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# Specific heat study and Landau analysis of the phase transition in $\text{PbTiO}_3$ single crystals

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## Abstract

The specific heat of pure lead titanate ( $\text{PbTiO}_3$ ) crystals grown by the float-zone method is reported at temperatures of 325–1250 K. The excess specific heat associated with the ferroelectric phase transition was analysed using a 2–4–6 Landau potential to self-consistently determine the Curie–Weiss temperature, the  $m3m \leftrightarrow 4mm$  transition points, the total transition enthalpy, as well as the latent heat and entropy discontinuity at the first-order phase change. The temperature ranges over which various excess thermodynamic quantities obeyed the mean-field predictions of the Landau theory were investigated. The coefficients of the Landau potential were also determined, and the results compared to corresponding measurements made on pure polycrystalline lead titanate specimens. The implications of the results with respect to prior discrepancies reported for the first-order character of the phase transition in lead titanate crystals are discussed.

## 1. Introduction

The discovery of ultrahigh piezoelectric coefficients and electromechanical coupling factors in multi-domain crystals of  $\text{PbTiO}_3$  in solid solution with the complex perovskite compounds  $\text{Pb}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$  (where  $\text{B}' = \text{Mg}$  or  $\text{Zn}$ ,  $\text{B}'' = \text{Nb}$ ) has stimulated renewed interest in the fundamental aspects of phase transitions and structure–property relations in Pb-based ferroelectric single crystals [1]. The tetragonal ( $P4mm$ ) compound  $\text{PbTiO}_3$  has long been regarded as an archetypal representative of this large family of oxygen octahedra ferroelectrics and exhibits a high transition temperature ( $T_t = 763 \pm 5$  K) and an unusually large spontaneous strain (tetragonal axial ratio  $c/a = 1.065$ ) at room temperature [2]. A number of studies

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have examined the dielectric properties of  $\text{PbTiO}_3$  single crystals as functions of temperature and pressure [3–7], yet inconsistencies remain concerning the thermodynamic parameters characterizing the first-order nature of the  $m3m \leftrightarrow 4mm$  phase change. For example, the Curie–Weiss constant has been variously reported to be in the range of  $C_{\text{cw}} \sim 1.1 \times 10^5$ – $4.1 \times 10^5$  K, and the Curie–Weiss temperature to be in the range  $T_0 \sim 715$ – $758$  K. Consequently, if the difference ( $T_t - T_0$ ) is taken as a measure of the first-order character of the phase change, then the observed value of this quantity varies quite substantially, by as much as 45 K.

Although there are several reports of the dielectric [3–7], soft-mode [8], structural [2, 9, 10], and elastic properties [11] of  $\text{PbTiO}_3$  single crystals, the behaviour of the specific heat has not been investigated in detail. Early studies carried out to measure heat capacity and estimate transition energies were performed on ceramic specimens [12] while subsequent measurements on flux-grown single crystals made using adiabatic calorimetry [13] and AC calorimetry [4] were not suitable for quantitative analysis. In determining the thermodynamic parameters characterizing the phase transition in lead titanate, detailed studies of the specific heat have several advantages. The specific heat integrates over all contributions to the free energy occurring on the timescale of the measurement. These contributions include not only the thermal evolution of the order parameter (i.e. the spontaneous polarization) but also contributions arising from coupling with other possible relaxations of the structure. Also, from specific heat measurements alone it is possible to determine the Curie–Weiss temperature and locations of phase equilibrium points, and to obtain the total transition enthalpy, the latent heat, and the entropy discontinuity at the first-order phase change [14]. Deviations of the observed behaviour of the specific heat and excess entropy from the mean-field predictions of the Landau theory, which may be influenced by lattice imperfections, strain inhomogeneities, etc, can then be readily assessed.

The lack of complete thermophysical data for  $\text{PbTiO}_3$  crystals is attributable at least in part to the difficulty encountered in growing large single crystal specimens without additives. Crystals of sizes suitable for property measurements have invariably been grown from KF or PbO fluxes and the resulting crystals have contained significant impurities, from the flux, that may alter the properties of the pure material. Flux-grown crystals become conductive at elevated temperatures and so have been doped with charge compensators such as  $\text{U}^{3+}$  to enhance resistivity and enable more reliable dielectric measurements [4, 6]. Alternatively, stoichiometric  $\text{PbTiO}_3$  powders with high chemical and phase purity can be readily obtained by a variety of chemical methods. To circumvent problems associated with crystal growth, lattice parameter [15, 16] and specific heat [16] measurements carried out on well-crystallized sol–gel derived powders have been more recently used to indirectly deduce the single crystal properties from the appropriate thermodynamic relations involving these quantities. Although self-consistent agreement between independent property estimates has been obtained from these studies, the inherent uncertainties in the elastic boundary conditions in polycrystalline specimens, which may vary with crystallite size, shape, and distribution, have been shown to significantly influence the behaviour of the specific heat in  $\text{PbTiO}_3$  powders with crystallites in the sub-micron size range [17].

