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Specific heat of nearly-one-dimensional tetramethyl ammonium manganese trichloride (TMMC) and tetramethyl ammonium cadmium trichloride (TMCC)

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The specific heat of tetramethyl ammonium manganese trichloride and its cadmium isomorph is measured for $2 < T < 52$ K. The temperature dependence of the lattice specific heat of the cadmium compound could be fitted with an expression based upon a pseudoelastic approach of the lattice vibrations in this low-dimensional system. Application of this approach to the manganese compound yields a magnetic contribution which fits the overall behavior of a one-dimensional Heisenberg model with an intrachain interaction of $J/k = -6.7 \pm 0.5$ K. Inspection of the low-temperature region yields a satisfactory agreement with the expression $C_m = 1.1|kT/J| + 0.5|kT/J|^2 - 0.13\,|kT/J|^3$, predicted by recent calculations.

INTRODUCTION

Tetramethyl ammonium manganese trichloride (TMMC) is considered as one of the best one-dimensional antiferromagnetic compounds known at this moment. Recent publications have shown that the Ni (TMNC) and the diamagnetic Cd (TMCC) compounds can be considered as isomorphic.[1] The one-dimensional magnetic behavior of TMMC originates from the crystallographic arrangement of isolated Cl_3–Mn–Cl_3 chains separated from each other by $N(CH_3)_4$ groups. The ratio of inter- to intrachain exchange interactions $|J'/J|$ has been estimated to range between 10^{-3} and 10^{-5}.[2] The exchange can be considered as highly isotropic, small anisotropy effects have only been observed in susceptibility measurements.[2,3] Neutron-diffraction experiments have shown that the correlation lengths and the dispersion relations of the spin waves are consistent with a highly one-dimensional behavior with Heisenberg exchange, although there is some discrepancy between the inferred values for the intrachain exchange coupling.[4,5] Although a large number of papers have been devoted to the magnetic properties of TMMC, the over-all behavior of the *magnetic* specific heat does not seem to have been reported. In a previous paper, the total specific heat up till 4.2 K, including the behavior near the ordering temperature ($T_N = 0.835$ K) was reported.[6] Recently Dietz *et al.*[7] and Vis *et al.*[8] published their specific-heat results in the range 0.3–300 K. The specific heat of the isomorphous TMCC from 1.7 to 18 K was reported by Blacklock *et al.*[9]

Our aim was to obtain an estimate for the *magnetic* contribution to the specific heat of TMMC and compare it with the extended theoretical estimates for a $S = \frac{5}{2}$ Heisenberg linear system reported in recent publications.[10–12] The main difficulty, however, is the lack of information about the temperature dependence of the lattice contribution. The low dimensionality of the system prevents the application of standard expressions for the lattice heat capacity based on purely isotropic and elastic behavior. Therefore we used a recently developed theory for anisotropic media based on a pseudoelastic approach.[13] The specific heat of the diamagnetic Cd^{++} isomorph was used to establish a functional form for the over-all lattice heat capacity of TMMC, containing a minimum of adjustable parameters.

PREPARATION AND EQUIPMENT

Specific heat measurements were performed on samples consisting of 0.1 mole of small crystals (average dimensions 5 mm). The specimen was sealed inside a copper capsule with a small quantity of ^3He exchange gas. The capsule was suspended inside an evacuated can placed inside a ^4He cryostat. Between the capsule and the outer can a temperature-controlled heat screen was fitted, which enabled us to perform very accurate measurements at temperatures up to about 50 K. Temperature readings were obtained from a calibrated germanium thermometer which was attached to the capsule and measured with an ac resistance bridge operating at 172 Hz. An over-all check of the accuracy of the system was performed by measuring the specific heat of 99.999% spectrographic pure copper. The data below 25 K were compared with the copper reference equation of Osborne *et al.*,[14] those above 25 K with the selected values evaluated by Furukawa *et al.*[15] The precision of the measurements was estimated to be better than ~ 1% in the whole temperature region.

