temperature given by Emin [13]. This is also found to be true for the other solid solutions.

Since a similar calculation of thermopower for a small polaron hopping process has not been carried out, comparison with our thermopower data is not possible. Nevertheless, the foregoing analysis appears to lend support to small polaron hopping as the transport mechanism in these compounds.

Acknowledgment

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