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Calorimetric studies of phase transitions in imidazolium perchlorate crystal

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Abstract

The first precise measurements of specific heat changes have been performed for a $C_3N_2H_5ClO_4$ crystal using an ac calorimeter. Phase transitions at about 373 and 219 K were revealed. The continuous second-order phase transition at 373 K to the ferroelectric phase is described by the Landau model using specific heat and linear birefringence data. The Landau expansion coefficients B and C are of the same order of magnitude as those obtained for hard ferroelectric materials. Thermal parameters (such as the excess enthalpy, ΔH , and the excess entropy, ΔS) of the continuous transition were estimated and discussed. During the first cooling, a distinct (~ 2 K) supercooling effect was observed at the discontinuous transition at about 219 K.

1. Introduction

Organic–inorganic crystals are often the subject of studies, because they exhibit structural phase transitions. Among them, the crystals of pyridinium perchlorate [1], pyridinium fluoroborate [2], and pyridinium periodate [3] are found to undergo ferroelectric and other structural phase transitions related to the ordering of cations and anions. Another subfamily that exhibits ferroelectric phase transitions is imidazolium salts. So far, ferroelectric phases have been found in imidazolium fluoroborate [4], imidazolium perchlorate [5], and imidazolium chlorobismuthate [6].

The imidazolium perchlorate $C_3N_2H_5ClO_4$ is a newly synthesized salt, isomorphous to the fluoroborate analogue [4], which can be classified as a disordered molecular–ionic crystal of pseudopentagonal cation symmetry. Structural, dielectric and optical studies [5] were performed above a temperature of 90 K and two phase transitions were found at about 373 K (I–II) and 210 K (II–III), whereas for the fluoroborate analogue three phase transitions (at about 294.4, 200 and 140.5 K on cooling) were reported. The crystal symmetry of both crystals at room temperature is trigonal with noncentrosymmetric group $R3$. A second-order phase transition in $C_3N_2H_5ClO_4$ at about 373 K, postulated as the ferroelectric one, is accompanied by

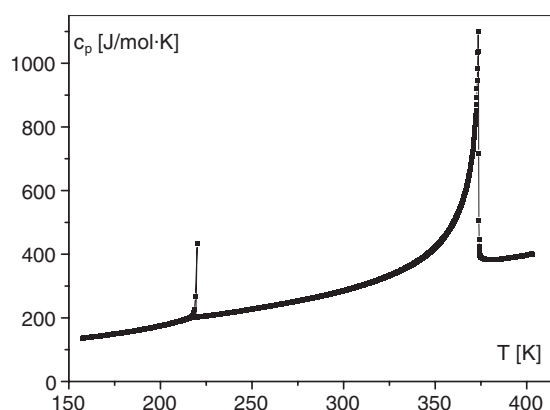


Figure 1. Temperature dependence of the specific heat observed during the first cooling process.

a large anomaly in the electric permittivity measured along the rhombohedral [111] direction. Curie–Weiss constants for the para- and ferroelectric phase are equal to 1411 and 329 K, respectively. The crystal is optically uniaxial in the para- and ferroelectric phase. Hence the expected change of symmetry at the ferroelectric–paraelectric transition is $R3 \leftrightarrow R\bar{3}$. An order–disorder character of the transition is supported by the ratio of the Curie constant $C_{\text{para}} = 1411$ K to the transition temperature $T_C = 373.65$ K, equal to 3.78, which is close to the value of 3 found for a Lorentz factor of the classical statistical model of the order–disorder transition [7]. The first-order phase transition was found at about 210 K on cooling; optical observations were not possible below this transition temperature because samples were internally cracked and non-transparent. At about 486 K, the crystal starts to melt. Differential scanning calorimetry (DSC) studies were performed only for the imidazolium tetrafluoroborate crystal at a rather high scanning rate. To describe thermal parameters of phase transitions, we decided to measure the temperature dependence of the specific heat of $\text{C}_3\text{N}_2\text{H}_5\text{ClO}_4$ using the ac calorimeter.

