LETTER TO THE EDITOR

Specific heat and linear birefringence behaviour of 4-aminopyridinium tetrachloroantimonate (III), [4-NH$_2$C$_5$H$_4$NH][SbCl$_4$]

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Abstract
Thermal (specific heat) and optical (linear birefringence) studies were performed for a new ferroelectric crystal [4-NH$_2$C$_5$H$_4$NH][SbCl$_4$]. Four phase transitions were confirmed and described. Thermal parameters (ΔH, ΔS) of the normal–incommensurate, N–IC, and incommensurate–ferroelectric commensurate, IC–F(C), phase transitions are given. The order–disorder mechanism of the N–IC phase transition is proved but the displacive one for the IC–F(C) transition can be proposed. The critical index value ($2\beta = 0.68 \pm 0.02$) estimated from the linear birefringence measurements indicates that the N–IC phase transition can be described in terms of the 3d XY model.

Introduction

4-aminopyridinium tetrachloroantimonate (III) (4-APCA), [4-NH$_2$C$_5$H$_4$NH][SbCl$_4$], is a member of the family of general formula R$_a$M$_b$X$_{3b+a}$ (where R = organic cations, M = Sb, Bi and X = Cl, Br, I) [1–6]. The crystal structure of 4-APCA is made of polyanionic chains of (SbCl$_4^-$) and 4-aminopyridinium cations connected via weak hydrogen bonds to the chlorine atoms [7]. 4-APCA is a unique structurally incommensurate (IC) ferroelectric crystal with the following sequence of phase transitions [7, 8]:

phase	(V) P2$_1$/c	(IV) Cc	(III) Cc (0β0)	(II) C/2c (0β0)s0	(I) C2/c
	nonpolar	ferroelectric (IC)	ferroelectric C	incommensurate IC	paraelectric N
cooling/heating	240/245 K	248/250 K	270.5/271 K	304/304 K	

Recent x-ray studies by Pietraszko *et al* [8] showed that phase (II) is characterized by a modulation wavevector $\mathbf{q} = \beta\mathbf{b}^*$, with the modulation parameter β changing from 0.58 at

300 K to 0.66 at 270 K, whereas $\beta \approx 0.66$ in the commensurate structure of ferroelectric phase (III). In the paraelectric phase (I) the 4-aminopyridinium cation is distributed between two positions with occupancy factor 0.5/0.5, whereas in the ferroelectric phase all organic cations (three types) are ordered. In view of recent x-ray studies the ordering of cations is expected to contribute to the normal–incommensurate (N–IC) phase transition mechanism at 304 K. The measurements of the complex dielectric constant of $[4\text{-}NH_2C_5H_4NH][SbCl_4]$ over the IC phase (II) in the frequency range 200 Hz–1 MHz revealed a significant dielectric dispersion below 304 K. The dielectric relaxation was characterized by the apparent critical slowing down with $\tau \approx 1 \times 10^{-4}$ s close to T_C.

4-APCA seems to be a very attractive polar material from the viewpoint of critical phenomena because of its interesting sequence of phase transitions. As with other ferroelectric crystals with IC modulation, linear birefringence (LB) and ac calorimetry measurements have been very useful methods to investigate critical behaviour in 4-APCA.

The aim of present studies is to characterize this quite complex phase sequence using precise thermal and optical techniques.

1. Thermal studies

The ac calorimetry was used for detailed studies of the heat capacity of the 4-APCA crystal. The method seems to be very effective in the study of phase transition because it offers high resolution and detailed temperature dependence of the specific heat near transition temperatures. A computer controlled ac calorimeter (Sinku-Riko ACC 1M/L) equipped with a PID temperature programmer was used. The ac calorimetric measurements were made with a chopping frequency of 2 Hz during heating and cooling at a rate of 0.05 K min^{-1}. Chromel–constantan thermocouple wires of 25 μm were attached to the rear face of a thin ($\sim$0.2 mm) sample. It should be taken into account that absolute values of the specific heat could be determined only in a relative way, by a comparison with a response of the model sapphire sample, and they were not compared with the c_p-values obtained by an adiabatic calorimeter.

