

The specific heat of $N(CH_3)_4MnBr_3$ by adiabatic calorimetry

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 2259

(<http://iopscience.iop.org/0953-8984/11/10/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.214

The article was downloaded on 15/05/2010 at 07:11

Please note that [terms and conditions apply](#).

The specific heat of $N(\text{CH}_3)_4\text{MnBr}_3$ by adiabatic calorimetry

I Ruiz-Larrea†, J Díaz-Hernández‡, A Fraile-Rodríguez§, A Arnaiz||,
E H Bocanegra† and A López-Echarri§

† Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco,
Apdo 644, 48080 Bilbao, Spain

‡ Facultad de Ciencias Físico-Matemáticas, Universidad Autónoma de Puebla, Apdo 1152,
72000 Puebla, Mexico

§ Departamento de Física de la Materia Condensada, Facultad de Ciencias,
Universidad del País Vasco, Apdo 644, 48080 Bilbao, Spain

|| Departamento de Química Inorgánica, Facultad de Ciencias, Universidad del País Vasco,
Apdo 644, 48080 Bilbao, Spain

Received 9 October 1998, in final form 4 December 1998

Abstract. The specific heat of $N(\text{CH}_3)_4\text{MnBr}_3$ has been measured by adiabatic calorimetry, using both static and dynamic methods. The obtained results have permitted the *calorimetric* characterization of the phase transition which the crystal shows at 143 K. The comparison with other compounds of the family has been used to generate an adequate baseline for the normal lattice contribution to the specific heat. These results allow for an accurate estimation of the phase transition thermodynamic functions: $\Delta H = 218 R K$ and $\Delta S = 1.58 R$. The calorimetric data are very close to those found for the isomorphous $N(\text{CH}_3)_4\text{CdBr}_3$ and suggest a similar frequency spectrum for the lattice vibrational modes and the anharmonic contributions to the specific heat.

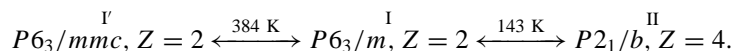
1. Introduction

Tetramethylammonium tribromomanganate $N(\text{CH}_3)_4\text{MnBr}_3$ (TMMB for short) belongs to the well known family of crystals $N(\text{CH}_3)_4\text{MX}_3$ ($M = \text{Mn}, \text{Cd}, \dots$; $X = \text{Cl}, \text{Br}, \dots$). These compounds undergo a number of structural phase transitions leading to different ordering of the tetramethylammonium (hereafter TMA) groups in the low temperature phases [1–6]. These crystals, with hexagonal symmetry at room temperature and space group $P6_3/m$ with two molecules per unit cell ($Z = 2$), show infinite linear chains made of face-sharing MX_6 octahedra parallel to the c crystallographic axis. The TMA units, which exhibit a dynamic orientation disorder, are located between the chains.

The difficulties found in the crystal synthesis of TMMB have limited the experimental studies, otherwise abundant in other members of this family. However, experimental works such as x-ray [7, 8], optical spectroscopy measurements [9], magnetic susceptibility [10, 11], DSC [10], neutron diffraction [12], dielectric measurements [6, 13], AC calorimetry [14], EPR [9] and AFMR [15] measurements have been reported.

As cited above, at room temperature this compound presents a hexagonal structure with space group $P6_3/m$ (phase I); in particular, $a = b = 9.4299(45) \text{ \AA}$, $c = 6.7821(17) \text{ \AA}$, at 268 K [8]. It undergoes a structural first order phase transition about 143 K. More recently a new second order phase transition at 384 K has been detected by AC calorimetry [14]. A comparison with similar ABX_3 compounds suggests the existence of a hexagonal $P6_3/mmc$ (phase I') above this temperature, but x-ray measurements have not been performed to confirm

this point. The TMMB first order phase transition below room temperature is governed by the ordering processes of the TMA groups. Although x-ray measurements suggested hexagonal symmetry for this low temperature phase (phase II) [8], more recently it has been considered to be monoclinic, most probably $P2_1/b$. Two reasons support this assignment: first, TMMB is believed to be isostructural with phase II of TMCC and secondly, the neutron diffraction experiments carried out by Visser and McIntyre [12]. This symmetry also agrees with the three-dimensional magnetic ordering at very low temperatures ($T_N = 2.54$ K) [11]. All these considerations have permitted us to establish the following phase transition sequence for TMMB:



However, some new unexpected results derived from x-ray [16] and NMR [17] measurements on the cadmium chloride compound (TMCC) in phase I might change the symmetries cited above. The possibility of two independent substructures associated with the inorganic chains and the TMA layers has arisen. The confirmation of these last results could support the incommensurate character of this phase in TMCC and affect the corresponding symmetry assignment to phase I in the remaining members of this family.

