# Optical anisotropy of $(C_3H_7NH_3)_2CuCl_4$ and $(C_3H_7NH_3)_2MnCl_4$ crystals

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## Abstract

Using the Senarmont and the universal null-polarimetric techniques, the birefringence, optical indicatrix orientation and the gyration of (001) bis-propylammonium tetrachlorocuprate crystal are studied above the room temperature. The indicatrix rotation and the normal light wave ellipticity related to the gyration effect are found to be less than $\sim 10^{-4}$ and $\sim 2\cdot 10^{-4}$, respectively, including the temperature region of the incommensurate γ phase. The birefringence of iso-propylammonium tetrachloromanganate crystal is also measured and the second-order phase transition at 38 °C is found.

**Key words:** phase transitions, incommensurate phase, symmetry, gyration, polarimetry

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## Introduction

Tetrachlorocuprate and tetrachloromanganate of propylammonium, $(C_3H_7NH_3)_2CuCl_4$ and $(C_3H_7NH_3)_2MnCl_4$, abbreviated to PACC and PAMC in the following text are representatives of a general family of $A_2BX_4$ crystals which belong to the group $(C_nH_{2n+1}NH_3)_2MeCl_4$, where $n = 3$ and Me = Mn, Cu. Recently, the above materials have attracted much attention of researchers since they manifest a variety of structural phase transitions, including ferroelectric, ferroelastic and incommensurately modulated ones [1]. Another interesting point is the existence of the two isomorphic modifications of their propylammonium cation, the so-called *bis*- and *iso*- forms. As a result, the corresponding modifications of PACC and PAMC crystals differ notably in their physical properties. So, the crystals of *bis*-PACC have a layered structure and possess rich sequence of structural phases, of which high-temperature part is illustrated in Fig.1. The incommensurate γ phase of a "re-enter" type [1] is rather unusual as it is located between the β and δ phases described by the same orthorhombic space symmetry groups. As it is seen from Fig.1, some contradiction still remains with respect to the phase transition points [2-7]. It should be noted that the *iso*-modifications of PACC and PAMC crystals are studied in a much less detail. It is only known that *iso*-PACC exhibits the ferroic and thermochromic properties (see [7]).

Some optical properties of PACC and PAMC have been reported in [2,5-7], in particular optical absorption and the linear birefringence. Besides, the authors [8] have observed a controversial effect of optical activity in the γ phase of *bis*-PAMC, despite of

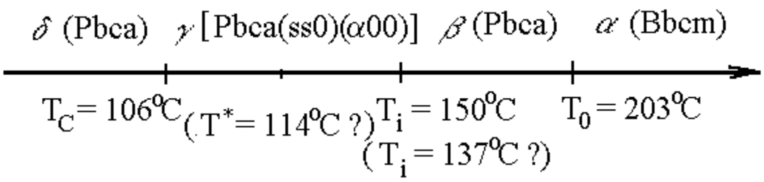


**Fig.1.** Schematic representation of high-temperature structural transformations in *bis*-PACC and the temperatures of phase transitions according to the data [2,4,6,7].

that this phase should be macroscopically characterized by the inversion point group *mmm* of the β and δ phases, and so the effect might have been symmetry forbidden. This fact encourages further crystal optical experiments on the above materials. In this work we report the results of our combined studies of the birefringence, the optical indicatrix rotation and the optical activity in *bis*-PACC and partly *iso*-PAMC, performed with both commonly known Senarmont technique and the universal null-polarimeter [9,10].

## Experimental

We prepared several bis-PACC samples with their optical surfaces parallel to the (001) cleavage plane and typical thicknesses of about 0.1 mm. The 0.44 mm thick (001) *iso*-PAMC sample was obtained with the standard methods of crystal polishing. Due to specific features of our temperature controlling apparatus, we worked only in the temperature range above the room temperature. The sample temperature was controlled with the accuracy of ~ 0.05 °C and measured with the copper-constantan thermocouple. The experiments according to the universal null-polarimetric method were carried out in the regime of temperature stabilization. Typical times for stabilization of each temperature point were from 40 min to 1 h, because we had clearly seen that a drift of the measured data took place with less times (see also [11]). The Senarmont measurements were performed so that the sample temperature was being scanned continuously in the heating run. The 50 mW He-Ne laser with the wavelength $\lambda = 632.8$ nm was used as a light source.