Figure 1 shows the temperature dependence of the specific heat during cooling in the limited temperature range. Four anomalies connected with the previously mentioned phase transitions were detected at temperatures 304, 270, 247 and 241 K. Since the ac calorimeter can be used only for qualitative studies of first order transitions one can notice a temperature hysteresis during heating and cooling for both transitions at 247 K (of 0.4 K) and 241 K (of 1.8 K) respectively; see figure 2. It was concluded from dielectric studies that the ferroelectric phase transition took place at about 270 K.

The N–IC phase transition was registered at about 304 K. This most pronounced anomaly, presented in figure 3, is very typical for a second order phase transition. There was no temperature hysteresis observed during heating and cooling. We tried to estimate the excess enthalpy associated with the transition after subtracting the approximate background. Integrating the excess specific heat Δc_p one can get $\Delta H_{\text{N–IC}} = 1855$ J mol^{-1}. The excess entropy change $\Delta S_{\text{N–IC}}$ was determined by integrating $\Delta c_p/T$ over the same temperature range as above (277.67–324.95 K) giving 6.23 J mol^{-1} K^{-1}. The obtained value is very close ($\approx$1.08) to $R \ln 2$, where R is the gas constant, and it suggests that the 4-aminopyridinium cation can take up one of two possible sites.

The transition to the ferroelectric phase at about 270 K can be regarded as the transition to the commensurate phase (III) [8]. In our transients one can only notice at this temperature region a slightly diffused cusp (see figure 4), but it shows a sharp increase on the low temperature side and a more gradual fall on the high temperature side. This specific feature has been observed earlier for lock in transitions [9, 10]. It was rather difficult to estimate a regular
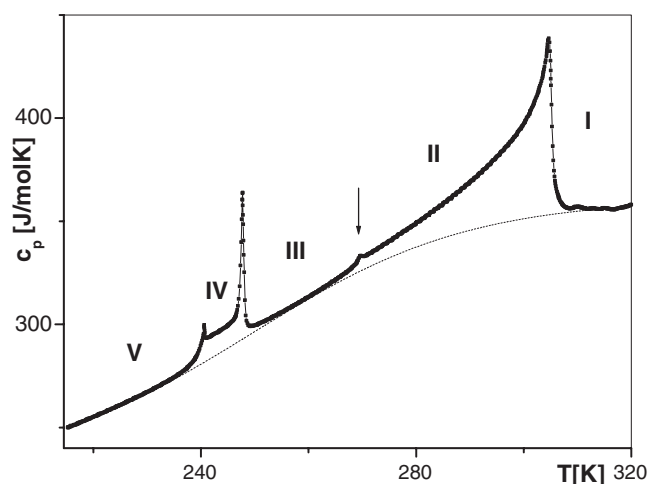
Figure 1. Temperature dependence of the specific heat for the 4-APCA crystal. The approximate lattice contribution is presented. The arrow points to the small anomaly connected with the II → III ferroelectric phase transition.
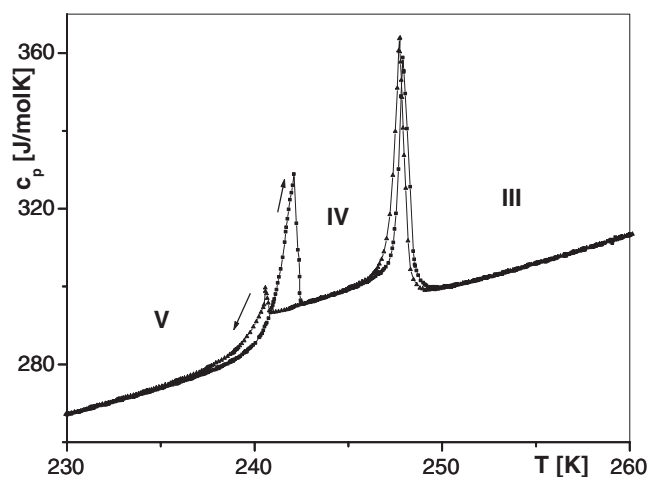

Figure 2. Temperature hysteresis observed during heating and cooling for two first order phase transitions: lock in from the ferroelectric C to ferroelectric IC and ferroelectric IC to nonpolar phase.

background contribution to the specific heat. This is why the cusp shown in the figure 4 was obtained after subtraction from the prolonged $c_p(T)$ dependence. We have determined the thermodynamic properties of the transition II → III as $\Delta H_{IC-F(C)} = 11.62$ J mol^{-1}, and $\Delta S_{IC-F(C)} = 0.043$ J mol^{-1} K^{-1}, respectively. These values are quite close to those reported for lock in transitions in Rb$_2$ZnCl$_4$ and Rb$_2$ZnBr$_4$ [9, 10].