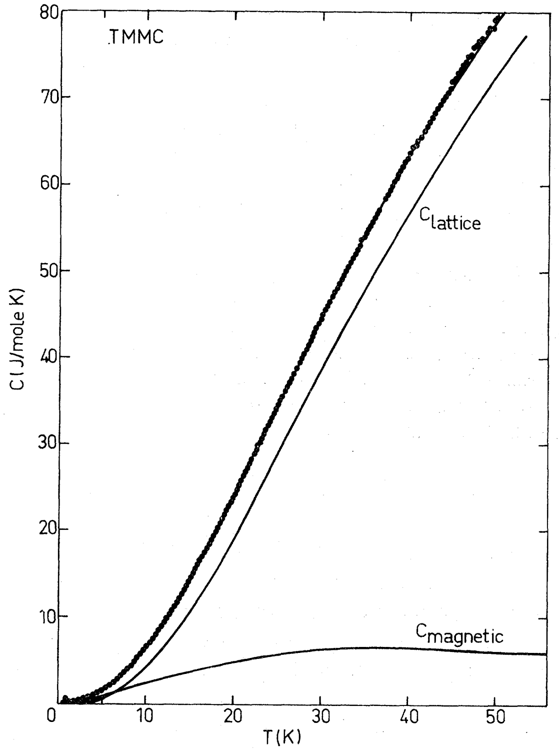

FIG. 1. Specific heat of TMMC. Drawn line through the data points represents the best fit to the total heat capacity. Lattice and magnetic contribution are drawn separately.

The crystal samples were grown by slow evaporation of equimolar solutions of the appropriate chlorides and NH_4Cl in water. The starting materials contained less than 0.1% impurities.

RESULTS AND DISCUSSION

The specific heat of both TMMC and TMCC was measured from 2 to 52 K. The experimental results on TMMC are shown in Fig. 1. Representative data for both compounds are tabulated in Table I. A general inspection of the data shows that the results for TMMC below 4 K and for TMCC below 18 K are in good agreement with the earlier published results.[7–9] At low temperatures the specific heat of TMMC rises above that of TMCC, because of the increasing relative magnitude of the additional magnetic contribution in the Mn compound. At high temperatures the specific heat of TMCC is slightly larger than the specific heat of TMMC, which is not surprising in view of the larger mass of the Cd^{++} ion.

In order to get information about the magnetic contribution to the specific heat, we have to perform a separation of the magnetic and lattice contribution. In the majority of cases such a separation is obtained, at least in a restricted temperature region, by utilizing established limiting temperature dependences of both contributions and fitting the coefficients to the experimental data (e.g., $C_p=aT^{-2}+bT^3$). In our case such a procedure does not seem possible for several reasons. As we stated before, our aim was to establish the overall magnetic contribution in the temperature range studied. So it is not enough, for this purpose, to know the limiting temperature dependence. Moreover, our experimental data points are restricted to relatively low and intermediate temperatures. As we shall argue further on neither the low-temperature behavior of the magnetic contribution nor that of the lattice contribution is known to a sufficient degree of accuracy. Of course, one may speculate on a certain limiting low-temperature behavior. For instance, the specific heat of TMMC in the region $2<T<6$ K can be represented fairly well as $C_p=0.098T+0.046T^2$, a relation also reported by Vis *et al.*[8] with slightly different coefficients. One may argue that the first term arises from the magnetic contribution and confront it with the theoretical expression for C_m from linear spin-wave theory. However, in the temperature region $4<T<10$ K, the total specific heat can equally well be described by $C_p=0.21T+0.0044T^3$. The same procedure will give quite different results now. We will return to this low-temperature behavior more specifically in a later stage but will conclude that, unless more detailed information on the behavior of both the lattice and the magnetic contribution is available, procedures of this kind should only be applied with great care.

