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Magnetic susceptibility of heavy rare-earth molybdates

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Results of the molar magnetic susceptibility (χ_m) measurements of heavy rare-earth (RE) molybdates of the type $RE_2(MoO_4)_3$ with RE = Gd, Dy, Ho, Er, Tm and Yb are reported in the temperature range 3 to 300 K at a magnetic field of 3.2×10^5 A m^{-1}. All molybdates show ferrimagnetic behaviour with ferrimagnetic Néel temperatures lying in the range 15 to 24 K. Evaluated magneton numbers agree fairly well with those for free tripositive rare-earth ions. Various magnetic parameters are evaluated using appropriate models.

1. Introduction

Molybdates of the type $RE_2(MoO_4)_3$ (where RE = Sc, Y and La to Lu) are some of the most important compounds of rare-earth elements and some of them show interesting piezoelectric, ferroelectric, ferroelastic, fluoroscent and non-linear optical properties [1–10]. The interest in these compounds is recent and it is only in the last two decades that reasonably pure rare-earth molybdates were prepared, identified and studied. Obviously they are new compounds and non of the physical properties of the members of this series are completely understood. Thus, the study of $RE_2(MoO_4)_3$ is interesting as well as important. For the last few years a study into the magnetic, dielectric and electrical properties of rare-earch compounds such as sesquioxides [11–13], tungstates [14–18], garnets [19–20], orthochromites [21, 22] has been undertaken, and molybdates have been recently included in the program. Some of the earlier studies on these compounds are reported elsewhere [23–26]. The present work reports low temperature (3 to 300 K) magnetic susceptibility studies on heavy rare-earth molybdates.

$RE_2(MoO_4)_3$ crystallise in variety of structures depending upon the method of their preparation, the annealing temperature used and the rare-earth ionic radius. The details are given elsewhere [10]. Among the heavy rare-earth molybdates Gd, Tb, Dy and Ho usually crystallize in their α-form which is monoclinic [α-$Eu_2(WO_4)_3$ type, space group C_2/c] with four molecules per unit cell [6, 8]. The α-phase is stabilized only when both firing and annealing temperatures are kept below the α-β phase transition temperature, otherwise the metastable β′ phase and the β-phase co-exist with α-phase. The rare-earth ion in such an (α-phase) arrangement is surrounded by eight oxygen ions at the corners of a slightly distorted cubic cell. The molybdates formed with Er to Lu are reported to have orthorhombic structure, i.e. the are [$Sc_2(WO_4)_3$] type, again with four molecules per unit cell. In such an arrangement, the rare-earth ion co-ordinates with six oxygen ions, at the corners of a slightly distorted octahedral cell [6].

2. Material and experimental techniques

The molybdates were prepared using the method reported by Brixner *et al.* [8]. The starting materials, for the preparation of Gd and Dy to Yb molybdates, were the relevant sesquioxide [obtained from Rare-Earth Products, England, with a stated purity of 99.99 percent] and MoO_3 [obtained from Bond, India, again with a stated purity of 99.99 percent] which were both dried at 200° C before use. Stoichiometric amounts of

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the starting materials were thoroughly mixed, made into pellets and fired at 600° C for 6 h in a platinum crucible in air. The reaction product was reground, again made into pellets and fired at 700° C for more than 24 h. The melting points of the final products were found to be nearly the same as those reported by other workers [10].

X-ray diffraction patterns of the prepared powders were taken using a CuKα source at 295 K. The diffraction patterns of Dy and Ho molybdates were identified as being similar to those of the α-$Eu_2(WO_4)_3$ type structure, whereas the diffraction patterns of Tm and Yb molybdates were found to be similar to those of the $Sc_2(WO_4)_3$ type (orthorhombic structure). The X-ray diffraction pattern of Er molybdate differs from that of Yb, but does not exactly resemble the pattern of Ho. Probably Er molybdate has some intermediate structure, but no attempt was made to resolve the structure.

