

Thermodynamics of the phase transitions in ferroelectric pyridinium perchlorate,
 $[\text{C}_5\text{NH}_6]^+\text{ClO}_4^-$

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

2002 J. Phys.: Condens. Matter 14 3321

(<http://iopscience.iop.org/0953-8984/14/12/318>)

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

Download details:

IP Address: 171.66.16.104

The article was downloaded on 18/05/2010 at 06:22

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

Thermodynamics of the phase transitions in ferroelectric pyridinium perchlorate, $[\text{C}_5\text{NH}_6]^+\text{ClO}_4^-$

Izabela Szafraniak¹ and Piotr Czarnecki

Institute of Physics, A Mickiewicz University, ul. Umultowska 85, 61-614 Poznan, Poland

E-mail: izaszaf@main.amu.edu.pl

Received 18 October 2001, in final form 6 February 2002

Published 15 March 2002

Online at stacks.iop.org/JPhysCM/14/3321

Abstract

Calorimetry, linear thermal expansion, volumetric dilatometry and dielectric methods were applied to investigate the phase transitions of pyridinium perchlorate, $[\text{C}_5\text{NH}_6]^+\text{ClO}_4^-$. Anomalies of the physical properties measured, related to the first-order phase transitions, were observed at $T_1 = 248$ K and $T_2 = 233$ K. The values of the entropy change indicate their order-disorder character. An additional thermal anomaly observed at $T_3 = 236$ K is connected with the next continuous phase transition. The mechanism of the phase transitions is proposed in this paper. The results suggest that the character of the phase transitions do not change up to 800 MPa. On the basis of the high-pressure studies the p - T phase diagram is obtained. The pressure dependences of the phase transition temperatures agree well with the values estimated from the Clausius–Clapeyron relationship. The uniaxial pressure dependences of the phase transition temperatures are estimated.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the last decade ferroelectric materials attracted considerable attention from physicists. Their ferroelectric, dielectric and piezoelectric properties were found to be promising for microelectronic and micromechanical applications [1, 2]. On the other hand, problems associated with applications of these materials, such as the ‘size effect’, stimulated intensive research on the fundamental properties of ferroelectrics [3–5]. Searching for new ferroelectrics and their characterization is still an important scientific topic. This paper, in which we describe the thermodynamical aspect of phase transitions of pyridinium perchlorate, $[\text{C}_5\text{NH}_6]^+\text{ClO}_4^-$, denoted as PyClO_4 , is connected to the last subject. Although ferroelectricity in PyClO_4 crystals was discovered in 1994, information about its properties has been scarce [6–8].

¹ Present address: Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany.

PyClO₄ belongs to a large family of pyridinium salts. The majority of pyridinium salts reveal one phase transition, although in ferroelectric ones a sequence of at least two phase transitions has been observed. The additional phase transition, taking place at higher temperature, is usually a ferroelectric one. Many pyridinium salts crystallize in the trigonal system $R\bar{3}m$ or $R3m$, in which the planar pyridinium cations are parallel to each other [7, 9]. According to the results of earlier studies, PyClO₄ shows two discontinuous phase transitions at $T_1 = 248$ K and at $T_2 = 233$ K and the sequence of its structural transformations is $R3m \xrightarrow{245\text{ K}} Cm \xrightarrow{233\text{ K}} ?(Pm)$ [7]. At room temperature both anions and cations are dynamically disordered [7]. Each cation has six equivalent positions. It has been observed for different pyridinium salts that with decreasing temperature the cation reorientation slows down [10, 11]. It was suggested that this process usually induced symmetry breaking connected with phase transition. A similar behaviour of cations in PyClO₄ was observed on the basis of NMR and dielectric measurements [6–8]. In this paper we propose a more detailed model of phase transitions obtained from analysis of our calorimetric and dilatometric studies. An additional phase transition at $T_3 = 236$ K was found in differential scanning calorimetry (DSC) investigations and we performed dielectric measurements under ambient and high hydrostatic pressure to obtain more information about its nature.

Because of the planar arrangement of the cations in the crystal lattice, the largest anisotropy of physical properties is expected in the directions along and perpendicular to the threefold symmetry axis of the trigonal system. So far only the anisotropy of dielectric properties in single crystals of PyClO₄ has been described [7]. Large anisotropy of dielectric properties and linear thermal expansion of pyridinium tetrafluoroborate PyBF₄, which has similar structure, have also been reported [9, 12]. Moreover, results of our high-pressure measurements enabled a construction of a p – T phase diagram and its analysis on the basis of the Clausius–Clapeyron equation.

