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The heat capacity of $KDy(MoO_4)_2$ near the magnetic phase transition

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Abstract. The results of the heat capacity measurements are compared with theoretical prediction for Ising 2D and 3D models. The behaviour of the heat capacity at temperatures $T > T_c$ is described by the 2D Ising model. At temperatures below T_c the crossover of the magnetic dimensionality was observed from 2D to 3D Ising-like behaviour near T_c.

$KDy(MoO_4)_2$ forms orthorhombic crystals belonging to the space group D_{2h}^{14} at room temperature. The primitive cell dimensions are $a = 1.820$ nm, $b = 0.795$ nm and $c = 507$ nm and there are four formula units in the primitive cell (Klevtsova and Borisov 1968). This layered crystal undergoes a crystallographic second-order phase transition of the Jahn–Teller type to an antiferro-distortive phase below 14 K. Above this temperature the Dy^{3+} ions have a low-lying doublet 18 cm^{-1} above the ground doublet state. When the substance is cooled through the transition temperature, these doublets move symmetrically apart in energy to a low-temperature splitting of 28 cm^{-1} (Cooke *et al* 1976). Spectroscopic and magnetic investigations have shown that the structural phase transition behaviour in a magnetic field resembles the phenomena associated with magnetic spin-flip transitions but involving energies characteristic of spin–lattice rather than spin–spin interactions (Leask *et al* 1981). Recently, two inequivalent magnetic states above 14 K and four inequivalent magnetic states below 14 K were found by EPR spectroscopy investigation (Bagulya *et al* 1988). A phase transition into a complex magnetic ordered state was found at 1.1 K from magnetic susceptibility measurements (Cooke *et al* 1976).

In this paper, we report the results of the heat capacity measurements of $KDy(MoO_4)_2$ in the vicinity of the magnetic phase transition with the aim of contributing to the understanding of the magnetic behaviour of $KDy(MoO_4)_2$.

Typical crystals with dimensions $8 \times 12 \times 1$ mm^3 were grown by the flux method. The heat capacity was measured by the usual quasi-adiabatic heat pulse method.

The heat capacity of the crystal from 0.6 to 6 K is shown in figure 1. The heat capacity curve in zero magnetic field shows a λ-type peak at 1.000 ± 0.005 K corresponding to the magnetic phase transition. The resulting magnetic contribution C_M to the heat capacity (shown in figure 2) was obtained by subtracting the lattice part ($\Theta_D = 137.4$ K) and the part caused by the crystal-field splitting (the Schottky anomaly) from the total measured heat capacity (Orendáčová *et al* 1989). Because the ground state in the low-temperature phase has an Ising-like **g**-tensor (Leask *et al* 1981, Bagulya *et al* 1988) an

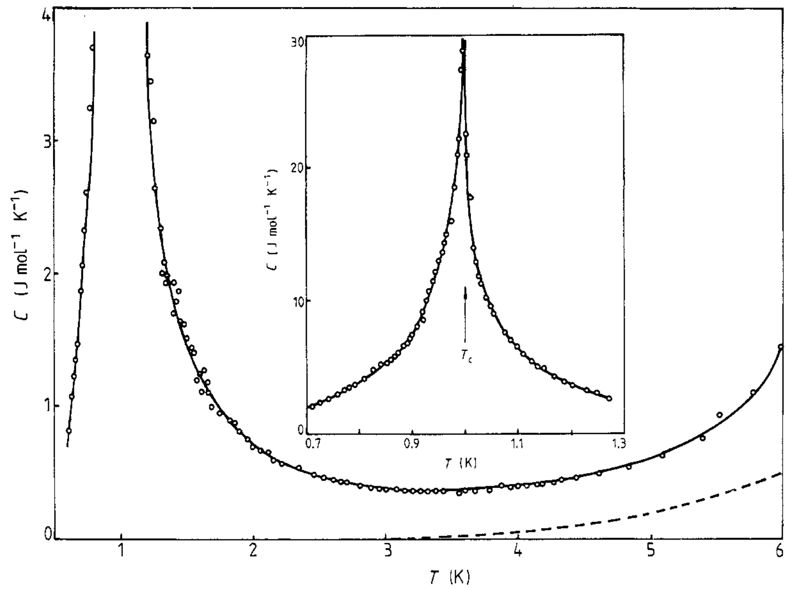

Figure 1. Total heat capacity of $KDy(MoO_4)_2$ near T_c: ○, experimental data; ---, Schottky contribution; ——, guide for the eye.

