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Theoretical and experimental magnetic specific heat of $CsMnCl_3 \cdot 2H_2O$

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Detailed specific-heat measurements between 1.1 and 52 K on the $S = 5/2$ Heisenberg linear-chain system $CsMnCl_3 \cdot 2H_2O$ are reported. The results could be interpreted with the aid of newly developed theoretical estimates for the magnetic contribution and a lattice contribution characteristic for a chemically layered compound. A value of $J/k = -3.3 \pm 0.3$ K is obtained, which will be compared with the results from other studies.

I. INTRODUCTION

Magnetically one-dimensional model systems have attracted considerable attention of both theoreticians and experimentalists over the past decade. In spite of the simplifications introduced by the low dimensionality, reliable predictions for the behavior of the thermodynamic properties of infinite ensembles of interacting spins are available only in a few cases, mostly with $S=\frac{1}{2}$. As there exists a still-growing number of compounds reflecting linear-chain characteristics with $S>\frac{1}{2}$, we thought it worthwhile to try to obtain a reliable estimate of the specific heat and the magnetic susceptibility of these systems. This paper will deal with the theoretical and experimental specific heat of the $S=\frac{5}{2}$ linear Heisenberg system $CsMnCl_3 \cdot 2H_2O$.

A considerable number of experimental investigations have been devoted to this compound.[1,2] These studies reveal that above $T \simeq 9$ K the magnetic behavior can be very well described by a system of isolated linear chains of $S=\frac{5}{2}$ ions with an antiferromagnetic intrachain interaction of about 3 K. Relatively small interchain interactions are present, giving rise to a three-dimensional ordering at $T_N = 4.89$ K.[3] The interchain interaction was estimated by a Green's-function method[3] and has been experimentally determined from neutron-diffraction[4] and EPR linewidth[5] studies. The available evidence indicates that this interaction is smaller by two orders of magnitude.

Up till now no detailed specific-heat measurements have been reported. The main reason for this may be found in the fact that no reliable estimate was available for either the magnetic or the lattice contribution to the specific heat. Fischer's classical spin model,[6] although satisfactorily used in the interpretation of both paramagnetic susceptibility[1] and neutron-diffraction experiments,[4] fails to give a correct description of the magnetic heat capacity of systems with finite spins. The predicted specific heat is nonphysical in the zero-temperature limit, while the error at intermediate temperatures $[kT \simeq JS(S+1)]$ may be rather large.

Weng obtained an estimate of C for $S=\frac{5}{2}$ from interpolation between $S=\frac{1}{2}$, $S=1$, and $S=\infty$.[7] However, the reliability of his results is not clear. For the ferromagnetic case Green's-function calculations have been reported.[8] To our knowledge no predictions have been reported for the antiferromagnetic chain with a sufficient degree of accuracy to enable a reliable separation of the magnetic and the lattice contribution. On the other hand, an accurate evaluation of the lattice contribution in this compound was ruled out by the fact that all attempts to grow a diamagnetic isomorph were unsuccessful.

In many cases the lattice contribution may be determined independently from heat-capacity measurements in an external magnetic field sufficiently large to saturate the magnetic system. However, in view of the reported values for the exchange interaction in this compound, magnetic fields large compared to 150 kOe would be required.

II. THEORY

At temperatures sufficiently large compared to the ordering temperature the magnetic contribution to the specific heat of this compound may most likely be described by the heat capacity of a system of isolated linear chains. The theoretical estimate for the heat capacity of such a system was composed from the results of different approximation procedures. The heat capacity at high temperatures was calculated from high-temperature series expansions that were analyzed with a Padé-approximant method giving a good convergence at temperatures down to $kT \simeq JS(S+1)$. The relative error of our estimate in this temperature region amounts to less than 0.1%. The heat capacity at intermediate temperatures was obtained by extrapolation of the results for finite chains; the accuracy of the limit for $N\rightarrow\infty$ was estimated to be better than 1%. The low-temperature behavior was approximated by expanding the heat capacity in a series of the reduced temperature kT/J. The coefficients were obtained by matching the series to our estimate for the specific heat at intermediate temperatures and to the—independently determined—limiting behavior at $T=0$, with the condition that the total magnetic entropy gain should amount to $R\ln(2S+1)$. The specific heat in the zero-temperature limit was found to obey the relation $C=\alpha T$. In general, the constant α was obtained from extrapolation of the results of finite rings and chains according to a procedure described by Bonner and Fischer.[9]