We have recently grown millimetre-sized  $\text{PbTiO}_3$  crystals without additives by the containerless float-zone method and have characterized their chemical, microstructural, and dielectric properties [18]. In this communication we report an analysis of the specific heat measured for these crystals by high temperature differential scanning calorimetry. In particular, we compute the excess specific heat associated with the  $m3m \leftrightarrow 4mm$  phase transition and interpret the results using a 2–4–6 Landau potential. The temperature range of validity of the mean-field theory near the first-order phase change is investigated. Excess thermodynamic

quantities describing the phase change are estimated and compared to corresponding data obtained on pure polycrystalline lead titanate specimens. The implications of the results with respect to the discrepancies concerning the first-order nature of the phase change as observed in prior dielectric studies of flux-grown crystals are discussed.

## 2. Materials and methods

The crystals used in this study were grown by the float-zone method, the details of which have been reported previously [18]. Briefly, the growth procedure consisted of heating 99.9% pure ceramic PbTiO<sub>3</sub> feed rods in a pure oxygen atmosphere above the congruent melting temperature ( $T_m = 1563$  K). A single ellipsoid image furnace heated by 1.5–5.4 kW lamps was used with the growing crystal subject to combined specimen translation and rotation. Cylindrical single crystal specimens as large as 7 mm in length and 2 mm in diameter were obtained, though they invariably showed evidence of cracking during cooling through the phase change to room temperature. Electron probe microanalysis showed that the crystals were extremely uniform at these dimensions with the weight percentage of Pb varying by  $\pm 0.5\%$  and the weight percentages of Ti and O varying by  $\pm 0.2\%$ . The as-grown multi-domain crystals were somewhat deficient in Ti and O and had an average formula of  $\text{PbTi}_{1-\gamma}\text{O}_{3-\Delta}$  with  $\gamma \approx 0.015$  and  $\Delta \approx 0.375$ . X-ray powder diffraction patterns collected at room temperature for crushed crystals showed no second phases and the refined lattice parameters were  $a = 0.3901$ ,  $c = 0.4153$  nm and  $c/a = 1.0644$  as expected on the basis of prior single crystal studies [2, 9].

The specific heat ( $C_p$ ) measurements were made using a Netzsch (Burlington, MA, USA) STA 449C high temperature differential scanning calorimeter from 323 to 1273 K. The measurements were made under an air atmosphere flowing at 40 ml min<sup>-1</sup>. The data were acquired on heating in temperature intervals of 0.5 K using a scan rate of 20 K min<sup>-1</sup>. The PbTiO<sub>3</sub> specimen consisted of a single monolithic piece of crystal of mass  $42.07 \pm 0.01$  mg that was separated from the parent float-zone crystals and was placed in good thermal contact within covered Pt metal crucibles. Heat capacities of the specimen after calorimeter calibration were determined by subtracting the data acquired for the empty crucibles from data acquired on the crucibles plus sample.

The temperature calibration of the instrument was determined by measuring the melting points of a series of pure metal standards (In, Sn, Bi, Zn, Al, Ag, Au) that spanned the temperature range of interest (429–1337 K). Over this range of temperature the measured temperatures agreed with the known melting points of the metals to within  $\pm 1$  K without the need to apply any internal instrument correction factors. The calorimeter was calibrated for  $C_p$  from measurements made on a sapphire crystal and the calibration polynomial for the calorimeter was then computed from the standard reference data for synthetic sapphire (NIST Standard Reference Material, SRM 720). The reproducibility of the values of  $C_p$  obtained in successive runs made on the sapphire crystal was typically  $\pm 1\%$ . To estimate uncertainties in the computation of  $C_p$  for the PbTiO<sub>3</sub> specimen introduced by errors in specimen mass, specimen placement, and other experimental factors,  $C_p$  was again computed at temperatures of 323–1273 K from measurements made under identical conditions on a high purity  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> sample. These data were then compared against the sapphire reference data. The agreement of the measured values for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> sample with the standard reference values were typically  $\pm 1\%$  to  $\pm 2\%$  with a maximum deviation at the highest temperatures of approximately  $\pm 3\%$ . At temperatures near the expected phase transition temperature for PbTiO<sub>3</sub> (763 K) this corresponds to an uncertainty in  $C_p$  of  $\pm 2$  J mol<sup>-1</sup> K<sup>-1</sup>.

