Ferromagnetism in Some Semi-Conducting Heavy Rare-Earth Molybdates

H. B. Lal and R. N. Pandey

Department of Physics, University of Gorakhpur, Gorakhpur 273001, India

Measurements of the magnetic susceptibility of powdered samples of $Dy_2(MoO_4)_3$, $Ho_2(MoO_4)_3$ and $Er_2(MoO_4)_3$ in the temperature range 300 to 920 K are reported. The Curie Weiss Law is obeyed and yields the magneton numbers 10.72, 10.68 and 9.68 for the Dy^{3+}, Ho^{3+} and Er^{3+} ions, respectively, the theoretical values being 10.63, 10.60 and 9.60. The results are analysed in terms of molecular field theory and it is predicted that $Dy_2(MoO_4)_3$, $Ho_2(MoO_4)_3$ and $Er_2(MoO_4)_3$ become ferromagnetic below 12, 17 and 5 K, respectively.

Decades back ferromagnetism in insulating rare-earth compounds was considered a rare phenomenon [1, 2], however with the discovery of ferromagnetism in EuO, EuH_2, $EuSe$, $ErCrO_3$, $ErFeO_3$, $YbCrO_3$, $Er_2(WO_4)_3$ etc. and the understanding of indirect and super exchange interaction it has become a familiar, yet interesting occurrence. Ferromagnetic semiconductors [1] are still somewhat rare and quite interesting to investigate both from the theoretical [2, 3] and applicational point of view. Some rare-earth molybdates are of interest because of their ferroelectric, ferroelastic and non-linear optical properties [4—7]. These are the right materials for searching for a coexistence of ferroelectricity and ferromagnetism. We have been investigating the electrical, dielectric and magnetic properties of rare-earth compounds for the last six years [8—10]. This note reports on preliminary results obtained on three of the six heavy rare-earth molybdates.

The starting materials Dy_2O_3, Ho_2O_3 and Er_2O_3 with a stated purity of 99.99 percent were procured from Rare-earth Product, England, and MoO_3 (99.99 percent — German made) from Bond, India. With these the molybdates were prepared and checked using standard methods reported in the literature [11]. $Dy_2(MoO_4)_3$ (white), $Ho_2(MoO_4)_3$ (light-yellow) and $Er_2(MoO_4)_3$ (light-red) have tetragonal lattice structures [12].

The magnetic susceptibilities of the powdered samples have been measured using a magnet with

tapered pole-pieces (Polytronic, India) and a sensitive non-magnetic projection type balance (type K-11, Keroy India) employing the standard Faraday method. $Gd_2(WO_4)_3$ (from Rare-earth Product England) has been used as standard material. Due corrections for the container have been made. The over-all accuracy of the measurements is about 2.5 percent at 300 K and decreases with increase of temperature to become about 5 percent at 800 K.

The magnetic susceptibilities of the starting materials have been measured to check for their purity. The paramagnetic temperatures (θ) were found by $- 2.9$ K for Dy_2O_3, 3.1 K for Ho_2O_3 and $- 11.8$ K for Er_2O_3 in agreement with the results of other workers [13, 14]. The magneton numbers have also been found to be approximately those expected for Dy^{3+}, Ho^{3+} and Er^{3+} ions, indicating the purity of our starting materials. The magnetic susceptibility of MoO_3 has been found to be very small ($\sim 10^{-6}$ per g at 300 K) with almost no temperature dependence. These observations ruled out the existence of ferromagnetic impurities in the starting materials.

The results of our magnetic measurements on the molybdates (Fig. 1) show a linear dependence of χ_m^{-1} on T suggesting a Curie Weiss law [$\chi_m = C_m/(T - \theta)$] behaviour of the samples. The paramagnetic Curie temperature (θ) and the Curie constant [$C_m = dT/d(\chi_m^{-1})$] have been evaluated from the intercept and the slope of the curves. These values are given in Table 1. It is observed from this table that the θ values are positive suggesting a ferromagnetic behaviour at lower temperatures. From the θ and C values, the molecular field constant ($\gamma = \theta/C_m$) and magneton numbers ($p = \sqrt{3kC_m/N\beta^2}$, where k is Boltzmann constant, N is the number of paramagnetic ions per g mole and $\beta = 0.927 \times 10^{-20}$ erg/Oe is the Bohr-magneton) have been evaluated and are also given in the Table 1.