The relative error in the low-temperature region generally may amount to a few percent. Further details of the calculation, including the computational methods and a justification of the extrapolation procedures, will be presented elsewhere.[10] We only mention that the results in the limit $N\rightarrow\infty$ for $S=\frac{1}{2}-\frac{5}{2}$ are tabulated and are available on request.

III. EXPERIMENTAL

Crystals of $CsMnCl_3 \cdot 2H_2O$ were grown by slow evaporation of an equimolar solution of CsCl and $MnCl_2 \cdot 4H_2O$. They showed the morphology described by Jensen *et al.*[11]

A specimen consisting of 38.11 g of small crystals was sealed inside a vacuum calorimeter of conventional design, which was fitted with a temperature-controlled heat screen to enable very accurate measurements at temperatures up to about 50 K. Temperature readings were obtained from a calibrated germanium thermometer that was measured with an ac resistance bridge operating at 175 cps. The experimental data between 1.1 and 52 K are shown in Fig. 1.

IV. INTERPRETATION

As already mentioned, the reported experimental results on $CsMnCl_3 \cdot 2H_2O$ indicate that the interchain interactions may most likely be neglected above 9 K. The relative error of our theoretical estimate for the heat capacity of an infinite $S=\frac{5}{2}$ antiferromagnetic chain amounts to less than 1% at temperatures above $T\simeq 3J/k$. Therefore this estimate was used to describe the magnetic contribution to the specific heat above 12 K.

The rather low symmetry and the complexity of the chemical structure of this compound precludes a rigorous and meaningful calculation of the lattice specific heat, given the large number of unknown parameters involved. However, since lattice specific heats generally vary smoothly with temperature and are not influenced greatly by the details of the structure, a description by relatively simple models often appears to be very satisfactory.

As a first approximation, the lattice heat capacity was described by the three-dimensional Debye model. The number of "heavy" atoms in a formula unit was assumed to be seven. A least-squares fit of both J and the characteristic Debye temperature Θ_3 to the experimental data between 12 and 52 K yielded $J/k=-2.8\pm0.7$ K and $\Theta_3=205\pm3$ K. However, the fit revealed a large systematic error, which gave rise to deviations that were nearly two orders of magnitude larger than the scatter in the experimental data points (0.3%).

A possible explanation for this may be found in the typical chemical structure of $CsMnCl_3 \cdot 2H_2O$. In the c direction the chemical structure is held together by hydrogen bonds. Since the ab plane appears to be a perfect cleavage plane and no other cleavage planes are present we assume that, from a chemical point of view, this compound may be described by a system of loosely coupled layers. If the coupling between the layers is relatively small, the lattice heat capacity might reflect some characteristics of the two-dimensional Debye model. This was checked by a least-squares fit of both J and the characteristic Debye temperature

