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The magnetic phase transition in layered cesium rare earth metal dimolybdates

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Résumé. — Des mesures de chaleur spécifique de CsGd (MoO₄)₂, CsDy (MoO₄)₂ et CsDy₀.₉₅Eu₀.₀₅ (MoO₄)₂ montrent des anomalies aiguës à Tc = 0.448 K, Tc = 1.288 K et Tc = 1.227 K, respectivement. Les résultats sont comparés aux prédictions du modèle d'Ising à 2D et 3D.

Abstract. — Heat capacity measurements on CsGd (MoO₄)₂, CsDy (MoO₄)₂ and CsDy₀.₉₅Eu₀.₀₅ (MoO₄)₂ show that sharp anomalies occur at Tc = 0.448 K, Tc = 1.288 K and Tc = 1.227 K, respectively. The heat capacity behaviour is compared with 2D and 3D Ising model.

The chain-layered rare earth dimolybdates have the general formula AR (MoO₄)₂ (A = Cs, K, Rb...; R = Eu, Gd, Dy...) . Most of these compounds crystallise with the orthorhombic structure. According to their low temperature properties they belong to one of three categories: a) there are only a crystallographic phase transitions, e.g. CsLu (MoO₄)₂ [1]; b) there are a crystallographic phase transition and magnetic ordering, e.g. CsGd (MoO₄)₂ [2]; c) there are two phase transitions, the symmetry is lowered by a cooperative Jahn-Teller effect and at some lower temperature there is an additional magnetic ordering, e.g. CsDy (MoO₄)₂ [3]. This work contains the results of the heat capacity measurements of single crystals CsGd (MoO₄)₂, CsDy (MoO₄)₂ and CsDy₀.₉₅Eu₀.₀₅ (MoO₄)₂ and their comparison with suitable magnetic models.

All single crystal samples were prepared by the flux method and show an orthorhombic crystallographic structure (space group D₃₂) at room temperatures. Chains of the rare earth ions alternate with chains of Cs ions along b axis. Each of rare earth ions resp. Cs ions is located in the center of an octaeder formed by oxygen atoms. Unit cell parameters are a = 0.952 nm, b = 0.805 nm, c = 0.507 nm for CsGd (MoO₄)₂ and a = 0.951 nm, b = 0.797 nm, c = 0.505 nm for CsDy (MoO₄)₂ and CsDy (MoO₄)₂ with 5% of Eu. The energy levels of the ⁴S₇/₂ ground state of Gd³⁺ in CsGd (MoO₄)₂ are separated by ΔE₁ = 0.8 K, ΔE₂ = 1.33 K and ΔE₃ = 1.59 K.
respectively, the lowest energy level corresponding to $S = \pm 7/2$. For CsDy (MoO$_4$)$_2$ the energy levels of the $^6H_{15/2}$ ground state are separated by $\Delta E_1 = 32$ K but the lowering of the symmetry due to a cooperative Jahn-Teller effect occurs at 42 K and the energy levels are separated by $\Delta E_1 = 158$ K [4]. The CsDy$_{0.95}$Eu$_{0.05}$ (MoO$_4$)$_2$ differs from pure CsDy (MoO$_4$)$_2$ in the temperature of the phase transition into the low symmetry phase ($T_{RT} = 11$ K). Crystals were typically 18 x 16 x 1 mm with average weight 1.8 g. The specific heat was measured by means of the usual heat pulse method with the accuracy of 1%.

Fig.1 — Magnetic heat capacity of CsGd (MoO$_4$)$_2$ near $T_c$.

The specific heat $C_M$ of magnetic origin is plotted in figure 1 were the sharp maximum correspond to the onset of the long range ordering with $T_c = (0.448 \pm 0.005)$ K. This magnetic contribution was obtained by subtracting the lattice part ($\theta_D = 174$ K) and the part caused by the crystal field splitting (Schottky anomaly) from the total measured capacity. It was compared with the theoretical prediction for a 2D Ising model using a new type of the correlated effective field approximation (full curve in Fig. 1.) [5]. In the temperature range well above the phase transition the constant of the exchange interaction $J_1/k_B = 0.56$ K was obtained. Using the expression from reference [5]

$$e^{-J_1/k_BT_c} + e^{-(J_1/k_BT_c)\alpha} = 1$$

where $\alpha = J_2/J_1$ is the ratio of interchain to intrachain exchange interactions the numerical value $\alpha = 0.03$ was determined. We suppose that the heat capacity of CsGd (MoO$_4$)$_2$ may be described by the above mentioned model.

