Specific heat and critical behaviour of $CsMnI_3$

1993 J. Phys.: Condens. Matter 5 6289

(http://iopscience.iop.org/0953-8984/5/34/015)

J. Phys.: Condens. Matter 5 (1993) 6289–6294. Printed in the UK

Specific heat and critical behaviour of $CsMnI_3$

D Beckmann†, J Wosnitza†, H von Löhneysen† and D Visser‡

† Physikalisches Institut der Universität Karlsruhe, Engesserstrasse 7, 76128 Karlsruhe, Federal Republic of Germany

‡ University of Technology, Department of Physics, Loughborough, LE11 3TU, UK

Received 18 May 1993

Abstract. We report on measurements of the specific heat, C, of the triangular lattice antiferromagnet $CsMnI_3$ in the vicinity of the two successive phase transitions at $T_{N1} = 11.28$ K and $T_{N2} = 8.19$ K and in magnetic fields up to 6 T applied perpendicular to the c axis. Near T_{N2} the data can be fitted with a critical exponent $\alpha = -0.05 \pm 0.15$ for $B = 0$ compatible with the prediction of three-dimensional ordering with XY symmetry for this transition. Within the experimental uncertainty, the critical behaviour is not affected by a magnetic field.

1. Introduction

Recently much effort has been devoted to determining the critical exponents of magnetic phase transitions in stacked triangular-lattice antiferromagnets. Within the renormalization group theory, the critical behaviour of these transitions is supposed to be different from the behaviour predicted by ordinary universality classes. Kawamura [1] proposed new universality classes for transitions with triangular spin structures, characterized by the symmetry of their order parameter, $Z_2 \times S_1$ or SO(3) for the cases of XY and Heisenberg models, respectively. These classes lead to unusual critical exponents which have been confirmed experimentally, for example in $CsMnBr_3$ [2–5], which exhibits an easy-plane anisotropy thus representing the XY model with chiral symmetry.

$CsMnI_3$ is a triangular-lattice Heisenberg antiferromagnet with an Ising anisotropy. The crystal structure is hexagonal. $CsMnI_3$ shows two successive phase transitions to a three-dimensionally ordered state [6–8]. The magnetic structure is the same as in $CsNiCl_3$ [9–11]. It is a six-sublattice spin structure with one third of the spins aligned parallel to the c axis and two thirds canted away from the c axis with an angle θ ($\theta \approx 50°$ in $CsMnI_3$). The ordering of the spin components parallel and perpendicular to the c axis takes place at $T_{N1} = 11.28$ K and $T_{N2} = 8.19$ K, respectively. The magnetic structure has been discussed in detail by other authors [6, 8, 11, 12]. Theory predicts both transitions to be conventional XY-like [13]. In this article we report on specific-heat measurements in applied magnetic fields of up to 6 T in order to shed more light on the nature of the magnetic phase transitions.

2. Results and discussion

Single-crystalline samples of $CsMnI_3$ were grown by the Bridgman technique. We measured the specific heat C with a standard heat-pulse method in a ^{4}He cryostat. The relative temperature resolution was of the order 10^{-5}, giving an accuracy of $\Delta C/C \approx 1\%$ with

0953-8984/93/346289+06\$07.50

relative temperature increments near the phase transitions of $\Delta T/T \approx 10^{-3}$ (see also [5, 14]). Measurements were carried out in zero magnetic field in a temperature range 1.4–30 K and in the vicinity of the transition temperatures with magnetic fields of 1.5, 3 and 6 T applied perpendicular to the c axis of the hexagonal crystal.

In figure 1 the specific heat data for zero field are shown in a linear plot of C/T against T. The two magnetic transitions at T_{N1} = 11.28 K and T_{N2} = 8.19 K are clearly visible as small anomalies on a large regular background. The anomaly near T_{N2} is better resolved in figure 2, where the data for different applied fields are shown. A small but well resolved λ-type anomaly is visible. With the application of field, the anomaly keeps its overall shape in C/T against T but shifts to higher temperatures. At T_{N1} only a broader weak structure in C is observed, which also shifts to higher temperatures in a magnetic field.

