THE SPECIFIC HEAT OF THE FERROELECTRIC PHASE TRANSITION IN N(CH₃)₄CdBr₃

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Abstract

The specific heat of N(CH₃)₄CdBr₃ from 50 to 300 K has been measured by adiabatic calorimetry, using both static and dynamic methods. The obtained results have permitted a careful study of the ferro-paraelectric phase transition the crystal shows at 160 K. The available spectroscopic data have been used to generate a reliable baseline which accounts for the normal lattice contribution to the specific heat. These results allow for an accurate estimation of the phase transition thermodynamic functions: $\Delta H = 2620$ J·mol^{-1} and $\Delta S = 18.04$ J·(mol°C)$^{-1}$. These high values are in agreement with the predictions of the 6 well potential Frenkel model.

Keywords: adiabatic calorimetry, ferroelectricity, phase transitions, specific heat

Introduction

The tetramethylammonium tetrabromocadmate, N(CH₃)₄CdBr₃ (TMCB for short) belongs to the well known family of N(CH₃)₄MX₃ crystals (M = Mn, Cd; X = Cl, Br). These compounds undergo a number of structural phase transitions leading to different ordering of the tetramethylammonium groups in the low temperature phases [1, 2]. Above 390K, TMCB shows a prototype disordered structure with space group P6₃/mmc and Z = 2, similar to that found in N(CH₃)₄MnCl₃ and N(CH₃)₄CdCl₃ [2, 4]. Below 390 K, the crystal belongs to the space group P6₁ /m, Z = 2, down to 160 K, where and additional phase transition leads to an ordered improper ferroelectric phase with space group P6₁–P6₅ and Z = 6 [3].

In this paper we present the specific heat of TMCB from 50 to 340 K as a contribution for a more general study of the ferro-paraelectric phase transition around 160 K.

Experimental

The measurements have been performed on an automatic adiabatic calorimeter described previously [5, 6]. For this purpose, a calibrated copper vessel of about 30 cm^3, was used. The sample vessel was also filled with helium gas at low pressure to favour the thermal equilibrium after heating. Points have been obtained by the conventional pulse technique throughout the whole temperature range of measurements. Temperature steps of about 1.5°C were previously fixed by means of the computer program. In addition, continuous heating curves were also performed around 160 K. This technique permits a better definition of the specific heat curve around the phase transition temperature. Both procedures guarantee a 0.1% accuracy for the obtained C_p.

Results and discussion

The experimental results are shown in Fig. 1. The specific heat anomaly presents a neat first-order character with a sharp maximum of C_p as high 11750 J·(mol°C)$^{-1}$ at $T_c = 161.27 \pm 0.01$ K. This value has been obtained from a heating curve. This dynamic technique usually shifts the C_p values and precludes a precise determination of the phase transition temperature. However, in the present case, the temperature heating rate around T_c went down to 0.02 °C/h, due to the very high values of C_p. In these conditions, the accuracy of the T_c value approaches the calibration of the platinum resistance thermometer (1 mK). This result agrees with previous DSC measurements [3], showing that the thermal hysteresis does not exceed 1 K, but is somewhat at odds with that of Gesi [7], who found $T_c = 156$ K.

In order to determine the excess thermodynamic functions associated with the phase transition, we have to establish carefully the regular lattice specific heat contribution (baseline). For this purpose we have adopted the procedure described in previous works [8]. The harmonic contribution to the lattice specific heat has been identified with C_v, once the difference between constant volume and constant geometry is discarded.

This contribution has been established by means of the lattice mode frequencies obtained from Raman experiments on TMCB [9]. The frequencies of the Raman inactive modes have been estimated from data obtained from related compounds [8, 10, 11], specially those concerning the high frequency internal modes of the tetramethylammonium group. These high frequency modes are only weakly coupled with the lattice external modes and do not present noticeable changes among the various crystals [8]. The lattice contribution of these optical modes was obtained by means of Einstein functions, weighted by the corresponding degeneracies. On the other hand, the contribution of the acoustic

modes was calculated by a Debye function with a Debye characteristic frequency: $\nu_D = 50$ cm^{-1}, as estimated from the Raman spectra and from the dispersion curves in TMCB. It has been shown that the contribution of these modes attains their classical saturation values at relatively low temperatures. As a consequence, they do not practically affect the shape of the specific heat curve above 50 K. In fact, the behaviour of C_p from 100 to 300 K is mainly governed by the vibrational modes with frequencies between 100 and 1500 cm^{-1}, which were well determined.
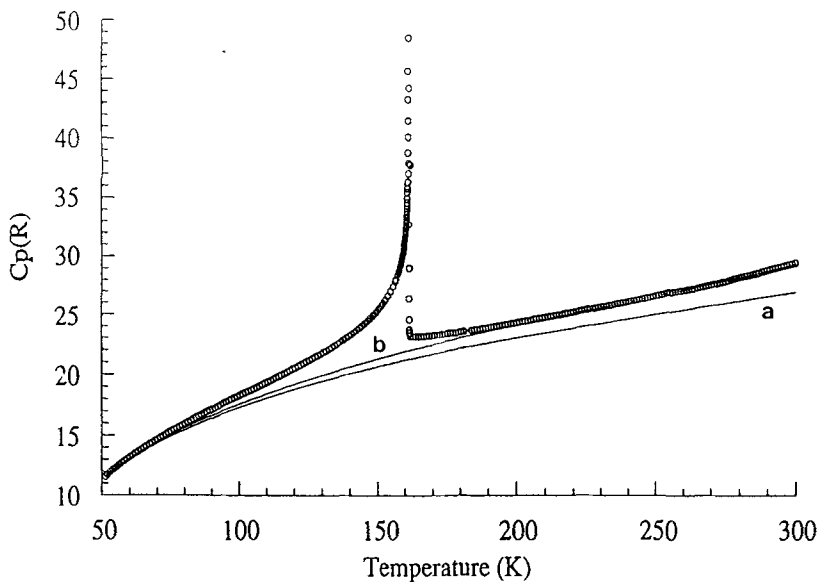