**Table 1.** Specific heat of single crystal PbTiO<sub>3</sub> at 325–1250 K.

$T$ (K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$T$ (K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )
325	115	770	140
375	117	800	124
425	120	850	124
475	122	900	124
525	124	950	125
575	126	1000	125
625	130	1050	125
675	135	1100	125
725	144	1150	128
750	158	1200	123
760	432	1250	122

### 3. Results and discussion

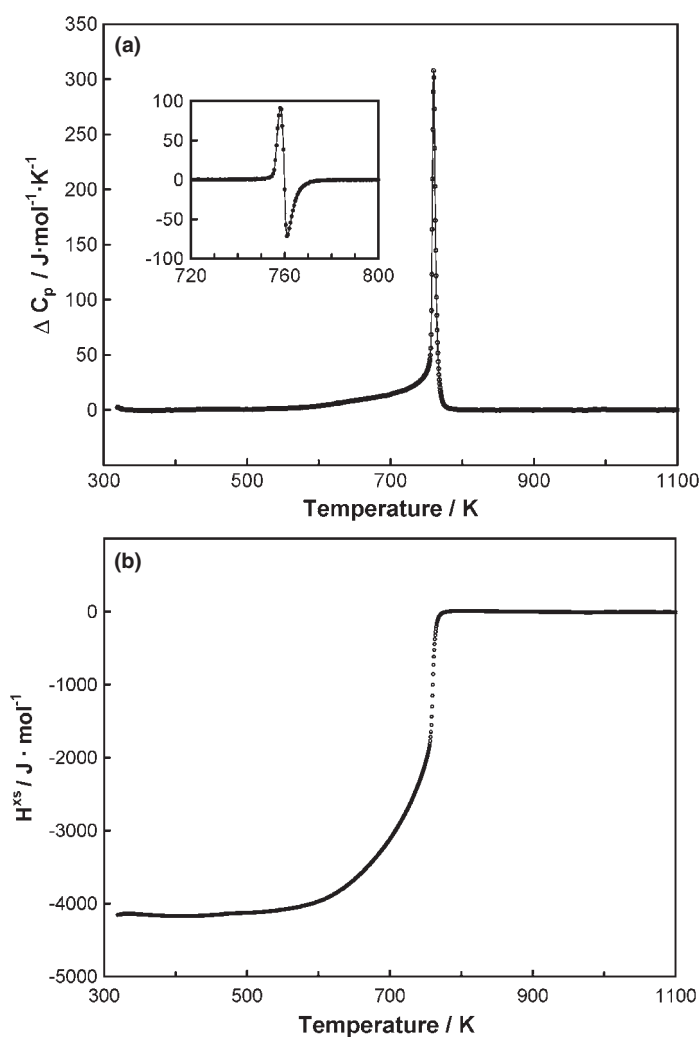
Table 1 reports the heat capacity measured at selected temperatures from 325 to 1250 K. In the tetragonal phase at temperatures of 325 to 750 K  $C_p$  increases monotonically from 115 to 158 J mol<sup>-1</sup> K<sup>-1</sup>. The peak near the phase change at 750–770 K is very large (>430 J mol<sup>-1</sup> K<sup>-1</sup>) and narrowly centred close to 760 K. In the cubic phase above 800 K the heat capacity is constant with an average value  $C_p(\text{cubic}) = 125$  J mol<sup>-1</sup> K<sup>-1</sup> with a standard deviation of  $\pm 1$  J mol<sup>-1</sup> K<sup>-1</sup> to temperatures as high as 1250 K. The average value of  $C_p(\text{cubic})$  is nearly identical to the classical Dulong–Petit limit,  $C_V \approx C_p = 3nk_B N_A = 124.7$  J mol<sup>-1</sup> K<sup>-1</sup>, where  $n = 5$  is the number of atoms per unit cell,  $k_B$  is Boltzmann's constant, and  $N_A$  is Avagadro's number. This same result was observed for micron-sized sol–gel derived powders [16] confirming that PbTiO<sub>3</sub> has the full equipartition density of vibrational modes in the cubic phase.

To obtain the excess specific heat a procedure similar to that described in [14] was adopted. The background or 'hard-mode' specific heat ( $C_p^0$ ) was estimated by extrapolating the data in high temperature phase at  $T \geq 800$  K to the data at  $T \leq 450$  K, where the soft-mode contributions are essentially frozen out, using a single fourth-order polynomial fit over the entire temperature range. The excess specific heat  $\Delta C_p = (C_p - C_p^0)$  was computed and is shown in figure 1(a). The inset of the figure shows the first derivative of the  $\Delta C_p(T)$  curve which exhibits two sharp extrema located near  $T_1 = 758$  K and  $T_2 = 762$  K. The excess enthalpy ( $H^{\text{XS}}$ ) and entropy ( $S^{\text{XS}}$ ) were determined by integration of  $\Delta C_p(T)$  with  $H^{\text{XS}} = \int \Delta C_p(T) dT$  and  $S^{\text{XS}} = \int [\Delta C_p(T)/T] dT$ . It is clear from figure 1(b) that the total energy of the  $m3m \leftrightarrow 4mm$  phase transition asymptotes to  $E = 4150$  J mol<sup>-1</sup> with an estimated uncertainty in the integration of  $\pm 50$  J mol<sup>-1</sup>.