2. Experiment and results

The imidazolium perchlorate single crystals were grown from a saturated water solution of dissolved polycrystals by a slow evaporation method at a constant temperature of 303 K. The polycrystals were obtained from stoichiometric quantities of imidazolium and perchloric acid. The computer-controlled ac calorimeter (Sinku–Riko ACC 1 M/L) equipped with a PID temperature programmer was used. Chromel–constantan thermocouple wires of $25 \mu\text{m}$ were attached to the rear face of a thin (~ 0.3 mm) crystal sample. The front face of the sample was blackened for better absorption of the heat pulse. The ac calorimetric measurements were made at a chopping frequency of 1 Hz during the heating and cooling process at a temperature rate of 0.05 K min^{-1} . It should be taken into account that absolute values of the specific heat could be determined only in a relative way, by comparison with the ac temperature response of the model sapphire sample. Figure 1 shows the temperature dependence of the specific heat during cooling in the limited temperature range. Two anomalies connected with the previously mentioned phase transitions were detected at the temperatures 373.5 and 219 K. The high-temperature specific heat anomaly is typical of the second-order phase transition. No temperature hysteresis was observed during heating and cooling for this transition.

Further cooling leads to the first-order transition at about 219 K. The ac calorimeter can be used only for qualitative studies of the first-order transitions, but some specific features of the

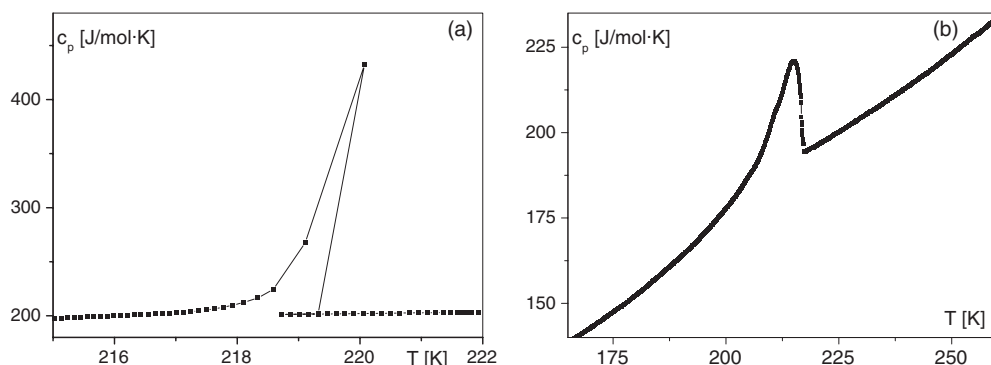


Figure 2. (a) First-order transition anomaly observed during the first cooling in the vicinity of the first-order phase transition. (b) Low-temperature anomaly corresponding to the first-order phase transition recorded during the second cooling.

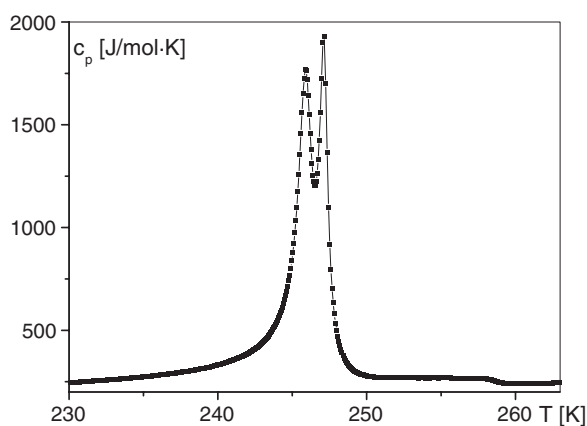


Figure 3. Two peaks and step recorded during heating at the lower-temperature phase transition.

transition could still be clearly registered. The first-order phase transition observed during the first cooling process is rather unusual. In the figure 2(a) this anomaly is presented, showing a large (~ 2 K) supercooling effect. The effect was connected to a temperature leap and release of the latent heat, so the observed response of the measuring system was only an indication of the first-order transition.

We checked that this first cooling process caused an internal micro-cracking effect in the sample, as it was observed under a polarizing microscope. The second cooling to phase III was not accompanied by the supercooling effect (figure 2(b)). One could assume that the crystal behaves as if it were composed of micro-crystals. Then the crystal was heated and a large temperature hysteresis of about 27 K during heating and cooling was noticed for the lower-temperature transition (figure 3). The anomaly during heating was composed of two peaks and a broad step, reaching a temperature of about 258 K. A similar step-like transition during heating was recorded in dielectric studies [5].