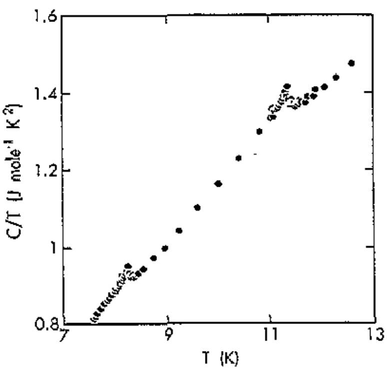

Figure 1. C/T against T near the two transition temperatures.

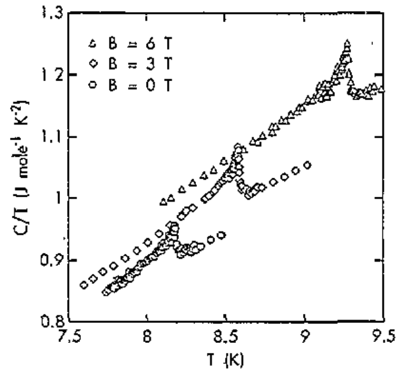

Figure 2. C/T against T near T_{N2} with magnetic field $B \perp c$.

The entropy changes associated with the two transitions were determined to $\Delta\eta_1 = 0.045$ J mol^{-1} K^{-1} for T_{N1} and $\Delta\eta_2 = 0.020$ J mol^{-1} K^{-1} for T_{N2} by subtracting a smooth background. The entropy of the completely disordered magnetic system is $\eta_{max} = Nk_B \ln(2S+1) = 14.89$ J mol^{-1}K^{-1} ($S = 5/2$). Thus we find $\Delta\eta_1/\eta_{max} = 0.3\%$ and $\Delta\eta_2/\eta_{max} = 0.14\%$. These small values can be explained by the fact that above T_{N1} the magnetic system is not completely disordered but shows antiferromagnetically ordered chains along the c axis. Only very little entropy is left to be removed when the three-dimensional ordering occurs driven by the weak inter-chain coupling. Comparable results have been found in $CsMnBr_3$ [15].

The magnetic phase diagram for $B \perp c$ is shown in figure 3, where T_{N1} and T_{N2} are plotted for the different fields. The phase diagram is similar to that of $CsNiCl_3$ for the same orientation of the field, reflecting the fact that both substances have the same magnetic structure with an easy-axis anisotropy. This type of phase diagram has, to some extent, been investigated experimentally [16] as well as theoretically by means of a Landau-type free energy calculation [17], with good agreement between experiment and theory.

The specific heat near the phase transitions can be described by [18]

$$C = \frac{A}{\alpha}|t|^{-\alpha} + B + Et \qquad (\text{for } T > T_c)$$
$$C = \frac{A'}{\alpha}|t|^{-\alpha} + B + Et \qquad (\text{for } T < T_c) \qquad (1)$$

with $t = (T - T_c)/T_c$. The fit function consists of the regular contribution approximated by a linear t dependence $(B + Et)$ close to T_c and the power law for the leading contribution to the singularity in C. The fitting procedure is described in detail elsewhere [18]. The fitted critical exponents for the lower transition, $T_c = T_{N2}$, are $\alpha = -0.05 \pm 0.15$ for $B = 0$, $\alpha = 0.05 \pm 0.1$ for $B = 3$ T and $\alpha = 0.05 \pm 0.15$ for $B = 6$ T. Within the experimental uncertainty, the critical behaviour is not affected by the applied field. Due to the small contribution of the singularity to C, relatively large error bars are given. The complete sets of fit parameters for the three magnetic fields are given in table 1.

Table 1. Parameters of equation (1) describing the behaviour at the lower phase transition $T_c = T_{N2}$.

	T_c	A	A'	B	E	α	A/A'
$B = 0$ T	8.185	0.08495	0.06993	8.857	18.19	-0.05 ± 0.15	1.215
$B = 3$ T	8.59	0.06812	0.08230	6.890	19.41	0.05 ± 0.1	0.828
$B = 6$ T	9.28	0.09053	0.10909	8.477	23.93	0.05 ± 0.15	0.830

The data analysis to extract α is illustrated in figure 4, where the specific heat is plotted against reduced temperature near $T_c = T_{N2}$ for $B = 0$. The open and full circles represent data below and above T_c respectively. The full curves show the best fit to the data, with $\alpha = -0.05$. The broken curves show an attempt to fit the data with a critical exponent $\alpha = 0.32$, as predicted by the hyperscaling relation $\alpha = 2 - d\nu$ ($d = 3$), with a value of $\nu = 0.56$ for the critical exponent of the correlation length recently obtained from neutron diffraction measurements [6]. This fit does not reproduce the data close to T_c, in particular for $T < T_c$, even if one includes a Gauss-distributed smearing of T_c [5] which is not shown here. Note that T_c is a free parameter. The same T_c was assumed for $\alpha = 0.32$ as for $\alpha = -0.05$ in comparing the fits. A change of T_c would not improve the fit with $\alpha = 0.32$. Thus fits with a large positive value of α (0.24 or 0.34), as predicted for universality classes with chiral symmetry [1], do not match the experimental data.