To determine the values for the Curie–Weiss temperature  $T_0$  and the transition temperature  $T_t$  (i.e. the temperature at which the cubic and tetragonal phases are in thermodynamic equilibrium) the data in figure 1 were analysed using a conventional 2–4–6 Landau potential for the excess free energy, expanded in even powers of the dimensionless order parameter  $Q$ :

$$G^{\text{XS}} = A Q^2 + B Q^4 + C Q^6 \quad (1)$$

with  $A = A_0(T - T_0)$  where the prefactor  $A_0$  is related to the Curie–Weiss constant. The higher order coefficients  $B$  and  $C$  were assumed to be independent of temperature and for a proper ferroelectric of point symmetry  $4mm$  it is expected that the uniform spontaneous strain  $[(c/a) - 1] \propto Q^2$ . From equation (1) the excess entropy is  $S^{\text{XS}} = -(\delta G^{\text{XS}}/\delta T) = -A_0 Q^2$ . These relations may be rearranged in a form convenient for the analysis of the experimental



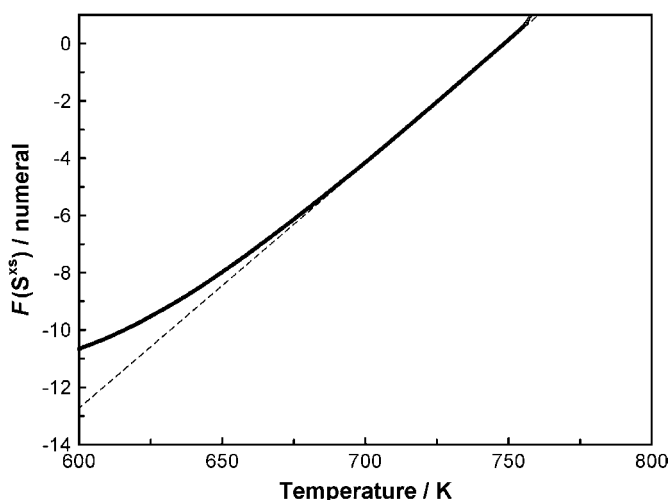
**Figure 1.** Plot of the excess specific heat (a) and excess enthalpy (b) of PbTiO<sub>3</sub> crystals as functions of temperature. The inset in (a) shows the first derivative of the excess specific heat versus temperature curve near the phase transition.

$S^{\text{XS}}$  data [14]:

$$F(S^{\text{XS}}) \equiv \frac{4}{3} \left\{ - \left[ \frac{3T_1 S^{\text{XS}}}{2L} - 1 \right]^2 + 1 \right\} = \frac{(T - T_0)}{(T_1 - T_0)} \quad (2)$$

where  $L$  is the latent heat at the first-order phase change and  $\Delta S^{\text{XS}}$  is the corresponding discontinuity in excess entropy,  $T_1 \Delta S^{\text{XS}} = L$ .

A plot of  $F(S^{\text{XS}})$  versus  $T$  gives  $T_0$  at  $F(S^{\text{XS}}) = 0$  and the slope is  $(T_1 - T_0)^{-1}$ , from which  $T_1$  may be obtained. The broad temperature range over which  $H^{\text{XS}}$  varies as shown figure 1(b) and the non-equilibrium nature of the scanning calorimetry experiment made the direct evaluation of  $L$  impractical. Rather than evaluating  $L$  using arbitrary integration limits on  $\Delta C_p(T)$ , which may result in a large error [14], we instead take  $L$  as the heat evolved above the temperature  $T_1$ . In the scanning experiment, this temperature defines the maximum



**Figure 2.** Plot of the function  $F(S^{XS})$  versus temperature (see equation (2)) for  $\text{PbTiO}_3$  crystals. The dashed line is a least squares fit ( $R^2 = 1$ ) to the data above 700 K. The intersection of the line at  $F(S^{XS}) = 0$  defines the Curie–Weiss temperature  $T_0 = (748 \pm 2)$  K.

rate of change of  $\Delta C_P$  with respect to  $T$  on heating and it is expected that  $T_1 \approx T_t$  at the scan rate used. At the temperature resolution of our measurements this procedure gave  $L = (1550 \pm 100)$  J mol $^{-1}$  and this value was inserted in equation (2).

