Journal of Thermal Analysis, Vol. 40 (1993) 341-347

MAGNETIC SPECIFIC HEAT AND SPIN-GLASS-LIKE ORDERING IN THE PYROCHLORES: $RE_2Mo_2O_7$ (*RE* = Y, Sm, Gd, Ho)

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The pyrochlores $RE_2Mo_2O_7$ (*RE* = Y, Sm, Gd, Ho) display, with the exception of $Ho_2Mo_2O_7$, magnetic transitions at 18 K, 68 K, 55 K, respectively. No long-range order occurs. The rare-earth atoms remain in the paramagnetic state down to 1.5 K. The magnetic specific heat behaviour is explained by spin-glass-like ordering of Mo^{4+} ions, imposing a molecular field of random character on the rare-earth ions, and by crystalline field-splitting effects.

Keywords: magnetic specific heat, pyrochlores, spin-glass-like ordering

Introduction

The face-centered cubic compounds $RE_2Mo_2O_7$ (*RE* = Nd, ...Yb and Y) belong to the pyrochlore group with the general formula $A_2B_2O_7$ [1]. Characteristic features of these compounds are that, for each of the metal atoms A and B, there exist two (magnetic) sublattices and that each forms a three-dimensional network of corner-sharing tetrahedra. Such an arrangement leads to a very high degree of magnetic frustration if nearest-neighbour interaction is antiferromagnetic. An extremely large variety of physical properties has been found in pyrochlores [2–14]. The Mo-compounds also display very different properties. $RE_2Mo_2O_7$ (*RE* = Nd, Sm, Gd) are metallic [7, 8, 10]. Spontaneous magnetization occurs at 96 K, 80 K and 57 K, respectively. $Tb_2Mo_2O_7$ is semi-metallic and shows magnetic ordering phenomena near 25 K [11]. The remaining $RE_2Mo_2O_7$ compounds are insulating and do not exhibit any cooperative magnetic ordering above 4 K [8, 9]. $Y_2Mo_2O_7$, where Mo^{4+} is the only magnetic ion, is semiconducting with a magnetic transition near 18 K [6, 7, 12]. The magnetic susceptibility curves clearly indicate spin-glass-like behaviour. However, earlier specific heat

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measurements and neutron diffraction studies did not indicate long-range order at low temperatures [4]. $Y_2Mo_2O_7$ is a very interesting magnetic system: i.e. there is no crystallographic disorder and therefore the observed spin-glass behaviour must originate from the topological frustration of the Mo-sublattice only. A very limited number of specific-heat measurements has been reported for pyrochlores [e.g. 4, 13].

We have systematically studied for the first time the specific heat of molybdenum-pyrochlores [13]. In particular, we investigated their magnetic heat in the temperature range 2 K to 300 K, in order to elucidate the complex magnetic structure and the interplay of the two magnetic sublattices built up by molybdenum and rare-earth atoms. The specific heat of non-magnetic $Y_2Ti_2O_7$ was used to reconstruct the pure lattice heat of the magnetic pyrochlores. In this paper, we present the specific heat of the pyrochlores $Y_2Mo_2O_7$, $Sm_2Mo_2O_7$, $Gd_2Mo_2O_7$ and $Ho_2Mo_2O_7$ below 100 K. These data, and detailed susceptibility studies reported in [13], substantiate that some Mo-pyrochlores behave like spin-glasses.

Experimental

Polycrystalline, single-phase pellets of $RE_2Mo_2O_7$ (*RE* = Y, Sm, Gd, Ho) were prepared by solid-state reaction as described in [13]. The observed lattice constants were in excellent agreement with those reported in the literature. [2, 8, 9]. The susceptibilities (ac- and dc-), as well as magnetization curves, were measured using a purpose-built ac-susceptometer at a frequency of 117 Hz and a SQUID magnetometer (Quantum Design, San Diego). Specific heats from 1.5 K to 150 K were determined with a fully-automated quasi-adiabatic calorimeter equipped with commercially calibrated platinum or germanium resistance thermometers [15]. The absolute error of the C_p-measurement was less than 1.5%. The average data scatter amounted to 0.8%.