We have estimated the excess enthalpy, ΔH , associated with the second-order phase transition after subtracting an approximate background (figure 4). The polynomial background function up to the fourth order was fitted to the experimental data. Integrating the excess specific heat, Δc_p , one can get $\Delta H_{I-II} = 6200 \text{ J mol}^{-1}$.

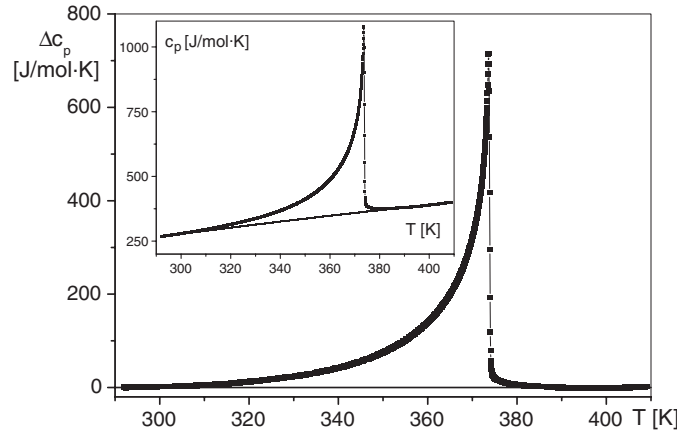


Figure 4. Specific heat increment, Δc_p , at the second-order transition anomaly. In the inset, the $c_p(T)$ —dependence and the approximate background are presented.

In order to describe the second-order transition, a Landau theory was applied. The Landau expansion of the excess free energy, often referred to as the 2-4-6 potential, can be written in the form [7, 8]:

$$\Phi = \Phi_0 + \frac{1}{2}A(T - T_C)Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}CQ^6 \quad (1)$$

where A , B and C are treated as temperature-independent coefficients. The equilibrium order parameter can be obtained from the expression $(\frac{\partial \Phi}{\partial Q})_{Q=Q_0} = 0$ and

$$Q_0 = \left[\frac{-B + [B^2 - 4AC(T - T_C)]^{1/2}}{2C} \right]^{1/2}. \quad (2)$$

The excess entropy can be correlated with the order parameter as $\Delta S = -\frac{1}{2}AQ_0^2$. The specific heat increment is:

$$\Delta c_p = T \left(\frac{\partial S}{\partial T} \right) = \left(\frac{A^3}{16C} \right)^{1/2} \frac{T}{\left(T_C + \frac{B^2}{4AC} - T \right)^{1/2}}. \quad (3)$$

A more convenient representation can be used for the determination of the Landau coefficients A , B and C :

$$\left(\frac{T}{\Delta c_p} \right)^2 = \frac{4B^2}{A^4} + \frac{16C(T_C - T)}{A^3}. \quad (4)$$

In figure 5(a), $(T/\Delta c_p)^2$ is plotted as a function of $(T_C - T)$ in the ferroelectric phase. The A coefficient can be determined from dielectric measurements: $A = (\epsilon_0 C_{\text{para}})^{-1} = 8.00 \times 10^7 \text{ V m C}^{-1} \text{ K}^{-1}$. We have estimated the coefficients B and C from the equation of the straight line (linear regression): $(T/\Delta c_p)^2 = 0.27231 + 0.29456 \cdot (T_C - T)$. Taking into account the molar volume $V_m = 10.592 \times 10^3 \text{ mol m}^{-3}$, the coefficients $B = (2.13 \pm 0.02) \times 10^{11} \text{ V m}^5 \text{ C}^{-3}$ and $C = (1.34 \pm 0.02) \times 10^{14} \text{ V m}^9 \text{ C}^{-5}$ could be found, respectively. The A coefficient is two times as much, whereas the B and the C coefficients are of the same order of magnitude as those determined for the hard ferroelectric crystal of telluric acid ammonium phosphate (TAAP). The 2-6 Landau potential cannot be applied for the imidazolium perchlorate crystal. In figure 4(b), calculated and measured increments of specific heat are plotted. Very good approximation holds up to about 5–6 K below the transition temperature.