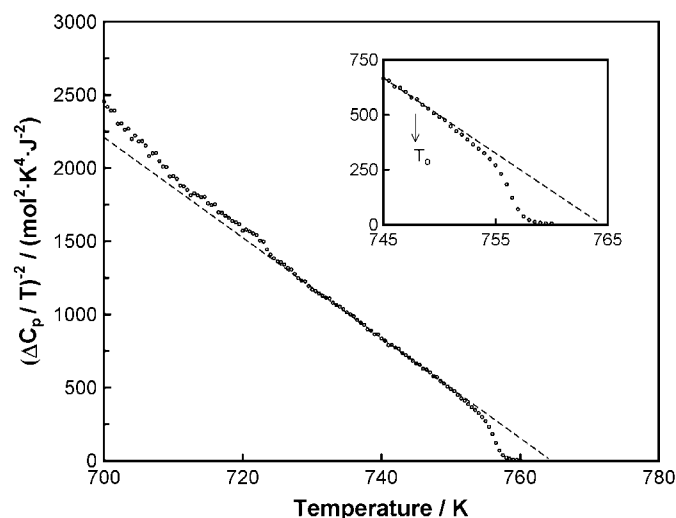
Figure 2 shows a plot of  $F(S^{XS})$  versus  $T$ . The data are well described by a straight line ( $R^2 = 1$ ) of slope  $0.086$  K $^{-1}$  above 700 K. From this line it was found that  $T_0 = (748 \pm 2)$  K,  $T_t = (760 \pm 2)$  K and  $(T_t - T_0) = (12 \pm 3)$  K. From  $T_t$  determined in this way we may compute the entropy discontinuity to be  $\Delta S^{XS} = (2.0 \pm 0.1)$  J mol $^{-1}$  K $^{-1}$ . Alternatively, for a first-order transition, it is possible to obtain two relations between the Landau coefficients in equation (1) directly from the heat capacity data by expressing the temperature dependence of  $\Delta C_P = T(\delta S^{XS}/\delta T)$  in the general form [14, 19]:

$$\left(\frac{\Delta C_P}{T}\right)^{-2} = \frac{4(B^2 - 3A'C)}{A_0^4} + \frac{12C}{A_0^3}(T_t - T) \quad (3)$$

where the first term defines the discontinuity in  $\Delta C_P$  at  $T_t$  and  $A' = A_0(T_t - T_0)$ . Equation (3) predicts that a plot of  $(\Delta C_P/T)^{-2}$  versus  $T$  is linear over some range of reduced temperature  $\tau = (T_t - T)/T_t$ . Figure 3 shows the plot constructed from the  $\Delta C_P$  data and it was found that equation (3) holds well ( $R^2 = 0.999$ ) over the interval  $\tau = 0.013$ – $0.049$ . This interval of  $\tau$  is somewhat smaller than expected as compared with other perovskite crystals with displacive transitions lying closer to a mean-field tricritical point [19]. The more strongly first-order character of the phase change in  $\text{PbTiO}_3$  makes equation (3) applicable only in the monophasic tetragonal state below  $T_0$  [20], as seen more clearly in the inset of the figure. However, extrapolation of the data in the linear range at  $730$  K  $\leq T \leq 750$  K to  $(\Delta C_P/T)^{-2} = 0$  gives  $T^* = (764 \pm 2)$  K in agreement with the relation [19]

$$T^* = \frac{(T_t - T_0)}{4} + T_t \quad (4)$$

where  $T^*$  is the highest temperature to which the tetragonal state will remain stable in the absence of an externally applied field. Consequently, we expect that the maximum temperature range of coexistence of the cubic and tetragonal states is  $(T^* - T_0) = (16 \pm 3)$  K, a finding that



**Figure 3.** Plot of the reciprocal of the square of the excess specific heat divided by temperature versus temperature (see equation (3)) for PbTiO<sub>3</sub> crystals. The dashed line is a least squares fit ( $R^2 = 0.999$ ) to the data at  $730 \text{ K} \leq T \leq 750 \text{ K}$ . The inset shows the deviation from linear behaviour at temperatures above the Curie–Weiss temperature of  $T_0 = (748 \pm 2) \text{ K}$ .

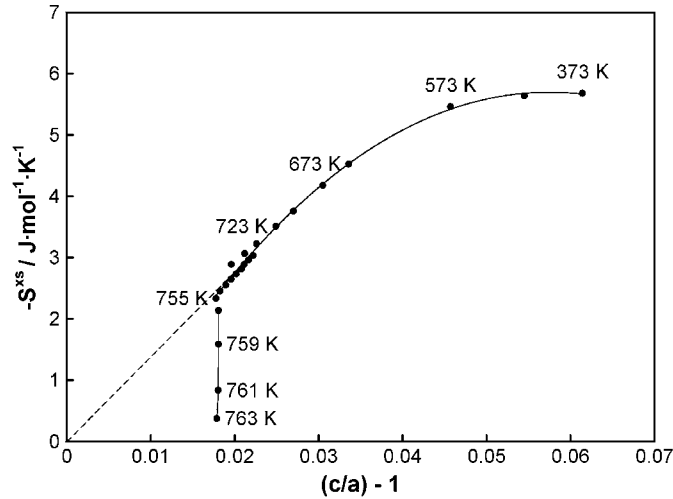
is in good agreement with direct observations of the symmetry changes made on polycrystalline specimens by high resolution x-ray diffraction [16].

