

## Quasi-one-dimensional behavior of $(\text{CH}_3)_2\text{NH}_2\text{MnCl}_3$ (DMMC)

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The heat capacity of dimethyl ammonium manganese trichloride has been investigated for  $1.6 < T < 50$  K. A transition to a three-dimensional antiferromagnetically ordered state has been observed at 3.60 K, which is supported by nuclear-magnetic-resonance and susceptibility measurements. The critical entropy did amount to 3.4%. The magnetic heat capacity in the paramagnetic region could be described very well by a  $S = 5/2$  Heisenberg linear chain system with  $J/k = -5.8 \pm 0.7$  K. The data for  $kT/|J| < 1.5$ , together with the earlier data on  $(\text{CH}_3)_4\text{NMnCl}_3$ , corroborate the suggested low-temperature behavior of such a system.

### INTRODUCTION

Dimethyl ammonium manganese trichloride (DMMC) can be considered as a promising example of a low-dimensional  $S = \frac{5}{2}$  Heisenberg system. The structure of DMMC is built up from linear chains of face-shared  $[\text{MnCl}_6]$  octahedra separated by organic cations. DMMC may be considered as the low-symmetry analog of  $(\text{CH}_3)_4\text{NMnCl}_3$  (TMMC),<sup>1</sup> since the chains in both substances are largely similar. TMMC has been the subject of a large number of experimental investigations, and was found to display almost pure one-dimensional characteristics.<sup>2</sup> At present, the magnetic interactions in DMMC are not very well established. The powder susceptibility has been measured for  $1.6 < T < 130$  K by Caputo *et al.*<sup>1</sup> who reported a broad maximum near 60 K, a minimum near 20 K, and a very pronounced divergence as the temperature approaches zero. In their experiments no evidence for the onset of a three-dimensional ordering has been observed. The data were fitted to a mean-field corrected Fisher model, which yielded an intrachain exchange coupling  $J/k = -6.9$  K. Up till now no additional measurements have been reported.

In view of the rather high value of  $J/k$  and the analogy with TMMC one may anticipate that this system will display rather pure one-dimensional characteristics. Therefore we thought it worthwhile to investigate some thermodynamic properties. In this paper we will focus our attention mainly on the behavior of the magnetic specific heat.

### EXPERIMENTAL

Crystals of DMMC were grown by cooling a saturated solution of equimolar quantities of anhydrous  $\text{MnCl}_2$  and  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$  in absolute ethanol from 60 to 20 °C. The pink needle-shaped crystals appeared to be rather hygroscopic. X-ray exam-

ination revealed the structure reported by Caputo *et al.*<sup>1</sup>

A specimen consisting of 18.1 grams of small crystals was sealed inside a vacuum calorimeter of conventional design, which was fitted with a temperature-controlled heat screen to enable accurate measurements at higher temperatures. Temperature readings were obtained from a calibrated germanium thermometer that was measured with an audio frequency resistance bridge using synchronous detection.

### SPECIFIC HEAT

The experimental data between 1.6 and 50 K are shown in Fig. 1. The  $\lambda$ -shaped anomaly at 3.60 K that is shown in the insert in more detail is associated with the onset of three-dimensional ordering. In order to obtain an estimate for the critical entropy, the entropy gain between 1.6 and

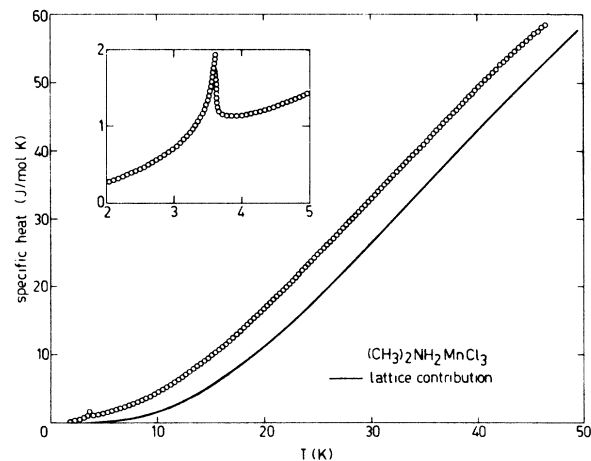


FIG. 1. Experimental heat capacity of  $(\text{CH}_3)_2\text{NH}_2\text{MnCl}_3$  between 1.6 and 50 K. The drawn curve denotes the inferred lattice contribution. The insert shows the low-temperature region in more detail.