Here we present the specific heat capacity measurements on TMMB as an additional contribution to similar previously published works on other crystals of this family [18–20].

2. Experiment

Single crystals of TMMB were grown by slow evaporation of aqueous solutions containing stoichiometric amounts of tetramethylammonium bromide and anhydrate manganese bromide at about 30 °C. The solutions were acidified by adding 10% HBr unless they deposited orthorhombic $[N(CH_3)_4]_2MnBr_4$ (TMMB₄) crystals. Grown crystals were hexagonal prismatic, pink coloured and highly hygroscopic. Their chemical composition was confirmed by atomic spectroscopy. Small amounts of TMMB were used in DSC measurements with 1–10 °C min⁻¹ heating and cooling rates from 170 K to 300 K. These measurements confirm the absence of significant TMMB₄ traces. X-ray powder diffraction has been also used at room temperature to confirm the crystallographic quality of the sample. The assignment of the reflections observed was in good agreement with previous results of cell parameters.

Specific heat measurements from 60 to 340 K have been performed by making use of an automatic adiabatic calorimeter described in [21–23]. The calorimeter vessel was filled with a powder sample of TMMB and helium gas at low pressure to improve the sample thermal conduction. As we have described in previous works, two different methods were used to measure the specific heat in this range: discontinuous heating (pulse) and continuous heating (thermogram) techniques. Both methods give an accuracy better than 0.1% for the specific heats obtained. The automatic data acquisition of C_p measurements permitted us to study the thermal relaxation after each heating period. The appropriate fit gives an easy way to study the behaviour of the thermal conduction near solid–solid phase transitions [24].

3. Results and discussion

Preliminary DSC measurements on a powder sample showed the expected phase transition around 140 K, the results of which are presented in figure 1. The observed thermal hysteresis confirms the first order character assigned to this phase transition.

The experimental specific heat points obtained by adiabatic calorimetry are presented in figure 2. In agreement with the measurements referred to above, only one phase transition is

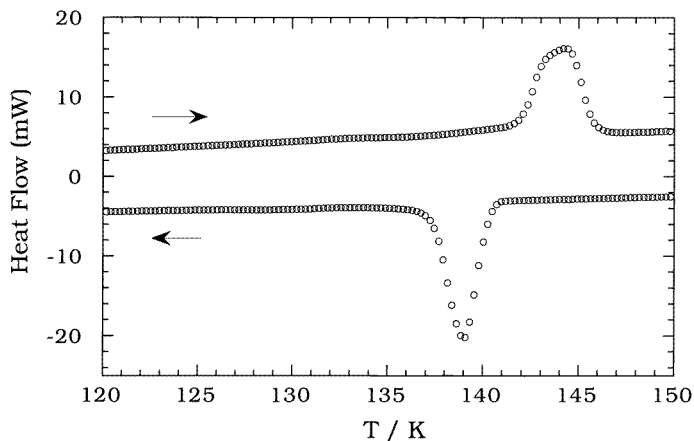


Figure 1. DSC heating and cooling curves for TMMB showing the thermal hysteresis of the phase transition.

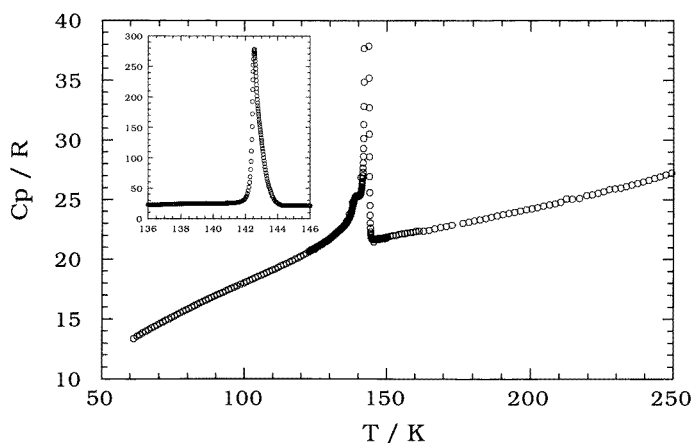


Figure 2. The specific heat of TMMB measured by adiabatic calorimetry. Dots represent the experimental points. Only some of them have been plotted for clarity. Both pulse and thermogram techniques have been used. The inset shows the total specific heat curve around the phase transition.

found between 60 and 340 K. As usual, various heating thermograms were performed in the proximity of the phase transition, in order to obtain a better definition of the specific heat curve in this temperature range. The shape of the curves is dependent on the thermogram rates, the peak being slightly displaced when it is increased. However, rates below $0.5\text{ }^\circ\text{C h}^{-1}$ lead to reproducible curves within the limits of the experimental accuracy. The apparent sharpness of the peak indicates again the first order nature of this phase transition. A very small anomaly, reproducible in all the experiments, was also found at 139.0 K. However, no reference to a possible new phase transition is found in the literature.