2. Experimental details

The PyClO₄ salt is formed in the reaction between pyridine and perchloric acid. PyClO₄ crystals were grown from a water solution by slow evaporation at a constant temperature. The maximum size of the trigonal prism crystals was $3 \times 3 \times 20$ mm³.

DSC measurements were carried out on a Perkin–Elmer DCS-2 in the temperature range from 160 to 290 K, at different heating rates from 2 to 10 K min^{−1}. Small single crystals were used for these measurements.

The specific volume and the linear thermal expansion of the crystal were measured with a Netzsch dilatometer TMA402 in the temperature range from 170 to 300 K at the heating rate of 0.5 or 1 K min^{−1}. The influence of hydrostatic pressure on the specific volume of the crystal was tested by pressure–volume dilatometry on home-made equipment [13, 14]. Measurements of the specific volume were performed at a rate of 0.5 K min^{−1} under isobaric conditions for a few pressures from the range 10–100 MPa. Isothermal measurements were performed for a few temperatures from 230 to 300 K at a rate of 10 MPa min^{−1}. The measurements were carried out in a high-pressure chamber filled with silicon oil (AK12500, Wacker Chemie). As the silicon oil freezes at about 230 K, measurements below this temperature could not have been performed. For the linear thermal expansion investigation we used samples cut from the single crystals as rectangular prisms oriented along the threefold axis of the trigonal system or perpendicular to it. Measurements of volumetric thermal expansion under ambient and high pressure were carried out for polycrystalline samples, pressed into cylinders of 5.8 mm in diameter and 10 mm in length.

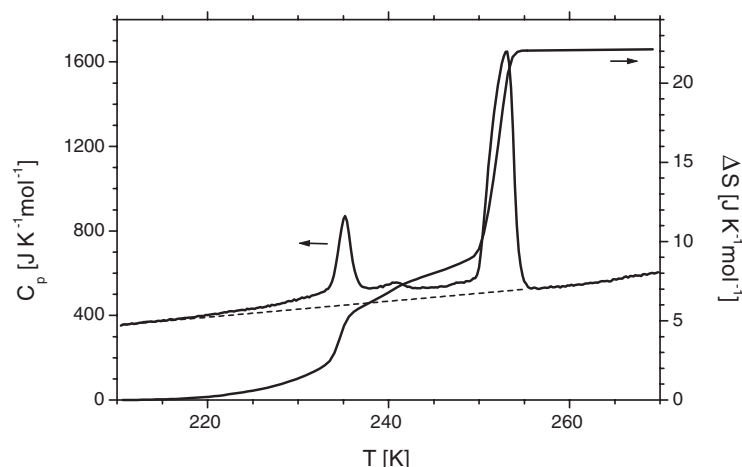


Figure 1. Temperature dependence of specific heat C_p (left) and the entropy change ΔS (right) obtained from the DSC measurement at a rate of 5 K min^{-1} .

The dielectric properties were measured using a Hewlett-Packard 4192A impedance analyser at frequency 50 kHz. The measuring ac electric field was about 1 V cm^{-1} . For the high-pressure dielectric measurements, the high-pressure chamber was connected to a gas compressor GCA-10 Unipress. The pressure was measured, using a manganin sensor, with the accuracy of $\pm 2 \text{ MPa}$. The high-pressure dielectric measurements were obtained at a few values of hydrostatic pressure from the range 50–900 MPa in the temperature range 150–300 K. Measurements of the pyroelectric effect were made by a Keithley 6514 electrometer. For these measurements we used samples of 0.5 mm in thickness and 10 mm^2 area cut out of the single crystal. Gold electrodes were evaporated on the surface parallel or perpendicular to the threefold crystal axis.

3. Results

3.1. DSC measurements

Several DSC runs at different rates were made and a remarkable repeatability of results was achieved. The temperature dependence of specific heat is shown in figure 1, and reveals two sharp anomalies related to the phase transitions at $T_1 = 248 \text{ K}$ and $T_2 = 233 \text{ K}$. The character of these anomalies is typical of discontinuous phase transitions. Temperature hystereses ($\Delta T \sim 2.5 \text{ K}$) between heating and cooling are observed. The anomalous changes in specific heat C_p , observed on heating on the low-temperature side, suggest that the pretransition effects play an essential role in these phase transitions. These effects, starting several tens of degrees below the phase transition temperatures, have been observed in other pyridinium salts [12, 15, 16].

An additional anomaly is observed between two sharp peaks. Several runs at different heating rates on different crystals were performed to examine this anomaly. The shape of this peak as well as the lack of temperature hysteresis indicates a continuous or weakly first-order phase transition at $T_3 = 236 \text{ K}$. The results of dielectric measurements, reported in [7], showed a change of dielectric permittivity slope near this temperature but the authors of [7] did not connect this anomaly to a phase transition.