The measured specific heats C_p consisted of contributions from the lattice C_L and from the magnetic heat C_M. Since an independent determination of both contributions was not possible, the lattice heat had to be evaluated by an appropriate procedure. First, the specific heat of $Y_2Ti_2O_7$, which is isostructural to $RE_2Mo_2O_7$ and non-magnetic, was measured. Second, the temperature-dependent Debye temperatures $\Theta(T)$ were calculated for all samples according to the Debye function. The Θ-values of $Y_2Ti_2O_7$ were multiplied by a scaling factor such that the scaled Θ-values of $Y_2Ti_2O_7$ and a given sample of $RE_2Mo_2O_7$ were equal above the magnetic transition temperatures. Third, the scaled $\Theta(T)$ *vs.* T curve of $Y_2Ti_2O_7$ was then converted back into specific heat, which represented the lattice heat C_L of the corresponding compound. Finally, C_M was obtained by subtracing the derived C_L from the measured C_p-curve.

Results

Measured specific heats are shown in Fig. 1. Comparison of the non-magnetic reference material, $Y_2Ti_2O_7$, with the Mo-compounds reveals broad anomalies for the $RE_2Mo_2O_7$ (*RE* = Y, Sm, Gd, Ho), but no sharp, λ-type transition was observed. These additional specific heats, which apparently are of magnetic origin, become clearly visible in Figs 2 and 3 after subtraction of the lattice heats. For $Y_2Mo_2O_7$ the magnetic heat is linear below 15 K and is centered near 20 K (Fig. 2), in agreement with the peak of zero-field cooled susceptibility at about 18 K. The deduced magnetic entropy at the transition temperature, 18 K, is 1.6 J/mol·K. The effective magnetic moment was found to be 1.7 μ_B per Mo^{4+} (Curie constant, 0.35 emu/molK).

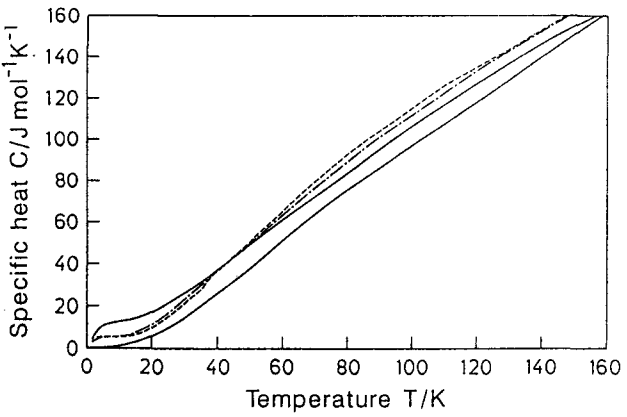

Fig. 1 Specific heat of some molybdenum pyrochlores. For clarity the more than 300, individually measured, data-points are given as continuous curves: —— lower curve: $Y_2Mo_2O_7$; —— upper curve: $Gd_2Mo_2O_7$; – – – $Sm_2Mo_2O_7$; – · – · – $Ho_2Mo_2O_7$

The paramagnetic Curie temperature of –28 K indicates antiferromagnetic exchange interaction. (The considerable reduction of the effective moment of Mo from 2.8 μ_B, which is expected for a d^2-configuration leading to a $S = 1$ triplet ground state, is ascribed to noticeable spin-orbit splitting effects of the 4*d* electrons [13]). Our study clearly reveals spin-glass-like behaviour of $Y_2Mo_2O_7$:

i) strong differences in field-cooled (FC) and zero-field cooled (ZFC) susceptibilities

ii) a broad anomaly for C_M with a maximum at the spin-glass freezing temperature T_F

iii) a linear temperature dependence of C_M below T_F

iv) recovery of only about 15% of the expected magnetic entropy for Mo, namely $\Delta S_M = R\ln(2S + 1) = 5.76$ J/mol·K. We note that similar findings have been reported for $Y_2Mn_2O_7$ [14].

The specific heat of $Ho_2Mo_2O_7$ displays a Schottky anomaly at low temperatures which presumably is induced by crystal-field interaction. The susceptibility data indicate a weak anti-ferromagnetic interaction (Curie temperature, –3 K; Curie constant, 25.2 emu/mol·K). A more detailed discussion must be postponed since further investigation is required.