A more direct approach to the problem seems to be the subtraction of the specific heat of a diamagnetic isomorph. The only available compound for this purpose is TMCC. However, owing to the rather large mass difference between the Mn^{++} and the Cd^{++} ion, the scaling procedure as suggested by Stout and Catalano[16] may introduce serious errors in this case. Moreover it has been shown that, in general, the scaling factor is slightly temperature dependent, so that one probably cannot scale the whole region of interest with one single parameter. Despite this, the resulting magnetic specific heat after subtraction of the scaled heat capacity of TMCC was rather realistic. The scaling factor was determined to be 1.083 through the conditions that $C_m>0$ at higher temperatures and the total magnetic entropy gain should equal $R\ln(2S+1)$. The curve showed a maximum of $\simeq 6.8$ J/mol K at $T\simeq 40$ K, which is in agreement with the behavior of a Heisenberg $S=\frac{5}{2}$ linear chain system with $J/k\simeq -7.5$ K.[10–12] However, the experimental curve showed serious systematic deviations from the calculated curves for such a system. Partially this might have been expected because, in contrast to the description of the total specific

TABLE I. Representative values of the specific heat of TMMC and TMCC.

T (K)	C_{Mn} (J/mole K)	C_{Cd} (J/mole K)	T	C_{Mn}	C_{Cd}	T	C_{Mn}	C_{Cd}
2.00	0.370	0.026	8.40	4.373	3.255	21.50	27.257	25.725
2.20	0.423	0.035	8.60	4.601	3.482	22.00	28.291	26.716
2.40	0.488	0.047	8.80	4.826	3.702	22.50	29.337	27.777
2.60	0.555	0.061	9.00	5.067	3.924	23.00	30.388	28.813
2.80	0.621	0.081	9.20	5.301	4.165	23.50	31.409	29.825
3.00	0.689	0.105	9.40	5.545	4.400	24.00	32.349	30.854
3.20	0.764	0.137	9.60	5.797	4.629	25.00	34.497	32.910
3.40	0.843	0.174	9.80	6.057	4.887	26.00	36.568	34.992
3.60	0.925	0.216	10.00	6.317	5.139	27.00	38.613	37.091
3.80	1.013	0.266	10.50	6.994	5.798	28.00	40.620	39.117
4.00	1.100	0.320	11.00	7.719	6.538	29.00	42.546	41.130
4.20	1.192	0.378	11.50	8.475	7.303	30.00	44.725	43.360
4.40	1.286	0.440	12.00	9.237	8.129	31.00	46.767	45.057
4.60	1.387	0.513	12.50	10.036	8.947	32.00	48.504	46.951
4.80	1.491	0.594	13.00	10.881	9.621	33.00	50.439	49.010
5.00	1.596	0.680	13.50	11.735	10.505	34.00	52.202	50.797
5.20	1.704	0.771	14.00	12.601	11.362	35.00	54.027	52.760
5.40	1.826	0.873	14.50	13.495	12.230	36.00	56.107	54.862
5.60	1.941	0.980	15.00	14.384	13.118	37.00	57.876	56.653
5.80	2.066	1.095	15.50	15.292	13.997	38.00	59.710	58.663
6.00	2.196	1.214	16.00	16.208	14.882	39.00	61.721	60.473
6.20	2.323	1.341	16.50	17.138	15.845	40.00	63.793	62.836
6.40	2.496	1.476	17.00	18.174	16.517	41.00	65.141	64.885
6.80	2.815	1.773	17.50	19.159	17.725	42.00	66.695	66.939
7.00	2.986	1.931	18.00	20.108	18.706	43.00	68.524	67.892
7.20	3.163	2.097	18.50	21.092	19.662	44.00	70.210	70.764
7.40	3.347	2.271	19.00	22.120	20.638	45.00	72.009	71.972
7.60	3.540	2.456	19.50	23.020	21.636	46.00	73.599	73.642
7.80	3.734	2.640	20.00	24.070	22.628	48.00	76.759	76.329
8.00	3.945	2.838	20.50	25.189	23.619	50.00	79.370	80.142
8.20	4.157	3.045	21.00	26.220	24.674	52.00	81.988	83.423