Table 1. Thermodynamics parameters of phase transition of PyClO₄. ⊥, || denote directions perpendicular and parallel to the threefold axis.

	$T = 233 \text{ K}$	$T = 236 \text{ K}$	$T = 248 \text{ K}$
$\Delta S \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}^{\text{a}}$	5.4 (± 0.2)	1.7 (± 0.1)	14.5 (± 0.2)
$\Delta S_{T_0} \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}^{\text{b}}$	2.90 (± 0.08)	<0.02	13.0 (± 0.2)
$\Delta \left(\frac{\Delta l}{l_0} \right)_{\perp} 10^{-3}$	-1.70 (± 0.05)	<0.02	14.0 (± 0.1) ^c
$\Delta \left(\frac{\Delta l}{l_0} \right)_{\parallel} 10^{-3}$	2.30 (± 0.05)	<0.02	2.90 (± 0.05)
$\Delta V \text{ (cm}^3 \text{ mol}^{-1}\text{)}$	0.20 (± 0.02)	<0.01	1.00 (± 0.02)

^a Total value connected with phase transition (with pretransition effects).

^b Value of change at phase transition temperature (without pretransition effects).

^c The value was changed (see the text).

The phase transition temperatures detected from DSC are slightly higher than observed in previous measurements [6]. These differences are mainly induced by the different heating rates used in various methods. It seems that dielectric methods, which are usually performed at low rate (e.g. 0.05–0.1 K min⁻¹ near phase transition), attain a more realistic phase transition temperature.

The entropy change at the phase transition significantly depends on the choice of the baseline and the range of integration. Moreover, the relatively small pretransitional effects bring a significant contribution to the total change of entropy. The total change of entropy (figure 1) determined from the above measurements varies from $\Delta S = 20$ to $26 \text{ J K}^{-1} \text{ mol}^{-1}$, depending on the choice of the baseline and integration range. It is very difficult to establish precisely the change of entropy in particular transitions, because of overlapping effects connected to these transitions. The changes of entropy at the phase transitions are given in table 1.

3.2. Dilatometric measurements

Measurements of the linear thermal expansion were performed in the two most anisotropic directions—along the threefold axis and perpendicular to it. The temperature dependence of linear expansion is shown in figure 2. In the temperature range in which the effects connected to the phase transitions are not observed, the changes are greater in the direction parallel to the threefold axis, so perpendicular to the pyridinium ring planes. This anisotropy follows from the structure and is probably a result of the planar arrangement of the cations in the crystal lattice. Temperature can modify more easily interactions and distance in the direction perpendicular to the planar pyridinium cations. A similar anisotropy of the linear thermal expansion was discovered in the PyBF₄ crystals [12].

The anomaly connected with the phase transition at T_3 is not detectable in our dilatometric measurements. At T_1 and T_2 the temperature dependence of linear expansion in both directions reveals jumpwise changes. The extracted values of these changes are collected in table 1. It is worth noticing that at the Curie point the crystal dimensions decrease with decreasing temperature in all directions while at the low-temperature transition the crystal expands in parallel to the threefold axis and shortens in the directions perpendicular to the threefold axis. The values of the dimension change at T_1 in the direction perpendicular to the threefold axis decrease after each cooling run, which was interpreted as a result of an increasing number of defects after each cooling run through the phase transition. From dilatometric measurements the linear expansion coefficients $\alpha_l = (1/l)(\partial l/\partial T)_p$ were calculated and their values are placed in table 2.

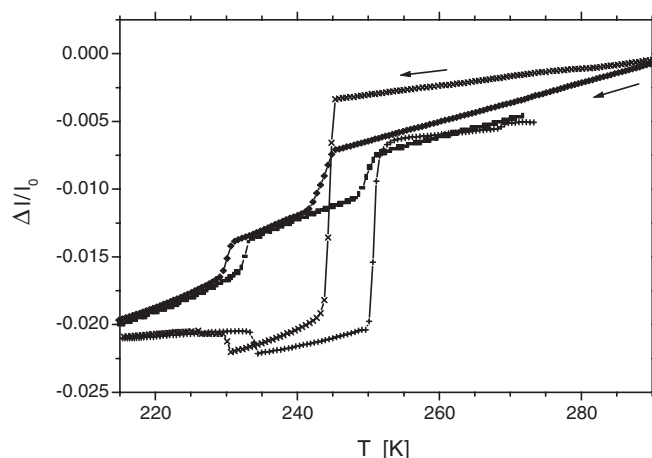


Figure 2. Temperature dependence of the linear thermal expansion $\Delta l/l_0$ measured along (squares) and perpendicular (crosses) to the threefold axis. The arrows indicate cooling and heating runs.

