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# Specific heat and thermodynamic functions for $\text{Cs}_2\text{CdBr}_4$ phase transitions

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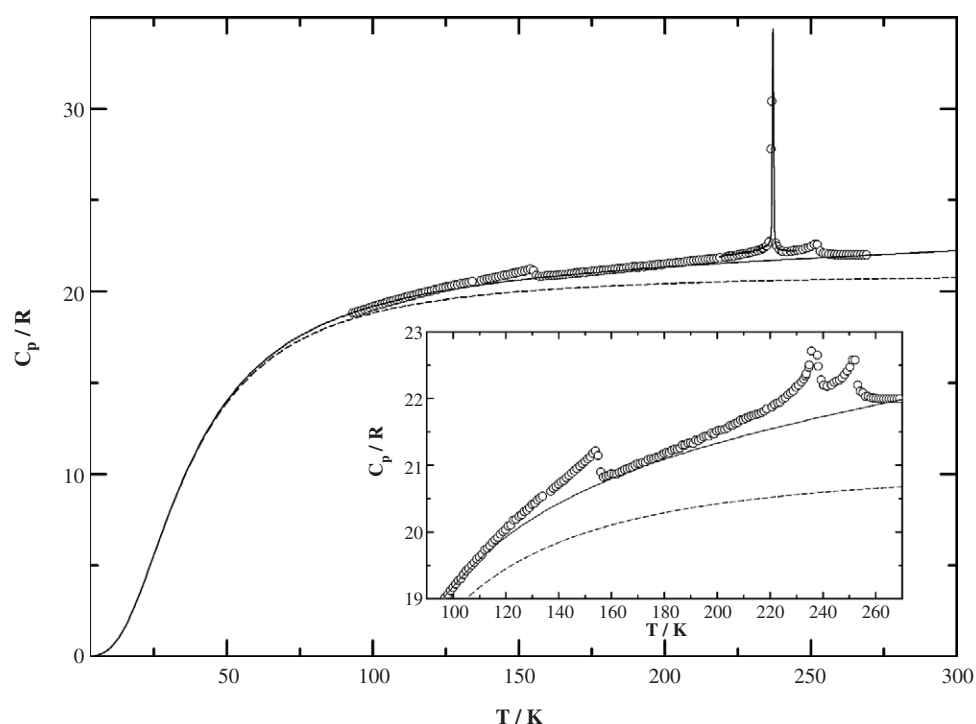
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## Abstract

Adiabatic calorimetry measurements have been performed on  $\text{Cs}_2\text{CdBr}_4$  from 90 to 270 K. Phase transitions at 252.03, 237.02, and 154.88 K were found. The thermal expansion coefficients and the elastic constant values were used to separate the harmonic and anharmonic contributions to the specific heat, which permitted us to establish a baseline for the precise determination of the thermodynamic functions associated with the phase transitions. Anharmonic quantities, such as the Grüneisen parameter and the isothermal compressibility, were also calculated. Finally, no experimental evidence of the suggested transitions at 208 and 130 K was found.

## 1. Introduction

$\text{Cs}_2\text{CdBr}_4$  belongs to the widely studied family of  $\text{A}_2\text{BX}_4$  compounds [1–5]. Many of them show an orthorhombic phase at room temperature and exhibit successive structural phase transitions at lower temperatures. Incommensurate phases are also commonly present. For this crystal, the incommensurability was first suggested by Altermatt *et al* [6] and confirmed by Plesko *et al* [1]. The space group symmetry of  $\text{Cs}_2\text{CdBr}_4$  was found to be  $Pnma$  at room temperature [6]. Below 252 K, the incommensurate phase with superspace group  $Pnma(\alpha, 0, 0)\bar{1}SS$  [7] is stable down to 237 K, where the lock-in phase transition in the centre of the Brillouin zone takes place. This ferroelastic commensurate phase with space group  $P2_1/n$  [1] undergoes another phase transition at 156 K. Below this temperature the crystal shows a monoclinic phase with space group  $P\bar{1}$  ( $Z = 4$  in all phases) [8, 9]. This phase transition sequence and the physical properties of the various phases have been studied by means of different experimental techniques which include dilatometry [10], dielectric [8, 10], NQR [11, 12], Raman scattering [13, 14], ultrasonic [15, 16], and x-ray diffraction [6, 7, 9, 17] approaches.