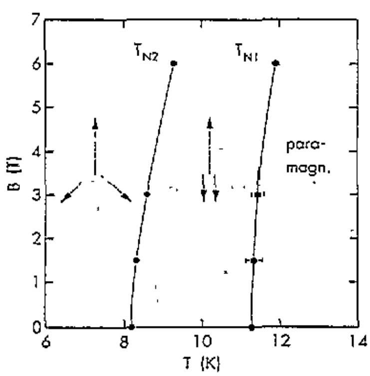

Figure 3. Magnetic phase diagram of $CsMnI_3$ with $B \perp c$. The arrows are schematic pictures of the three sublattice magnetizations. The full lines are guides to the eye. For the lower transition the error bars are smaller than the size of the points.

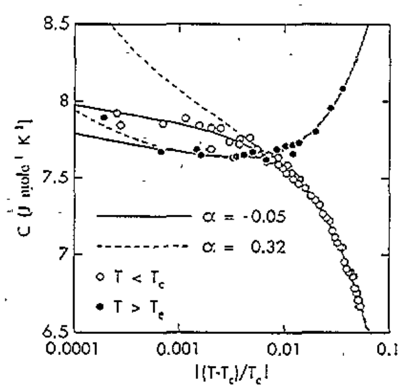

Figure 4. C against reduced temperature near $T_c = T_{N2}$ in zero field. The full and broken curves are theoretical fits with $\alpha = -0.05$ and $\alpha = 0.32$ respectively.

For the phase transition from the paramagnetic to the first antiferromagnetic phase at T_{N1} no reliable extraction of the critical exponent was possible. The reason why the shape of this anomaly is broader is not clear. Possibly this transition is more sensitive to sample inhomogenities.

Recent neutron diffraction measurements [6, 7] revealed critical exponents $\beta = 0.35 \pm 0.01$, $\gamma = 1.04 \pm 0.03$ and $\nu = 0.56 \pm 0.02$ for the spontaneous sublattice magnetization, susceptibility, and correlation length, respectively. The experimental values, together with theoretical predictions for several different three-dimensional models, are shown in table 2. While γ and ν would fit the new $Z_2 \times S_1$ and SO(3) classes, β, and also the value of α close to zero, are consistent with the prediction of the conventional XY model. Of course, the values of the Ising and the Heisenberg models are also consistent within the error bars. However, the scaling and hyperscaling relations $\alpha + 2\beta + \gamma = 2$ and $\alpha = 2 - d\nu \quad (d = 3)$ are violated, with deviations somewhat beyond the experimental uncertainty. A possible explanation for this discrepancy might be that some of the measurements were not performed close enough to T_c for the asymptotic critical behaviour to be seen, and that the reported exponents are therefore just effective experimental values.

Table 2. Critical exponents for several three-dimensional universality classes together with experimental values for $CsMnBr_3$ and $CsMnI_3$.

	α	β	γ	ν
Ising [19]	0.106	0.326	1.238	0.631
XY [19]	−0.01	0.345	1.316	0.669
Heisenberg [19]	−0.121	0.367	1.388	0.707
SO(3)[1]	0.24	0.30	1.17	0.59
$Z_2 \times S_1$[1]	0.34	0.25	1.13	0.54
$CsMnBr_3$	0.40 ± 0.05 [5]	0.25 ± 0.01 [3]	1.10 ± 0.05 [4]	0.57 ± 0.03 [4]
$CsMnBr_3$	0.39 ± 0.09 [20]	0.21 ± 0.02 [2]	1.01 ± 0.08 [2]	0.54 ± 0.03 [2]
$CsMnI_3$ (T_{N1})	no data	0.32 ± 0.01 [7]	1.12 ± 0.07 [6]	0.59 ± 0.03 [6]
$CsMnI_3$ (T_{N2})	-0.05 ± 0.15†	0.35 ± 0.01 [7]	1.04 ± 0.03 [6]	0.57 ± 0.02 [6]

†This work.