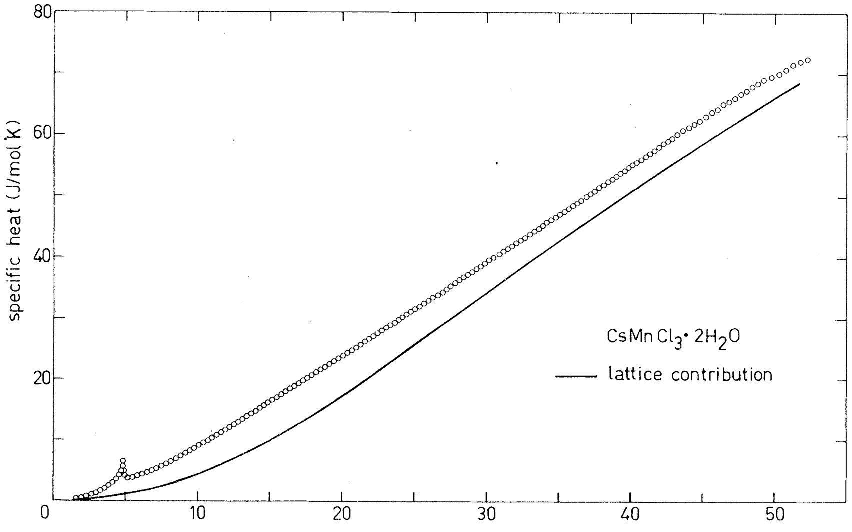

FIG. 1. Experimental specific heat of $CsMnCl_3 \cdot 2H_2O$ between 1.1 and 52 K. The drawn curve denotes the inferred lattice contribution

Θ_2 to the data between 12 and 52 K. The fit yielded $J/k=-2.95\pm0.25$ K and $\Theta_2=255\pm1.5$ K, and resulted in a systematic error that was about three times smaller than the error in the "pure" three-dimensional description.

In a more detailed description of the lattice system, the modes of vibration parallel and perpendicular to the layers should be treated separately, since they give rise to rather different restoring forces. As a first approximation one might assign two different characteristic Debye temperatures $\Theta_{2,\parallel}$ and $\Theta_{2,\perp}$ to the parallel and perpendicular modes of vibration, respectively. This would give the following expression for the lattice heat capacity:

$$C_L=7[\tfrac{2}{3}D_2(\Theta_{2,\parallel})+\tfrac{1}{3}D_2(\Theta_{2,\perp})]\,, \tag{1}$$

where D_2 stands for the two-dimensional Debye function. Despite the simplicity of this model, a least-squares fit between 12 and 52 K of J, $\Theta_{2,\parallel}$, and $\Theta_{2,\perp}$ gave an excellent agreement with the experimental data, the maximum deviation being less than 1.2%. The parameter values obtained were $J/k=-3.32\pm0.02$ K, $\Theta_{2,\parallel}=391\pm1$ K, and $\Theta_{2,\perp}=158.6\pm0.2$ K.

In the description so far, the coupling between the layers has been neglected completely. As long as this coupling is relatively small, the heat capacity at higher temperatures may be satisfactorily described by Eq. (1), but at lower temperatures the predicted lattice heat capacity is too high.[12-14] Therefore the inferred lattice contribution cannot safely be extrapolated below $T=12$ K. This may be checked by a calculation of the experimental magnetic entropy increase between $T=0$ and $T=\infty$.

The experimental magnetic specific heat was obtained by subtracting the inferred lattice contribution from the experimental data. Below 1.1 K the (rather small) entropy gain was estimated by approximating the magnetic heat capacity down to $T=0$ with the relation $C_M=\alpha T^{\beta}$. At higher temperatures the entropy increase was obtained by numerical integration of C_M/T, while the extrapolation to $T=\infty$ was performed using our estimate for the heat capacity of an infinite $S=\frac{5}{2}$ antiferromagnetic chain. The total evaluated entropy increase did amount to $1.69R$, which is about 6% smaller than the theoretical value $R\ln(2S+1)=1.792R$. This discrepancy lies well outside the experimental error.