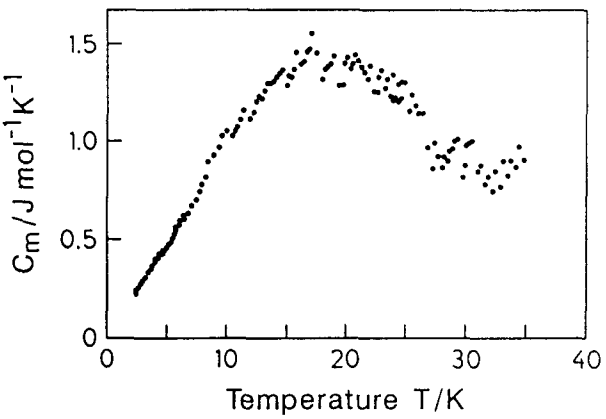

Fig. 2 Magnetic specific heat of $Y_2Mo_2O_7$

Analysis of the specific heats of $Sm_2Mo_2O_7$ and $Gd_2Mo_2O_7$ reveal two anomalies for each compound. In Fig. 3, C_M of $Gd_2Mo_2O_7$ is plotted as an example. The C_M curve of the Sm compound is nearly identical; for more details refer to [13]. A pronounced Schottky-type anomaly exists near 30 K. Surprisingly, there is no corresponding feature detected in the magnetic susceptibility. A second, broad, smeared-out anomaly is found for C_M around 65 K. (At this temperature the lattice heat is still dominant, contributing about 80% to C_p). It is evident from Fig. 3 that C_M increases linearly above 40 K. These C_M anomalies at higher temperatures are accompanied by sharp rises in susceptibilities of $Sm_2Mo_2O_7$ and $Gd_2Mo_2O_7$ indicating transition temperatures of 58 K and 55 K, respectively. In a similar manner to $Y_2Mo_2O_7$, splitting of ZFC and FC susceptibilities occur below these transition temperatures. In contrast to $Y_2Mo_2O_7$, the observed positive paramagnetic Curie temperatures of 53 K and 101 K indicate ferromagnetic interaction for $Sm_2Mo_2O_7$ and $Gd_2Mo_2O_7$. Preliminary values of C_M for $Gd_2Mo_2O_7$, measured at high magnetic fields, as shown in Fig. 3, support this finding because the C_M maximum shifts to higher temperatures with increas-

ing magnetic field. The saturation magnetic moments (at 5 Tesla) are in agreement with previous studies. We measured 2.2 μ_B and 14.7 μ_B, and Curie constants of 0.55 and 7.80 emu/mol·K, for the Sm and Gd compounds, respectively. The two anomalies (near 30 K and 70 K) can be separated reasonably well in the vicinity of 40 K. Thus the magnetic entropies can be calculated separately for each anomaly. For the anomalies at higher temperatures, ΔS_M equals 1.8 J/mol·K per formula unit of $Sm_2Mo_2O_7$ and 0.9 J/mol·K for $Gd_2Mo_2O_7$. These entropy values are comparable to the value for $Y_2Mo_2O_7$ which has been attributed to spin-glass ordering [13, 14]. The magnetic entropies associated with the Schottky-like anomalies at lower temperatures amount to 5.7 J/mol·K and 15.3 J/mol·K for $Sm_2Mo_2O_7$ and $Gd_2Mo_2O_7$, respectively. These values are close to Rln2 for $Sm_2Mo_2O_7$ and Rln8 for $Gd_2Mo_2O_7$, indicating the expected two-level and eight-level magnetic ground states.