Magnetic suceptibility of small sample (50 to 100 mg) of the molybdates was measured using the Faraday method, employing a compensation type electromagnetic balance. The sample was suspended in the constant $H(\mathrm{d}H/\mathrm{d}z)$ region using a copper sample holder, and the force exerted on the sample was recorded in the temperature range 3 to 300 K. Low temperatures were obtained by using a cryostat employing the continuous helium vapour flow method, and the temperature was monitored using platinum (300 to 30 K) and carbon (40 to 30 K) standard resistors. Mohr salt was used as a standard material for calibration. The details are described elsewhere [27].

3. Results and discussion

The variation of inverse molar magnetic susceptibility, χ_M^{-1}, with temperature, over the range 3 to 300 K of all the molybdates studied are shown in Figs 1 to 3. The χ_M^{-1} against T curves for all molybdates are almost linear above 100 K but at lower temperatures show a downward drop towards the temperature axis. Below 20 K all the curves again show an extended and almost linear χ_M^{-1} against T plot down to 3 K.

The rare-earth ions are the only magnetic ions

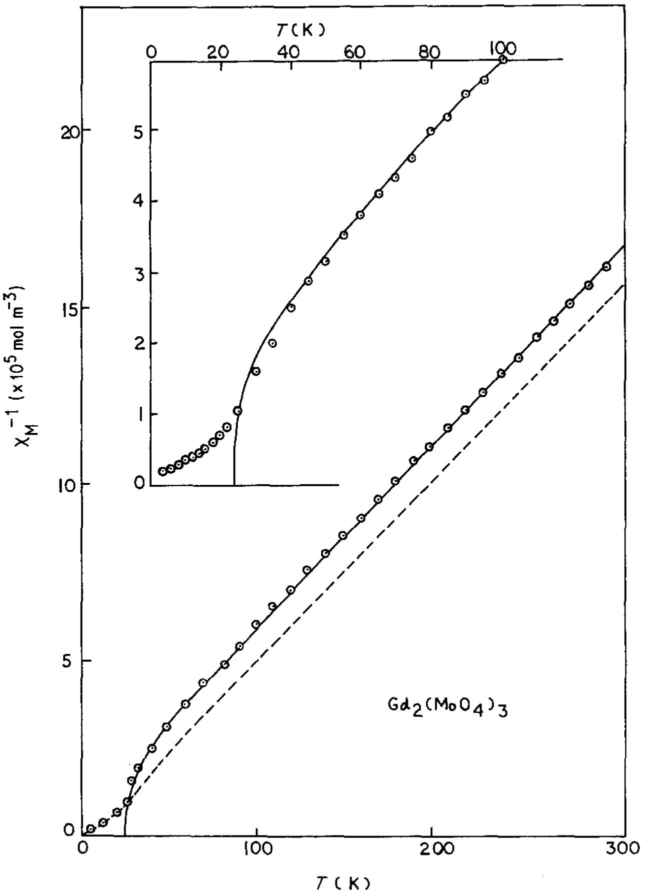

Figure 1 A plot of the inverse molar magnetic susceptibility χ_M^{-1}, against Temperature, T, for $Gd_2(MoO_4)_3$ powders in a field of 3.2×10^5 A m^{-1}. The experimental points are shown by circles, the dotted lines represent χ_M^{-1} calculated according to Equation 1 and the unbroken line represents χ_M^{-1} calculated according to Equation 2.

in these molybdates, and they are presumed to exist in the trivalent state.There are $2N_A$, where N_A is the Avogardo number, rare-earth ions in each mole of these compounds. The multiplet separation of a heavy rare-earth (RE) ion (RE = Gd to Yb) is much larger than the thermal energy at room temperature [28] and, hence, all the ions remain in their ground state at normal temperature. The magnetic susceptibility, χ, of such non-interacting magnetic ions is given by the relationship

$$\chi = \frac{ngJ\mu_0\mu_\beta}{H} B_J(a), \qquad (1)$$

where n is the number of rare-earth ions, g is spectroscopic splitting factor, J is the total angular momentum of the rare-earth ion in the ground state, μ_0 is the magnetic constant, μ_β is the Bohr magneton, $B_J(a)$ is the Brillouin function, H is the applied magnetic field and $a = gJ\mu_\beta H/kT$, k being the Boltzmann constant.