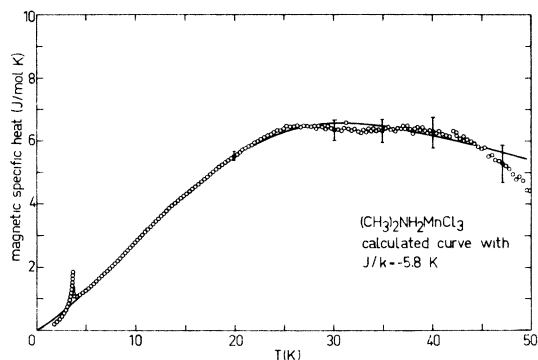


FIG. 2. Magnetic specific heat of  $(\text{CH}_3)_2\text{NH}_2\text{MnCl}_3$ . The circles are the experimental data corrected for the lattice contribution. The drawn curve denotes our estimate for an infinite Heisenberg chain with  $J/k = -5.8$  K. The error bars reflect the uncertainty in the determination of the total heat capacity.

3.60 K was evaluated by numerical integration of  $C/T$ . Below 1.6 K, the heat capacity was approximated by the relation  $C = \alpha T^6$ . The critical entropy was found as  $0.061R$ , which corresponds to 3.4% of the theoretical value  $R \ln 6$ .

As the crystal structure of DMMC consists of linear chains of  $[\text{MnCl}_6]$  octahedra separated by organic complexes, a large amount of elastic anisotropy may be present. Hence we described the lattice heat capacity of this compound by a pseudo-one-dimensional model.<sup>3</sup> In view of the analogy with TMMC, the expression for the lattice heat capacity  $C_L$  has been modified as follows

$$C_L = F_1(\Theta_l, \Theta_c, T) + F_1(\Theta_t, \Theta_c, T) + F_2(2\Theta_l, 2\Theta_c, T), \quad (1)$$

which contains three independent parameters. In this expression  $F_1$  and  $F_2$  are certain combinations of Debye functions of various dimensionality.<sup>3</sup> For the description of the magnetic heat capacity we used the theoretical and numerical estimates for a  $S = \frac{5}{2}$  Heisenberg linear chain system.<sup>4</sup> A least-squares fit of  $C_M + C_L$  to the experimental data between 8 and 50 K yielded  $J/k = -5.8 \pm 0.7$  K,  $\Theta_l = 366 \pm 5$  K,  $\Theta_t = 201 \pm 3$  K, and  $\Theta_c = 64.8 \pm 0.5$  K. The rms deviation of the fit was less than 0.4%, which is of the same order of magnitude as the scatter in the experimental data. The inferred lattice contribution is represented by a solid curve in Fig. 1. In Fig. 2 the resulting magnetic heat capacity is plotted. The dots represent  $C_{\text{exp}} - C_{L,\text{calc}}$ , the drawn curve denotes the theoretical estimate for a  $S = \frac{5}{2}$  Heisenberg linear chain system with  $J/k = -5.8$  K. The error bars reflect the possible error in the experimental data (0.8%). The slowly varying systematic deviations of  $C_{\text{exp}} - C_{L,\text{calc}}$  are mainly

due to small errors in the calibration of the germanium thermometer that was used in the measurements. They are most pronounced for  $T > 20$  K, since in that region  $C_M \ll C_L$ .

