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Calorimetric study of the pyrochlore compounds $Gd_2Mo_2O_7$ and $Sm_2Mo_2O_7$

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Abstract

The heat capacity $c_p(T, H)$ in magnetic fields up to 14 T for polycrystalline samples of $Gd_2Mo_2O_7$ and $Sm_2Mo_2O_7$ pyrochlore compounds is presented. In contrast to previous work, for both compounds well defined peaks in $c_p(T, H = 0)$ at 73 K (Gd) and 70 K (Sm) mark the onset of ferromagnetic order in the Mo subsystem. For $Gd_2Mo_2O_7$ a small step-like anomaly at 11.3 K on top of a large Schottky-like anomaly indicates partial magnetic ordering in the Gd subsystem. The magnetic contributions to $c_p(T)$ are estimated by comparing with a proper lattice reference and the evolution of magnetic entropies with temperature and external field is analysed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Pyrochlore compounds $A_2B_2O_7$ have attracted broad interest due to their exotic low temperature magnetic properties. The magnetism of these materials is largely governed by geometric frustration since the two cationic subsystems are arranged in networks of corner sharing tetrahedra. $RE_2Mo_2O_7$ (RE = rare earth ion) compounds have received special attention since the character of the magnetic transition of Mo can be tuned via the rare earth's mean ionic radius [1]. While Mo pyrochlores with Nd, Sm and Gd are metallic and show ferromagnetic ordering (in the Mo subsystem), those with smaller RE are non-metallic and display spin glass-like behaviour. Overviews are given in [2–4].

There seems to be no apparent long range magnetic ordering of the RE subsystem in any Mo pyrochlore compound studied so far. For example, broad Schottky-like anomalies (which did not show up in magnetic susceptibility) have been found in the zero-field specific heat of $Gd_2Mo_2O_7$ and $Sm_2Mo_2O_7$ [5]. These have been successfully modelled assuming a random Zeeman splitting of the spin-only and the crystal electric field (CEF) ground states of the Gd^{3+} and the Sm^{3+} ions, respectively. Here, we present new specific heat data and obtain the magnetic contribution to the heat capacity by comparing with an improved lattice reference.

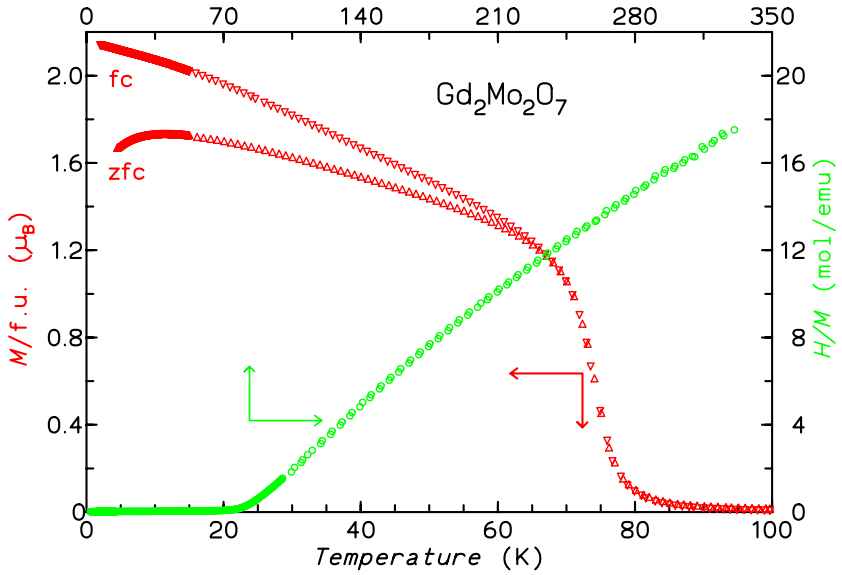

Figure 1. Magnetization $M(T)$ of $Gd_2Mo_2O_7$ in an external field of 0.01 T versus temperature (zfc, △; fc, ▽) and $H/M(T)$ measured in a field of 0.1 T (○).

In addition, we studied the influence of magnetic fields up to 14 T on the low temperature magnetic properties.