heat of TMMC with linear and quadratic terms in the region $2 < T < 6$ K, the specific heat of the Cd compound in that same region could only be described with cubic and higher-order terms. Whereas the lattice contribution in TMMC at those temperatures amounts to roughly 50%, this presents a strong indication that simple scaling, as we argued before, will not hold.

Of course the rather complicated behavior of the lattice contribution is not surprising in view of the fact that the crystallographic structure of TMMC and TMCC can be described as a system built up from chemically loosely coupled chains. It has been shown both theoretically and experimentally that in such cases a description of the lattice specific heat in terms of three-dimensional Debye functions is not realistic. Tarasov, for instance, concluded that in a first—rather crude—elastic approach it can be shown that the specific heat of such a system is described by a combination of one- and three-dimensional Debye functions.[17] This may give rise to temperature regions where a dominant three-dimensional or a dominant one-dimensional behavior can be detected. A modification of this theory was used to explain the specific heat of $\mathrm{CsMnCl_3 \cdot 2H_2O}$.[18]

A somewhat more refined model was proposed by Kopinga *et al.*[13] In a pseudoelastic approximation in which dispersion effects for the low-energy vibrational modes are taken into account, the specific heat of a one-dimensional system can be expressed as the sum of the contributions of the three vibrational modes:

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

The functions F_1 represent the contribution from the longitudinal and transverse modes with displacements perpendicular to the chain direction, while F_2 represents the mode with displacements in the chain direction. The variables Θ_l, Θ_t, and Θ_c are related to the elastic constants and the eventual additional bending stiffness due to covalent bonding effects. The functions F_1 and F_2 can be expressed as combinations of suitably normalized one-, two-, and three-dimensional Debye functions.

A fit of (1) to our specific-heat data on TMCC with Θ_l, Θ_t, and Θ_c as variables, gives an over-all agreement (see Fig. 2) better than ~2% for $4 < T$

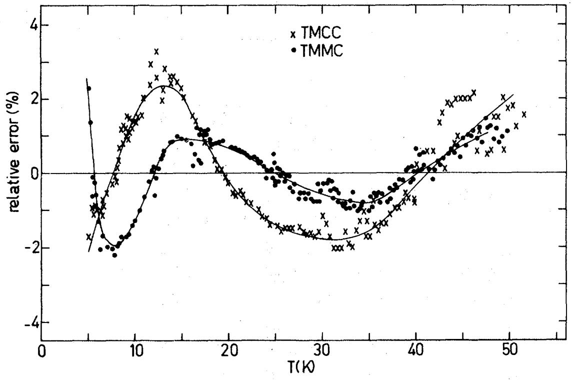

FIG. 2. Relative error in the fit to the experimental specific heat of TMMC and TMCC as a function of temperature.

< 50 K with $\Theta_l = 442$ K, $\Theta_t = 154$ K, and $\Theta_c = 36.5$ K, which is quite satisfactory considering the rather large temperature interval. In view of this good fit and the isomorphy of TMCC and TMMC, we may expect that the same model will apply to the latter compound with roughly the same lattice-parameter values. We therefore tried to fit the total specific heat of TMMC simultaneously varying the lattice parameters in the expression for the *lattice* specific heat as well as the exchange parameter J in the expression for the *magnetic* specific heat. For the magnetic contribution we took the results of the extended high-temperature series expansion combined with results of the extrapolation of finite chains for the $S=\frac{5}{2}$ Heisenberg model as published recently.[10–12,18]

