

Heat capacity of tetramethylammonium trichloromanganate(II) from 1.5 to 300 K

ANTHONY G. DUNN,[†] MICHAEL JEWESS,^{‡§}
LIONEL A. K. STAVELEY, and RICHARD D. WORSWICK[•]

*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road,
Oxford OX1 3QR, U.K.*

(Received 8 October 1982)

The heat capacity of tetramethylammonium trichloromanganate(II), $N(CH_3)_4MnCl_3$, from 1.5 to 300 K is reported. The principal novelty of the results is in the region above 52 K, for which only a very small-scale plot has previously been published. From our results we estimate the anomalous molar entropy gain associated with the monoclinic-to-hexagonal transition ($T_c = 126$ K) as $R \ln 2.8$.

1. Introduction

Tetramethylammonium trichloromanganate(II), $N(CH_3)_4MnCl_3$, (commonly known as TMMC, short for tetramethylammonium manganese chloride), has been the subject of several previous heat-capacity studies.⁽¹⁻⁴⁾ All of these included measurements below 4 K reported in at least fair detail. One of them⁽⁴⁾ included additionally measurements from 4 to 52 K reported in detail. Another⁽²⁾ included measurements from 4 to 300 K, which however were reported only in the form of a small-scale plot.

TMMC is of thermodynamic interest in two main respects. Firstly, it is a remarkably good approximation to a one-dimensional Heisenberg antiferromagnet; long-range three-dimensional magnetic order breaks down at 0.84 K, but short-range magnetic ordering within linear chains of Mn atoms persists for many tens of kelvins above this.^(5,6) Secondly, there is a monoclinic-to-hexagonal phase change at 126 K involving orientational disordering of the tetramethylammonium ions.⁽⁷⁾ The previous reports of heat-capacity work referred to above are sufficiently detailed (below 52 K) to permit a satisfactory thermodynamic analysis of the development of

[†] Present address: British Telecom Southend-on-Sea Area, 45 Victoria Avenue, Southend-on-Sea SS2 6BA.

[‡] Present address: British Telecom Intellectual Property Unit, 151 Gower St, London WC1E 6BA.

[§] To whom correspondence concerning this work should be addressed.

Present address: Uplands, Dunstan Road, Old Headington, Oxford OX3 9BY.

[•] Present address: AERE Harwell, Oxon OX11 0RA.

magnetic disorder, but are not sufficiently detailed (above 52 K) to permit a satisfactory thermodynamic analysis of the disordering of the tetramethylammonium ions. The present paper aims to remedy this deficiency.

2. Experimental

Two different samples were used, both prepared by dissolving tetramethylammonium chloride and manganese(II) chloride tetrahydrate, the latter in 5 moles per cent excess, in the minimum quantity of aqueous hydrochloric acid and crystallizing the product by cooling over many hours. Batch I was prepared with concentrated hydrochloric acid⁽⁸⁾ and batch II with acid of concentration $2 \text{ mol} \cdot \text{dm}^{-3}$.⁽⁹⁾

The hexagonal rose-pink crystals, which can deliquesce, were stored in a desiccator. The batch I crystals had linear cross-section of about 3 mm; the batch II crystals were several times smaller.

Mass fractions w found by chemical analysis were as follows.

	Mn	Cl	C	N	H
I	0.232	0.452	0.204	0.057	0.051
II	—	0.451	0.200	0.059	0.051
calculated	0.2333	0.4517	0.2041	0.0595	0.0514

Debye-Scherrer X-ray powder diffraction photographs of I and II could be indexed on the unit cell determined by the single-crystal method,⁽¹⁰⁾ with the exception of weak lines at 0.863, 0.737, and 0.415 nm and (in the case of sample II) of weak lines that could be indexed on the unit cell of $[\text{N}(\text{CH}_3)_4]_2\text{MnCl}_4$.⁽¹¹⁾ However, these lines do not necessarily indicate any impurity phases in I and II, since the finely ground powder specimens may have reacted with the (moist) atmosphere⁽¹²⁾ during the X-ray exposure.

Heat-capacity measurements below 80 K were performed on about 0.1 mol of batch I in "calorimeter B" described elsewhere.⁽¹³⁾ Measurements above 80 K were performed on about 0.2 mol of batch II in a calorimeter used for several previous investigations in this laboratory and similar to that described by Andrews *et al.*⁽¹⁴⁾ Calorimeter B was operated with ^3He exchange gas inside the sample-containing vessel (about 10 μmol) and the other calorimeter with ^4He exchange gas. Both calorimeters were operated by the method of intermittent electrical heating.