2. Sample preparation and experimental details

Single-phase polycrystalline samples of $RE_2Mo_2O_7$ (RE = Sm, Gd) were prepared from RE_2O_3 and MoO_2, which were mixed thoroughly and pressed into pellets. The pellets were placed in an alumina crucible and heated in a flowing Ar atmosphere at 1350 °C for ≈24 h. $LaZr_2O_7$ was prepared similarly, from La_2O_3 and ZrO_2 at 1300 °C.

The magnetization was measured in a SQUID magnetometer in zero-field cooling (zfc) and field cooling (fc) modes in 0.01 and 0.1 T external fields.

The heat capacity was determined with a quasi-adiabatic step-heating method [6]. The sample masses were ≈230 mg ($Gd_2Mo_2O_7$) and ≈690 mg ($Sm_2Mo_2O_7$). The inaccuracy of $c_p(T)$ amounts to ≈1% between 2.2 and 30 K and increases to ≈2% at 100 K. For $H \neq 0$ the temperature calibration of the sample holder thermometer was corrected for magnetoresistive effects. An additional zero-field measurement was performed in a ^{3}He cryostat (0.6 K $< T <$ 2.2 K; inaccuracy about 2%). Zero-field measurements up to 200 K with a scanning calorimeter revealed no further anomalies.

3. Results and discussion

Magnetization data for $Gd_2Mo_2O_7$ are given in figure 1. $M(T)$ for $H_{ext} = 0.01$ T increases strongly below ≈77 K indicating the onset of the ferromagnetic ordering in the Mo subsystem. The fc magnetization in this low field at the transition is only 1.0 μ_B/fu but $M(T)$ strongly increases with an unconventional temperature dependence towards lower temperatures (cf the data in [7]). In a field of 1 T the magnetization reaches 2.0 μ_B/fu at 73 K and increases to 8.6 μ_B/fu at 2.0 K, which is still far below the experimental and theoretical saturation values

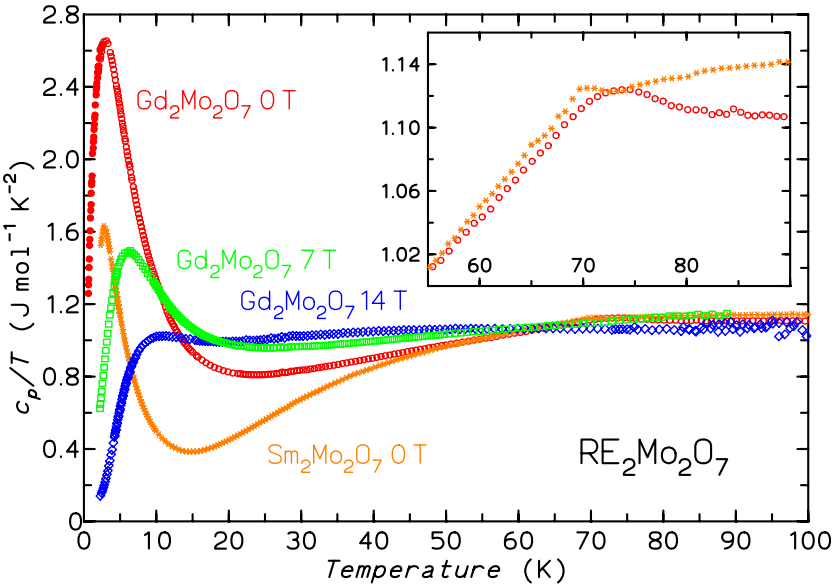

Figure 2. Specific heat capacity $c_p(T)/T$ of $Gd_2Mo_2O_7$ in zero (○, ● mark additional data from 0.6 to 2.6 K), 7 T (□) and 14 T (◇) magnetic fields and $c_p(T)/T$ of $Sm_2Mo_2O_7$ in zero field (∗). The inset displays a magnified view around $T_{C,Mo}$.

(cf [4, 5]). In the paramagnetic range $H/M(T)$ cannot be described by a Curie–Weiss law at all. Only at the highest temperatures (280–330 K) does the linearly fitted slope of $H/M(T)$ (corresponding to 8.4 μ_B/0.5 fu) approach the value expected for the sum of the free Gd and spin-only Mo effective moments (8.43 μ_B/0.5 fu). The resulting Weiss parameter $\Theta = +20$ K is, however, much smaller than the transition temperature of the molybdenum subsystem.