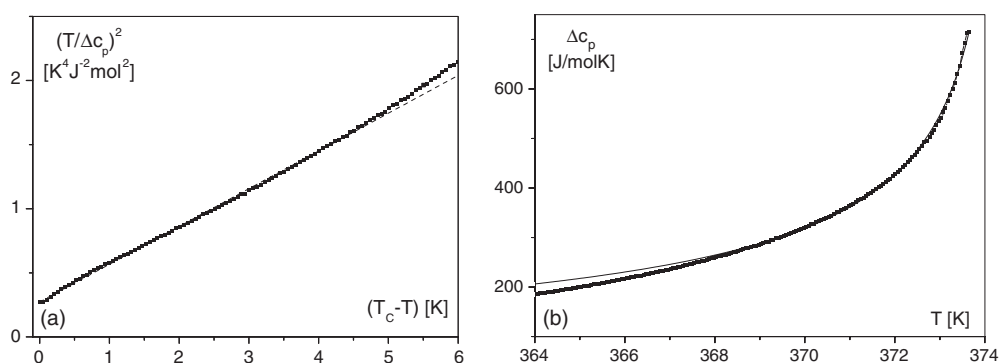


Figure 5. (a) $(\Delta c_p/T)^{-2}$ as a function of $(T_c - T)$ close to the ferroelectric transition. (b) Specific heat increment Δc_p in the ferroelectric phase, measured and calculated (thin line) using the Landau coefficients (formula (3)).

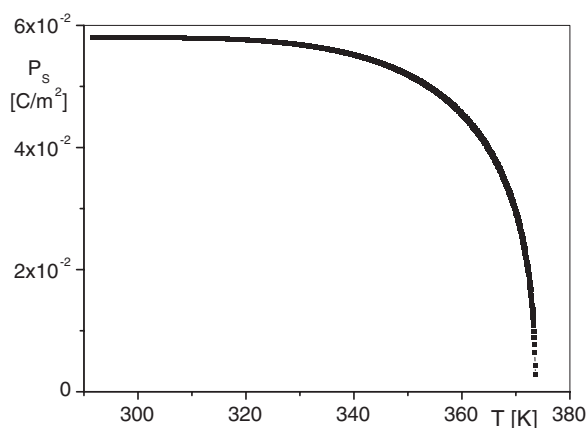


Figure 6. $P_S(T)$, calculated from formula (5).

Since the ratio of the Curie constants below and above the transition is equal to 4.3, which is close to the value of 4 corresponding to a tricritical point, we have tried to compare values of parameters indicating a proximity to the tricritical point. The parameters defined as $V = B/(AC)^{1/2}$, or the more universal dimensionless $K = B^2/4ACT_c$ [9], can be used for the estimation of the proximity to the tricritical point. The value of the V -parameter for the second-order transitions is positive, but it is negative for the first-order transitions. In our case $V = 2.06$, clearly showing that the transition is rather far from the tricritical point. The K -parameter gives 2.8×10^{-3} , which is a one order of magnitude greater value than that obtained for triglycine selenate (TGSe), which is often regarded as a model crystal exhibiting tricritical behaviour. The transition temperature is $T_c = 373.648 \text{ K}$ and the tricritical point should be located rather far ($\sim 0.9 \text{ K}$) from T_c . Since our trials to obtain a dielectric hysteresis loop have been unsuccessful because of a very high coercive field [2], we propose to determine the provisional temperature dependence of the order parameter (the spontaneous polarization at the ferroelectric phase) using the results of the calorimetric studies. It is possible to evaluate the $P_S(T)$ -dependence by using the above-mentioned formula for Q_0 and by taking calculated values of coefficients A , B and C . Figure 6 presents the $P_S(T)$ -dependence calculated from