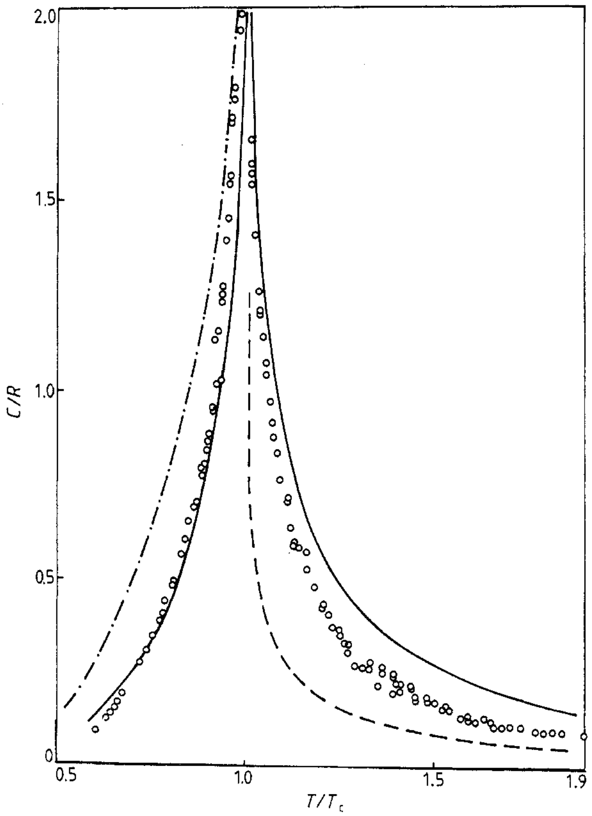

Figure 2. Magnetic heat capacity compared with theoretical prediction for 2D and 3D Ising models: ○, experimental data; ——, theoretical prediction for a simple quadratic lattice; ---, theoretical prediction for a simple cubic lattice; -·-, theoretical prediction for a tetrahedral lattice.

Table 1. The theoretical values of entropy and enthalpy below and above T_c are taken according to Domb (1960) and De Jongh and Miedema (1974).

	Ising (simple quadratic lattice) 2D theory	$KDy(MoO_4)_2$, experimental	Ising (tetrahedral lattice) 3D theory
S_c/R	0.306	0.346	0.511
$(S_\infty - S_c)R$	0.387	0.315	0.182
$(H_c - H_0)/RT_c$	0.258	0.303	0.420
$-H_c/RT_c$	0.623	0.493	0.320

Table 2. The set of values of J/K obtained by various methods.

	Method	Equation	J/k
Theoretical prediction	Ising tetrahedral lattice	$kT_c/zJ = 0.676$	0.369
Theoretical prediction	Ising simple quadratic lattice	$kT_c/zJ = 0.567$	0.44
Experimental value	High-temperature part of C_M	$C_M T^2/R = zJ^2/2k^2$	0.404
Experimental value	Total enthalpy	$H_{tot}/R = zJ/4k$	0.398

attempt was made to describe the magnetic heat capacity behaviour by the 2D and 3D Ising magnetic models. Neither of these models provides a good fit to the measured values in the whole temperature range (figure 2). Similarly, the thermodynamic quantities (entropy S and enthalpy H) calculated from the heat capacity lie between the theoretical predictions for the two Ising models (table 1). The total entropy of $KDy(MoO_4)_2$ is in a good agreement with the theoretical value $R \ln 2$, leading to the conclusion that the Dy^{3+} ions have an effective spin of $\frac{1}{2}$.

The coupling parameter J/k was estimated (for the number of nearest neighbours equal to 4) from the total enthalpy H_{tot}, from the high-temperature part of the magnetic heat capacity and from the theoretical expressions for the 2D and 3D Ising models (using the value of the temperature T_c of a magnetic phase transition). The results obtained are shown in table 2 and here again the values of J/k determined from enthalpy and from the high-temperature part of the heat capacity fall between the values for the Ising 2D and 3D models.