The equation of the line shown in figure 3 has a slope  $-34 \text{ mol}^2 \text{ K}^3 \text{ J}^{-2}$  and we find by extrapolation that the first term in equation (3) is  $158 \text{ mol}^2 \text{ K}^4 \text{ J}^{-2}$  at  $T_t$ . From these values the coefficients  $B$  and  $C$  in equation (1) may be obtained if the value of  $A_0$  is known. Noting that the temperature dependence of the lattice parameters measured for polycrystalline and single crystal specimens are virtually identical [9, 15, 16]  $A_0$  may be determined from the expected proportionality  $[(c/a) - 1] \propto Q^2$  by plotting  $-S^{\text{XS}}$  as obtained here for PbTiO<sub>3</sub> single crystals versus  $(c/a) - 1$  as measured previously for polycrystalline specimens [16].

Such a plot is shown in figure 4 where it is seen that the curve is linear ( $R^2 = 0.979$ ) with slope  $A_0 = (138 \pm 4) \text{ J mol}^{-1} \text{ K}^{-1}$  at temperatures in the range 673–757 K when the fitted line is constrained to pass through the origin. The corresponding reduced temperature range over which the proportionality holds is then  $\tau = 0.006$ – $0.11$ . Over this temperature interval a plot of  $\log(-S^{\text{XS}}/Q^2)$  versus  $\log(\varepsilon)$  with  $\varepsilon = 1 - (T/T_0)$  has zero slope as expected for transitions showing classical mean-field Landau behaviour [21]. Also, using the values estimated for  $\Delta S^{\text{XS}}$  and  $A_0$  we may deduce that at  $T_t$  the discontinuity  $\Delta Q^2 \propto \Delta(c/a - 1) = (0.015 \pm 0.001)$ . Figure 4 shows that this is in fact the case with a constant measured value of  $\Delta(c/a - 1) = 0.018$  extending across the phase coexistence region. The reasonable agreement of the measured and derived values of  $\Delta Q^2$  validates the method used for approximating the latent heat  $L$  at  $T_1 \approx T_t$ . From the derived value of  $\Delta Q^2$ , the higher order Landau coefficients  $B = -2A'/\Delta Q^2$  and  $C = A'/\Delta Q^4$  may also be computed, and these compared well with those obtained directly from the parameters of the linear fit to equation (3).

The thermodynamic quantities characterizing the  $m3m \leftrightarrow 4mm$  phase transition in PbTiO<sub>3</sub> single crystals are summarized in table 2 together with the Landau coefficients determined as described above. In the prior studies of polycrystalline PbTiO<sub>3</sub> specimens [15, 16] the more common Landau–Devonshire (LD) form of equation (1) for proper ferroelectrics was used, i.e. the order parameter  $Q \equiv P_s$  is the zero-field spontaneous





**Figure 4.** Plot of the negative excess entropy versus uniform spontaneous strain for  $\text{PbTiO}_3$ . The excess entropy is the crystal result reported here. The spontaneous strain is the polycrystalline result reported in [16]. The dashed line is a least squares fit ( $R^2 = 0.979$ ) for data at  $673 \text{ K} \leq T \leq 757 \text{ K}$  and is constrained to pass through the origin. The data labels show selected measurement temperatures and the vertical line above  $757 \text{ K}$  defines the measured discontinuity in spontaneous strain  $\Delta(c/a) - 1 = 0.018$ .

polarization vector directed along the crystallographic  $c$ -axis:

$$G^{\text{LD}} = \alpha P_s^2 + \beta P_s^4 + \delta P_s^6. \quad (5)$$

The coefficients in equation (1) for  $G^{\text{XS}} (\text{J mol}^{-1})$  are related to those of equation (5) for  $G^{\text{LD}} (\text{J m}^{-3})$  by the factor  $(\rho_M q^n)$ , where  $\rho_M$  is the molar density ( $2.63 \times 10^4 \text{ mol m}^{-3}$  for  $\text{PbTiO}_3$ ),  $n = 1, 2, 3$  for the prefactors of  $Q^2$ ,  $Q^4$ , and  $Q^6$ , respectively, and  $q$  is assumed to be a temperature-independent electrostrictive coupling factor. If the value  $P_s = 0.75 \text{ C m}^{-2}$  for undoped flux-grown crystals is adopted [5, 7], then  $q = 0.116 \text{ m}^4 \text{ C}^{-2}$  satisfies the relation  $(c/a) - 1 = q P_s^2$  at room temperature. Table 2 shows that the values of  $A_0$ ,  $B$ , and  $C$  for the single crystal and polycrystalline specimens compare favourably, indicating that the assumptions regarding  $P_s$  and  $q$  are appropriate for both forms of material. We further note that the Landau coefficients in table 2 are in agreement with those reported in the development of a full three-dimensional energy function used to describe the anisotropic property responses in  $\text{PbTiO}_3$  crystals and ceramics [15].