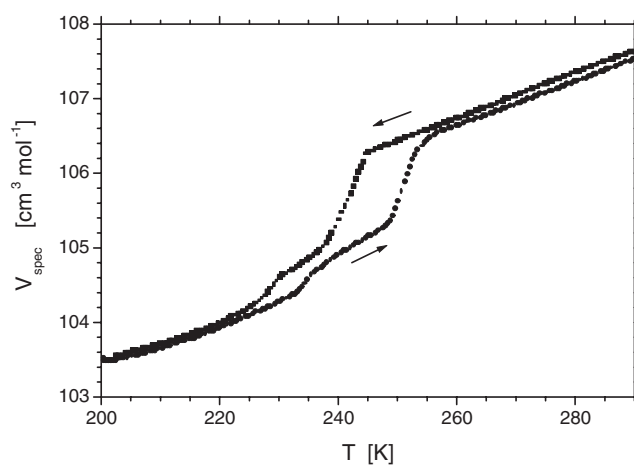


Figure 3. Temperature dependence of the specific volume obtained on heating and cooling at the rate of 1 K min^{-1} .

Table 2. Thermal expansion coefficients and compressibility of PyClO₄. \perp , \parallel denote directions perpendicular and parallel to the threefold axis.

	$T < 233 \text{ K}$	$233 \text{ K} < T < 248 \text{ K}$	$T > 248 \text{ K}$
$\alpha_{\perp} 10^{-4} (\text{K}^{-1})$	$0.20 (\pm 0.05)$	$1.55 (\pm 0.08)$	$0.53 (\pm 0.05)$
$\alpha_{\parallel} 10^{-4} (\text{K}^{-1})$	$2.15 (\pm 0.05)$	$2.10 (\pm 0.08)$	$1.65 (\pm 0.05)$
$\alpha_V 10^{-4} (\text{K}^{-1})$	$2.55 (\pm 0.08)$	$4.95 (\pm 0.09)$	$2.90 (\pm 0.05)$
$\beta 10^{-10} (\text{Pa}^{-1})$			$1.20 (\pm 0.05)$

A typical temperature dependence of specific volume under atmospheric pressure, shown in figure 3, reveals two anomalies at T_1 and T_2 . At the phase transitions the volume increases jumpwise on heating of the crystal. The volume expansion coefficients $\alpha_V = (1/V)(\partial V/\partial T)_p$ determined from the above measurements are given in table 2.

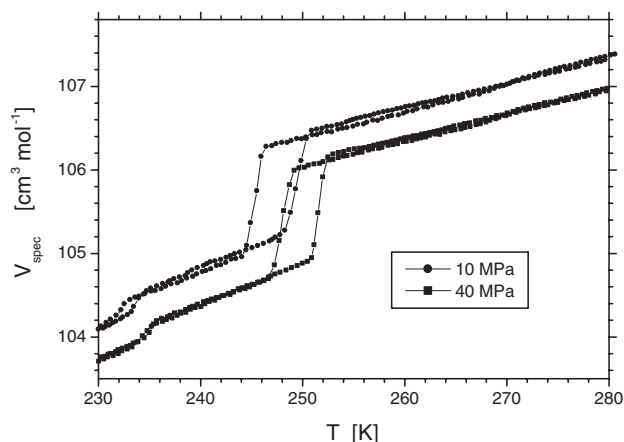


Figure 4. Temperature dependence of the specific volume under 10 MPa (circles) and 40 MPa (squares).

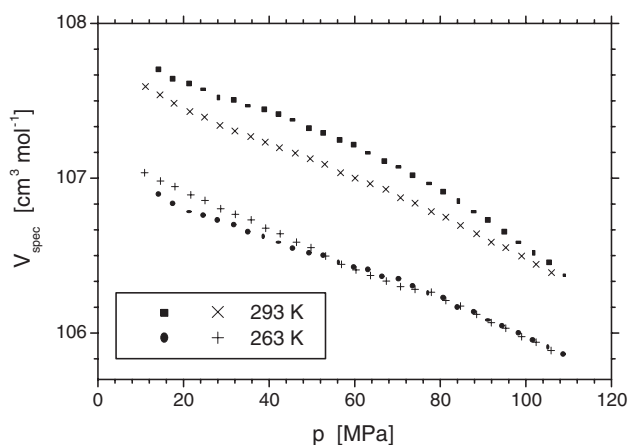


Figure 5. Specific volume versus hydrostatic pressure obtained during increasing (filled symbols) and decreasing pressure (crosses).