It can be concluded from our specific heat measurements that the N → IC phase transition at about 304 K can be regarded as of the 'order–disorder' type. This conclusion is confirmed and supported by crystallographic x-ray studies [8]. It was shown that the reorientation of the 4-aminopyridinium cation can be regarded as the main mechanism of the transition. It should be underlined that a similar model, based on averaging of the structure of phase (II),
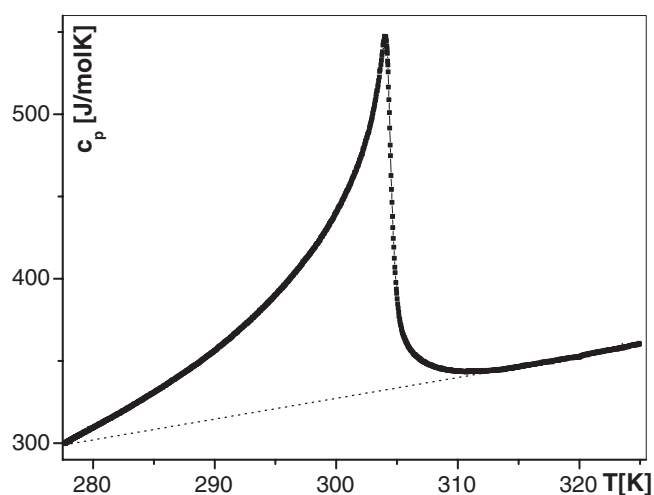
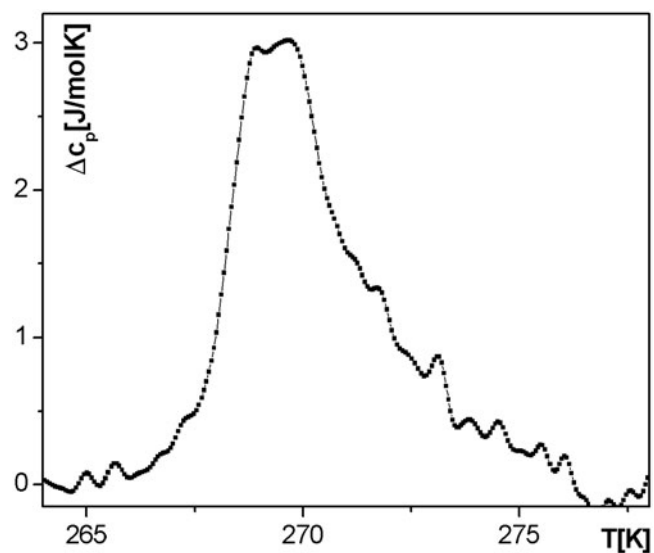**Figure 3.** The specific heat transient at the N–IC (I → II) phase transition.

Figure 4. The excess specific heat at the incommensurate–ferroelectric commensurate (II → III) phase transition at 270 K.