In further comparing the specific heat data obtained here for single crystal samples with those reported for polycrystalline materials [16] several observations are appropriate. At temperatures  $375 \text{ K} < T < 750 \text{ K}$ , the absolute values of  $C_P$  agree to within 4%, and both forms of material showed constant heat capacities of  $C_P = C_V$  (classical) in the cubic phase at  $T > 800 \text{ K}$ . In contrast, the peak in specific heat for the single crystals was larger by  $> 100 \text{ J mol}^{-1} \text{ K}^{-1}$  ( $\sim 25\%$ ) and the difference in the extrema  $(T_2 - T_1) = 4 \text{ K}$ , which measures the sharpness of the peak in  $\Delta C_P$ , was about half the value observed for the polycrystalline material as determined under equivalent measurement conditions. Also, the relations of equations (2) and (3) were better obeyed (i.e. showed less curvature) for the single crystal specimens compared to the polycrystalline material over similar intervals of  $\tau$ . Because the sol-gel derived powders showed a high degree of chemical and phase purity it seems likely that these differences may arise due to differing elastic boundary conditions on individual crystallites having a distribution of sizes within the sample [17, 22]. Nonetheless, the parameters derived

**Table 2.** Thermodynamic properties of single crystal and polycrystalline PbTiO<sub>3</sub>.

Property	Units	Single crystal (this study)	Polycrystalline [16]
Transition energy, $E$	J mol <sup>-1</sup>	4150 (±50) <sup>a</sup>	5250
Latent heat, $L$	J mol <sup>-1</sup>	1550 (±100) <sup>a</sup>	1910
Entropy change at $T_t$ , $\Delta S^{XS}$	J mol <sup>-1</sup> K <sup>-1</sup>	2.0 (±0.1) <sup>b</sup>	2.5
Transition temperature, $T_t$	K	760 (±2) <sup>c</sup>	764
Curie–Weiss temperature, $T_0$	K	748 (±2) <sup>c</sup>	752
Upper phase stability limit, $T^*$	K	764 (±2) <sup>c</sup>	769
Temperature difference, $(T_t - T_0)$	K	12 (±3) <sup>d</sup>	12
Temperature difference, $(T^* - T_0)$	K	16 (±3) <sup>d</sup>	17
Second-rank Landau prefactor, $A_0$	J mol <sup>-1</sup> K <sup>-1</sup>	138 (±4) <sup>c</sup>	146
Fourth-rank Landau coefficient, $B$	J mol <sup>-1</sup>	$(-2.2 \pm 0.8)^b \times 10^5$	$-2.2 \times 10^5$
Sixth-rank Landau coefficient, $C$	J mol <sup>-1</sup>	$(7.5 \pm 3.5)^b \times 10^6$	$6.4 \times 10^6$

<sup>a</sup> Estimated uncertainty in the integration of the  $C_p(T)$  curves.

<sup>b</sup> Standard propagated error in the derived quantity as defined by the relations given in the text.

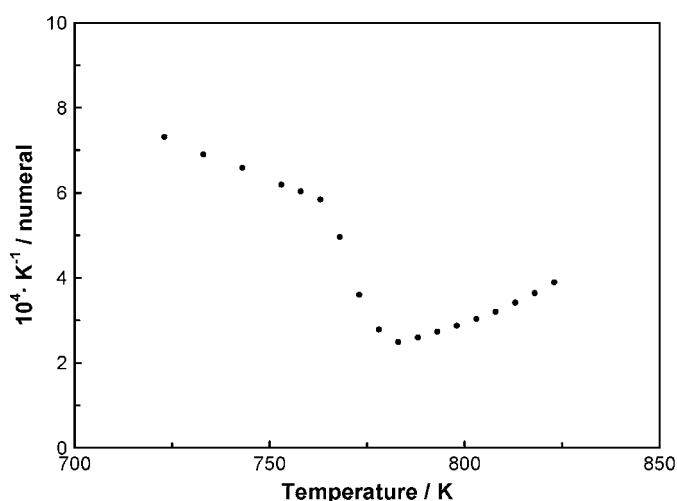
<sup>c</sup> Twice the experimental error in  $T$  or  $C_p$ .

