The specific heat of $KEr(MoO_4)_2$ - a quasi-one-dimensional Ising ferromagnet

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A Orendáčová†, M Orendáč†, V Bondarenko‡, A Feher† and A G Anders‡

† Faculty of Science, P J Šafárik University, Park Angelinum 9, 041 54 Košice, Slovakia
‡ Institute for Low Temperature Physics and Engineering, Lenin Avenue 47, 310164 Kharkov, Ukraine

Abstract. The specific heat of a layered single crystal, KEr(MoO$_4$)$_2$, was measured in the temperature range 0.45 K–6.5 K in zero magnetic field. A λ-type anomaly found at $T_c = 0.955$ K $\pm$ 0.005 K is associated with a phase transition into the ordered state. The experimental values of the magnetic entropy indicate deviations from two-dimensional behaviour of the magnetic system. Honmura's model of a 2D assembly of coupled $S = 1/2$ Ising ferromagnetic chains was used for the specific heat data analysis. The estimated value of the intrachain interaction is $J_1/k_B = 1.42$ K and that of the interchain interaction is $J_2/k_B \approx 0.03$ K; these were obtained from the fitting procedure for the ordered phase. The fit for the paramagnetic phase yields $J_1/k_B = 0.93$ K and $J_2/k_B \approx 0.07$ K. The comparison of the results of the analysis with theoretical calculations made on the assumption of a pure dipolar character of the magnetic correlations is discussed.

1. Introduction

In the last few years many theoretical studies [1–3] have revealed more complex spin dynamics in one-dimensional (1D) magnetic systems. This has stimulated renewed interest in the experimental study of the excitation spectrum and thermodynamic properties of linear chain compounds. Several classes of 1D magnetic materials have been reported, enabling investigators to study the influence of the anisotropy and spin value on the character of magnetic excitations [1, 4, 5].

One of the extensively studied class of low-dimensional materials is represented by a large series of ionic compounds with the general formula AR(MO$_4$)$_2$, where A $=$ Cs, K, Rb, ..., R $=$ La, Ce, Pr, ..., Lu and M $=$ Mo, W [6]. The compounds are characterized by a layered crystal structure and low-dimensional magnetic behaviour. In these ionic crystals the R^{3+} ions occupy sites which are sufficiently far apart from one another that dipolar coupling represents the dominating interaction among magnetic moments [7]. The moments of the rare-earth ions in an AR(MO$_4$)$_2$ lattice are often very anisotropic, in some cases leading to good approximations of the Ising model [8].

One of the best-studied compounds from this group is CsDy(MoO$_4$)$_2$ which has undergone an intensive experimental and theoretical investigation [9]. In this compound the separation between the two lowest Kramers doublets of the ground state ^{6}H$_{15/2}$ is 158 K [10]. At helium temperatures, Dy^{3+} behaves as an Ising ion with an effective spin 1/2. Thermodynamic studies [11] showed that the magnetic heat capacity in the critical region corresponds to the behaviour of the two-dimensional Ising system. Theoretical calculations

considering only dipolar interactions [12] revealed that the magnetic structure of the ground state consists of weakly coupled ferromagnetic chains of Dy^{3+} ions parallel to the c-axis with magnetic moments oriented along the chains. Good agreement was obtained when comparing magnetic specific heat data with the high-temperature expansions of the specific heat assuming only dipolar coupling [12].

The aim of this paper is to analyse the specific heat data for $KEr(MoO_4)_2$. This compound belongs to the aforementioned class; thus we assume dominating dipolar interactions in this system also. Nevertheless, since no corresponding high-temperature expansion for $KEr(MoO_4)_2$ is available yet, the data were analysed within the approximation of the exchange-coupled Ising model. The results of the analysis are compared with theoretical predictions [13] in which it is assumed that there are dipolar interactions only. The information obtained on the nature of magnetic interactions may indicate whether this compound could be suitable for the study of spin-cluster excitations (bound magnon states)—the lowest-lying excitations in 1D Ising systems [14].

2. Crystallography and experimental details

The crystal structure of $KEr(MoO_4)_2$ is orthorhombic, with space group D_{2h}^{14}; the parameters of the unit cell are $a = 5.063$ Å, $b = 18.25$ Å, $c = 7.915$ Å, and the cell contains four formula units. The chains of Er^{3+} ions which are located in the centre of eight-coordination oxygen polyhedra are parallel to the c-axis of the crystal. The intrachain distance of the ions is 3.957 Å [13].