The baseline required to separate the phase transition specific heat and the corresponding thermodynamic functions from the remaining contribution of the crystal lattice can be constructed by different procedures depending on the available experimental information. In some previous works (see for example [20]) the harmonic and anharmonic contributions to C_p

were determined from group theory, by using spectroscopic, elastic and expansivity data, but, unfortunately, this information is not available for TMMB. However, the experimental specific heat of this crystal, with exception made of the temperature range where the phase transition takes place, attains similar values to those of the isomorphous cadmium compound (TMCB), as can be seen in figure 3. As the lattice contribution of this last crystal was calculated in a previous work [19], a common baseline can be used for both compounds, only with small corrections based on a corresponding states law. A temperature scaling factor of 1.12 fits quite well this baseline to the TMMB specific heat at both sides of the peak. Similar results for the specific heat of isomorphous compounds of this family are also found in the chloride crystals TMCC and TMMC [20]. Finally, the phase transition enthalpy and entropy were calculated as usual by numerical integration after subtraction of the baseline values from the experimental specific heat. These values are:

$$T_c = 142.55 \text{ K}$$

$$\Delta H = 218 \text{ R K}$$

$$\Delta S = 1.58 \text{ R.}$$

The high value for the entropy, although lower than in the case of TMCB ($\Delta S = 2.18 \text{ R}$), is the one expected for an order–disorder phase transition, through which the tetramethylammonium groups attain the disordered state in the high temperature hexagonal phase. This is a fact established in the remaining isomorphous compounds by using various experimental techniques. However, discrepancies appear when a correct interpretation of the disordered state is attempted. In fact, the number of possible reorientations of the organic groups and the theoretical models used for the description of the physical mechanisms of these phase transitions are still under discussion [19, 20]. Two-, three- or six-well Frenkel models have been used [25, 26], but up to now, the main features of the disordered state are still unclear. Of course, the axial structure of these crystals plays an outstanding role in the progressive disorder of the TMA groups when the temperature is increased. As expected, the linear thermal expansion of TMMB in the plane perpendicular to the hexagonal axis (a , b) is found to be higher than along the axis itself. In the hexagonal phase, the three quantities are nearly temperature constant with $\alpha_a = \alpha_b \approx 3.4\alpha_c$ [8]. This represents an increase of about 0.8% for the cell dimensions a and b , from the low temperature phase to room temperature (but only 0.27% for c). As a consequence, the main effect of the thermal expansion is to separate the inorganic chains as temperature increases, favouring the tetramethylammonium reorientations.

The phase transition entropy values for the two chloride crystals are quite similar, 0.99 R for TMCC and 1.02 R for TMMC, and suggest three independent orientations for the TMA groups. However, the higher phase transition temperature together with the different entropy values found for the bromide crystals imply that the inorganic octahedra also play an active role in the transition mechanisms. As concerns TMMB, the lack of any additional experimental information, specially the doubtful symmetry assignment for the low temperature phase which up to now is not firmly established, excludes a detailed study of this phase transition, even its description by the usual phenomenological models.

As direct spectroscopic information about the TMMB crystal is not available, an accurate calculation of the harmonic contribution to the specific heat is impossible. However, the good fit of the normal lattice specific heat of both bromide compounds TMMB and TMCB [19], shown in figure 3, suggests a similar frequency spectrum for the normal vibrational modes in both compounds. The harmonic specific heat (C_v) and hence the anharmonic contribution to C_p estimated for TMCB probably applies also well to TMMB, and estimates of the Gruneisen parameter and the isothermal compressibility could be made.

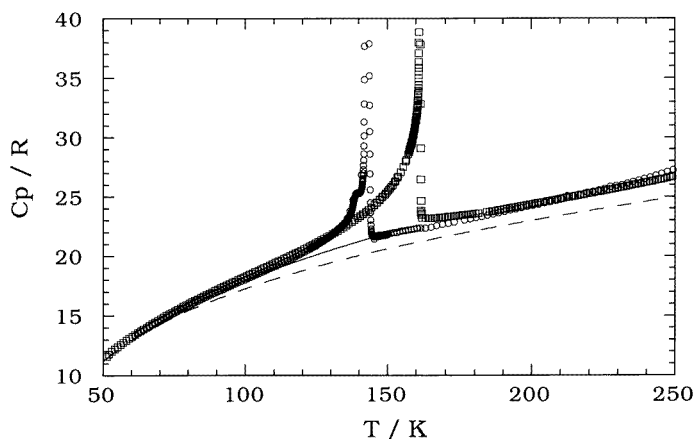


Figure 3. The specific heat of TMMB (○) and TMCB (□). The continuous curve is the baseline assigned to TMMB, obtained by means of a corresponding states law (see text). The dashed line is the TMCB harmonic specific heat, calculated from the frequencies of the vibrational spectrum.