The heat capacity data in different external magnetic fields are shown in figure 2. In a previous calorimetric investigation [5] broad humps due to the magnetic contributions of the RE and Mo had been detected. In contrast, for the current samples a rather sharp peak is visible at 73 K ($Gd_2Mo_2O_7$) and 70 K ($Sm_2Mo_2O_7$) in zero field, marking the magnetic ordering of the Mo subsystem in good agreement with the magnetization study and data in [5]. The peak in $c_p(T)$ of $Gd_2Mo_2O_7$ is found exactly at the mid-temperature of the step in $M(T)$ (see figure 1).

To estimate the lattice contribution to $c_p(T)$ of the magnetic pyrochlores, the heat capacity of $Y_2Ti_2O_7$ had been used before by Raju *et al* [5]. Since the atomic masses in $Y_2Ti_2O_7$ deviate significantly from those of Gd, Sm and Mo, we considered non-magnetic pyrochlores containing heavier atoms. Therefore, we prepared and measured the heat capacity of two more non-magnetic pyrochlore compounds, namely $Y_2Sn_2O_7$ and $La_2Zr_2O_7$, and found $La_2Zr_2O_7$ best applicable for constructing a lattice reference within Debye theory. Within error bars our data for $La_2Zr_2O_7$ are in agreement with those given by Bolech *et al* [8]. The heat capacity of $La_2Zr_2O_7$ was converted to the corresponding Debye temperature $\Theta_D(T)$, scaled by $\sqrt{M/M'}$, where M and M' are the molar masses of the lattice reference and the magnetic sample, respectively, and reconverted to specific lattice reference values $c_{\mathrm{lat,(Gd/Sm)}}(T)$. The magnetic specific heat contributions $c_{\mathrm{mag}} = c_p - c_{\mathrm{lat}}$ are given in figures 3 and 4, respectively. The magnetic entropies (including an extrapolation with T^3 to zero for $T < T_{\mathrm{min}}$) are shown in figure 5.

The zero-field magnetic contribution for $Gd_2Mo_2O_7$ is characterized by two distinct anomalies. At lower temperatures a pronounced Schottky-like anomaly originating from the

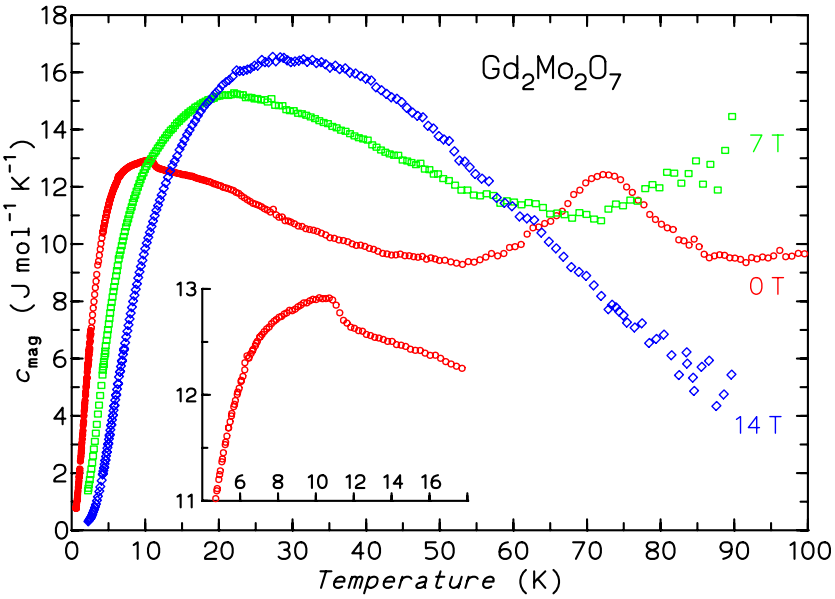

Figure 3. Magnetic specific heat contributions c_{mag} of $Gd_2Mo_2O_7$ in different magnetic fields (0 T, O; 7 T, □; 14 T, ◇). The inset is a magnified view around 11 K ($H = 0$ T).