Temperature dependences of the volume thermal expansion, measured under two pressures, are presented in figure 4. The phase transition temperatures increase with increasing pressure, but the character of the anomalies in the vicinity of the phase transitions does not change in the pressure range studied. Results of the isothermal studies are given in figure 5 and the value of the compressibility $\beta = -(1/V)(\partial V/\partial p)_T$ is equal to $1.2 \times 10^{-10} \text{ Pa}^{-1}$ in the high-temperature phase. The pressure dependences of the temperature of the phase transition T_1 are shown in the p - T phase diagram, figure 6.

3.3. Measurements of spontaneous polarization by the pyroelectric effect

The temperature changes of spontaneous polarization determined on the basis of pyroelectric effect measurements are plotted in figure 7. The pyroelectric effect was measured in the range from 160 to 270 K. To pull the crystal into the single-domain state, it was cooled at the rate of 2 K min^{-1} in an electric field of the order of 4000 V cm^{-1} . The heating rate during the

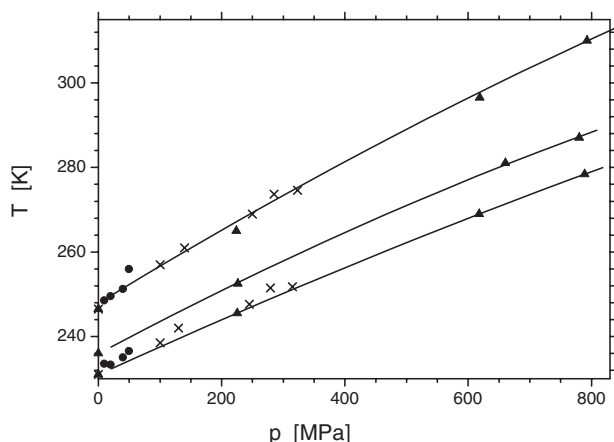


Figure 6. The p - T phase diagram of PyClO_4 obtained from our dilatometric (circles) and dielectric (triangles) measurements and from DTA (crosses) studies [7].

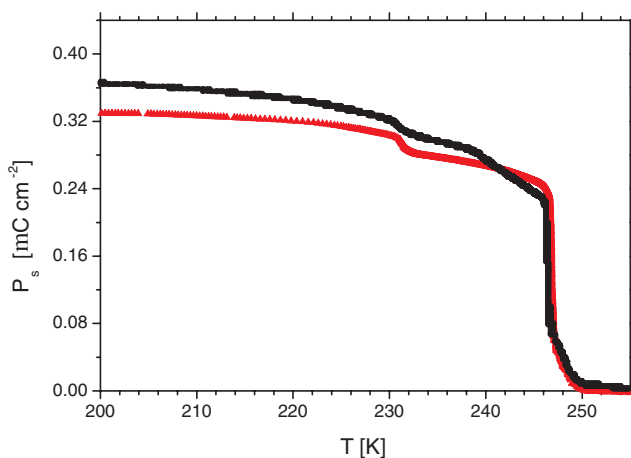


Figure 7. Temperature dependence of spontaneous polarization obtained from the pyroeffect measurements in the direction perpendicular (triangles) and parallel (circles) to the threefold axis.

measurements was 0.5 K min^{-1} . The value of spontaneous polarization is nonzero below T_2 . The nonferroelectric transition at T_3 is manifested as a small anomaly in the temperature dependence of the spontaneous polarization. This anomaly is clearly seen in the direction parallel to the threefold axis.

3.4. Dielectric measurements

All anomalies of the physical properties related to the new phase transition at T_3 are very weak. The analysis of dielectric measurements performed earlier on PyClO_4 showed that this phase transition was quite readily detectable for a low measuring frequency (lower than 1 MHz). To obtain more information about this phase transition we decided to measure dielectric permittivity in the direction perpendicular to the threefold axis at 50 kHz under ambient and high hydrostatic pressure. Figure 8 shows the temperature dependences of ϵ' recorded for a few pressures.

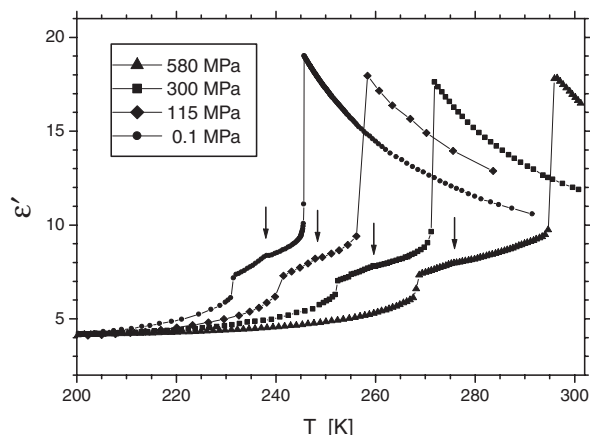


Figure 8. Temperature dependence of the real part of dielectric permittivity measured for a few pressures. The arrows indicate the phase transition at T_3 .