As a final point, we briefly discuss the low-temperature behaviour of the specific heat. The magnetic structure of $CsMnI_3$ exhibits antiferromagnetically ordered chains along the c axis. For antiferromagnetic Heisenberg chains, several theoretical studies [21–24] suggest a T-linear contribution $C/R = \kappa k_B T/|J_0|$ at low temperatures, where J_0 is the intra-chain exchange constant. Different attempts have been made to estimate the constant κ which determines the exact magnitude of this contribution for spin-5/2 Heisenberg chains, including spin-wave theory ($\kappa = 0.209$ [21]) and numerical calculations ($\kappa = 0.138$ [24], $\kappa = 0.17$ [23]). Experimental studies confirmed the existence of such a contribution in the ABX_3 compound $CsNiCl_3$ [25] above the three-dimensional ordering temperature, and in $CsMnBr_3$ the linear contribution persists even in the three-dimensionally ordered phase [15, 26].

In figure 5 the low-temperature data are plotted as C/T against T together with a fit to the function

$$C = aT + bT^3. \tag{2}$$

The fitted parameters are $a = 0.093$ J mol^{-1} K^{-2} and $b = 0.0177$ J mol^{-1} K^{-4}. From this fit, and with $|J_0|/k_B = 9.1$ K extracted from ESR measurements [27], we obtain $\kappa = 0.102$. This value is only slightly smaller than the theoretical predictions [21, 23, 24]. This is surprising because for three-dimensionally ordered antiferromagnets one might expect a T^3

dependence of C at low temperatures (or an even stronger T dependence for an anisotropic antiferromagnet) and the low-energy excitations of the one-dimensional antiferromagnetic chains should be absent. This point requires further study.

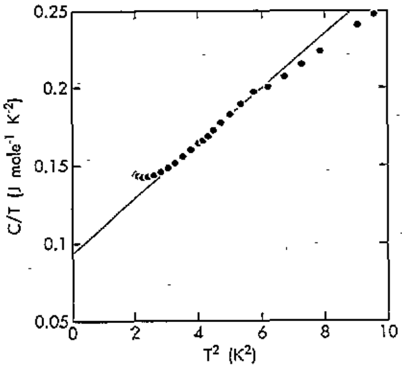

Figure 5. C/T against T^2 at low temperatures. The full line is a fit to $C/T = a + bT^2$.

Taking the Debye temperature $\theta_D = 153$ K of the isostructural non-magnetic compound $CsMgBr_3$ [25] as a crude estimate, the Debye contribution b_D would only be 15% of b. The rather large coefficient b of the T^3 term indicates that it also contains a large magnetic contribution b_M. Such a large magnetic T^3 contribution below the three-dimensional ordering temperatures in related compounds has been reported by other authors [28]. We took the spin-wave expression $C/R \approx 5.07 \times 10^{-4}(k_B T/|J|)^3$ for $S = 5/2$ Heisenberg antiferromagnets with NaCl structure [21] to estimate $|J|$. Of course, for an exact calculation one would have to consider an anisotropic spin-wave model on the triangular lattice (see [29]). From our estimate we get an 'effective exchange constant' $|J_e|/k_B = 0.65$ K. This value lies between the intra-chain exchange constant $|J_0|/k_B = 9.1$ K and the inter-chain exchange constant $|J_1|/k_B = 0.075$ K [27]. Thus the magnitude of the magnetic T^3 contribution seems to be roughly compatible with spin-wave theory.

However, the fit with equation (2) has to be taken with some care. As can be seen in figure 5, the chosen temperature range for the fit is somewhat ambiguous and the fit does not represent the data very well. Furthermore, measurements on different samples of $CsMnI_3$ indicate a strong dependence of the low-temperature specific heat on impurities, which might also be the reason for the small upturn towards low temperatures.