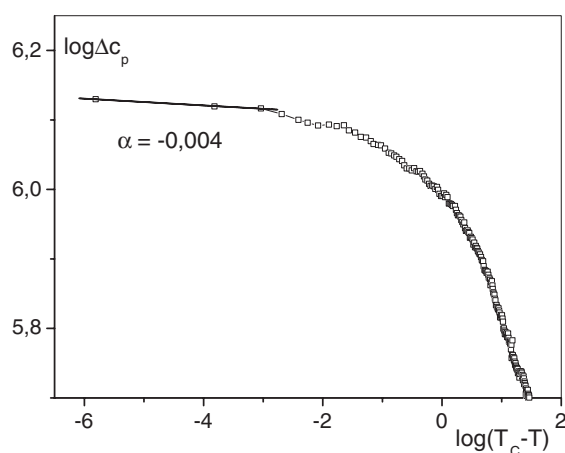


Figure 7. The specific heat critical index, α , determined as the slope of $\ln \Delta c_p$ versus $\log(T_c - T)$.

the relation:

$$P_S^2(T) = \int_{T_c}^T \frac{2\Delta c_p}{AT} dT \quad (5)$$

The maximum of the P_S value reaches $5.8 \times 10^{-2} \text{ C m}^{-2}$, which is about seven times greater than the P_S value estimated for the imidazolium fluoroborate crystal. An estimation of the critical index for the order parameter from the calculated $P_S(T)$ -dependence gives $\beta = 0.45$, indicating that the system can be described by the mean field model of the transition. The specific heat critical index $\alpha = -0.004$ is very close to zero (figure 7), which confirms this approximation [10].

An alternative method for estimating the Landau expansion coefficients can also be derived from the formula:

$$T_c - T = \frac{B}{A} P_S^2 + \frac{C}{A} P_S^4, \quad (6)$$

obtained from equation (2); ($Q_0 = P_S$).

Assuming that $|\Delta S| = \frac{A}{2} P_S^2$ and taking into account the relation $\delta(\Delta n) = R^* P_S^2$, one should expect a linear proportionality of $\delta(\Delta n)$ and ΔS . This linear correlation is satisfactory up to about 12 K below T_c , as is shown in figure 8(a). The slope of the straight line equals $a = 5.373 \times 10^{-5} \text{ mol K J}^{-1}$. Then

$$R^* = a \frac{A}{2} \quad \text{and} \quad T_c - T = \frac{2B}{A^2} \frac{\delta(\Delta n)}{a} + \frac{4C}{A^3} \frac{[\delta(\Delta n)]^2}{a^2}. \quad (7)$$

The estimation of the parabolic parameters from the approximation plotted in figure 8(b) gives the Landau expansion coefficients B and C as $B = 1.44 \times 10^{11} \text{ V m}^5 \text{ C}^{-3}$ and $C = 9.65 \times 10^{13} \text{ V m}^9 \text{ C}^{-5}$, respectively. The coefficients that are obtained are close to those calculated from the increment in the specific heat.

The change in entropy at the ferroelectric transition is presented in figure 9. The excess entropy, ΔS_{I-II} , was determined by integrating $\Delta c_p/T$ in the temperature range 280–410 K giving, for several, transients 18.6–19.3 $\text{J mol}^{-1} \text{ K}^{-1}$.

The value that is obtained is close to $R \ln 10$ and rather high, as one can expect for an order–disorder transition; significantly higher than $\Delta S_{I-II} = 5.5 \text{ J mol}^{-1} \text{ K}^{-1}$ reported for the

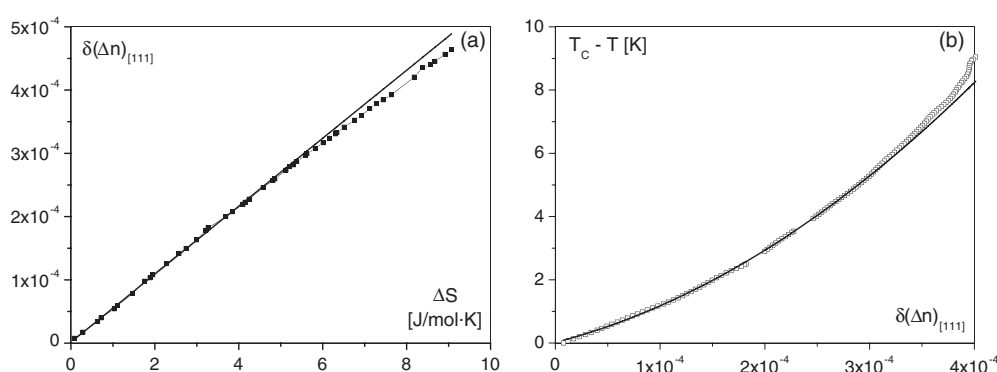


Figure 8. (a) The increment in linear birefringence, $\delta(\Delta n)_{[111]}$, versus the increment in the entropy, $[\Delta S]$. (b) $(T - T_C)$ as a function of the increment in the birefringence, $\delta(\Delta n)_{[111]}$. The parabolic approximation is also presented.

