

## Magnetic susceptibility of the compounds $(\text{Dy}_x\text{Y}_{1-x})_2\text{Mo}_2\text{O}_7$ in the temperature range 600–4.2 K

N P Raju, G Rangarajan and R Srinivasan

Department of Physics, Indian Institute of Technology, Madras 600 036, India

Received 3 February 1988, in final form 25 May 1988

**Abstract.** The magnetic susceptibilities of the compounds  $(\text{Dy}_x\text{Y}_{1-x})_2\text{Mo}_2\text{O}_7$  for  $x = 1.0, 0.8, 0.6, 0.4$  and  $0.2$  have been measured in the temperature range 600–4.2 K to check whether any magnetic ordering is found at low temperatures and to separate the contributions from  $\text{Dy}^{3+}$  and  $\text{Mo}^{4+}$  to the susceptibility in the paramagnetic region. The effective magnetic moment of  $\text{Dy}^{3+}$  was found to be less than that of the free-ion magnetic moment and is attributed to the crystal-field splitting of the energy levels.

### 1. Introduction

The rare-earth molybdenum pyrochlores  $\text{RE}_2\text{Mo}_2\text{O}_7$  with  $\text{RE} \equiv \text{Nd–Yb}$  form an interesting class of compounds. They crystallise in the face-centred cubic structure with the space group  $Fd\bar{3}m$ . There are eight formula units in the unit cell. The synthesis and the lattice constants of these compounds have been reported in [1].

The magnetic susceptibility of the compounds with  $\text{RE} \equiv \text{Gd–Yb}$  was studied below room temperature in [2]. They also studied solid solutions with  $\text{RE} \equiv \text{Nd}_{1-x}\text{Yb}_x$  and  $\text{Nd}_{1-x}\text{Er}_x$ . While evidence for magnetic ordering was found in the Nd solid solutions in Gd and in Sm compounds in the temperature range 73–97 K, it was inferred that the other compounds also ordered at lower temperatures. This was speculative.

Recently the magnetic susceptibility of the above compounds including  $\text{RE} \equiv \text{Nd}$  from 300 to 4.2 K has been studied [3]. It was found from a Curie–Weiss plot that the compounds with  $\text{RE} \equiv \text{Nd, Sm}$  and Gd indicate magnetic ordering around 90 K. The precise ordering temperatures were then found by magnetisation measurements but, in the other rare-earth molybdenum pyrochlores, no evidence was found for magnetic ordering down to 4.2 K.

Meanwhile, we improved the magnetic susceptibility set-up to give increased precision and extended the temperature range down to 4.2 K. Simultaneously we could also make measurements from 300 to 600 K using a PAR model 155 vibrating-sample magnetometer. We studied solid solutions of  $(\text{Dy}_x\text{Y}_{1-x})_2\text{Mo}_2\text{O}_7$  with  $x = 1.0, 0.8, 0.6, 0.4$  and  $0.2$  to check whether any magnetic ordering is found at low temperatures and to separate the contributions from  $\text{Dy}^{3+}$  and  $\text{Mo}^{4+}$  to the susceptibility in the paramagnetic region. The results are reported in this paper.

## 2. Sample preparation

High-purity powders of  $\text{Dy}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{MoO}_2$  (made by the reduction of  $\text{MoO}_3$ ) are mixed in stoichiometric proportions and pressed into a pellet. The pellet is put in a quartz tube which is then evacuated and sealed. The evacuated tube is heated to  $1300^\circ\text{C}$  for 24 h. The pellet is taken out, reground and repelletised, and the heat treatment is repeated. The process is continued until the reaction is complete and x-ray diffraction photography reveals a single-phase material. The x-ray diffractogram of the compound  $\text{Y}_2\text{Mo}_2\text{O}_7$  studied here is reproduced in figure 1 and agrees well with the neutron diffractogram reported in [4].