Our optical thermostat did not contain any optical windows in order to avoid the errors originated from the stress-induced birefringence and optical activity in those windows [9]. This imposed certain experimental problem, since, in the open atmosphere, the optical surfaces of both crystals had appeared to loss their quality and get "muddy" at high temperatures. The latter fact evidently contradicted the requirements of accurate temperature stabilization, especially in the case of measurements with the universal null-polarimetric method, and caused the limitations of the temperature range under test. Our practical way out lied in measurements on several samples. In the particular case of PACC, we performed three experiments C2, C3 and C4, using the samples with the thicknesses $d_{C2} = 0.08$ mm, $d_{C3} = 0.16$ mm and $d_{C4} = 0.13$ mm.

The Senarmont technique is well described in the open literature. As for the universal null-polarimetric technique, the determination of crystal optical properties is based on measuring, at each temperature, the parameters

$$d\chi / d\theta = \cos\Delta, d\varepsilon / d\theta = \sin\Delta, \quad (1)$$

$$\varepsilon_0 = 2k - p_0 + \delta\chi \cot(\Delta/2), \quad (2)$$

$$\theta_0' = \theta_{orig} + \Delta\theta + (k - p)\cot(\Delta/2) + \delta\chi / (1 - \cos\Delta). \quad (3)$$

Here $\chi$ and $\varepsilon$ are the azimuth and the ellipticity of the light emergent from the crystal, $\theta$ the incident light azimuth lying in the HAUPregion (see, e.g., [8,9]), $\Delta = (2\pi d / \lambda)\Delta n$ the phase retardation (with $\Delta n$ being the birefringence), $k = g_{33} / (2\bar{n}\Delta n)$ the ellipticity of normal light waves in crystal (with $g_{33}$ being the gyration tensor component and $\bar{n}$ the mean refractive index), $\Delta\theta$ the orientation angle of the optical indicatrix, $p$, $p_0$ and $\delta\chi$ the effective parameters of imperfection of the polarizers, and $\theta_{orig}$ the apparatus constant (see, e.g., [9]).

## Results and discussion

The temperature dependence of the birefringence of *iso*-PAMC crystal obtained with the Senarmont technique is presented in Fig.2. We were unable to derive data above 53 °C because of a progressive light scattering at the sample surfaces. As it is seen from Fig.2, the birefringence variations in the overall temperature range are approximately $2 \cdot 10^{-4}$. A clear change in the temperature slope occurs at $T_C$ = 38 °C, testifying the second-order phase transition at this point. The critical exponent calculated on the basis of spontaneous increment of the birefringence in the course of the phase transition is determined to be β = 0.52. A nature of this structural transformation, as well as the temperature behaviour of the other crystal optical parameters of *iso*-PAMC, will be elucidated in detail elsewhere.

The appropriate results derived with the Senarmont technique of the *bis*-PACC sample with the thickness $d_{C1}$ = 0.06 mm are depicted in Fig.3. As to the PAMC crystal, the deficiency in the sample surface quality did not allowed us to study the birefringence up to the phase transition temperature $T_i$ equal 137 °C [6,7] (or 150 °C [2,4]). For this reason, the experimental accuracy in the high-temperature region gradually decreased. It is seen from Fig.3 that the birefringence changes almost monotonously with temperature, unlike the results [2] where the phase transitions effect is very clear. The main features of the temperature behaviour found here are in general similar to those reported in [5,6], in particular the total variation range and the temperature slopes at lower and higher temperatures. In contrast to the data [6], however, we cannot say anything certain of the temperature point $T^*$ = 114 °C. Slight anomalies visible in the vicinity of $T^*$ may be a very good result of inadequate accuracy. So the nature of the birefringence peculiarity [6] at $T^*$ awaits its