All the ions, except the rare-earth ions, are diamagnetic and give a negligible contribution to χ_M in these molybdates. Therefore χ_M for these compounds can be obtained by using Equation 1 and by replacing n by $2N_A$. The calculated values of χ_M for Gd molybdate at different temperature are given in Fig. 1 by the dotted curve. It can be seen from this figure that there exists significant differences between calculated and experimental values of susceptibility. Similar differences also occur for all other molybdates. The measured magnetic susceptibility remains less than the calculated susceptibility at all temperatures. The reasons for this discrepancy might be (a) crystal field effects, (b) dipolar interaction or (c) exchange interaction. The dipolar interaction between the rare-earth ions in the solid state are very weak and are seldom significant above 2 K, which falls below the lowest temperature limit of the present study. Furthermore, in $Gd_2(MoO_4)_3$, because of the spherically symmetrical nature of Gd^{3+} magnetic ion, crystal field effects are insignificant. Hence the discrepancy between experimental and theoretical χ_M values is due to exchange interaction.

From Fig. 1 it can be seen that the experimental χ_M^{-1} against T plot is almost linear at higher temperatures but starts bending towards the temperature axis below 100 K. The curve in general looks similar to a standard curve for a ferrimagnetic material. The deviation from linearity and systematic downward drop of the χ_M^{-1} against T curve indicates the onset of short range ordering just above the ferrimagnetic Néel temperature (T_N). For a wide temperature range (25 to 300 K) the data for χ_M of $Gd_2(MoO_4)_3$ can be expressed by the following equation [29]

$$\frac{1}{\chi_M} = \frac{T-\theta_p^2}{C} - \frac{\theta_b^2}{C(T-\theta)}, \qquad (2)$$

where C is the Curie constant for the material, θ_p is the paramagnetic (asymptotic) Curie temperature, and θ and θ_b are parametric temperatures.

The ordering temperature, T_N, (usually referred to as the ferrimagnetic Néel temperature or some times as the ferrimagnetic Curie temperature) is obtained by the constraint that as $T \rightarrow T_N$, $\chi_M^{-1} \rightarrow$

TABLE I Some magnetic parameters of heavy rare-earth molybdates $RE_2(MoO_4)_3$

Parameters	Molybdates*					
	Gd	Dy	Ho	Er	Tm	Yb
Bulk Nature	FeM	FeM	FeM	FeM	FeM	FeM
C (10^5 K m^3 mol^{-1})	19.8	35.5	35.4	28.6	18.1	7.3
C_1 (10^5 K m^3 mol^{-1})	14.6	21.0	22.7	21.6	15.8	6.2
C_2 (10^5 K m^3 mol^{-1})	5.2	14.5	12.7	7.0	2.3	1.1
p (exp)	7.94	10.63	10.62	9.55	7.60	4.82
p (theo)	7.94	10.63	10.60	9.60	7.60	4.54
T_N (K)	24	22	20	15	22	24
θ_p (K)	−20	−18	−10	−15	−30	−65
θ (K)	21.0	20.0	19.0	13.0	16.0	20.0
θ_b (K)	11.5	9.0	5.5	7.8	17.7	18.9
α	0.019	0.043	0.28	−0.05	−0.16	−0.37
β	0.019	0.043	0.28	−0.05	−0.16	−0.37
$n \times 10^4$ (kg m^{-3})	1.02	8.55	7.32	1.06	4.19	135.9

*All molybdates were found to be ferrimagnetic.

0. The values of these parameters (θ, θ_b, θ_p, T_N and C) for the best fit to the experimental points are given in Table I. For simplification a molecular field treatment and the Néel two sublattice model (NTSM) are used to find the exchange field parameters of $Gd_2(MoO_4)_3$.