In addition, the experimental data on the heat capacity near T_c were compared directly with the theoretical prediction for the magnetic models using the procedure proposed by Fisher (1964). For this comparison the following models were used:

(i) the 2D Ising model with Onsager's solution for $\varepsilon = |1 - T_c/T| > 6 \times 10^{-2}$ and with the asymptotic form $C_M R = -0.4945 \ln|1 - T_c/T| - 0.29$ for $\varepsilon < 6 \times 10^{-2}$, the agreement between the two solutions being 3% at $\varepsilon = 6 \times 10^{-2}$;

(ii) the approximate solution of the 3D Ising model for $T > T_c$ (simple cubic lattice (Sykes *et al* 1972)) and for $T < T_c$ (tetrahedral lattice (Gaunt and Domb 1968)).

Comparison of the experimental data with the 2D and 3D Ising models is shown in figure 3 for $T > T_c$ and in figure 4 for $T < T_c$. The behaviour of the heat capacity of $KDy(MoO_4)_2$ above T_c shows the logarithmic tendency which is characteristic of the 2D Ising model. The most interesting feature of the heat capacity below T_c is the crossover

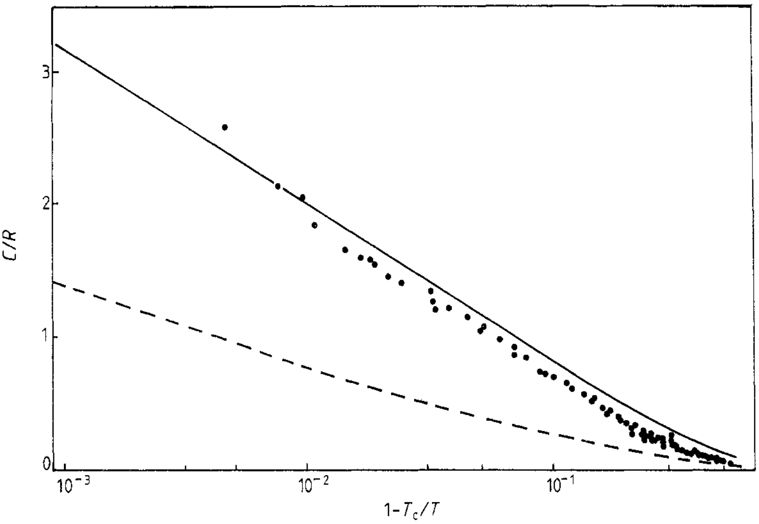

Figure 3. Critical behaviour of heat capacity for $T > T_c$: ●, experimental data; ——, theoretical prediction for a simple quadratic lattice; – – –, theoretical prediction for a simple cubic lattice.

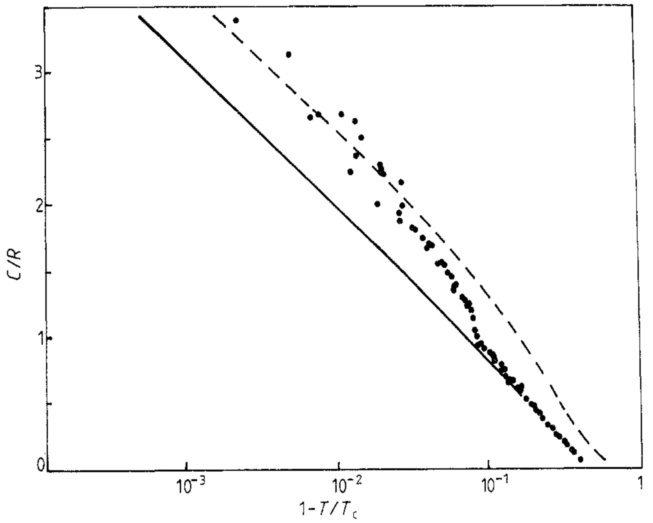

Figure 4. Critical behaviour of heat capacity for $T < T_c$: ●, experimental data; ——, theoretical prediction for a simple quadratic lattice; – – –, theoretical prediction for a tetrahedral lattice.

from 2D behaviour (for $\varepsilon > 10^{-1}$) to 3D behaviour. Dimensional type of crossover can be seen in the magnetisation behaviour of weakly coupled magnetic layers in Heisenberg-type crystals (De Jongh and Miedema 1974). However, the appearance of such a crossover from 2D to 3D behaviour at $\varepsilon = 10^{-1}$ in the heat capacity was rather unexpected (Liu and Stanley 1973). We assume that it can be regarded as the first direct observation of crossover from 2D to 3D behaviour in heat capacity. We believe that the crossover