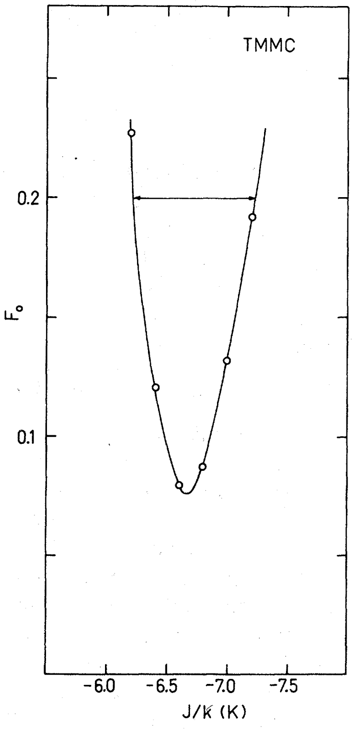

FIG. 3. Squares sum of the fit to the specific heat of TMMC vs the intrachain exchange interaction.

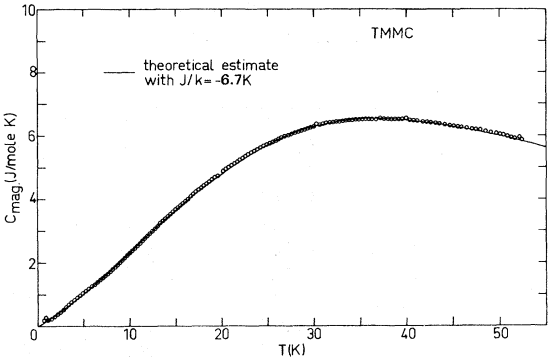

FIG. 4. Magnetic specific heat of TMMC. Open circles are the experimental data points corrected for the lattice contribution. Drawn curve represents the theoretical estimate for a Heisenberg linear chain with $J/k = -6.7$ K.

A least-squares fit to the experimental data points yielded $J/k = -6.7 \pm 0.5$ K, $\Theta_l = 473$ K, $\Theta_t = 169$ K, and $\Theta_c = 39$ K. Comparison of these results with the parameters for TMCC confirms the conjectures made before, to the extent that the Θ values increase about 8% for TMMC, which is not surprising, considering the smaller mass of the Mn^{++} ion. The results of this fit are shown in Figs. 1 and 2. Figure 3 gives the best-fit squares sum as a function of the fixed J/k value. The uncertainty in J/k is estimated from the width of this curve as 0.5 K.

In Fig. 4 we show the magnetic specific-heat data points obtained by subtraction of the calculated lattice contribution from the total experimental specific heat, corrected in the sense that the remaining deviations, as shown in Fig. 2, are contributed to the lattice and magnetic system proportional to their relative magnitude. As one can

TABLE II. Values for the intrachain exchange interaction J in TMMC obtained from several experimental techniques.

Technique	J/k (K)	Reference
Susceptibility	-6.3	2
Susceptibility	-6.47 ± 0.13	5
Neutron scattering	-7.7 ± 0.3	5
Spin-wave dispersion	-6.6 ± 0.15	5
Specific heat, direct fit	-6.7 ± 0.5	present work