The only magnetic ions in these solids are the trivalent rare-earth ions. Thus the theoretical value of p can be evaluated from the ground state of these ions [15]. There is a good agreement between the theoretical and experimental values of p (cf. Table 1). This and the finding that χ_m^{-1} depends linearly on T even at higher temperatures suggests that the $4f$ magnetic electrons are completely localized at the ions. Thus the question of
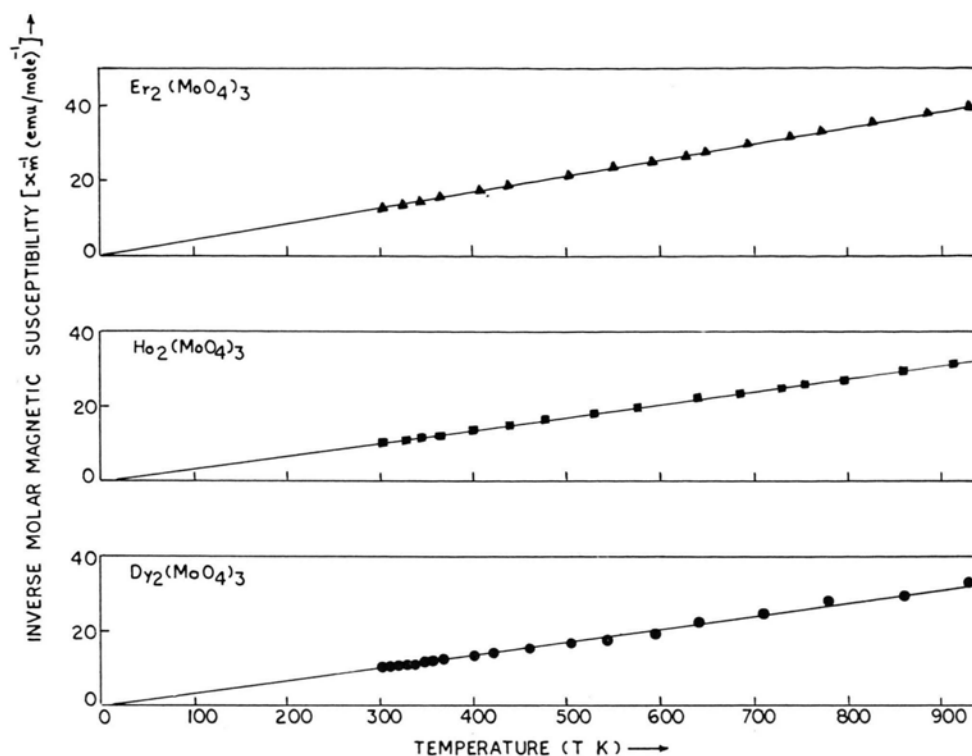
Fig. 1. Variation of inverse of molar magnetic susceptibility with temperature.

Table 1. Some magnetic parameters of heavy rare-earth molybdates.

Material	Magnetic ion	Ground state of magnetic ion	Curie constant C_m $\left(\frac{e.m.u}{g\text{-mole}}\right)$	Paramagnetic Curie temp. (θ K)	Experimental value of magneton number (p)	Theoretical value of p		Mol. field constant (γ_{gm}) $\times 10^2$	Exchange energy parameter J_e(K)
						Hund's value	Van Vleck and Frank's value		
$Dy_2(MoO_4)_3$	Dy^{3+}	$^6H_{15/2}$	28.75	12	10.72	10.63	10.60	3.37	.036
$Ho_2(MoO_4)_3$	Ho^{3+}	$^5I_8$	28.50	17	10.68	10.60	10.60	4.83	.045
$Er_2(MoO_4)_3$	Er^{3+}	$^4I_{15/2}$	23.44	5	9.68	9.59	9.60	1.74	.015

their participation in the electrical conduction does not arise and some other electrons must be responsible for the semi-conducting properties of the compounds.

A rough estimate of the average exchange energy parameter ($J_e = ng^2\beta^2\gamma/2Z$, where Z is the number of nearest neighbours) can be made using molecular field theory. The calculated values of J_e are given in Table 1. It is difficult to say anything about the

nature of the exchange interaction. Anderson type super-exchange between the rare-earth ions (Ln^{3+}) may be the reason for the long range magnetic ordering in these compounds at lower temperatures. For better understanding of the Ln^{3+}-O-Mo-O-Ln^{3+} interaction low temperature studies of the magnetization and the magnetic structure (neutron-diffraction studies) of the compounds would be needed. We are hoping to create facilities for such studies.

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