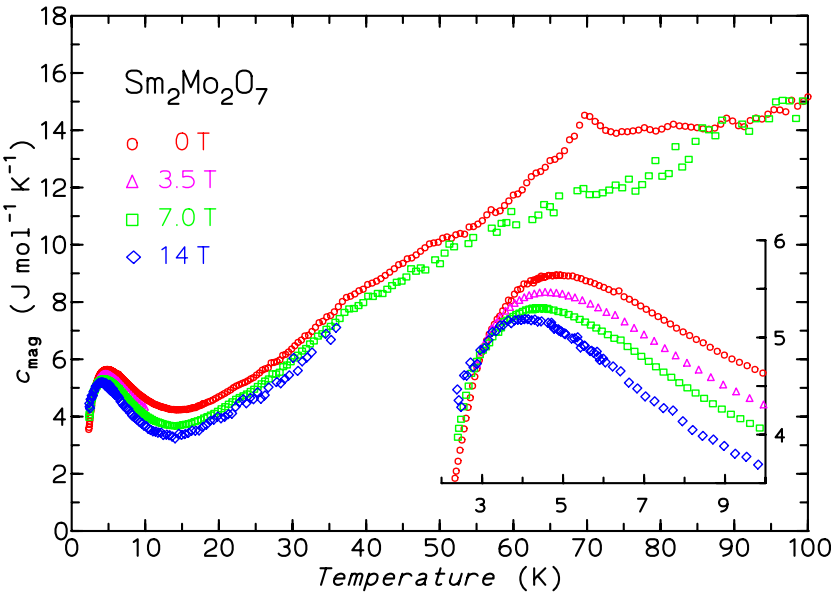

Figure 4. Magnetic specific heat capacities c_{mag} of $Sm_2Mo_2O_7$ in different magnetic fields (0 T, O; 3.5 T, △; 7 T, □; 14 T, ◇). The inset shows a magnification.

spin levels of the $^8S_{7/2}$ ground state of Gd^{3+} split by the exchange field of the Mo subsystem is observed. Additionally, a small kink at 11.3 K on top of the broad anomaly is visible. This kink seems to indicate long range ordering in the Gd subsystem, however, the entropy involved is much too small to account for complete ordering of all spins.

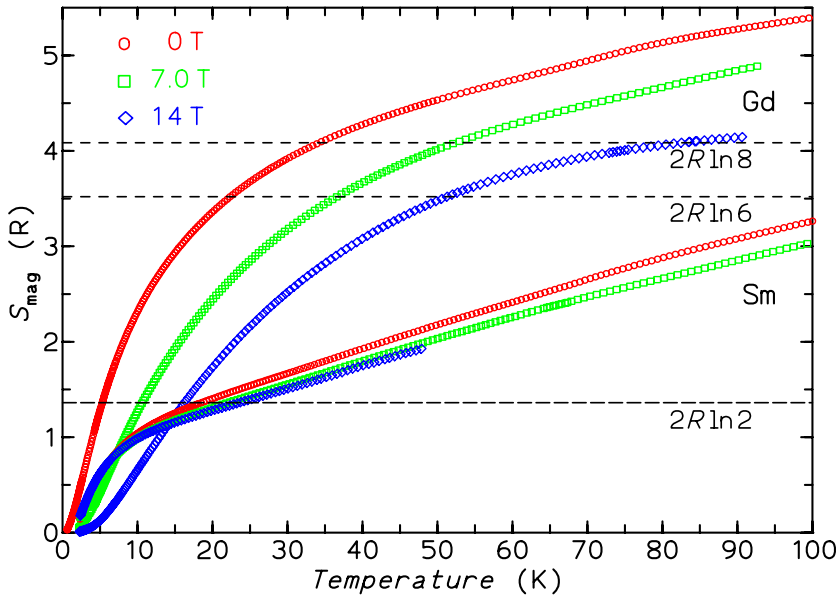

Figure 5. Magnetic entropies S_{mag} of $Gd_2Mo_2O_7$ and $Sm_2Mo_2O_7$ in different magnetic fields (0 T, ○; 7 T, □; 14 T, ◇). The levels indicate the entropies expected for the respective RE ground state multiplets (Gd, Sm) or an isolated doublet (Sm).