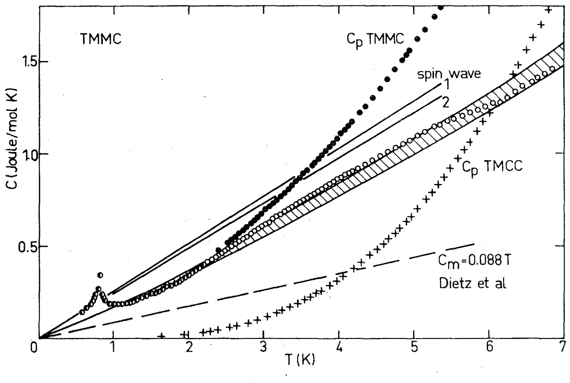

FIG. 5. Total specific heat of TMMC and TMCC (● and +, respectively). Open circles represent $C_{m,\mathrm{TMMC}}$ and are obtained from $C_m(T) = C_{p,\mathrm{TMMC}}(T) - C_{p,\mathrm{TMCC}}(T/1.08)$. Below $T=2$ K the magnetic and total specific heat almost coincide. Shaded area is the estimated low-temperature limit for C_m in the case of Heisenberg exchange with $J/k=-6.7$ K. Curve denoted by spin wave 1 represents the linear spin-wave prediction for this case with $J/k=-6.7$ K. Curve denoted by spin wave 2 represents the result for C_m obtained from direct integration of the experimental dispersion relation (Ref. 7).

see, the agreement with the theoretical estimate is very good over the whole temperature range $2 < T < 50$ K. The value of $J/k = -6.7 \pm 0.5$ K inferred from this experiment compares favorably with the values cited in literature deduced from susceptibility, magnetization, and neutron-diffraction experiments, as can be seen in Table II. In view of this we may conclude that we have shown the applicability in this case of both the expressions for the lattice and the magnetic specific heat derived for low-dimensional systems like TMMC and TMCC.

Because of the small ratio $|J'/J|$ and the low three-dimensional ordering temperature, TMMC offers a good opportunity to get experimental evidence of the limiting low-temperature behavior of the magnetic specific heat of an antiferromagnetic $S=\frac{5}{2}$ Heisenberg system. In fact, the experimental information on this point seems rather scarce, while the theoretical predictions contradict. Therefore we will now focus our attention to the relative low-temperature region in more detail. In Fig. 5 the data points below 7 K are shown, The points of the magnetic specific heat curve are obtained by

$$C_m(T) = C_{p,\mathrm{Mn}}(T) - C_{p,\mathrm{Cd}}(T/1.08). \qquad (2)$$

We have chosen here for subtracting a scaled heat capacity of TMCC to avoid any interference between the magnetic and the lattice contribution which might arise from simultaneous fitting procedures. In this temperature range the magnetic contribution obtained by scaling lies within 2% of the curve obtained by the procedure outlined before. The scaling factor 1.08 was chosen as an average of the factors following from the increase of Θ_l, Θ_t, and Θ_c. Otherwise the curve does not change significantly upon varying the scaling factor because we are still in the range where $C_L < C_m$. For the sake of completeness we have also reproduced the total specific heat of both compounds. The shaded area through the data points represents the estimate for the low-temperature limiting behavior of a linear antiferromagnetic Heisenberg $S=\frac{5}{2}$ system calculated by De Neef *et al.*[10–12]:

$$C_m = 1.1\,|kT/J| + 0.5\,|kT/J|^2 - 0.13\,|kT/J|^3, \quad (3)$$

with $J/k = -6.7$ K.

The agreement is rather satisfactory. The slight systematic deviations are comparable with the estimated inaccuracy which amounts to 4%. The value for the intrachain coupling is the same as the value found from the over-all fit, and compares very well with those obtained from inelastic neutron scattering and susceptibility measurements. We thus feel confident to state that the suggested low-temperature limit (3) is in good agreement with the experimental evidence.

The linear term in (3) is about 50% smaller than the one expected on the basis of linear noninteracting spin-wave theory.[19] A similar fact was observed by Bonner and Fisher for a $S=\frac{1}{2}$ Heisenberg linear chain.[20] The discrepancy in that case amounts to a factor of about three. Apparently the spin-wave approximation yields a better result when the spin value increases. The region in Fig. 5 where C_m can be approximated by the linear term only is greatly obscured by the three-dimensional ordering phenomena. However, this region does not extend above ≈2 K, which corresponds to $kT/|J| \simeq 0.3$. In view of this fact it seems to us that the validity range of the linear behavior of the specific heat is somewhat overestimated in earlier publications.[7] For comparison two of these estimates are reproduced in Fig. 5.

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