Table 3. Pressure dependences of phase transition temperature.

$T(p = 0.1 \text{ MPa})$	$T(p)$	$(dT/dp)_{\text{exp}}^{\text{a}}$ (K MPa $^{-1}$)	$(dT/dp)_{\text{theor}}^{\text{b}}$ (K MPa $^{-1}$)
248	$248 \text{ K} + 0.09 \text{ (K MPa}^{-1}) \times p - 1.4 \times 10^{-5} \text{ (K MPa}^{-2}) \times p^2$	$0.090 (\pm 0.004)$	$0.077 (\pm 0.005)$
236	$236 \text{ K} + 0.068 \text{ (K MPa}^{-1}) \times p$	$0.068 (\pm 0.004)$	—
233	$231 \text{ K} + 0.07 \text{ (K MPa}^{-1}) \times p - 1.7 \times 10^{-5} \text{ (K MPa}^{-2}) \times p^2$	$0.070 (\pm 0.004)$	$0.069 (\pm 0.005)$

^a Low-pressure value obtained from p - T diagram.

^b Value calculated from Clausius–Clapeyron relationship.

With increasing pressures, the temperatures of the phase transition anomaly are shifted toward higher values. Any change in character was not observed in the studied pressure range. The phase diagram of PyClO_4 obtained from high-pressure measurements is shown in figure 6. As follows from the results, the temperatures of phase transitions show non-linear changes with pressure and the dependences are described in table 3.

The Curie–Weiss temperatures were estimated from the temperature dependence of dielectric permittivity for various pressures. The values of the Curie–Weiss temperatures are lower by about 58 K than T_1 in the whole pressure range studied. The character of ferroelectric phase transition does not change up to 800 MPa. This means that there is no tricritical point on the p - T diagram at this pressure. This is consistent with the theoretical predictions for the phase transition with the index equal to three [17]. The phase transition index is defined as the ratio of the order of the paraelectric symmetry class to the order of the ferroelectric class [18].

4. Discussion

The anomalous part of ΔS obtained from calorimetric measurements brings important information about the phase transition nature. The theoretically established entropy change of the order–disorder phase transition is equal to $R \ln 2$ or larger. A smaller value of ΔS suggests a displacive character of the phase transition. In the real crystal the situation is more complicated and often both mechanisms are involved [19]. The precise value of entropy change is especially important for a strongly disordered structure. In this case results of the x -

ray and neutron diffraction studies do not permit exact determination of the number of possible positions of ions in particular phases.

Three phase transitions are observed in PyClO₄ and the accompanying entropy changes are given in table 1. A small value of the entropy change at T_3 suggests a displacive nature of this phase transition. Also dielectric measurements do not show any characteristic changes near this temperature, which could be connected to a change of the electric dipole reorientation. Probably this transition is related to a slight ion deformation or a very small displacement of ions. Because the changes were observed in the direction parallel to the threefold axis (see figures 7 and 8) displacement along this direction can be expected. To prove our supposition, precise structural investigation near this phase transition is required.

The other phase transitions are accompanied by larger values of ΔS , which suggests their order–disorder characters. The total change in entropy at a first-order phase transition is a sum of the orientational entropy ΔS_O and the volume entropy ΔS_V :

$$\Delta S = \Delta S_O + \Delta S_V.$$

In order to find out the exact number of possible inequivalent positions of the ions, the value of the volume entropy is needed. One of the methods of its estimation is based on the following formula [20–22]:

$$\Delta S_V = \Delta V \frac{\alpha_V}{\beta}.$$

Assuming that the compressibility coefficient β is similar in all phases, the value of ΔS_{V1} is $2.5 \text{ J K}^{-1} \text{ mol}^{-1}$ at T_1 and ΔS_{V2} is $0.4 \text{ J K}^{-1} \text{ mol}^{-1}$ at T_2 . The total change in the volume part of the entropy ΔS_V is $2.9 \text{ J K}^{-1} \text{ mol}^{-1}$. This value is relatively low compared with the total entropy, which means that the main contribution to the change in entropy of PyClO₄ originates from the orientational part of the entropy, that indicates a change in the dynamics of the ions. Knowing the change of the orientational entropy, the change in the number of inequivalent positions can be estimated from the relation