3. Results

The calorimetric results are presented in table 1 and figure 1. Curvature corrections were generally negligible and were not attempted in the neighbourhood of the anomaly.

The fraction of the total measured heat capacity which was due to the sample varied in calorimeter B from 90 per cent or more at 1.5 to 7.2 K to 65 per cent at 79 K. In the other calorimeter, this fraction varied from 55 to 60 per cent away from the anomaly to 80 per cent in the region of the peak of the anomaly.

TABLE 1. Molar heat-capacity of N(CH₃)₄MnCl₃(s)

(a) At temperatures below 80 K								
T	ΔT	$C_{p,m}$	T	ΔT	$C_{p,m}$	T	ΔT	$C_{p,m}$
K	K	J·K ⁻¹ ·mol ⁻¹	K	K	J·K ⁻¹ ·mol ⁻¹	K	K	J·K ⁻¹ ·mol ⁻¹
1.529	0.0242	0.253	6.055	0.565	2.185	36.69	2.644	57.01
1.574	0.0629	0.266	6.593	0.535	2.621	38.64	1.270	60.24
1.636	0.0609	0.274	7.230	0.760	3.126	39.89	1.216	62.50
1.718	0.111	0.296	8.127	1.065	4.047	41.08	1.174	64.13
1.870	0.205	0.326	9.275	1.255	5.184	44.10	4.862	69.45
2.048	0.179	0.375	10.78	1.837	7.330	48.25	3.447	76.91
2.233	0.215	0.427	12.36	1.330	10.06	49.18	2.425	78.47
2.441	0.228	0.498	13.64	1.784	12.25	51.54	2.296	82.16
2.675	0.263	0.571	13.89	1.728	12.66	54.19	2.996	86.04
2.906	0.232	0.646	15.51	1.960	15.02	57.09	2.803	91.02
3.131	0.265	0.739	15.51	1.511	15.08	60.18	3.386	95.01
3.381	0.272	0.839	17.41	2.002	18.77	62.55	3.166	97.70
3.630	0.264	0.922	17.45	1.943	18.83	65.80	3.326	102.7
3.871	0.262	1.036	19.51	2.211	23.24	69.05	3.174	107.0
4.145	0.287	1.138	21.79	2.338	27.82	72.40	3.524	112.4
4.497	0.414	1.294	24.24	2.561	32.74	75.85	3.375	117.4
4.905	0.407	1.517	26.97	2.903	38.09	79.16	3.246	122.2
5.352	0.498	1.758	29.94	3.042	44.09			
5.850	0.513	2.060	33.42	3.903	50.74			

(b) At temperatures above 80 K							
T	$C_{p,m}$	T	$C_{p,m}$	T	$C_{p,m}$	T	$C_{p,m}$
K	J·K ⁻¹ ·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹
85.17	128.15	126.11	442	161.29	175.85	225.33	205.55
88.24	132.75	126.52	514	162.53	175.5	231.22	208.25
92.19	138.85	127.14	162.7	166.01	178.6	237.05	210.35
96.01	145.05	127.99	160.95	170.66	181.15	243.29	212.85
100.26	151.9	129.02	161.0	173.05	182.0	249.92	215.8
104.90	159.8	129.26	160.8	175.60	183.35	256.49	218.95
109.38	167.5	131.18	161.35	180.83	185.55	262.98	221.85
114.27	175.8	133.43	162.4	183.31	186.85	269.40	224.95
117.23	180.65	134.43	162.95	186.00	187.8	275.75	227.65
119.01	183.85	138.87	165.25	191.35	190.4	282.04	230.45
120.32	186.15	141.34	166.4	193.37	191.6	287.28	233.05
122.10	190.85	143.23	167.25	196.89	193.0	293.45	236.35
123.04	193.91	147.60	169.55	203.26	196.0	299.55	240.0
123.62	195.25	151.71	171.8	207.29	197.55		
124.77	200.0	152.58	172.15	213.37	200.2		
125.53	208.3	156.53	174.3	219.38	202.85		

The maximum in heat capacity at 126.52 K is so sharp that the transition, although initially gradual on the low-temperature side, might possibly be completed isothermally; however, we have not established this with certainty.

For comparison of our results with those reported by other workers, it is convenient to divide the temperature range into three parts: (a), below 4 K; (b), from 4 to 52 K; and (c), from 52 to 300 K.