Although this procedure yields rather satisfactory results, we feel that a simultaneous fit of  $C_M$  and  $C_L$  using four independent parameters may result in a rather large uncertainty in the value of  $J/k$ . Unfortunately, we did not succeed in growing a diamagnetic isomorph, and therefore we had to choose a somewhat different approach to estimate the influence of the lattice contribution. Inspection of Fig. 1 shows that the lattice heat capacity below 12 K amounts to less than one third of the total specific heat, and decreases rapidly at lower temperatures. Hence the details of the behavior of  $C_L$  will most likely have little influence in this region. As three-dimensional correlations seem to be present up till  $\sim 6$  K, we analyzed the data for  $6 < T < 10$  K with the simpler relation  $C = aT^3 + bT$ . A plot of  $C/T$  vs  $T^2$  yielded a fairly straight line with  $a = 2.1 \times 10^{-3}$  J/mol K<sup>4</sup> and  $b = 0.24$  J/mol K<sup>2</sup>. However, a much better fit to the experimental data was achieved by describing the magnetic contribution in this region by the expression  $C_M = \sum_i b_i (kT/J)^i$ , with the coefficients  $b_i$  given in Ref. 4. A least-squares fit of  $J/k$  and  $a$  to the experimental data between 6 and 10 K yielded  $J/k = -5.9 \pm 0.6$  K and  $a = 1.74 \times 10^{-3}$  J/mol K<sup>4</sup>. The value of  $J/k$  corresponds rather well with the value  $-5.8$  K obtained from the simultaneous fitting procedure for  $8 < T < 50$  K reported above.

The behavior of  $C_M$  in the low-temperature region was obtained as an average of the results of both separation procedures, and is plotted in Fig. 3 as a function of the reduced temperature

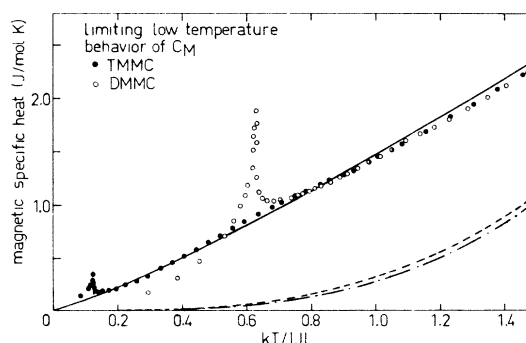


FIG. 3. Magnetic specific heat of DMMC and TMMC, denoted by  $\circ$  and  $\bullet$ , respectively, vs the reduced temperature  $kT/|J|$ . The solid line denotes the estimated behavior of an isolated antiferromagnetic  $S = \frac{5}{2}$  Heisenberg chain. The broken curves represent the two estimates for the lattice heat capacity considered in the text.

$kT/|J|$ . To indicate the uncertainty in  $C_M$ , the lattice contribution resulting from both procedures is also given. In the same figure we plotted the data on TMMC reported before.<sup>2</sup> The solid curve represents the low-temperature behavior calculated for an antiferromagnetic  $S = \frac{5}{2}$  Heisenberg linear chain system.<sup>4</sup> As this curve describes the data in the paramagnetic region for both TMMC and DMMC rather well, at least within the quoted accuracy of  $\sim 4\%$ , the expression given in Ref. 4 seems to be a fair estimate of the low-temperature behavior of a one-dimensional Heisenberg system.

#### DISCUSSION

The value for the intrachain exchange coupling  $J/k = -5.9$  K found from the heat-capacity measurements is significantly lower than the value  $J/k = -6.9$  K reported by Caputo *et al.*<sup>1</sup> Apart from the fact that the estimated inaccuracy of our value for  $J/k$  may be  $\sim 10\%$ , the difference may also arise from their interpretation of the powder susceptibility measurements. The reported measurements reveal a large divergence at low temperatures, which may have been caused by a small noncompensated moment which is allowed by symmetry. The presence of such a net moment may cast some doubt on the applicability of the expressions for a  $S = \infty$  antiferromagnetic linear chain to the powder susceptibility, especially at lower temperatures.

In contrast to the reported divergence, preliminary single-crystal measurements of the susceptibility in static fields show the regular behavior expected for a pseudo-one-dimensional antiferromagnetic system. When  $T$  decreases below  $T_N$ , the susceptibility along the  $a^*$  axis gradually drops to zero. As the susceptibility along the  $b$  and  $c$  axis slowly rises to a constant value, the  $a^*$  axis may be identified as the preferred direction of spin alignment. Preliminary nuclear magnetic resonance experiments support this conclusion.