As observed previously, c_{mag} drops linearly with temperature below the maximum of the Schottky-like anomaly [5]. Below 1 K c_{mag} decreases rather exponentially, indicating the opening of a spin gap towards lowest temperatures. The integrated entropy exceeds the $2R \ln 8$ value expected for Gd^{3+} at 34 K. Above this temperature the anomaly from the magnetic ordering in the Mo^{4+} subsystem ($S = 1$) gives rise to a further smooth increase of the entropy. At the maximum temperature of the measurement the integrated entropy tends to saturate at a value of about $6R$, close to ($2R \ln 8 + 2R \ln 3 = 6.36R$) as expected for the sum of the entropies of the two subsystems.

Magnetic fields have a surprisingly strong influence. The high temperature anomaly is smeared out. Significantly more entropy is acquired already at higher temperatures. In a field of 7 T (14 T) the entropy value $2R \ln 8$ is already reached at 53 K (85 K).

In magnetic fields one observes an extension of the low temperature exponential temperature dependence to higher temperatures indicating an increase of the spin gap due to Zeeman interaction. The gaps, Δ, deduced from an Arrhenius plot (see figure 6) amount to ≈1.3, 6.7 and 12.1 K for 0, 7 and 14 T, respectively. To a good approximation they rise linearly with magnetic field with a slope of 0.77 K T^{-1}.

A different picture arises for $Sm_2Mo_2O_7$. The zero-field magnetic contribution also shows a pronounced peak due to the magnetic ordering transition in the Mo subsystem. The peak is found at 70 K, almost the same temperature as for $Gd_2Mo_2O_7$. Other studies report the magnetic ordering at ≈60 K [7], 83 K [9, 10] or 73 or 77 K [11].

There is no sharp kink feature for the Sm subsystem contribution and the maximum of the Schottky-like anomaly of Sm is shifted to slightly lower temperatures with field (0 T: 4.80 K; 3.5 T: 4.55 K; 7 T: 4.40 K; 14 T: 4.05 K). Remarkably, the four curves $c_{mag}(T, H)$ all cross at 3.1 K. Further measurements to lower temperatures in high fields are necessary. There is also no increase of c_{mag} with H at higher temperatures. The entropy exceeds $2R \ln 2$ at 17 K, and increases almost linearly up to the maximum temperature of our study where it is still below

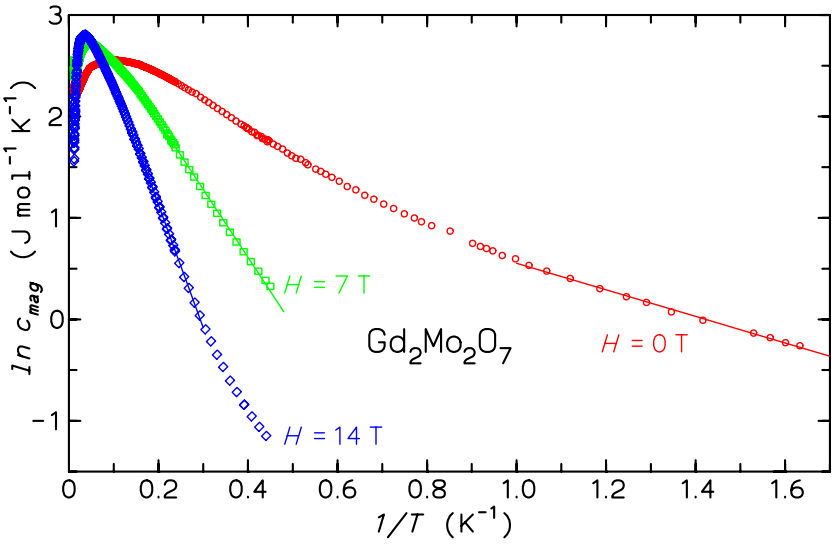

Figure 6. The magnetic contribution to the specific heat c_{mag} of $Gd_2Mo_2O_7$ plotted versus $1/T$, demonstrating that with increasing field an energy gap opens up.

$2R \ln 6$, the value expected for the Sm^{3+} ground state $^6H_{5/2}$. Obviously, a CEF doublet gives rise to the Schottky-like anomaly, the next excited CEF doublet accounts for the weak hump around 40 K and the third doublet is not yet populated at 100 K. From the field and temperature dependence of c_{mag} the Mo subsystem seems to be very similar to that in $Gd_2Mo_2O_7$.

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