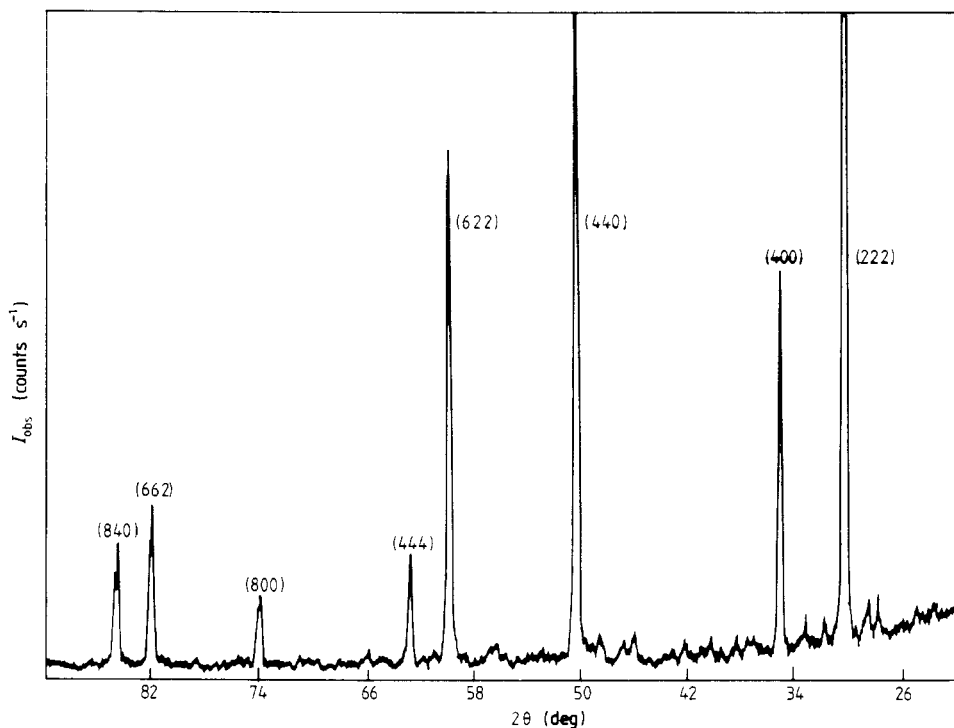


Figure 1. X-ray diffractogram of  $\text{Y}_2\text{Mo}_2\text{O}_7$ .

## 3. Experimental details

The measurements below room temperature were carried out with an AC mutual inductance bridge at 83 Hz. The coil system consists of one primary and two secondary coils. The primary coil of 3000 turns of SWG 36 insulated copper wire was wound uniformly over a length of 60 mm on a Perspex former with inner diameter 8 mm and outer diameter 10 mm. Two secondary coils, each consisting of 1200 turns, were wound on the primary coil. The primary coil was energised by the internal oscillator of a PAR lock-in amplifier model 5204. The output of the two secondary coils was fed into the lock-in amplifier in differential mode. By removing some of the turns of one of the secondary coils the output

of the lock-in amplifier was made zero and thus the bridge was balanced. When a sample in a fused quartz tube was introduced into the middle of the top secondary coil, the lock-in amplifier gives an output proportional to the sample's susceptibility. The constant of proportionality was determined using pure  $Gd_2O_3$ , the susceptibility of which is available down to 4.2 K in the literature [5–7]. This fact that the constant of proportionality was independent of temperature was verified.

The temperature of the sample was measured using a calibrated germanium thermometer below 35 K and a calibrated platinum thermometer above 35 K. These thermometers were mounted in the vicinity of the sample.

For measurements above room temperature a commercial PAR vibrating-sample magnetometer was used. This was calibrated using a pure nickel sphere supplied by the manufacturer. The temperature of the sample was measured with a chromel–alumel thermocouple. The susceptibility at room temperature measured in the two experimental arrangements agreed to within 1.5%.

#### 4. Results

Figure 2 shows the plots of inverse molar susceptibility against temperature in the range 4.2–600 K. It is seen that for all the materials the plot is linear from 600 to about 50 K. Below this temperature the curves show a concave upward trend. This is in agreement with the results in [3]. No ordering was seen in these compounds down to 4.2 K. Table 1 gives the parameters of the linear portion of the curves fitted to

$$\chi = C/(T - \theta).$$

For comparison the values of  $C$  and  $\theta_p$  obtained in [3] for  $Dy_2Mo_2O_7$  from measurements of susceptibility in the range 200–4.2 K are also given in table 1. It is seen that the value of  $C$  obtained in [3] is in good agreement with the present value. However, the value of  $\theta_p$  is distinctly higher in present measurements than that obtained in [3].