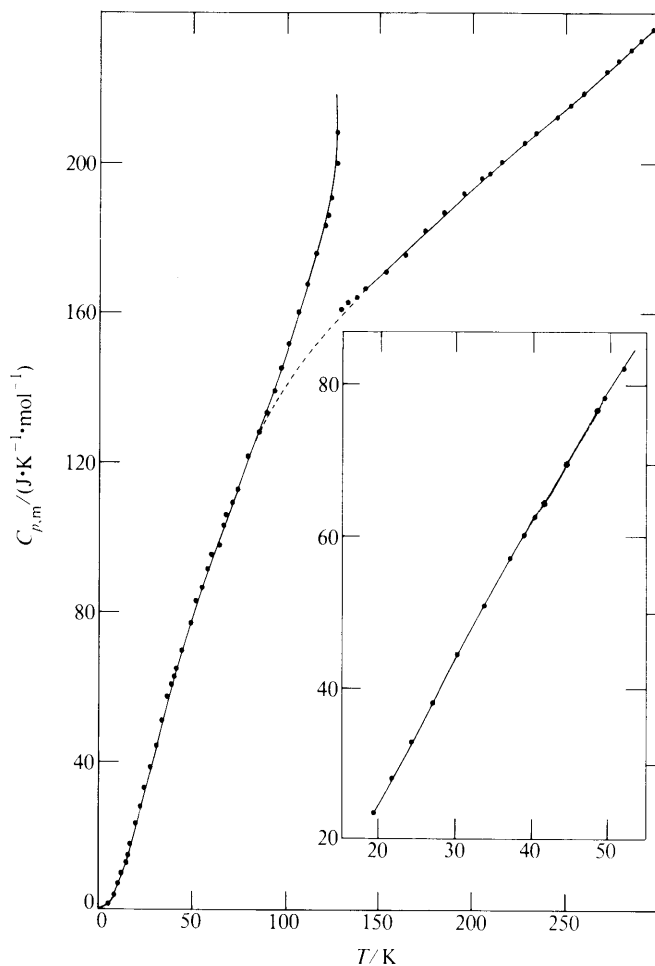


FIGURE 1. Molar heat capacity of $\text{N}(\text{CH}_3)_4\text{MnCl}_3(\text{s})$. To avoid congestion, only a limited number of points are plotted as dots. The broken line is the estimated baseline (or normal) heat capacity. The inset shows, on a larger scale, a region covering the transition proposed in reference 18.

(a), *Below 4 K.* Dietz *et al.*⁽²⁾ and Vis *et al.*⁽³⁾ while not quoting their actual experimental results, present plots showing a good fit with the equation $C_{p,m} = aT + bT^2$ from about 1.9 to 4 K, for values of $a/(\text{J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1})$ and $b/(\text{J}\cdot\text{K}^{-3}\cdot\text{mol}^{-1})$ of 0.088 and 0.047 and of 0.0858 and 0.048 respectively. We found that our 10 results from 1.87 to 3.87 K could be fitted, with a mean deviation of 0.0 per cent and an r.m.s. deviation of 0.8 per cent, to a similar equation with $a = 0.0883$ and $b = 0.0465$. Compared with this, the equation of Dietz *et al.* lies 0.4 per cent high at 1.9 K and 0.6 per cent high at 4 K, while that of Vis *et al.* lies 0.2 per cent high at 1.9 K and 1.3 per cent high at 4 K. De Jonge *et al.*⁽⁴⁾ quote "representative" (presumably smoothed) values from 2 to 4 K at 0.2 K intervals. Compared with our

line, these are 0.5 to 0.8 per cent high from 3.0 to 4.0 K but from 0.9 to 2.0 per cent high from 2.0 to 2.8 K. Takeda⁽¹⁾ presents his results only graphically, but some comparison is possible by reading from his graph. Notably, his value for the heat capacity at 4 K exceeds ours or those obtained by the other workers by about 10 per cent, this discrepancy diminishing towards lower temperatures.

(b), *From 4 to 52 K.* Over this range, de Jonge *et al.* quote "representative" values of the heat capacity at frequent intervals. Compared with a curve through these, our 32 results between 4 and 52 K have a mean deviation of -0.9 per cent and an r.m.s. deviation of 1.7 per cent. The latter probably includes a substantial contribution due to the smoothing by de Jonge *et al.* of genuine slight irregularities in the plot of $C_{p,m}$ against T ; but we cannot estimate this because they do not give their actual experimental results. Dietz *et al.* present their results in this range only on a very small-scale graph, not permitting detailed comparison with our results.