**Figure 1.** Specific heat measurements on  $\text{Cs}_2\text{CdBr}_4$  by adiabatic calorimetry using the pulse method from 90 to 270 K. One dynamical thermogram around the lock-in phase transition at 237 K is plotted. The harmonic approximation (dashed line) and the harmonic + anharmonic contribution (continuous line) are also shown. Details of these quantities around the phase transition sequence can be appreciated in the inset.

Two additional phase transitions at 208 K [8] and 130 K [17] are still under discussion [10, 18]. More recently, the specific heat results obtained by AC calorimetry [19] have given some additional evidence for these new phase transitions.

The aim of this work is to characterize the phase transition sequence of this crystal in two main respects by means of adiabatic calorimetry. The first task is examining the presence of these suggested new phase transitions and, secondly, we intend to obtain reliable values for the specific heat and for the phase transition thermodynamic functions.

## 2. Experimental results

Single crystals of  $\text{Cs}_2\text{CdBr}_4$  were obtained by the Bridgman method, using a stoichiometric mixture of  $\text{CsBr}$  and  $\text{CdBr}_2$ . The chemical analysis and the x-ray results confirmed the quality of the crystals, as cell parameters similar to those cited in the literature [6] were found at room temperature:  $a = 10.24 \text{ \AA}$ ,  $b = 7.95 \text{ \AA}$ , and  $c = 13.98 \text{ \AA}$ . The phase transition sequence of  $\text{Cs}_2\text{CdBr}_4$  has been studied by means of adiabatic calorimetry and dilatometric techniques. The specific heat was determined by means of an experimental installation described in [20]. The absolute temperature was measured by a Pt resistance thermometer calibrated from 4.2 to 370 K with a 1 mK resolution. The  $C_p$  accuracy is of about 0.1% throughout the temperature range from 10 to 350 K. Points were obtained by two different methods: the discontinuous pulse technique and dynamic heating thermograms. The best accuracy is attained by the first method,

whereas the second one is more appropriate for achieving a better resolution of the  $C_p$  curve around the phase transition peaks. Figure 1 shows the experimental results obtained by the first procedure in the 90–270 K temperature range, which covers the three main phase transitions previously reported. Peaks associated with these transformations are found at 252.03, 237.02, and 154.88 K, in agreement with previous results [1], and are associated with the  $Pnma$ –incommensurate ( $Pnma(\alpha, 0, 0)\bar{1}SS$ )– $P2_1/n$  (lock-in)– $P\bar{1}$  sequence. From the shape of the  $C_p$  curve, a second-order character should be assigned to the  $Pnma$ –Inc. and to  $P2_1/n$ – $P\bar{1}$  transitions, whereas the lock-in phase transition shows a first-order character.

Dynamic thermograms were also taken around the phase transition temperature ranges. Low heating rates of about 1 K h<sup>−1</sup> lead to a better resolution of the specific heat curve around the peaks and allow us to determine the three anomalies clearly. In particular, the thermogram around the lock-in transition at 237 K is plotted in figure 1. Special care has been taken in the measurements around 208 and 130 K, where two additional phase transitions were suggested to take place, but the various thermograms performed showed no anomalies within the experimental resolution.

Finally, dilatometric measurements were performed from 120 to 310 K along the three crystallographic axes. A thermal hysteresis of about 5 °C for the lock-in phase transition is observed, but no similar effect was found for the remaining phase transitions. These results confirm the order characters of the three phase transitions suggested by the calorimetric results. The thermal expansivity coefficients obtained at room temperature are:  $\alpha_1 = 3.15 \times 10^{-5} \text{ K}^{-1}$ ,  $\alpha_2 = 7.00 \times 10^{-5} \text{ K}^{-1}$ , and  $\alpha_3 = 3.75 \times 10^{-5} \text{ K}^{-1}$ , which are in very good agreement with the dilatometric data previously reported [10].

### 3. Discussion

The thermodynamic functions, such as the enthalpy and entropy associated with the respective phase transition mechanisms, are usually obtained from the specific heat of the materials by a previous subtraction of a conventional baseline, which accounts for the estimated normal lattice contribution to this quantity. The calculation of this baseline can be accomplished in two steps. The first one is an estimation of the specific heat at fixed strain ( $C_\varepsilon$ ) in the harmonic approximation, which in a first approach can be identified with the specific heat at constant volume ( $C_v$ ). Secondly, the anharmonic contribution to the specific heat can be calculated from the thermodynamic relation [21]

$$C_\sigma - C_\varepsilon = TVC_{ijkl}\alpha_{ij}\alpha_{kl} \quad (1)$$

where  $C_\sigma$  is the specific heat at constant stress (or  $C_p$ ),  $T$  is the absolute temperature, and  $V$  is the molar volume.  $C_{ijkl}$  are the elastic constants and  $\alpha_{ij}$  the thermal expansion coefficients.