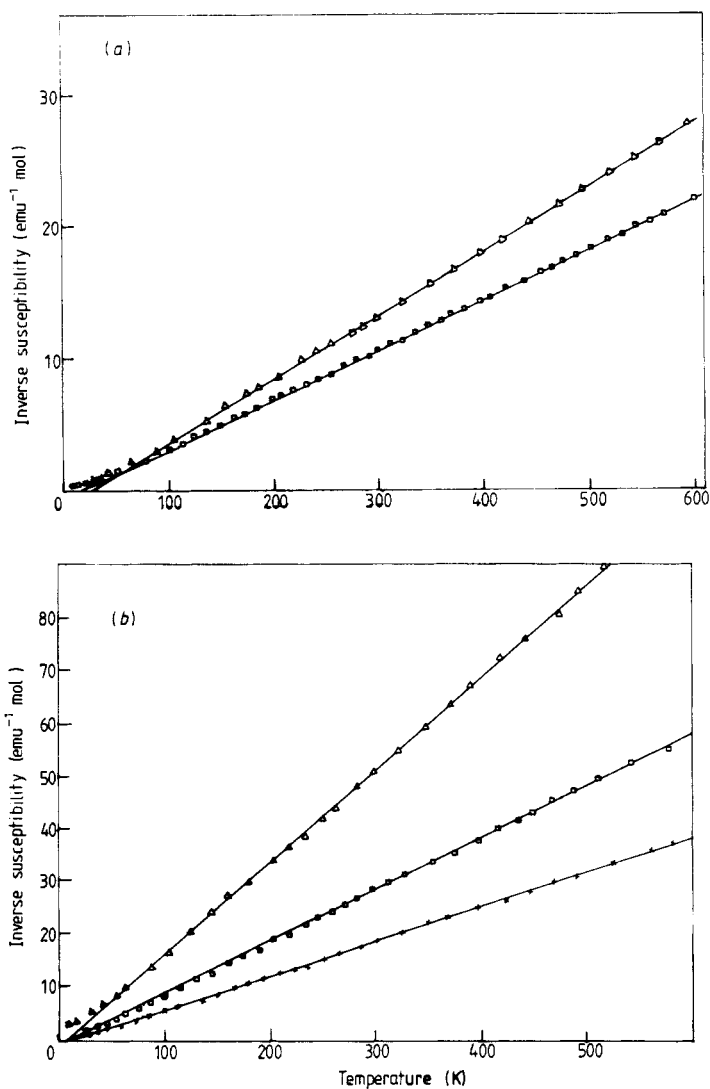
The susceptibility of  $Y_2Mo_2O_7$  from 200 down to 4.2 K has been measured [8] and it was found that above 100 K, the molar susceptibility  $\chi'$  obeys the equation

$$\chi' = 1.06/(T + 61) \text{ emu mol}^{-1}. \quad (1)$$

From the measured molar susceptibility  $\chi$  for the compound  $(Dy_xY_{1-x})_2Mo_2O_7$ ,  $\chi'$  is subtracted. The difference gives the contribution from  $Dy_x$  to the molar susceptibility of the compound. Figure 3 shows the plot of  $\chi^{-1}$  for  $Dy_x$  against  $T$ . A good straight-line

**Table 1.** The values of the Curie constant  $C$  and the paramagnetic Curie temperature  $\theta_p$  of compounds  $(Dy_xY_{1-x})_2Mo_2O_7$ .

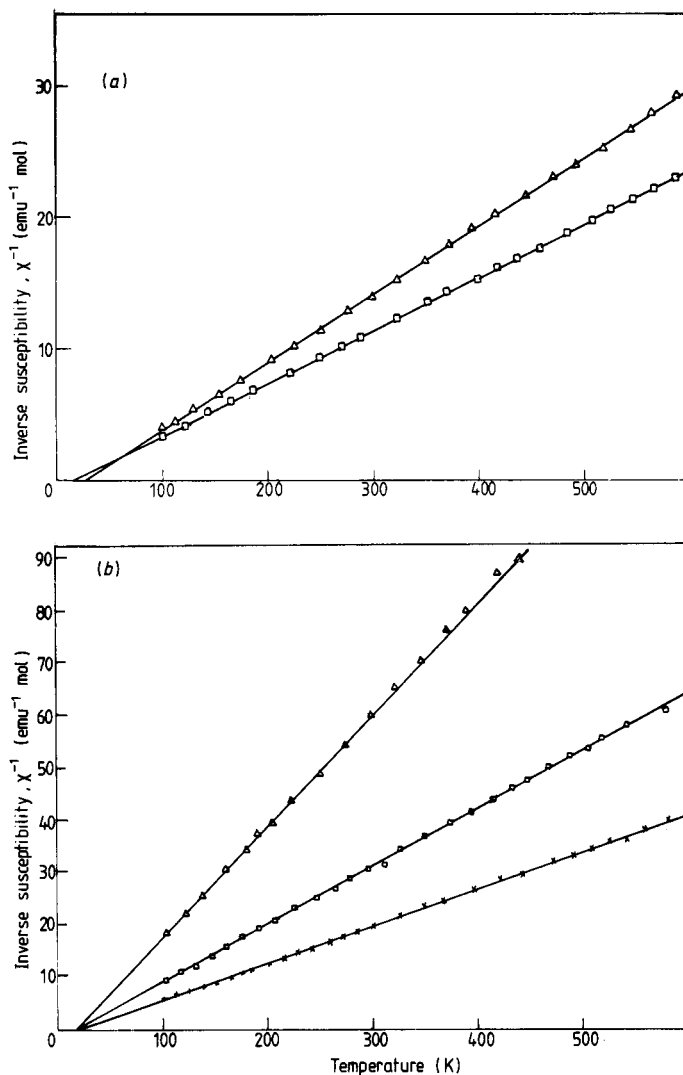
Sample number	$x$	$C$ (emu K mol <sup>-1</sup> )	$\theta_p$ (K)	$C$ (emu K mol <sup>-1</sup> )	$\theta_p$ (K)
1	1.0	26.21	18.1	26.72 [3]	10.0 [3]
2	0.8	20.43	22.3		
3	0.6	15.11	20.3		
4	0.4	10.16	12.7		
5	0.2	5.67	11.0		
6	0.0			1.06 [8]	-61.0 [8]