(c), *From 52 to 300 K.* Dietz *et al.* are the only other workers reporting results in this range, but once again detailed comparison with our results is not possible because they present their results only in the form of a very small-scale plot. They recorded a maximum heat capacity at 126.4 K, in satisfactory agreement with us (126.52 K).

4. Discussion

The magnetic contribution to the heat capacity below 52 K has already been comprehensively discussed⁽⁴⁾ with the aid of sophisticated theories.^(15,16)

We have estimated the anomalous contribution to the heat capacity in the region of the monoclinic-to-hexagonal transition by using a freehand baseline curve between about 90 and about 140 K as shown by the broken line in figure 1. On this basis the anomalous molar entropy gain was calculated as $8.51 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (about $R \ln 2.8$).† We consider that this is an underestimate rather than an overestimate. The structural significance of the anomalous molar entropy gain is discussed elsewhere.⁽¹⁷⁾

It has been suggested⁽¹⁸⁾ that the change in the proton n.m.r. spectrum at 39 K indicates a structural transition from one ordered arrangement of tetramethylammonium ions to another. Despite our use of small temperature intervals to cover 38.0 to 41.7 K, no evidence for such a transition was found (see inset to figure 1). In this we are in agreement with de Jonge *et al.*'s heat capacities and also with X-ray diffraction, Raman spectroscopy, and dielectric constants.⁽⁷⁾

We thank Dr J. W. White and Mr N. Brown of the Physical Chemistry Laboratory, Oxford, for helpful preliminary discussions, Dr M. T. Hutchings of AERE Harwell for commenting on the first draft of this paper, and Mr M. Gascoyne of this laboratory for preparing and analysing the samples.

† A preliminary statement of this result appeared in reference 19.

REFERENCES

1. Takeda, K. *Phys. Lett.* **1974**, 47A, 335.
2. Dietz, R. E.; Walker, L. R.; Hsu, F. S. L.; Haemmerle, W. H.; Vis, B.; Chau, C. K.; Weinstock, H. *Solid State Commun.* **1974**, 15, 1185.
3. Vis, B.; Chau, C. K.; Weinstock, H.; Dietz, R. E. *Solid State Commun.* **1974**, 15, 1765.
4. De Jonge, W. J. M.; Swüste, C. H. W.; Kopinga, K.; Takeda, K. *Phys. Rev. B* **1975**, 12, 5858.
5. Dingle, R.; Lines, M. E.; Holt, S. L. *Phys. Rev.* **1969**, 187, 643.
6. Walker, L. R.; Dietz, R. E.; Andres, K.; Darack, S. *Solid State Commun.* **1972**, 11, 593.
7. Peercy, P. S.; Morosin, B.; Samara, G. A. *Phys. Rev. B* **1973**, 8, 3378.
8. Adams, D. M.; Smardzewski, R. R. *Inorg. Chem.* **1971**, 6, 1127.
9. Hutchings, M. T.; Shirane, G.; Birgenau, R. J.; Holt, S. L. *Phys. Rev. B.* **1972**, 5, 1999.
10. Morosin, B.; Graeber, E. J. *Acta Crystallogr.* **1967**, 23, 766.
11. Morosin, B. Quoted in Wiesner, J. R.; Srivastava, R. C.; Kennard, C. H. L.; DiVaira, M.; Lingafelter, E. C. *Acta Crystallogr.* **1967**, 565. (Quotation on p. 573.)
12. Nagata, K.; Tazuke, Y. *J. Phys. Soc. Jpn* **1972**, 32, 337.
13. Jewess, M.; Lee-Bechtold, S.; Staveley, L. A. K. *J. Chem. Soc. Faraday Trans. II* **1980**, 76, 803.
14. Andrews, J. T. S.; Norton, P. A.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1978**, 10, 949.
15. Kopinga, K.; van der Leeden, P.; de Jonge, W. J. M. *Phys. Rev. B* **1976**, 14, 1519.
16. De Neef, T. *Phys. Rev. B* **1976**, 13, 4141.
17. Jewess, M. *Acta Crystallogr.* **1982**, B38, 1418.
18. Magnum, B. W.; Utton, D. B. *Phys. Rev. B* **1972**, 6, 2790.
19. Parsonage, N. G.; Staveley, L. A. K. *Disorder in Crystals*. Clarendon Press: Oxford. **1978**, pp. 365-366.

Available on
this web site.