A fairly simple model that takes into account the coupling between the layers has been proposed by Tarasov.[12] With some modifications to distinguish between the modes of vibration parallel and perpendicular to the layers, the lattice heat capacity can be written as

$$C_L=7\{\tfrac{2}{3}D_2(\Theta_{2,\parallel})+\tfrac{1}{3}D_2(\Theta_{2,\perp})+K[D_3(\Theta_3)-D_2(\Theta_3)]\}, \tag{2}$$

with

$$K=\tfrac{2}{3}\left(\frac{\Theta_3}{\Theta_{2,\parallel}}\right)^2+\tfrac{1}{3}\left(\frac{\Theta_3}{\Theta_{2,\perp}}\right)^2 .$$

In this expression Θ_3 represents the coupling between the layers. We found that the introduction of the parameter K did not significantly improve the agreement with the experimental data between 12 and 52 K. Since the four parameters ($\Theta_{2,\parallel}$, $\Theta_{2,\perp}$, J and K) appeared to be more or less correlated, the solution was obtained indirectly by minimizing the error with the additional condition that the total evaluated magnetic entropy increase should amount to $R\ln6$.

The fit that resulted from this procedure yielded

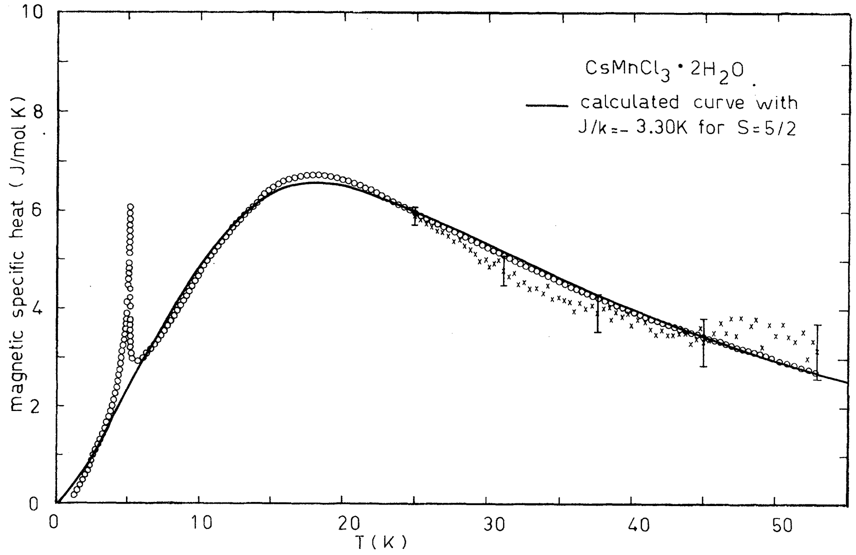

FIG. 2. Magnetic specific heat of CsMnCl$_3$ · 2H$_2$O between 1.1 and 52 K. The circles are the experimental data points corrected for the lattice contribution, while the crosses represent C (measured) $-C_L$(calculated). The drawn curve denotes our estimate for an infinite linear antiferromagnetic Heisenberg chain with $J/k=-3.3$ K.