The ground state of a free Er^{3+} ion is $^4I_{15/2}$, and in the crystal field of ortho-rhombic symmetry the energy level is split into eight Kramers doublets with the energies $E_0 = 0, E_1 = 13$ cm^{-1}, $E_2 = 32$ cm^{-1}, $E_3 = 74$ cm^{-1}, $E_4 = 185$ cm^{-1}, $E_5 = 258$ cm^{-1}, $E_6 = 317$ cm^{-1} and $E_7 = 324$ cm^{-1} [15]. Electron paramagnetic resonance experiments performed on single crystals of $KEr(MoO_4)_2$ [13] revealed that the magnetic axes are identical with the crystallographic a-, b-, c-axes. The Ising character of this compound is quite well established, with $g_c = 14.7$ and $g_a = 1.8$, $g_b < 0.9$ for the lowest doublet. The energy of the first excited doublet was re-estimated as $E_1 = 15 \pm 2$ cm^{-1} with corresponding g-factors $g_a' = 2.3$, g_b', $g_c' < 1$.

Table 1. Magnetic entropies below T_c ($S_{T<T_c}$) and above T_c ($S_{T>T_c}$) for $KEr(MoO_4)_2$ (this work), $CsDy(MoO_4)_2$ and theoretical predictions for the $S = 1/2$ 2D square (sq) and 3D simple cubic (sc) Ising lattices [8].

	$KEr(MoO_4)_2$	$CsDy(MoO_4)_2$	Ising (sq)	Ising (sc)
$S_{T<T_c}/R$	0.240	0.412	0.306	0.560
$S_{T>T_c}/R$	0.434	0.365	0.387	0.133

Single-crystal samples were prepared by the flux method [16], with typical dimensions $15 \times 10 \times 1$ mm^3 and weight of 1 g. The specific heat measurements were performed in two experimental devices. For temperatures above 2 K, standard adiabatic calorimetry was used in a ^{4}He cryostat equipped with a mechanical heat switch between the cold thermal reservoir and the sample cell. The sample temperature was measured using an RuO_2 resistor [17] calibrated against a commercial Lake Shore thermometer, GR 200A-500. For temperatures below 2 K, the dual-slope method [18] was used with an Oxford Instruments dilution refrigerator (model TLE 200). A RuO_2 thermometer, RCW-575, with a nominal value

of 4.7 kΩ, was calibrated against a commercial Lake Shore GR 500A-30 and served for measuring the sample temperature. The experimental data were corrected for additional contributions from the thermometer, the manganin heater and the varnish (GE 7031) used to anchor the specimen to the measuring platform. The overall 5% error of the experimental data was estimated on the basis of previous experiments performed on a copper reference specimen [19].

3. Results and discussion

The compound studied represents a magnetic insulator; therefore only magnetic and lattice systems are considered to contribute to the total specific heat. Since $KEr(MoO_4)_2$ has a layered crystal structure, the standard Debye approximation was not used. Instead, the specific heat of the diamagnetic isomorph, $KLu(MoO_4)_2$ [20], was used to separate the lattice contribution, applying a scaling procedure suggested by Stout and Catalano [21]. In this approximation $C(\text{lattice}, T) = C(KLu(MoO_4)_2, rT) + \mathrm{d}\ln r/\mathrm{d}\ln T$, where r is a scaling factor. In [15], where the specific heat of $KEr(MoO_4)_2$ was studied over the range 5 K–180 K, the aforementioned approximation for $r = 1$ was used successfully, and thus the same procedure was applied in the present work (figure 1). The magnetic specific heat obtained by this procedure is characterized by the dominating λ-anomaly observed at $T_c = 0.955 \pm 0.005$ K associated with a phase transition into the magnetically ordered state. The tendency of the specific heat to rise towards the higher temperatures is a manifestation of the Schottky anomaly due to the contribution of the higher energy levels of Er^{3+} in the crystal field. Since the energy separation Δ between the first excited doublet and the ground state is about 22 K, below helium temperatures higher energy levels will be considerably depopulated and in a first approximation only the ground doublet will be responsible for the behaviour of the magnetic system. This assumption led to the direct subtraction of the Schottky anomaly (figure 2). The temperature region in which we were interested was narrowed to one having an upper limit of about 4.5 K, where the relative occupation of the higher doublet n_1/n_0 (n_0 is associated with the lowest doublet) is about 1%. Magnetic entropy calculations for the temperature region 0.5 K–4.5 K yield the experimental value 5.603 J K^{-1} mol^{-1} which represents about 97% of the theoretical value $R\ln(2)$ for the $S = 1/2$ system. Table 1 contains $KEr(MoO_4)_2$ entropies compared with those for $CsDy(MoO_4)_2$ and theoretical predictions for Ising models. The value of the entropy found below the transition temperature is lower than the theoretical value for the $S = 1/2$ 2D Ising lattice while the entropy above this temperature is higher than the corresponding theoretical prediction. This fact indicates deviations from the 2D system towards quasi-1D behaviour.