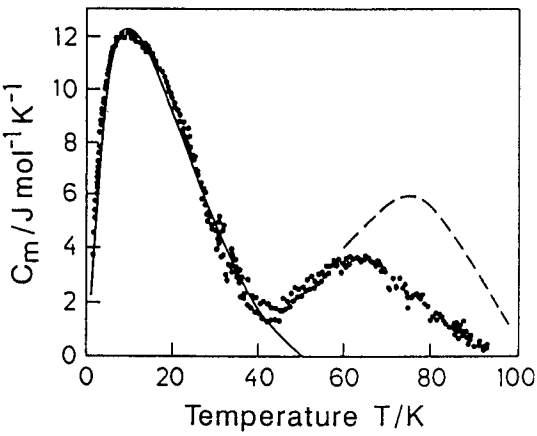

Fig. 3 Magnetic specific heat of $Gd_2Mo_2O_7$ in zero magnetic field (experimental data points) and in a magnetic field of 3 Tesla (dotted line). The solid curve was obtained from a theoretical fit to a two-level Schottky anomaly with Gaussian distribution and level splitting of 11 K. Further details of the model calculation are given in [13]

However, according to the magnetic measurements, obviously no magnetic long-range order occurs. The rare-earth ions apparently remain in the paramagnetic state. Similar specific heat anomalies have been detected in other $RE_2Mo_2O_7$ (*RE* = Dy, Ho and Yb) as depicted in Fig. 1 for $Ho_2Mo_2O_7$. We note that the experimental curves of the low-temperature anomalies (in Sm and Gd compounds) deviate significantly from what would be expected for a usual multi-level Schottky anomaly:

i) C_M increases linearly at low temperatures, instead of exponentially;
ii) the maximum is noticeably smaller;

iii) above the maximum C_M reduces more rapidly than one would expect from the characteristic T^{-2}-temperature dependence of a Schottky anomaly.

Recently we have given a detailed description and attempted to model the complex magnetic behaviour which appears to be typical of some pyrochlores which contain different magnetic sublattices [13]. Therefore only an outline explanation is given here. $Sm_2Mo_2O_7$ and $Gd_2Mo_2O_7$ display all the features of spin-glass-like behaviour near their transition temperatures (68 K and 55 K). We conclude, by comparison with $Y_2Mo_2O_7$, that the Mo^{4+} ions undergo spin-glass-like ordering in $Sm_2Mo_2O_7$ and $Gd_2Mo_2O_7$ near 70 K. The rare-earth sublattices remain paramagnetic. However, it is known that rare-earth ground-states are much affected by crystal electric fields and usually split by a Kelvin or less. In the present case, the interaction between molybdenum and rare-earth elements creates a molecular field at the rare-earth site which lifts the degeneracy of the magnetic ground states of Sm and Gd and leads to the appearance of the Schottky-like anomalies near 30 K. As a consequence of the spin-glass-like behaviour of the Mo sublattice, the molecular field imposed on the rare-earth ions is not unique but has a random character. We have to assume a field probability distribution. Simulation of the internal exchange field by a Gaussian distribution around 8 K for $Sm_2Mo_2O_7$ and 11 K for $Gd_2Mo_2O_7$, respectively, allows a quantitative description of the specific heat anomalies [13]. We emphasize that this first study of the specific heat of molybdenum pyrochlores unambiguously demonstrates that the Sm and Gd molybdenum pyrochlores exhibit spin-glass-like properties although the materials are crystallographically fully ordered. Therefore, these compounds represent very interesting and unique systems for the investigation of magnetic interactions.

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The authors thank Dr. R. K. Kremer for very helpful discussions and gratefully acknowledge the assistance of H. Bender, E. Brücher and K. Ripka in preparing the samples, and performing magnetic and calorimetric experiments, respectively. It is a pleasure for one of the authors (NPR) to gratefully acknowledge financial support from DAAD (German Academic Exchange Service).

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Zusammenfassung — Mit Ausnahme von $Ho_2Mo_2O_7$ zeigen die Pyrochlore $RE_2Mo_2O_7$ (*RE* = Y, Sm, Gd, Ho) Curie-Punkte bei 18K, 68K bzw. 55K. Es existieren keine Fernordnungen. Die Seltenerdenatome verbleiben im paramagnetischen Zustand bis herunter auf 1.5K. Das magnetische spezifische Wärmeverhalten wird mit Aufspaltungseffekten des Kristallfeldes und mit einer spin-glas-artigen Ordnung von Mo^{4+}-Ionen durch ein molekulares Random-Feld erklärt.