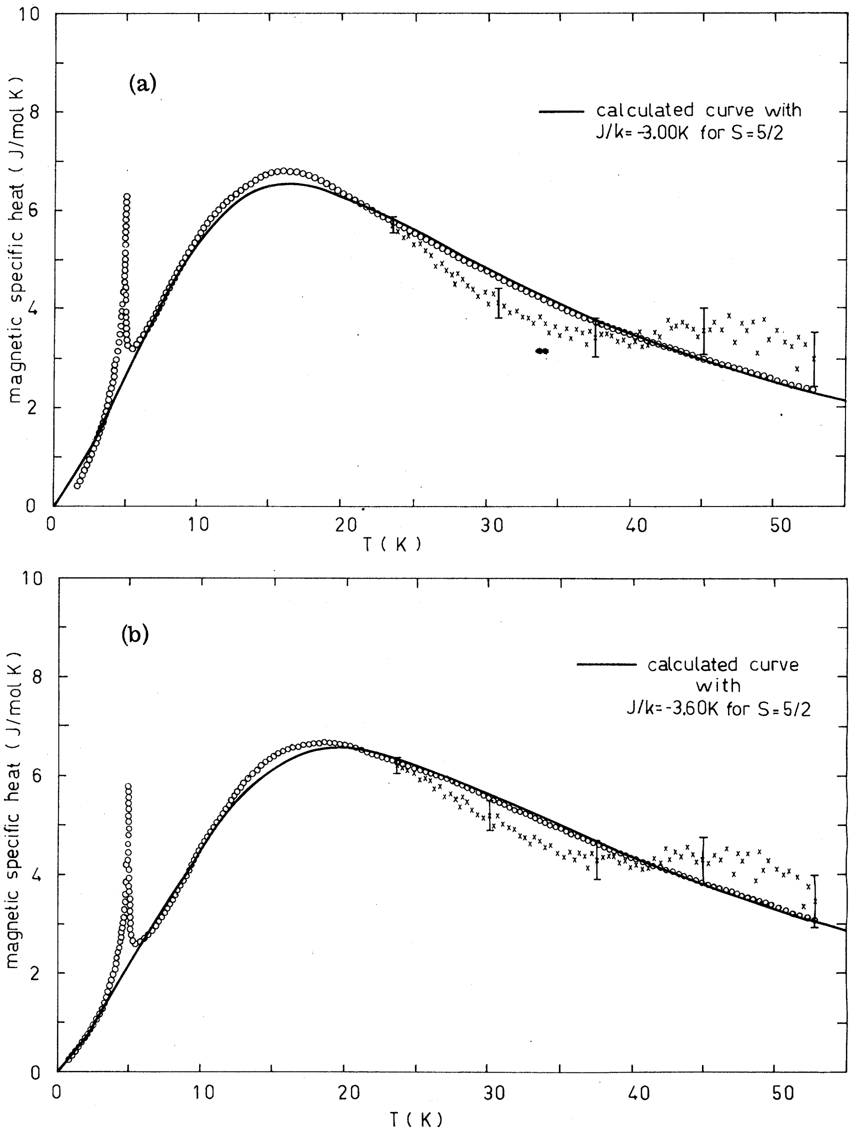

FIG. 3. (a) Magnetic specific heat of $CsMnCl_3 \cdot 2H_2O$ between 1.1 and 52 K. The circles are the experimental data points corrected for the lattice contribution, while the crosses represent C(measured) $- C_L$(calculated). The drawn curve denotes our theoretical estimate with $J/k = -3.0$ K. (b) Magnetic specific heat of $CsMnCl_3 \cdot 2H_2O$ between 1.1 and 52 K. The circles are the experimental data points corrected for the lattice contribution, while the crosses represent C(measured) $- C_L$(calculated). The drawn curve denotes our theoretical estimate with $J/k = -3.6$ K.

$J/k = -3.30$ K, $\Theta_{2,\parallel} = 395$ K, $\Theta_{2,\perp} = 156$ K, and $K = 0.03$. The inferred lattice contribution is shown as a solid line in Fig. 1, while the magnetic contribution resulting from the separation is shown in Fig. 2. In general, the magnetic contribution C_M is obtained by subtracting the inferred lattice contribution from the experimental data. Since this procedure ascribes both the experimental uncertainty in C(measured) and the total systematic error to the magnetic contribution, the relative error in C_M at higher temperatures, where the lattice contribution C_L is very dominant, will be rather large. This effect is shown by the crosses in Fig. 2, which represent C(measured) $- C_L$(calculated). The error bars reflect the experimental uncertainty in C(measured). We feel that a more realistic picture of the quality of the fit can be provided by ascribing the error at higher temperatures to C_L and C_M in proportion to their relative value. This is shown by the circles in Fig. 2. Since below $T = 20$ K the positions of the circles and the crosses are almost

TABLE I. Values for the intrachain exchange interaction J in $CsMnCl_3 \cdot 2H_2O$ obtained from several experimental techniques.