As was mentioned earlier, simplified theoretical calculations [13] based on the assumption of pure dipolar interactions showed that the calculated magnetic structure of $KEr(MoO_4)_2$ is similar to that of $CsDy(MoO_4)_2$. That is, in the ground state the magnetic moments are arranged in ferromagnetic chains running along the crystallographic c-axis which corresponds to the easy axis. The energy of the ground state with only dipolar coupling taken into account was evaluated to be $E_g = 1.28$ K [22], and the contribution to the binding energy among the chains arising from dipolar coupling was estimated from the energy difference $E_h - E_g = 0.005$ K [13]; E_g and E_h are energies corresponding to the configuration of the ground state and the next configuration in increasing order of energy, respectively. It should be noted that for $KEr(MoO_4)_2$ the dipolar coupling itself would lead to a 3D array of weakly coupled ferromagnetic Ising chains.

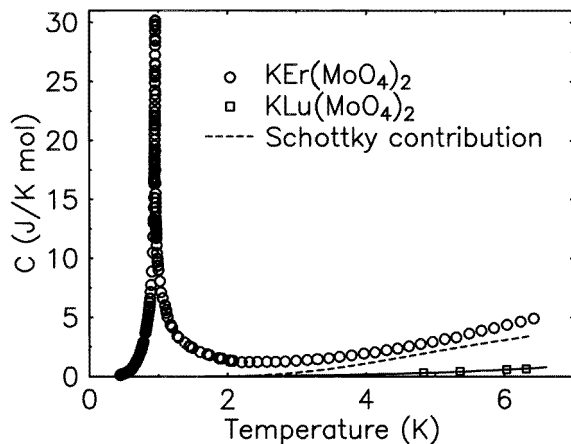The predicted Ising type of anisotropy corresponds to the aforementioned values of

Figure 1. The temperature dependence of the specific heat of a single crystal, $KEr(MoO_4)_2$, in zero magnetic field ($\bigcirc$) and a diamagnetic isomorph $KLu(MoO_4)_2$ ($\square$). The solid line is a low-temperature cubic extrapolation; the Schottky contribution is represented by a dashed line.
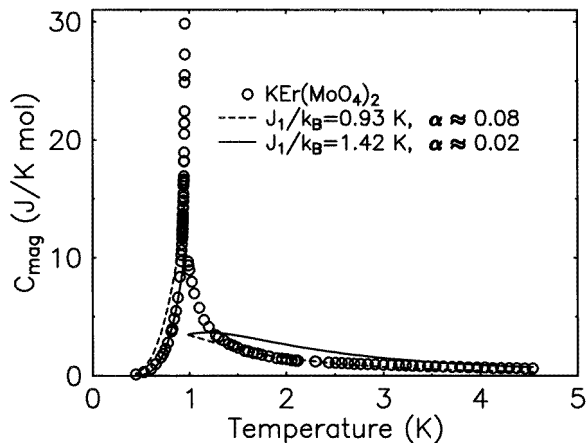

Figure 2. The temperature dependence of the magnetic specific heat resulting in zero magnetic field. The solid and dashed lines represent the best fits of Honmura's 2D model for $S = 1/2$ coupled Ising ferromagnetic chains obtained from the low-temperature and high-temperature regions, respectively.