$$\Delta S_O = R \ln N_1/N_2,$$

where N_1 and N_2 are the numbers of inequivalent positions in the high- and low-temperature phases and R is the gas constant. The total change of the orientational entropy is close to $\Delta S = R \ln 12$, so $N_1/N_2 = 12$. From previous investigation it is known that the pyridinium cation can take six inequivalent positions at room temperature [7]. This number is typical of pyridinium salts of the same structure, such as pyridinium iodide, pyridinium hexafluorophosphohate and pyridinium tetrafluoroborate [12, 23, 24]. In the low-temperature phase the cation reorientations stop. The number of cation positions in the low-temperature phase has not been determined, but it is reasonable to suppose that the phase is ordered and the number of possible cation positions is 1. In the high-temperature phase, the anion performs reorientations and has at least two possible positions. These reorientations slow down with decreasing temperature.

The orientational entropy change of PyClO₄ is about $\Delta S_1 = R \ln 4$ at the Curie point and about $\Delta S_2 = R \ln 3$ at the low-temperature phase transition. Assuming these values, the mechanism of the phase transition could be as follows: at the Curie point the pyridinium cation begins to perform jumps among three positions ($\Delta S = R \ln 6/3 = R \ln 2$); a change in the cation motion induces a change in the anion reorientations. The number of inequivalent positions of the anion is reduced twice. The entropy change related to the change in the anion dynamics is $\Delta S = R \ln 2$. At the low-temperature phase transition the cation dynamics changes. Instead of three positions in the intermediate phase it has only one position in the low-temperature phase. At this phase transition the change in entropy related to the change of

the cation's dynamics is $\Delta S_2 = R \ln 3/1$. The change in the ClO_4 anion's dynamics does not contribute to the change in entropy.

Assuming the total change of entropy $\Delta S \approx R \ln 12$, an alternative mechanism of the phase transitions is also possible. At the Curie point, the entropy can change by $\Delta S_1 = R \ln 6$, while in the low-temperature phase $\Delta S_2 = R \ln 2$. Assuming these values the mechanism of the phase transitions may be the following. Below the Curie point the pyridinium cation is completely ordered and the number of possible cation positions is unity ($\Delta S_1 = R \ln 6/1$). At the low-temperature phase transition the anion stops at one of two possible positions ($\Delta S_2 = R \ln 2/1$). The first mechanism of phase transitions is consistent with the results of earlier investigation of PyClO_4 in which a slowing down of cation motions was observed in the low-temperature phases [7, 8].

The part of orientational entropy change in all phase transitions connected with the pyridinium cation position change is equal to $14.9 \text{ J K}^{-1} \text{ mol}^{-1}$ ($R \ln 6$). The smaller part of ΔS_0 , equal to $5.76 \text{ J K}^{-1} \text{ mol}^{-1}$ ($R \ln 2$), is related to the change of ion position numbers. From the structural studies [7] it is known that the ClO_4 anion is strongly disordered. If anions stop at low temperature then the value of the total entropy which we have obtained from the calorimetric measurements seems to be underestimated. This difference could be explained in two ways. The anions stop with decreasing temperature but they do not have a preferred orientation. So dynamical disorder is placed by statistical disorder. On the other hand, the ion motions could be correlated. As a result of this correlation the total number of possible orientations is much lower in the high-temperature phase. Such suggestions were made on the basis of previous NMR measurements of some pyridinium salts [11].

The values of enthalpy ΔH from the calorimetric measurements and ΔV from the dilatometric measurements (see table 1) were used to obtain the pressure dependence of the phase transition temperatures from the Clausius–Clapeyron relationship:

$$\frac{\partial T_0(p)}{\partial p} = T_0(p=0) \frac{\Delta V}{\Delta H}.$$

The calculated values are given with those obtained from the p – T diagram in table 3. A very good agreement between the values is clear.

The magnitude of $\Delta l_i/l_i$ and its sign provide information about the uniaxial pressure dependence of T_0 :

$$\frac{\partial T_0(p)}{\partial p_i} \approx T_0(p=0) \frac{V_m}{\Delta H} \Delta \left(\frac{\Delta l_i}{l_i} \right)$$

where V_m is the molar volume. The $\partial T_1/\partial p_i$ values calculated from our measurements are positive for the ferroelectric phase transition temperature in both directions ($\partial T_1/\partial p_{\perp} = 0.12 \text{ K MPa}^{-1}$ and $\partial T_1/\partial p_{\parallel} = 0.02 \text{ K MPa}^{-1}$). $\partial T_2/\partial p_i$ is negative when pressure is applied perpendicular to the threefold axis $\partial T_2/\partial p_{\perp} = 0.06 \text{ K MPa}^{-1}$ and positive for uniaxial pressure applied in parallel to this axis and positive ($\partial T_2/\partial p_{\parallel} = 0.08 \text{ K MPa}^{-1}$). Similar results were obtained for the PyBF_4 crystal although its phase transitions are continuous [12].