Since this material contains only one type of magnetic ion, ferrimagnetic behaviour can occur only when a number of ions are different in the two sub-lattices. Such a situation can be anticipated in the case of $Gd_2(MoO_4)_3$. It has an α-$Eu_2(WO_4)_3$ type structure, which can be regarded as pseudo-scheellite [i.e. $CaWO_4$ type with an ordered replacement of three calcium ions by two tripositive rare-earth ions], or, can be regarded as more like a compound $RE_{2/3}\square_{1/3}WO_4$, where $\square$ represents a vacant site. Thus there are one third of the cation positions unoccupied by rare-earth ions in the scheellite structure. Dividing these vacancies into two sublattices, it is found that in the extreme case one of the two sublattice sites are fully occupied and the other is partially vacant. However this extreme case is not a common occurance, therefore, in general, the number of ions on two sublattices will be quite different. As per convention [29] we shall adopt the following terminology for the exchange field constants between Sublattices 1 and 2

$$W_{12} = -n, \quad W_{11} = n\alpha \quad \text{and} \quad W_{22} = n\beta \qquad (3)$$

where W refers to the exchange field constants between Sublattices 1 and 2 and α and β are dimensionless constants. These constants (n, α and β) are related to the parametric temperatures (θ, θ_b and θ_p) and C by the following equations

$$\theta_p = -\frac{n}{C}\left(2\,C_1C_2 - \alpha C_1^2 - \beta C_2^2\right) \qquad (4)$$

$$\theta = \frac{n}{C}\,[(C_1C_2)(2+\alpha+\beta)] \qquad (5)$$

$$\theta_b = \frac{n}{C}\left\{(C_1C_2)^{1/2}\right.$$
$$\left.[C_1(1+\alpha) - C_2(1+\beta)]\right\} \qquad (6)$$

$$T_N = \frac{1}{2}n\{[(\alpha C_1 - \beta C_2)^2 + 4C_1C_2]^{1/2}$$
$$+ \alpha C_1 + \beta C_2\} \qquad (7)$$

$$C = C_1 + C_2 \qquad (8)$$

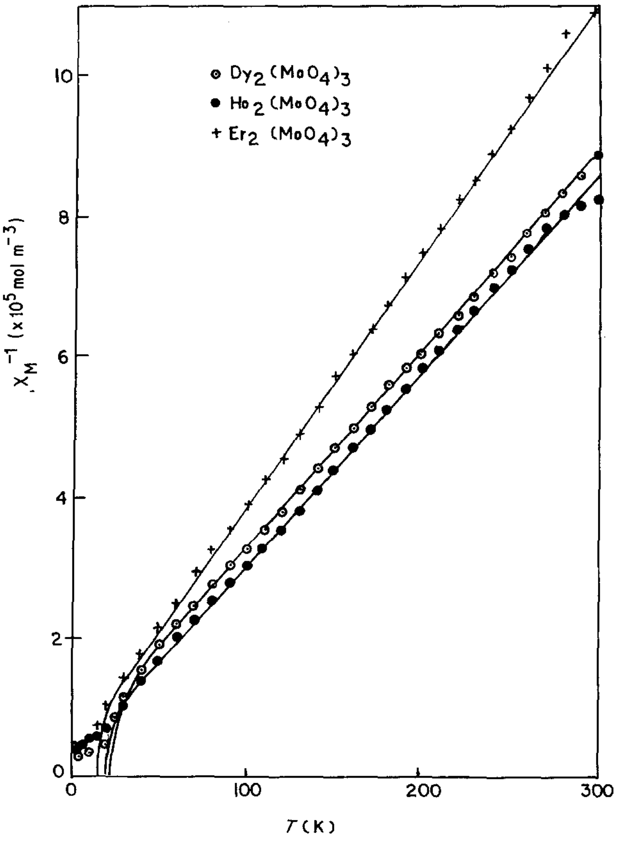

Figure 2 Plot of χ_M^{-1} against T for Dy, Ho and Er molybdates in a field of 3.2×10^5 A m^{-1}. The experimental points are shown by $\circ$ for Dy, ● for Ho and + for Er molybdates respectively and the unbroken line represents the best-fit curve according to Equation 2.

where C_1 and C_2 are Curie constants and T_N is the ferrimagnetic Néel temperature. The values of θ_p, θ, θ_b, T_N and C are known from the fitting of a curve to the experimental points in accordance with Equation 2. Therefore, in principle, five unknown quantities, namely α, β, n, C_1 and C_2, can be obtained by solving the above equations. However, this is not an easy exercize. To proceed, the assumption that $\alpha = \beta$ may be made. This assumption seems to be valid because the same type of magnetic ions are occupying the two sublattices and the distances between the Gd^{3+} ions are not very much different. On this assumption it becomes much easier to evaluate α, n, C_1 and C_2 using Equations 4 to 8. The calculated values are given in Table I. It is found that α and β are small and positive, which indicates a ground state in which all neighbouring Gd^{3+} ions are alligned antiparallel to each other.