Fig. 1 The specific heat of TMCB around the ferroparaelectric phase transition. Dots are the experimental points. The baseline (b) has been established from both the harmonic (a) and anharmonic contributions to the specific heat

Due to the lack of elastic and thermal expansivity data, which would permitted an accurate determination of the anharmonic contribution to the specific heat, we have used the approximation of the well known Nernst-Lindemann law for solid substances [12].

$$C_p - C_v = aTC_p^2 \qquad (1)$$

where a is related with the isobaric expansivity and with the isothermal compressibility. This factor is known to be practically temperature independent. This law permitted an easy empirical calculation of the anharmonic contribution to C_p. The best fit was obtained for $a = 1.11 \times 10^{-7}$ J^{-1}·mol. The baseline

calculated in this way is shown in Fig. 1, line (b); it matches the experimental points on both sides of the transition anomaly quite well.

The excess specific heat ΔC_p, can be readily figured out by substracting the baseline to the measured C_p. By means of a numerical integration of ΔC_p and $\Delta C_p /T$ respectively, we have obtained the following values for the phase transition thermodynamic functions:

$$\Delta H = 2620 \text{ J/mol}$$

$$\Delta S = 18.04 \text{ J/mol·K}$$

The errors to be assigned to these quantities should be briefly discussed. First of all, the numerical integration shows that up to 30% of both values appears in a very small temperature range (0.25°C) around the transition temperature. Due to the extremely high values of C_p in this range, one could expect high induced errors for ΔH and ΔS. However, we can affirm that they do not arise from the specific heat measurements errors, nor from the subsequent numerical integration. This conclusion is sustained by an independent and direct enthalpy measurements (enthalpymetry). This has been done by a continuous heating of the sample under adiabatic conditions from 50 to 240 K. The instantaneous electrical power supplied to the sample was carefully measured every 20 seconds during the whole heating period (about 6 h) and permitted a direct determination of the total enthalpy. Two of these enthalpymetries were performed, leading to the following values for the phase transition enthalpy: 2616 J/mol and 2611 J/mol, showing differences well below 0.5% when compared with the integrated C_p values. These results lead to the conclusion that the enthalpy and entropy errors do not significantly arise from the experiments themselves, but rather come from the baseline selection, and more specifically from the anharmonic term. Slight variations of the "a" constant in the Nernst-Lindemann law, compatible with the specific heat error above T_c, also limits both errors to below 1%. However, we should stress the empirical character of this law as the main responsible for noticeable ambiguities in the phase transition thermodynamic functions. Indeed, once different attempts in estimating reasonable anharmonic contributions to C_p have been done (for instance, if we assume a linear increase of the anharmonic contribution to C_p as temperature increases), it turns out that the reported ΔH and ΔS values could be overestimated by 5%.

It should be noticed that a tail in the ΔC_p values vs. T curve, develops well above T_c, ending around 200 K. Given this large temperature range (40 K) together with the rather first order character of the phase transition, it seems to us unlikely to assign this phenomenon to critical fluctuations of the order parameter. In fact, similar behaviour has already been reported in a number of

ferroelectric or ferroelastic materials and is commonly assigned to crystal inhomogeneities of various kind.

Although probably overestimated, the reported entropy value for this phase transition accounts for its order-disorder character. In fact this value approaches the prediction of the so-called 6W Frenkel microscopic model [13] which accounts for a reorientational ordering of the tetramethylammonium groups in a 6-well potential ($\Delta S = R\ln 6$).

Further studies which will include Raman experiments performed on TMCB together with a description of this phase transition within the frame of the Landau Theory, will be published elsewhere [9].

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Zusammenfassung — Unter Einsatz sowohl dynamischer als auch statischer Methoden wurde mittels adiabatischer Kalorimetrie die spezifische Wärme von $N(CH_3)_4CdBr_3$ zwischen 50 und 300 K gemessen. Die erhaltenen Resultate erlaubten eine behutsame Untersuchung der ferroparaelektrischen Phasenumwandlung, die das Kristall bei 160 K aufweist. Die zur Verfügung stehenden spektroskopischen Angaben wurden benutzt, um eine zuverlässige Basislinie zu erhalten, welche den normalen Gitterbeitrag zur spezifischen Wärme berücksichtigt. Diese Resultate erlauben eine genaue Schätzung der thermodynamischen Funktionen der Phasenumwandlung: $\Delta H = 2620$ J·mol^{-1} und $\Delta S = 18.04$ J·(mol°C)$^{-1}$. Diese hohen Werte stimmen mit den Vorhersagen der 6 besten Frenkel'schen Modelle überein.