**Figure 2.** Inverse magnetic susceptibility of the compounds  $(\text{Dy}_x \text{Y}_{1-x})_2 \text{Mo}_2 \text{O}_7$ : (a) when  $x = 1.0$  ( $\square$ ) and  $x = 0.8$  ( $\triangle$ ); (b) when  $x = 0.6$  ( $\times$ ),  $x = 0.4$  ( $\square$ ) and  $x = 0.2$  ( $\triangle$ ).

fit is obtained above 100 K. Table 2 gives the constants  $C_{\text{Dy}}$  and  $\theta_{\text{Dy}}$  obtained from the straight-line plots.

For  $\text{Dy}_2 \text{Ti}_2 \text{O}_7$  where  $\text{Dy}^{3+}$  is the only magnetic ion, the paramagnetic Curie temperature  $\theta_p$  was found to be 0.65 K [9]. Here the magnetic interaction is only between the  $\text{Dy}^{3+}$  ions. This interaction is very weak. Since the lattice parameters of the rare-earth molybdates are not very different from those of the rare-earth titanates, there is no reason to suppose that the RE-RE interaction is significantly stronger than that in the titanates. However, from table 2 it is seen that the  $\theta_p$ -values for dysprosium are around 20 K which is much higher than 0.65 K. Obviously there is a relatively stronger interaction between  $\text{Dy}^{3+}$  and  $\text{Mo}^{4+}$ .



**Figure 3.** Inverse magnetic susceptibility against temperature for  $Dy_x$ , obtained by subtracting the magnetic susceptibility of  $Y_2Mo_2O_7$  from  $\chi_{(Dy_xY_{1-x})_2Mo_2O_7}$  and inverting it: (a) when  $x = 1.0$  ( $\square$ ) and  $x = 0.8$  ( $\triangle$ ); (b) when  $x = 0.6$  ( $\times$ ),  $x = 0.4$  ( $\square$ ) and  $x = 0.2$  ( $\triangle$ ).

One may make an estimate of the strength of the ferromagnetic interaction on the basis of a mean-molecular-field theory assuming that

- (i) the strength of the Mo–Mo interaction has the same value in all the solid solutions as in  $Y_2Mo_2O_7$  and
- (ii) the Dy–Dy interaction can be neglected.

Then one obtains

$$\begin{aligned}\chi_{Dy} &= (1/x)[\chi_{(Dy_xY_{1-x})_2Mo_2O_7} - \chi'] \\ &= (C_{Dy}/T)[(1 + \beta\chi')^2/(1 - \beta^2\chi'xC_{Dy}/T)]\end{aligned}$$

**Table 2.** The values of the paramagnetic Curie temperature  $\theta_p$  and the Curie constant  $C$  obtained from the plots of  $\chi_{(\text{Dy}_x\text{Y}_{1-x})_2\text{Mo}_2\text{O}_7}^{-1} - \chi_{\text{Y}_2\text{Mo}_2\text{O}_7}^{-1}$  against  $T$ .

Sample number	$x$	$\theta_p$ (K)	$C_{\text{Dy}_x}$ (emu K mol $^{-1}$ )	$C_{\text{Dy}}$ (emu K mol $^{-1}$ )
1	1.0	20.0	24.78	24.78
2	0.8	26.6	19.32	24.15
3	0.6	20.2	14.22	23.70
4	0.4	18.6	9.06	22.65
5	0.2	18.8	4.69	23.45

where  $C_{\text{Dy}}$  is the Curie constant for the dysprosium sublattice in the absence of any magnetic interaction and  $\beta$  is the molecular-field constant representing the interaction between  $\text{Dy}^{3+}$  and  $\text{Mo}^{4+}$ .