5. Conclusions

An additional second-order or weakly first-order phase transition in PyClO_4 was discovered at $T_3 = 236 \text{ K}$. A small entropy change related to this phase transition suggests its displacive nature.

As follows from the character of anomalies established in calorimetric and dilatometric studies, the phase transitions in PyClO_4 at T_1 and T_2 are discontinuous. These phase transitions are of the order–disorder type, in which the dynamics of both cations and anions changes.

The values of the volume part of the entropy change (ΔS_V) are relatively low compared with the total entropy.

Although PyClO_4 and PyBF_4 have different orders of phase transitions, the mechanisms of their phase transitions are similar.

The pressure dependences of the phase transition temperatures obtained via the Clausius–Clapeyron relationship are in agreement with the p – T phase diagram. There is no change in the character of the first-order phase transitions up to 800 MPa.

Large anisotropy is expected in the presence of uniaxial pressure.

Acknowledgments

The authors wish to express thanks to Dr P U Mayr and Anne-Marie Saier for their help during dilatometric measurements and Dr G W H Höhne for his help in DSC measurements.

References

- [1] Scott J F 2000 *Springer Series in Advanced Microelectronics: Ferroelectric Memories* (Berlin: Springer)
- [2] Francombe M H (ed) 2000 *Handbook of Film Devices: Ferroelectric Film Devices* vol 5 (New York: Academic)
- [3] Zhong W L, Jiang B, Zhang P L, Ma J M, Cheng H M and Yang Z H 1993 *J. Phys.: Condens. Matter* **5** 2619
- [4] Shih W Y, Shih W H and Aksay I A 1994 *Phys. Rev. B* **50** 15 575
- [5] Ayyub P, Palkar V R, Chattopadhyay S and Multani M 1995 *Phys. Rev. B* **51** 6135
- [6] Czarnecki P, Nawrociak W, Pająk Z and Wąsicki J 1994 *J. Phys.: Condens. Matter* **6** 4955
- [7] Czarnecki P, Wąsicki J, Pająk Z, Goc R, Małuszyńska H and Habryło S 1997 *J. Mol. Struct.* **404** 175
- [8] Wąsicki J, Lewicki S, Czarnecki P, Ecolivet C and Pająk Z 2000 *Mol. Phys.* **98** 643
- [9] Czarnecki P, Katrusiak A, Szafraniak I and Wąsicki J 1998 *Phys. Rev. B* **57** 3326
- [10] Wąsicki J, Kozak A, Pająk Z, Czarnecki P, Belushkin A V and Adams M A 1996 *J. Chem. Phys.* **105** 9470
- [11] Wąsicki J, Pająk Z and Kozak A 1990 *Z. Naturf.* a **45** 33
- [12] Szafraniak I, Czarnecki P and Mayr P U 2000 *J. Phys.: Condens. Matter* **12** 643
- [13] Dollhopf W, Barry S and Strauss M J 1991 *Frontiers of High-Pressure Research* ed H D Hochheimer and R D Ethers (New York: Plenum) pp 25–32
- [14] Höhne G W H, Dollhopf W, Blankenhorn K and Mayr P U 1996 *Thermochim. Acta* **273** 17
- [15] Ripmeester J A 1976 *Can. J. Chem.* **54** 3453
- [16] Hanaya M, Ohta N and Oguni M 1993 *J. Phys. Chem. Solids* **54** 263
- [17] Toledano J-C and Toledano P 1987 *The Landau Theory of Phase Transition* (Singapore: World Scientific) p 186
- [18] Boccara N 1968 *Ann. Phys., NY* **47** 40
- [19] Perez-Mato I M, Ivantchev S, Garcia A and Etxebarria I 2000 *Ferroelectrics* **236** 93
- [20] Orani R A 1953 *J. Chem. Phys.* **19** 93
- [21] Karasz F E, Couchman P R and Klempner D 1977 *Macromolecules* **10** 88
- [22] Wurflinger A 1984 *Colloid Polym. Sci.* **262** 115
- [23] Lewicki S, Wąsicki J, Czarnecki P, Szafraniak I, Kozak A and Pająk Z 1998 *Mol. Phys.* **94** 973
- [24] Szafraniak I, Czarnecki P, Mayr P U and Dollhopf W 1999 *Phys. Status Solidi b* **213** 15