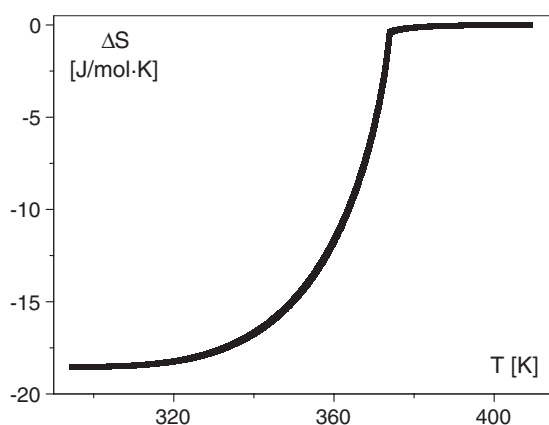


Figure 9. Temperature dependence of the entropy excess, ΔS_{I-II} , at the ferroelectric phase transition.

tetrafluoroborate analogue crystal at the respective transition [4]. A similar excess of entropy for the tetrafluoroborate analogue crystal can be measured for two consecutive transitions. It is rather difficult to estimate the change in entropy at the lower-temperature phase transition from the ac calorimetry. In order to evaluate contributions to ΔS_{I-II} , we must also take into account the ordering of the anion. There are two options, not confirmed by the structural studies: the low-temperature phase III can be ferroelectric or not. Assuming a single configuration order in the ferroelectric phase III, one can propose the cationic contribution as $R \ln 6$ and the anionic contribution as $R \ln 2$. The total ΔS_{I-II} could then be $R \ln 12 = 20.65 \text{ J mol}^{-1} \text{ K}^{-1}$. Slightly better agreement with the measured ΔS_{I-II} can be obtained by taking a sum of $R \ln 5$ and $R \ln 2$, which gives $R \ln 10 = 19.14 \text{ J mol}^{-1} \text{ K}^{-1}$. This estimation may reflect the pseudo-pentagonal symmetry of the cation. The second option, the non-ferroelectric phase III, assumes five positions of the anion in phase I and three positions in phase II. Taking the cationic contribution as $R \ln 6$ and the anionic contribution as $R \ln 5/3$ one can obtain $\Delta S_{I-II} = 19.14 \text{ J mol}^{-1} \text{ K}^{-1}$. Then, at the low-temperature transition, one can expect $\Delta S_{II-III} = R \ln 3/2 = 3.37 \text{ J mol}^{-1} \text{ K}^{-1}$, a value which is very close to the value roughly

estimated from the data presented in figure 2(b), i.e. $\Delta S_{\text{II-III}} = 3.06 \text{ J mol}^{-1} \text{ K}^{-1}$. We expect to collect more data in the near future to exclude one of the mechanisms presented above.

3. Summary

- (1) Specific heat measurements performed for the imidazolium perchlorate crystal using the ac method revealed anomalies at the second-order (at 373.5 K) and first-order (219 K) phase transition.
- (2) A strong supercooling effect ($\sim 2 \text{ K}$) was detected for the first cooling process at the first-order transition.
- (3) The Landau expansion coefficients B and C were estimated from the specific heat excess and the increment in linear birefringence for the second-order transition. Values obtained from both methods were very similar and close to those obtained for the hard ferroelectric crystals.
- (4) The parameters that indicated closeness to the tricritical point were an order of magnitude higher than those reported for the model tricritical crystal.
- (5) A temperature dependence of the order parameter (the P_S) was determined from the measurements of specific heat excess.
- (6) The entropy excess was evaluated and possible mechanisms leading to the obtained value of $\Delta S_{\text{I-II}}$ were proposed.

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