Neglecting  $\beta^2\chi'$  in comparison with equation (1) in the denominator and using equation (1) for  $\chi'$ , one may write

$$\chi_{\text{Dy}} = (C_{\text{Dy}}/T)(1 + 2\beta\chi') \approx C_{\text{Dy}}/T(1 - 2.12\beta)$$

$$\theta_{\text{Dy}} = 2.12\beta.$$

Therefore

$$\beta \approx 10 \text{ emu}^{-1} \text{ mol}.$$

The average value of  $C$  from table 2 is 23.74 with a mean-square deviation of 0.8. From this the magnetic moment  $p_{\text{eff}}$  is  $9.75\mu_{\text{B}}$ . This should be compared with the  $p_{\text{eff}}$  value of  $9.96\mu_{\text{B}}$  for  $\text{Dy}_2\text{Ti}_2\text{O}_7$  [9]. This value is smaller than the free-ion value of  $10.64\mu_{\text{B}}$  which is due to the crystal-field splitting of the energy levels. The data on  $\text{Dy}_2\text{Ti}_2\text{O}_7$  in [10] is analysed with a crystal field of the form

$$H_{\text{CF}} = \alpha B_2^0 O_2^0 - \beta_3^3 B_4^0 (O_4^0 - 20 \times 2^{1/2} O_4^3)$$

$$+ \gamma \frac{16}{9} B_6^0 \left( O_6^0 + \frac{35 \times 2^{1/2}}{4} O_6^3 + \frac{77}{8} O_6^6 \right)$$

which is appropriate for  $D_{3d}$  symmetry. Here, the  $B_n^m$ -values are the crystal-field parameters, the  $O_n^m$ -values are the Stevens' operator equivalents and  $\alpha$ ,  $\beta$  and  $\gamma$  are reduced matrix elements for the ground state of  $\text{Dy}^{3+}$  ions. This was also found to be satisfactory for  $\text{Yb}_2\text{V}_2\text{O}_7$  and  $\text{Tm}_2\text{V}_2\text{O}_7$  [11]. In the present case, this model may not be appropriate since a nearly pure  $|\pm \frac{1}{2}\rangle$  ground should lead to an ordering of the spins well above 4.2 K. The present observation that no ordering takes place down to 4.2 K may indicate the importance of crystal-field interactions in this case. The observed decrease in the effective moment from the free-ion value would then arise from admixtures of states such as  $|\pm \frac{3}{2}\rangle$  and  $|\pm \frac{5}{2}\rangle$  and  $|\pm \frac{7}{2}\rangle$ ; the extent of this admixture cannot be determined from powder susceptibility data alone, however.

The somewhat systematic variation obtained for  $C_{\text{Dy}}$  with  $x$  is surprising and may arise from a modification of crystal-field effects by the introduction of  $\text{Y}^{3+}$  ions. A more detailed analysis, however, can be meaningful only with single-crystal specimens and/or other measurements such as magnetisation, neutron scattering and electron spin resonance.

**References**

- [1] Subramanian M A, Aravamudan G and Subba Rao G V 1980 *Mater. Res. Bull.* **15** 1401
- [2] Ranganathan R, Rangarajan G, Srinivasan R, Subramanian M A and Subba Rao G V 1983 *J. Low Temp. Phys.* **52** 481
- [3] Sato M, Xu Yan and Greedan J E 1986 *Z. Anorg. (Allg.) Chem.* **540–541** 177–90
- [4] Blacklock K, White W H and Gurmen E 1980 *J. Chem. Phys.* **73** 1966
- [5] Mulay L N and Mulay I L 1974 *Anal. Chem.* **46** 490 R
- [6] Hacker H, Liu M S and Westrum E F 1964 *R.E. Research* ed. L R Eyring (New York: Gordon and Breach) p 93  
*Landolt–Börnstein, New Series* 1982 Group III, vol. 4a, ed. K-H Hellwege (Berlin: Springer) pp 94, 98
- [7] Miller A E, Jelinek F J, Gschneidner K A Jr and Gerstein B C 1971 *J. Chem. Phys.* **55** 2647
- [8] Greedan J E, Sato M and Xu Yan 1986 *Solid State Commun.* **59** 895–7
- [9] Cashion J D, Cook A H, Leask M J M, Thorp T L and Wells M R 1968 *J. Mater. Sci.* **3** 402
- [10] Townsend M G and Crossley W A 1968 *J. Phys. Chem. Solids* **29** 593
- [11] Soderholm L, Stager C V and Greedan J E 1982 *J Solid State Chem.* **43** 175