In addition the heat capacity of CsDy (MoO$_4$)$_2$ and CsDy$_{0.95}$Eu$_{0.05}$ (MoO$_4$)$_2$ were measured from 0.7 K to 6 K. The temperatures of the phase transitions were found as $T_c = (1.288 \pm 0.005)$ K for pure CsDy (MoO$_4$)$_2$ and $T_c = (1.227 \pm 0.005)$ K for CsDy$_{0.95}$Eu$_{0.05}$ (MoO$_4$)$_2$. The temperature range where the heat capacity can be described by $AT^{-2} + BT^3$ law was found (Fig. 2). The values of the Debye temperature were determined as $\theta_D = 171$ K for CsDy (MoO$_4$)$_2$, $\theta_D = 173$ K for CsDy$_{0.95}$Eu$_{0.05}$ (MoO$_4$)$_2$ and the corresponding lattice parts were subtracted. On the basis of the resulting magnetic heat capacity the thermodynamic quantitites (entropy $S$ and enthalpy $E$) were calculated below and above the critical point $T_c$ and were compared to the theoretical predictions of the Ising models (see Tab. I).
Table I

<table>
<thead>
<tr>
<th></th>
<th>CsDy (MoO₄)₂</th>
<th>CsDy (MoO₄)₂</th>
<th>Ising</th>
<th>Ising</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Sₐ - S₀) / R</td>
<td>0.412</td>
<td>0.395</td>
<td>0.306</td>
<td>0.560</td>
</tr>
<tr>
<td>(S₀ - Sₐ) / R</td>
<td>0.365</td>
<td>0.333</td>
<td>0.387</td>
<td>0.133</td>
</tr>
<tr>
<td>(Eₐ - E₀) / RTₐ</td>
<td>0.351</td>
<td>0.330</td>
<td>0.258</td>
<td>0.447</td>
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<tr>
<td>-Eₐ / RTₐ</td>
<td>0.573</td>
<td>0.530</td>
<td>0.623</td>
<td>0.218</td>
</tr>
<tr>
<td>Eₐ / RTₐ</td>
<td>0.924</td>
<td>0.860</td>
<td>0.881</td>
<td>0.665</td>
</tr>
<tr>
<td>-Eₐ / Eₐ</td>
<td>0.620</td>
<td>0.615</td>
<td>0.706</td>
<td>0.328</td>
</tr>
</tbody>
</table>

Fig. 2. The Debye temperature evaluation.

Fig. 3. Magnetic heat capacity compared with theoretical predictions for 2D and 3D Ising model.

The magnetic heat capacity results are shown in figure 3 together with the theoretical curves for 2D and 3D Ising model. The corresponding values J/k_B were calculated for CsDy (MoO₄)₂ : 0.568 K (2D Ising), 0.286 K (3D Ising) and for CsDy₀.₉₅Eu₀.₀₅ (MoO₄)₂ : 0.54 K (2D Ising), 0.272 K (3D Ising), respectively. We can conclude: a) CsDy (MoO₄)₂ and CsDy₀.₉₅Eu₀.₀₅ (MoO₄)₂ have predominantly 2D Ising character in spite of the fact that the total entropy are higher than the theoretical value for effective spin 1/2 for both samples; b) CsGd (MoO₄)₂ can be described by the 2D Ising model with nonequivalent interaction in plane unlike CsDy (MoO₄)₂ and CsDy₀.₉₅Eu₀.₀₅ (MoO₄)₂; it should be connected with the absence of the low symmetry structural phase in CsGd (MoO₄)₂.

References