3. Summary

We have presented measurements of the specific heat near the two antiferromagnetic transition temperatures $T_{N1} = 11.28$ K and $T_{N2} = 8.19$ K of $CsMnI_3$. Whereas at T_{N1} no determination of the critical exponent α of the specific heat was possible, for $T_c = T_{N2}$ we found $\alpha = -0.05 \pm 0.15$, with no significant change in magnetic fields of up to 6 T applied perpendicular to the c axis. This value, as well as the value of β found in neutron diffraction measurements, agrees with ordinary 3D-XY ordering, as predicted theoretically for this transition. The values of γ and ν deviate from this prediction. These contradictory results need further clarification. Measurements for B parallel to c are being carried out for $CsNiCl_3$, which exhibits the same magnetic structure, in order to investigate the critical behaviour near the multicritical point with chiral symmetry.

References

[1] Kawamura H 1988 *J. Appl. Phys.* **63** 3086; 1992 *J. Phys. Soc. Japan* **61** 1299
[2] Mason T E, Gaulin B D and Collins M F 1987 *J. Phys. C: Solid State Phys.* **20** L945; 1989 *Phys. Rev.* B **39** 586
Gaulin B D, Mason T E, Collins M F and Larese J Z 1989 *Phys. Rev. Lett.* **62** 1380
[3] Ajiro Y, Nakashima T, Unno Y, Kadowaki H, Mekata M and Achiwa N 1988 *J. Phys. Soc. Japan* **57** 2648
[4] Kadowaki H, Shapiro S M, Inami T and Ajiro Y 1988 *J. Phys. Soc. Japan* **57** 2640
[5] Deutschmann R, von Löhneysen H, Wosnitza J, Kremer R K and Visser D 1992 *Europhys. Lett.* **17** 637
[6] Kadowaki H, Inami T, Ajiro Y, Nakajima K and Endoh Y 1991 *J. Phys. Soc. Japan* **60** 1708
[7] Ajiro Y, Inami T and Kadowaki H 1990 *J. Phys. Soc. Japan* **59** 4142
[8] Harrison A, Collins M F, Abu-Dayyeh J and Stager C V 1991 *Phys. Rev.* B **43** 679
[9] Clark R H and Moulton W G 1972 *Phys. Rev.* B **5** 788
[10] Yelon W B and Cox D E 1973 *Phys. Rev.* B **7** 2024
[11] Kadowaki H, Ubukoshi K and Hirakawa K 1987 *J. Phys. Soc. Japan* **56** 751
[12] Chiba M, Ajiro Y, Kikuchi H, Maegawa S and Morimoto T 1992 *J. Phys. Soc. Japan* **61** 1758
[13] Kawamura H, Caillé A and Plumer M L 1990 *Phys. Rev.* B **41** 4416
[14] Wosnitza J and von Löhneysen H 1989 *Europhys. Lett.* **10** 381
[15] Ajiro Y, Kikuchi H, Nakashima T and Unno Y 1987 *Japan. J. Appl. Phys.* **26** suppl 775
[16] Johnson P B, Rayne J A and Friedberg S A 1979 *J. Appl. Phys.* **50** 1853
[17] Plumer M L, Hood K and Caillé A 1988 *Phys. Rev. Lett.* **60** 45
[18] Kornblit A and Ahlers G 1973 *Phys. Rev.* B **8** 5163; 1975 *Phys. Rev.* B **11** 2678
[19] Collins M F 1989 *Magnetic Critical Scattering* (New York: Oxford University Press) p 29
[20] Wang J, Belanger D P and Gaulin B D 1991 *Phys. Rev. Lett.* **66** 3195
[21] Kubo R 1952 *Phys. Rev.* **87** 568
[22] Bonner J C and Fisher M E 1964 *Phys. Rev.* A **135** 640
[23] Blöte H W J 1975 *Physica* B **79** 427
[24] de Neef T 1976 *Phys. Rev.* B **13** 4141
[25] Moses D, Shechter H, Ehrenfreund E and Makovsky J 1977 *J. Phys. C: Solid State Phys.* **10** 433
[26] Deutschmann R 1991 *Diploma Thesis* Universität Karlsruhe
[27] Tanaka H 1990 *J. Magn. Magn. Mater.* **90–91** 251
Tanaka H, Teraoka S, Kakehashi E, Iio K and Nagata K 1988 *J. Phys. Soc. Japan* **57** 3979
[28] Collocott S J and Rayne J A 1987 *J. Appl. Phys.* **61** 4404
[29] Plumer M L and Caillé A 1992 *Phys. Rev. Lett.* **68** 1042