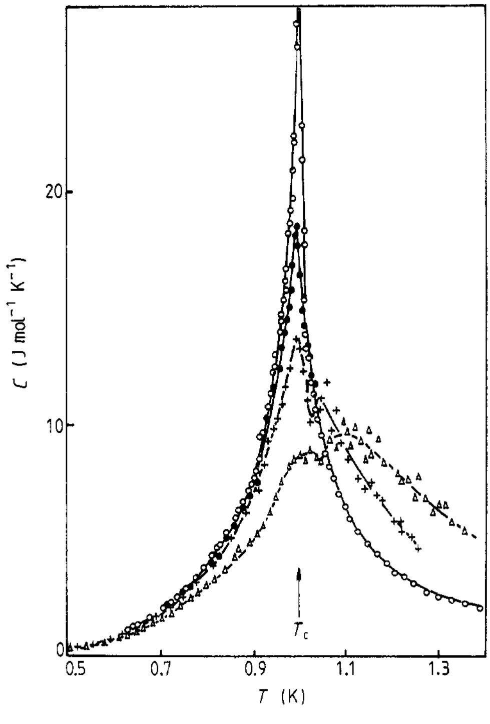

Figure 5. The heat capacity of $KDy(MoO_4)_2$ in small magnetic fields oriented along the c axis: ○, 0 mT; ●, 20 mT; +, 32 mT; △, 60 mT.

can be related to the particular behaviour of magnetic excitations in low-dimensional crystals, e.g. the existence of a weak dispersion in the energy spectrum which is responsible for the existence of magnetic excitations along the direction of weak coupling. It should be noted that we previously observed an analogous crossover in a $CsDy(MoO_4)_2$ crystal (Feher *et al* 1989).

In addition we examined the behaviour of the heat capacity of $KDy(MoO_4)_2$ in small magnetic fields along the c axis. As can be seen from figure 5, $KDy(MoO_4)_2$ shows ferromagnetic behaviour along the c axis. This supports the results of Cooke *et al* (1976). The anomalous dispersion in the experimental values of heat capacity was observed in the temperature range above T_c (see figure 5) and it is not an apparatus effect. We assume that this dispersion is due to the existence of low-dimensional magnetic domains above T_c (the effect of dispersion was not observable in the heat capacity of powdered samples of double molybdates) or to the influence of the magnetic field on the anisotropic paramagnet.

The results of the heat capacity measurements allow us to draw the following conclusions.

(i) $KDy(MoO_4)_2$ can be regarded as an Ising-like quasi-2D magnetic system.

(ii) The nature of the observed crossover of the magnetic dimensionality from 2D to 3D is not yet clear and further experiments are needed to determine the magnon dispersion curves.

(iii) Measurements of the heat capacity in small magnetic fields support the ferromagnetic character of the interaction along the c axis.

(iv) The origin of the dispersion of the experimental heat capacity data should be determined by more experiments at temperatures above T_c in magnetic fields.

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References

Bagulya B A, Zvyagin A I, Kobec M N, Stepanov A A and Zaika A S 1988 *Sov. J. Low Temp. Phys.* **14** 1493

Cooke A H, Davidson M M, England N J, Leask M J M, Lowry J B, Tropper A C and Wells M R 1976 *J. Phys. C: Solid State Phys.* **9** L573

De Jongh L J and Miedema A R 1974 *Adv. Phys.* **23** 1

Domb C 1960 *Adv. Phys.* **9** 245

Feher A, Stefanyi P and Orendáčová A 1989 *Acta Phys. Slovaca* at press

Fisher M B 1964 *Phys. Rev.* **136** A 1599

Gaunt D S and Domb C 1968 *J. Phys. C: Solid State Phys.* **1** 1038

Klevtsova R F and Borisov S V 1968 *Sov. Phys.-Dokl.* **12** 1095

Leask M J M, Tropper A C and Wells M R 1981 *J. Phys. C: Solid State Phys.* **14** 3481

Liu L L and Stanley H E 1973 *Phys. Rev.* B **8** 2279

Orendáčová A, Stefanyi P and Feher A 1989 *Acta Phys. Slovaca* at press

Sykes M F, Hunter D L, McKenzie D S and Heap B R 1972 *J. Phys. A: Math Gen.* **5** 667