The experimental χ_M^{-1} against T curves for all other rare-earth molybdates are also similar to ferrimagnetic material and therefore we have tried to express them by an equation similar to Equation 2. The best fit curves are shown in Figs 2 and 3 and values of various parameters are listed in Table I for different molybdates. It is seen that experimental points can be well represented by Equation 2 over a wide temperature range. This indicates that crystal field effects are not very important in these materials.

These curves can be analysed using the same procedure as has been employed for $Gd_2(MoO_4)_3$. The calculated value of different parameters (θ_p, θ, θ_b, T_N and C) and molecular field constants (α, β and n) and C_1 and C_2 are listed in Table I. It is found that α is positive and small for Dy and Ho molybdates but is negative, though less than unity, for molybdates of Er, Tm and Yb. Obviously the ground state of Dy and Ho molybdates is that of anti-parallel alignment. For the others however, a slight angular arrangement of the magnetic moment is espected in the ground state.

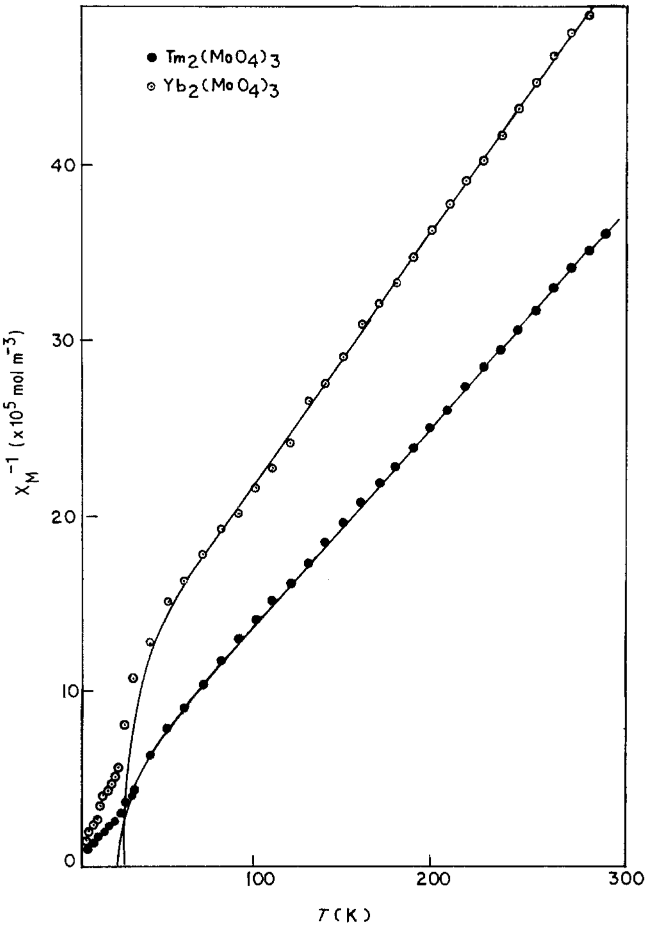

Figure 3 Plots of χ_M^{-1} against T for $Tm_2(MoO_4)_3$ and $Yb_2(MoO_4)_3$, in a field of 3.2×10^5 A m^{-1}. The best-fit curves obtained using Equation 2 are represented by an unbroken line and experimental points are shown by ● for Tm and ⊙ for Yb molybdates respectively.

The value of the magneton number (p) of the magnetic ions has been evaluated using the Curie constants and the relationship

$$p = \left(\frac{3kC}{2N_A \mu_0 \mu_\beta^2}\right)^{1/2} = 5.6411 \times 10^2 \, C^{1/2}. \quad (9)$$

These values, together with the theoretical value of p for tripositive rare-earth ions, are given in Table I. It is seen that there is a good agreement between the theoretical and experimental values of p for all tripositive rare-earth ions.

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