was proposed previously in [7] for the transition to the ferroelectric phase at 270 K. Our calorimetric studies unambiguously confirmed that the dynamics of organic cations mainly contributed to the phase transition (I → II) mechanism. The molecular mechanism of the transition from the incommensurate IC → F (ferroelectric) C, (II → III), at 270 K is still not fully clear. The cation dynamics seems to play an insignificant role, as can be concluded from the very small entropy change ($\Delta S_{IC-F(C)} = 0.043$ J mol^{-1} K^{-1}) at this transition. This may reflect the fact that the II → III phase transition has a displacive character.
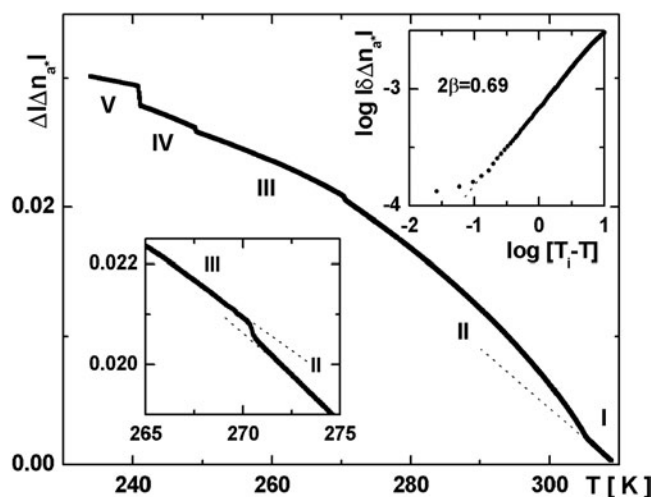
Figure 5. Temperature dependence of the LB change for the a^*-cut of the 4-APCA crystal. The insets show the small jump at about 270 K and a log–log plot of $\delta(\Delta n_{a^*})$ versus $(T_i - T)$.
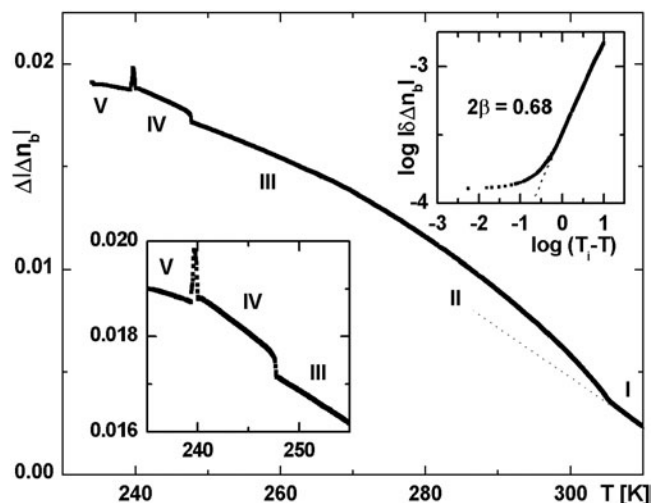

Figure 6. Temperature dependence of the LB change for the b-cut of the 4-APCA crystal. The insets show two first order phase transitions and a log–log plot of $\delta(\Delta n_b)$ versus $(T_i - T)$.

2. Linear birefringence studies

For better characterization of phase transitions in the [4-NH$_2$C$_5$H$_4$NH][SbCl$_4$] crystal we have also measured the temperature dependence of LB changes using the rotating analyser method [11]. Observations of the phase front with the aid of a polarizing microscope endowed with an Ehringhaus type optical compensator completed our method. At room temperature the crystal exhibited distinct optical anisotropy: $\Delta n_{a^*} \approx 0.13$ (direction of the obtuse bisectrix), and $\Delta n_b = n_c - n_a \approx 0.145$ (direction normal to the optical plane). These two chosen cuts of the studied crystal were explored. The first cut—close to a normal to the a-axis—showed four anomalies on the LB versus temperature curve (figure 5).

The phase transition at $T_i = 305$ K is of the continuous type, whereas anomalies at about 248 and 240 K confirm the discontinuous character of the phase transitions. The lowest one (IV $\rightarrow$ V) shows a thermal hysteresis of about 4 K. A small jump-like step was observed at 270 K. Similar results were obtained for the b-cut, but in this case the anomaly at 270 K was not detectable (see figure 6).

The phase transition N–IC at about 305 K may be characterized by a power dependence: $\delta(\Delta n_b) \sim (T_i - T)^{2\beta}$, where $2\beta = 0.68 \pm 0.02$, (β being the critical index of the order parameter). Theoretical predictions [12] ascribed the N–IC phase transition to the universal class of the three-dimensional XY model. For the three-dimensional two component ($n = 2$) Heisenberg model the 2β index was found to be equal to 0.70 ± 0.04 [13]. It seems clear that the N–IC phase transition at 305 K can be classified as the 3d XY type.

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