Ferromagnetism in Some Semi-Conducting Heavy Rare-Earth Molybdates

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Measurements of the magnetic susceptibility of powdered samples of Dy₂(MoO₄)₃, Ho₂(MoO₄)₃ and Er₂(MoO₄)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 Dy³⁺, Ho³⁺ and Er³⁺ 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 Dy₂(MoO₄)₃, Ho₂(MoO₄)₃ and Er₂(MoO₄)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, EuH₂, EuSe, ErCrO₃, ErFeO₃, YbCrO₃, Er₂(WO₄)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 nonlinear 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 Dy₂O₃, Ho₂O₃ and Er₂O₃ with a stated purity of 99.99 percent were procured from Rare-earth Product, England, and MoO₃ (99.99 percent — German made) from Bond, India. With these the molybdates were prepared and checked using standard methods reported in the literature [11]. Dy₂(MoO₄)₃ (white), Ho₂(MoO₄)₃ (light-yellow) and Er₂(MoO₄)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. Gd₂(WO₄)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 Dy₂O₃, 3.1 K for Ho₂O₃ and —11.8 K for Er₂O₃ in agreement with the results of other workers [13, 14]. The magneton numbers have also been found to be approximately those expected for Dy³⁺, Ho³⁺ and Er³⁺ ions, indicating the purity of our starting materials. The magnetic susceptibility of MoO₃ has been found to be very small (~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 χₘ⁻¹ on T suggesting a Curie Weiss law [χₘ = Cₘ/(T — θ)] behaviour of the samples. The paramagnetic Curie temperature (θ) and the Curie constant [Cₘ = dT/d(χₘ⁻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 (γ = θ/Cₘ) and magneton numbers (p = 1/3kCₘ/Nβ², where k is Boltzmann constant, N is the number of paramagnetic ions per g mole and β = 0.927 × 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 χₘ⁻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.

<table>
<thead>
<tr>
<th>Material</th>
<th>Magnetic ion</th>
<th>Ground state of magnetic ion</th>
<th>Curie constant Cm (e. m. u./g-mole)</th>
<th>Paramagnetic Curie temp. (θ K)</th>
<th>Experimental value of magneton number (p)</th>
<th>Theoretical value of p</th>
<th>Mol. field constant (γ_{nm}) × 10^2</th>
<th>Exchange energy parameter J_e(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy_2(MoO_4)_3</td>
<td>Dy^{3+}</td>
<td>6H_{15/2}</td>
<td>28.75</td>
<td>12</td>
<td>10.72</td>
<td>10.63</td>
<td>10.60</td>
<td>3.37</td>
</tr>
<tr>
<td>Ho_2(MoO_4)_3</td>
<td>Ho^{3+}</td>
<td>5I_8</td>
<td>28.50</td>
<td>17</td>
<td>10.68</td>
<td>10.60</td>
<td>10.60</td>
<td>4.83</td>
</tr>
<tr>
<td>Er_2(MoO_4)_3</td>
<td>Er^{3+}</td>
<td>4I_{15/2}</td>
<td>23.44</td>
<td>5</td>
<td>9.68</td>
<td>9.59</td>
<td>9.60</td>
<td>1.74</td>
</tr>
</tbody>
</table>

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.
Acknowledgement

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