	Technique	J/k (K)	Reference
I	Paramagnetic susceptibility	−3.12	1
II	I+quantum corrections	−3.00	1
III	Perpendicular susceptibility	−3.39	2
IV	Neutron scattering	−3.53	2, 4
V	EPR	−3.57	20
VI	Specific heat	−3.3	present work

identical, they are not shown separately. The drawn curve in Fig. 2 represents our limiting specific heat for an infinite $S=\frac{5}{2}$ chain with $J/k=-3.3$ K.

In the neighborhood of its minimum, the error of the four-parameter fit described above varied rather slowly with the magnitude of J. Since systematic errors of the same order of magnitude as the scatter in the experimental data points are still present, it may be incorrect to assume that the right solution corresponds exactly with the minimum error. To estimate the accuracy of the determination of the value of the intrachain exchange integral J, the fitting procedure was carried out for several fixed J values. In Figs. 3(a) and 3(b) the results are shown for $J/k=-3.0$ K and $J/k=-3.6$ K, respectively. In view of these results we quote as our estimate for the magnitude of the exchange integral $J/k=-3.3\pm 0.3$ K.

V. DISCUSSION

Although several simplifications were made in the evaluation of the relatively large lattice contribution to the specific heat, we feel confident to state that, given the characteristic properties of this compound, a fairly accurate determination of the value of the intrachain exchange integral has been possible. Some systematic errors in the description of the heat capacity are still present, which will most likely arise from the rather crude approximation of the lattice contribution. Apart from this, the small difference between the experimentally determined magnetic specific heat and the calculated behavior below $T\simeq 20$ K will probably be caused by the fact that the present calculations on C_M do not take into account the effect of anisotropy. It was shown for[8] $S=\frac{1}{2}$ and[10] $S=1$ that the presence of either dipolar or single-ion anisotropy will increase the magnitude of the specific-heat maximum, while the heat capacity at lower temperatures will be smaller than the isotropic value. A detailed specific-heat study of the effect of anisotropy in this compound will be hampered by the existence of interchain interactions. As can be seen from Fig. 2 these interactions—although rather small—give a significant contribution to the heat capacity below $T=7$ K. Since tetramethylammonium-manganese-trichloride (TMMC) has been found to be more chainlike in character,[15] we feel that an accurate determination of the magnetic specific heat of this latter compound will very likely provide more conclusive information.

As can be seen from Fig. 2, the maximum in the experimental heat capacity in the paramagnetic region occurs at $T_{C_{\max}}\simeq 17$ K, which may be compared with the temperature that corresponds to the maximum value of the paramagnetic susceptibility $T_{\chi_{\max}}\simeq 25$ K,[1] giving $T_{\chi_{\max}}/T_{C_{\max}}=1.5$. About 13% of the total magnetic entropy is removed below the ordering temperature ($T_N=4.885\pm 0.008$ K). The experimental magnetic energy gain amounts to 398 J/mol, which lies well within the rigorous bounds given by Anderson[16] for $Z=2$ and our result $J/k=-3.3$ K.

In Table I several experimental techniques that have been used to determine the magnitude of the intrachain exchange interaction in $CsMnCl_3\cdot 2H_2O$ are briefly summarized. It appears that the value of the exchange integral found in the present work is in satisfactory agreement with the majority of the reported experimental results. The magnitude of the exchange integral obtained by interpreting the susceptibility data in the paramagnetic region with the classical spin model seems relatively small. It should be noted that a similar effect does occur in TMMC.[15,17] The application of quantum corrections[1,18,19] as proposed by Weng and Griffiths even decreases the value of the exchange integral, although the fit to the experimental data is improved. We feel that a series of calculations on the susceptibility of linear chains of finite spins, according to the procedure that has been outlined briefly in the present work, might be necessary to clarify this question.

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