Since the perpendicular susceptibility  $\chi_\perp$  in the ordered state is related to the sum of the antiferromagnetic interactions, which is largely governed by the intrachain coupling, it is—in principle—possible to estimate a value for  $J/k$  from  $\chi_\perp$ . One should bear in mind, however, that for a pseudo one-dimensional (1D) system zero-point spin reduction may have a very drastic influence. Although a spin-wave analysis as performed for  $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$  (Ref. 5) is ruled out by the fact that at present the details of the magnetic space group are not known, one might try to obtain a rough estimate from the formulas

given by Keffer<sup>6</sup>:

$$\chi_\perp(T=0) = \frac{Ng\mu_B}{H_e + \frac{1}{2}H_a} \left( 1 - \Delta S/S - \frac{e(\alpha)}{(2+\alpha)zS} \right), \quad (2)$$

$$\Delta S/S = -(1/2S)[1 + (1/\pi)\ln 2\alpha]. \quad (3)$$

where  $H_e$  and  $H_a$  are the exchange field ( $2z|J|S/g\mu_B$ ) and the anisotropy field, respectively.  $e(\alpha)$  represents the antiferromagnetic ground-state energy,  $\Delta S/S$  denotes the zero-point spin reduction, and  $\alpha = H_a/H_e$ . For a linear chain system ( $z = 2$ ) and small values of  $\alpha$ , the expressions reduce to

$$\chi_\perp(T=0) = (Ng\mu_B/H_e)(1 - \Delta S/S - 0.0726), \quad (4)$$

$$\Delta S/S = -0.2[1 + (1/\pi)\ln 2\alpha]. \quad (5)$$

Measurements of the magnetic phase diagram reveal a spin-flop transition at  $H_{sf} = 18 \pm 1$  kOe. With the additional relation  $H_{sf} = (2H_e H_a)^{1/2}$ , Eqs. (4) and (5) may now be solved. Insertion of the observed value of  $\chi_\perp$  ( $1.6 \times 10^{-2}$  emu/mole) yields  $J/k = -7.6 \pm 1$  K,  $H_a = \sim 250$  Oe, and a zero-point spin reduction of  $\sim 25\%$ . A similar procedure for  $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$  shows that the value for  $\Delta S/S$  obtained from the expressions given above is a somewhat conservative estimate, and hence the resulting value for  $J/k$  will very likely be too high. A more reliable estimate, however, will have to await detailed information about the magnetic structure. Nevertheless, we may conclude that the intrachain interaction in DMMC is not very different from that in TMMC, as might have been conjectured already from the respective crystallographic structures. This analogy is corroborated by measurements of  $T_N$  as a function of the concentration of Cu impurities. At an impurity concentration of 2.1%, the decrease of  $T_N$  is about 36%, which is—within the experimental error—equal to the reported decrease in TMMC.<sup>7</sup> If one accepts the observed decrease of the ordering temperature to be mainly due to a suppression of the intrachain correlations by the substituted impurities, this result indicates that the intrachain exchange mechanism in both substances is largely identical.

The order of magnitude of the interchain interactions  $J'/k$  may be estimated by a Green's function method<sup>8</sup> from the value of  $J/k$  and  $T_N$ . If we use the values  $J/k = -6$  K and  $T_N = 3.60$  K this procedure yields  $J'/J = 1.2 \times 10^{-3}$ . In Table I the properties of DMMC are compared with those of TMMC and CMC. The entries of the table ( $J'/J$ ,  $S_{\text{crit}}$ , and  $kT_N/J$ ) are various entities by which the spatial magnetic dimensionality of the systems can be estimated. Inspection of this table shows that DMMC nicely fills the gap which exists between the two best-known approximations of a 1D Heisenberg system, TMMC, and

TABLE I. Comparison of the degree of one-dimensionality of  $(\text{CH}_3)_4\text{NMnCl}_3$  (TMMC),  $(\text{CH}_3)_2\text{NH}_2\text{MnCl}_3$  (DMMC), and  $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$  (CMC).

System	$ J'/J $	$S_{\text{crit}}$	$kT_N/J$	Reference
TMMC	$10^{-4}$	1%	-0.124	2
DMMC	$1.2 \times 10^{-3}$	3.4%	-0.627	Present work
CMC	$8 \times 10^{-3}$	13%	-1.48	5

$\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$ . This may be advantageous in studies which try to relate deviations from the pure model system and observable phenomena. Actually DMMC has been used already in our

systematic study on the field dependence of the ordering temperature of various pseudo-one-dimensional Heisenberg systems. Results of this study will be published elsewhere.

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