Relative values of the sample thermal diffusivity of the crystal as a function of temperature can also be obtained when the conventional pulse method is used. The automatic data acquisition permits to measure the thermal relaxation of the sample + calorimetric vessel after each heating period. The temperature–time curves obtained after each heating pulse are found to fit quite well an empirical relaxation law with two independent relaxation times respectively associated with the sample vessel and the sample itself [22]. Although both parameters are dependent on the characteristics of the experimental set-up and avoid absolute results, the last one shows a relative increase of about 40% in the sample thermal diffusivity from the low temperature monoclinic phase to the high temperature hexagonal one.

Acknowledgments

This work was supported by the Universidad del País Vasco under projects UPV 063.310-EA139/95 and UPV 063.310-EB046/93. One of the authors (J Díaz-Hernández) gratefully acknowledges the Universidad Autónoma de Puebla (Mexico) and the financial support from the CONACYT-Mexico.

References

- [1] Stucky G D 1968 *Acta Crystallogr. B* **24** 330
- [2] Peercy P S and Morosin D 1971 *Phys. Lett. A* **36** 409
- [3] Peercy P S, Morosin D and Samara G A 1973 *Phys. Rev. B* **7** 3378
- [4] Mlik Y and Couzi M 1982 *J. Phys. C: Solid State Phys.* **15** 6891
- [5] Levola T and Laiho R 1988 *Solid State Commun.* **66** 557
- [6] Gesi K 1992 *Ferroelectrics* **137** 209
- [7] Foster J J and Gill N S 1968 *J. Chem. Soc. A* **3** 2625
- [8] Alcock N W and Holt S L 1978 *Acta Crystallogr. B* **34** 1970
- [9] Putnick C F, Garret B B and Holt S L 1976 *Inorg. Chem.* **15** 2135
- [10] Visser D 1986 *J. Magn. Magn. Mater.* **54/57** 1489
- [11] Tanaka H, Tsuruoka F, Ishii T, Izumi H, Iio K and Nagata K 1986 *J. Phys. Soc. Japan* **55** 3269
- [12] Visser D and McIntyre G J 1989 *Physica B* **156/157** 259
- [13] Gesi K 1996 *J. Phys. Soc. Japan* **65** 1297

- [14] Gesi K and Osaka T 1995 *Solid State Commun.* **95** 639
- [15] Teraoka S, Kambe T, Koido N, Hirai S and Nagata K 1995 *J. Magn. Magn. Mater.* **140–144** 1659
- [16] Peral I, Madariaga G, Pérez-Etxebarria A and Breczewski T *Acta Crystallogr. B* submitted
- [17] Mulla-Osman S, Michel D, Czaplá Z and Hoffmann W D 1998 *J. Phys.: Condens. Matter* **10** 2465
- [18] Dunn A G, Jewes M, Staveley L A K and Worswick R D 1983 *J. Chem. Thermodyn.* **15** 351
- [19] Aguirre-Zamalloa G, Igartua J M, Couzi M and López-Echarri A 1994 *J. Physique I* **4** 1237
- [20] Díaz-Hernández J, Aguirre-Zamalloa G, López-Echarri A, Ruiz-Larrea I, Breczewski T and Tello M J 1997 *J. Phys.: Condens. Matter* **9** 3399
- [21] López-Echarri A and Tello M J 1981 *J. Phys. D: Appl. Phys.* **14** 71
- [22] Zubillaga J, López-Echarri A and Tello M J 1985 *Thermochim. Acta* **92** 283
- [23] Igartua J M, Ruiz-Larrea I, Zubillaga J, López-Echarri A and Tello M J 1992 *Thermochim. Acta* **199** 35
- [24] Ruiz-Larrea I, López-Echarri A and Tello M J 1988 *Ferroelectrics* **79** 311
- [25] Jewes M 1982 *Acta Crystallogr. B* **38** 1418
- [26] Aguirre-Zamalloa G, Madariaga G, Couzi M and Breczewski T 1993 *Acta Crystallogr. B* **49** 691