As can be seen in previous works [22, 23] the harmonic specific heat can be obtained from the vibrational spectrum using both Debye and Einstein functions for the acoustic and optical modes respectively. The requirements are a precise knowledge of all the normal mode frequencies and even their temperature evolution. In our case only some mode frequencies of Cs<sub>2</sub>CdBr<sub>4</sub> obtained from Raman and infrared spectroscopies are available in the literature [13, 14, 18], and up to now no neutron diffraction data have been reported. More recently, Shchur *et al* [24] reported normal mode data frequencies obtained by model calculations. One of the main characteristics of the Cs<sub>2</sub>CdBr<sub>4</sub> vibrational spectrum is the very low frequency values of the normal modes, both the ones obtained from the spectroscopic data and those from the calculations. The highest frequency is 210 cm<sup>−1</sup>. These results are a direct consequence of the high masses of the ions involved. In this situation we are not able to separate the internal modes of the CdBr<sub>4</sub> tetrahedra from the atomic displacements of this group

(rotation and translations) and from the Cs atomic translations. This approach has been useful for some other compounds [23, 25] but is not allowed in this case due to the high coupling of these two sets of crystal vibrations. On the other hand, this close grouping of the crystal mode frequencies in the low part of the spectrum suggests that a simple Debye model, which is not adequate for a precise description of the harmonic specific heat when high frequency optical modes are present, could be a reasonable approach for this compound. In agreement with the spectroscopic data, our experimental  $C_p$  curve shows a very flat shape from 90 to 270 K, the specific heat values increasing to a mere 15% in this range. This is a clear consequence of the low frequencies present in the crystal vibrational spectrum, as the contribution of such modes to the specific heat attains the classical saturated values at low temperatures. In this situation, an empirical selection of a Debye function with a characteristic temperature  $\theta_D = 150$  K has been found sufficient for a good description of the harmonic specific heat over the whole temperature range. As can be seen in figure 1 (dashed line), it approximates quite well the experimental curve at 90 K, where a very low anharmonic contribution is expected. It also shows a good agreement with the experimental  $C_p$  at room temperature after subtracting this contribution (see below). In fact, the harmonic specific heat at this temperature practically attains the saturated value of  $21 R$ , expected for a seven-atom molecule. Here  $R$  is the ideal gas constant ( $R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$ ).

The anharmonic contribution at  $T = 270$  K was calculated from the measured values for the nine independent elastic constants in the  $Pnma$  phase [15] together with the thermal expansion coefficient values obtained and a molar volume  $V = 1.714 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ , by using equation (1). This contribution is  $C_p - C_v = 1.12 R$  which represents a reasonable 5% of  $C_p$ . In previous works [22, 25] the decreasing of this contribution for lower temperatures is well described by the empirical Nernst–Lindemann law:

$$C_p - C_v = aTC_p^2 \quad (2)$$

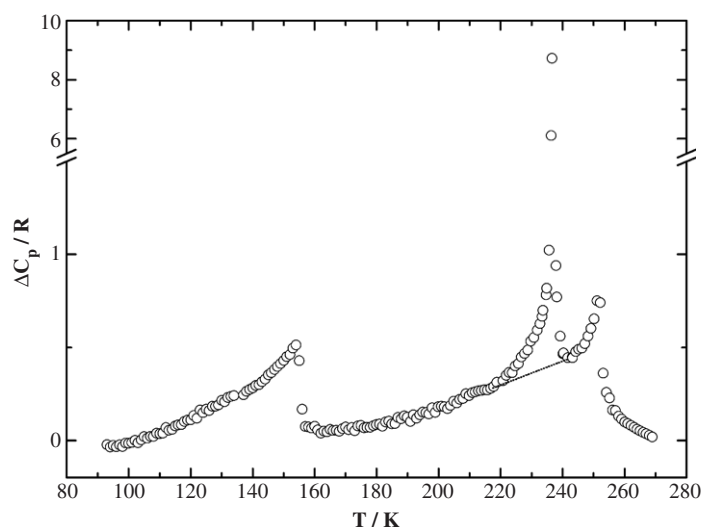
where

$$a = TVC_{ijkl}\alpha_{ij}\alpha_{kl}/C_p^2T \quad (3)$$

is found to be constant over a wide temperature range. Using the experimental values at room temperature in equation (3) we obtain  $a = 8.543 \times 10^{-6} R^{-1} \text{ K}^{-1}$ . This result can be used to obtain the isothermal compressibility  $k_T = V\alpha^2/aC_p^2 = 9.64 \times 10^{-11} \text{ Pa}^{-1}$  and the Grüneisen parameter  $\Gamma = \alpha V/k_T C_v = 1.48$  at room temperature. Here  $\alpha$  is the volume compressibility:  $\alpha = \alpha_1 + \alpha_2 + \alpha_3$ . A more direct way to calculate the isothermal compressibility from the elastic stiffness ( $s_{ij}$ ) values obtained from [15] leads to a very similar value  $k_T = \sum_{i,j=1}^3 s_{ij} = 9.89 \times 10^{-11} \text{ Pa}^{-1}$ .

However, a slightly different value for the constant in equation (3):  $a = 9.98 \times 10^{-6} R^{-1} \text{ K}^{-1}$ , permits a better approach for the anharmonic contribution as it provides the best fit to the experimental data from 90 to 270 K. It should be noted that discrepancies of about 15% are found for this constant when using different experimental expansivity data [10]. On the other hand, the lack of a complete set of elastic constant values for the various crystal phases prevents a precise calculation of the anharmonic contribution by using equation (1) and compels us to make use of the empirical Nernst–Lindemann approach. Within this approximation, a good baseline (figure 1) representing the normal lattice specific heat is obtained which, by subtraction from the  $C_p$  experimental values, permits a reliable determination of the specific heat excess associated with the phase transition sequence. This result is shown in figure 2.

As found for other related compounds of the  $A_2BX_4$  family with incommensurate phases [26, 27], the calorimetric signal associated with the lock-in phase transition appears superimposed on the second-order specific heat peak of the  $Pnma$  incommensurate phase



**Figure 2.** The phase transition specific heat of Cs<sub>2</sub>CdBr<sub>4</sub>, obtained by subtraction of the baseline plotted in figure 1. The dashed line represents the linear extrapolation used to calculate the thermodynamic functions of the lock-in phase transition.

**Table 1.** Thermodynamic functions of Cs<sub>2</sub>CdBr<sub>4</sub> phase transitions.

	$T$ (K)	$\Delta H$ (R K)	$\Delta S$ (R)
$T_1$	252.03	$25 \pm 3$	$0.110 \pm 0.015$
$T_2$	237.02	$11 \pm 1$	$0.047 \pm 0.003$
$T_3$	154.88	$11 \pm 1$	$0.082 \pm 0.007$

transition, the calorimetric contribution of which extends well down to the nominal transition temperature. A final empirical deconvolution was attained by a simple linear extrapolation (dashed line). After subtraction of the baselines, the enthalpy and entropy excesses are determined by means of a numerical integration of the experimental  $C_p$  using the expressions

$$\Delta H = \int C_p dt \quad \Delta S = \int \frac{C_p}{T} dt. \quad (4)$$

The results for the phase transition thermodynamic values are shown in table 1.

These values are lower than those reported in [19] where the authors point out the difficulties of the AC calorimetric technique for absolute value determinations of  $C_p$ . In fact, this last quantity attains 53  $R$  at 270 K in the cited work, whereas in our case a more reasonable value of 22  $R$  is found at this temperature.

In contrast with the extremely low entropy of the lock-in phase transitions exhibited by many of A<sub>2</sub>BX<sub>4</sub> crystals, the high value  $\Delta S = 0.05 R$  found for this crystal is explained by the correspondingly higher jump of the wavevector just at the transition temperature. It should be pointed out that a good correspondence is usually obtained for both quantities in other incommensurate compounds [28].

As regards the suggested phase transitions at 130 and 208 K, two small calorimetric signals have been recently reported [19]. However, these results are not reproducible and do not permit any definitive conclusions. In our case, the specific heat curve also shows some irregularities around these temperatures (see figure 2), although they lie within the limits of the experimental

resolution. Approximate calculations for the possible phase transitions limit their enthalpy values to  $\Delta H(130) < 0.07 R$  and  $\Delta H(208) < 0.10 R$  respectively.

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