<sup>d</sup> Square root of the sum of the squares of the error in  $T_0$ ,  $T_t$ , and  $T^*$ .

for both material forms (table 2) show good agreement overall. On average the transition energies and entropy ( $E$ ,  $L$ ,  $\Delta S^{XS}$ ) for the single crystals are all uniformly smaller, by about 20%, compared to the polycrystalline values estimated using similar experimental and data reduction methods. Similarly, the transition temperatures ( $T_0$ ,  $T_t$ ,  $T^*$ ) are all shifted to lower values by about 4 K so that the quantity  $(T_t - T_0)$  remains comparable for both forms of the material.

We may also use the tabulated value of the prefactor  $A_0 = (2q\varepsilon_0\rho_M C_{cw})^{-1}$  to compute a value for the Curie–Weiss constant  $C_{cw} = (1.3 \pm 0.1) \times 10^5$  K, where  $\varepsilon_0$  is the permittivity of free space. This value is on the lower end of the range reported for flux-grown or doped PbTiO<sub>3</sub> single crystals [3–7]. The Curie–Weiss plot in figure 5 for the float-zone crystals studied here gives some indication as to the possible origins of the seemingly large differences in  $C_{cw}$  and  $T_0$  observed in the prior studies. From figure 5 it was found that the best-fit line to the data in paraelectric phase gives  $C_{cw} = (3.0 \pm 0.5) \times 10^5$  K [18] though it is clear that the data is markedly nonlinear and that the slope determined above 805 K may be as much as a factor of 1.5 larger than the slope determined below 805 K. This variation translates into a shift in the extrapolated value of  $T_0 \approx 50$  K, as has been observed. Clearly, the dielectric permittivity is very sensitive at these temperatures to sample characteristics. For the present float-zone crystals this behaviour may be related to the measured oxygen nonstoichiometry. However, it is also worth noting here that very recent diffraction studies support prior observations [23] that there is a component of order–disorder behaviour extending to temperatures into the nominally paraelectric phase.

In contrast, even given the differences in physicochemical characteristics of the single crystal and polycrystalline materials studied, the average behaviour of the specific heat for PbTiO<sub>3</sub> does not vary greatly between the two sample types at these temperatures and leads to a well-constrained set of thermodynamic parameters. Notably, the quantity  $(T_t - T_0) \approx 12$  K is similar to that observed for BaTiO<sub>3</sub> crystals ( $\approx 10$  K) and is consistent with the observation that a tricritical point in PbTiO<sub>3</sub> crystals [10] and powders [24] occurs at a modest hydrostatic pressure of  $\sim 1.75$  GPa. Similarly, for tetragonal solid solutions of  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ , the onset of tricritical behaviour for both single crystal [25] and polycrystalline materials [26] becomes evident when the Zr substitution level is increased to values near  $x = 0.4$ .



**Figure 5.** Curie–Weiss plot of the reciprocal relative dielectric permittivity versus temperature for  $\text{PbTiO}_3$  crystals.

#### 4. Conclusions

The specific heat of pure, float-zone-grown  $\text{PbTiO}_3$  crystals was measured at temperatures between 325 and 1250 K. In the cubic phase above 800 K the average specific heat  $C_P(\text{cubic}) = (125 \pm 1) \text{ J mol}^{-1} \text{ K}^{-1}$  was found to be very close to the Dulong–Petit classical limit. A Landau analysis of the excess specific heat subject to the assumption that the higher order terms are temperature independent showed that the predictions of the mean-field theory were well obeyed over the reduced temperature range of  $\tau = (T_t - T)/T_t = 0.013\text{--}0.049$ . The expected proportionality between the spontaneous strain  $(c/a) - 1$  and excess entropy  $S^{\text{XS}}$  was maintained over a larger interval of  $\tau = 0.006\text{--}0.11$ . The first-order character of the  $m3m \leftrightarrow 4mm$  phase change was described using a latent heat  $L = (1550 \pm 100) \text{ J mol}^{-1}$ , an entropy discontinuity  $\Delta S^{\text{XS}} = (2.0 \pm 0.1) \text{ J mol}^{-1} \text{ K}^{-1}$ , a Curie–Weiss constant  $C_{\text{cw}} = (1.3 \pm 0.1) \times 10^5 \text{ K}$ , and a temperature difference  $(T_t - T_0) = (12 \pm 3) \text{ K}$  with Curie–Weiss temperature  $T_0 = (748 \pm 2) \text{ K}$ . These parameters, together with the Landau coefficients and the magnitude of the specific heat, were found to be in good agreement with the values previously reported for micron-sized sol–gel derived polycrystalline  $\text{PbTiO}_3$  materials. These results contrast with the large range of values for  $C_{\text{cw}}$  and  $(T_t - T_0)$  obtained from dielectric measurements, where experimental difficulties may complicate the determination of the relative permittivity at the temperatures of interest between  $T_t$  and 800 K.

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