the effective g-factor found for the lowest doublet, and the low-dimensional character of the magnetic correlations is indicated by magnetic entropy calculations. A study of phase transitions in $KEr(MoO_4)_2$ induced by an external magnetic field [23] revealed the influence of the exchange interaction and showed that the dominant exchange interaction can be, in the a-direction, estimated as $J_a/k_B \approx 0.1$ K. Consequently, the compound studied can be considered as a 3D array of ac-planes coupled in the b-direction due to dipolar interaction with energy $\sim E_h - E_g$ and a comparable exchange coupling. Thus, the magnetic specific heat was analysed in the framework of Honmura's model of 2D assembly of coupled $S = 1/2$ Ising ferromagnetic chains solved approximately using a correlated-effective-field theory [24]. The fitting of the experimental data was carried out at temperatures quite far from

the critical region (in the low-temperature region, $T < 0.95\,T_c$, and the high-temperature region, $T > 1.5T_c$). The main reason for this is that the effective-field approach does not yield accurate results in the critical region due to the absence of long-range fluctuations [24]. The fitting procedure in the low-temperature region yielded $J_1/k_B = 1.420$ K $\pm$ 0.020 K and $J_2/J_1 \approx 0.02$. The high-temperature results are $J_1/k_B = 0.935$ K $\pm$ 0.015 K and $J_2/J_1 \approx 0.08$ (J_1, J_2 are from the Ising Hamiltonian $H = -\sum J_{ij}\sigma_i^z\sigma_j^z$ with $\sigma_i^z = 2S_i^z$; J_{ij} takes the value J_1 for spins in the x-direction and J_2 for spins in the y-direction). The differences in the values are quite considerable (figure 2). There are several possible reasons for the observed discrepancies.

First at all, the effective-field approximation used itself involves inaccuracies despite the chosen region of application [25]. Furthermore, the compound system studied will in reality behave as a 3D magnet below T_c [4]. Consequently, using the 2D model for the ordered phase will lead to overestimation of the real value of J_1.

The incorrect subtraction of the Schottky anomaly due to the presence of magnetic correlations may deform the magnetic specific heat curve [26], but this only becomes important above 3 K (figure 1); as the high-temperature fitting interval was chosen to be from about 1.4 K to 4.5 K, this mechanism alone cannot explain such discrepancies in the J_1-values and α-values.

Finally, the observed discrepancy may be connected with the dipolar nature of the intrachain interactions. In the high-temperature region the interaction energy in dipolar chains will be reduced due to the chain clustering. As a result, the Ising model approach will yield a reduced value of the effective exchange parameter.

Nevertheless, both intrachain values of J_1 can serve as effective estimations of the ground-state energy corresponding to the magnetic structure determined by the dipolar approach; the ground-state energy of a pure dipole system, E_g, corresponds to the classical energy of 1D exchange-coupled systems, $4J_1S^2$ [7], which for $S = 1/2$ directly equals J_1. Furthermore, the estimation of interchain interaction in the ac-plane found from the present analysis $4J_2/k_B \approx 0.1$ K–0.3 K is also in good agreement with the aforementioned value of J_a/k_B (the factor 4 is used due to the type of Hamiltonian). This relatively good agreement may support the assumption of the dominant character of dipolar interactions in KEr(MoO$_4$)$_2$.

4. Conclusion

Specific heat studies of a single crystal, KEr(MoO$_4$)$_2$, carried out over the temperature range 0.45 K–6.5 K in zero magnetic field revealed deviations of the magnetic system from 2D towards 1D behaviour. The analysis of the specific heat data using Honmura's 2D model of coupled $S = 1/2$ Ising ferromagnetic chains yielded $J_1/k_B = 1.42$ K, $\alpha \approx 0.02$ and $J_1/k_B = 0.93$ K, $\alpha \approx 0.08$ in the low-temperature and high-temperature regions, respectively. The combination of potential mechanisms discussed above can explain the different evaluations of J_1 and α.

The J_1-values obtained correspond to the ground-state energy E_g calculated for KEr(MoO$_4$)$_2$ on the basis of pure dipolar interactions and the J_2-values are in good agreement with the value obtained in [23]. This may support the assumption of the dominating dipolar nature of magnetic correlations as for CsDy(MoO$_4$)$_2$. In view of this, it would be interesting to study the magnetic field dependence of the specific heat in the paramagnetic region below 2 K due to the contribution of non-linear excitations in $S = 1/2$ 1D ferromagnetic Ising chains [27].

Acknowledgments

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