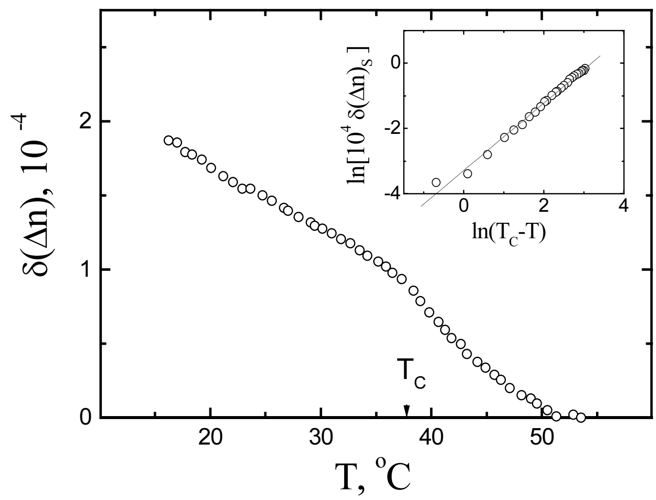


**Fig.2.** Temperature dependence of linear birefringence of *iso*-PAMC crystal with an arbitrarily taken origin (temperature scan rate $dT/dt$ = 21 °C/h). The inset shows the log-log plot of the spontaneous birefringence changes $\delta(\Delta n)_S$ at the phase transition versus ($T_C$ - $T$).

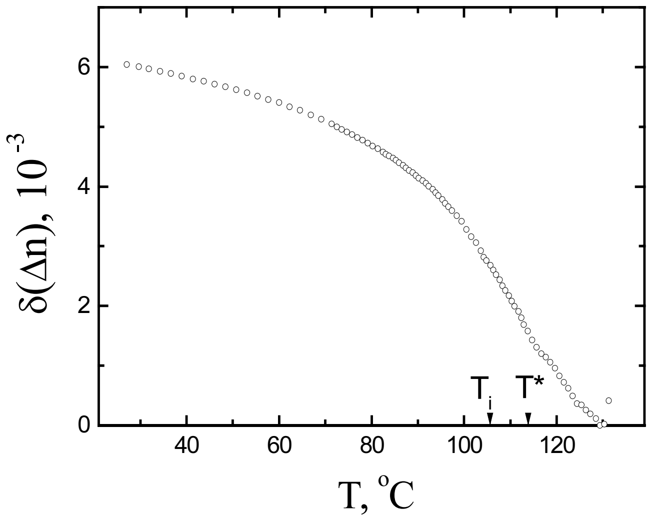


**Fig.3.** Temperature dependence of linear birefringence for *bis*-PACC crystal with an arbitrarily taken origin (temperature scan rate $dT/dt$ = 60 °C/h).

further clarification. We remind in this respect that the authors [2-5] do not report any phase transitions near $T$*. As for the transition point $T_C$, our data support the value $T_C$ = 106 °C, though in this case only the birefringence results can hardly be regarded as decisive (see discussion in [5]).

The temperature dependences of cos$\varDelta$, $\varepsilon_0$ and $\theta_0'$ quantities of the *bis*-PACC crystal measured in one of the experiments (C2) with the aid of the universal null-polarimetric technique are depicted in Fig.4-6, respectively. It is seen that the phase retardation $\varDelta$ tends to $2\pi m$ ($m$ being an integer) at T ≈ 85 °C, leading to a divergent temperature behaviour of the measured quantities. We omitted the measurements in the corresponding temperature region, since the contributions of the imperfection parameters to $\varepsilon_0$ and $\theta_0'$ there exceed much those of the optical parameters $k$ and $\Delta\theta$ (see formula (2) and (3)). Neglecting the thermal expansion contributions to $\delta(\Delta n)$, one can calculate from the data of curve 1 in Fig.4 the relative values of the birefringence

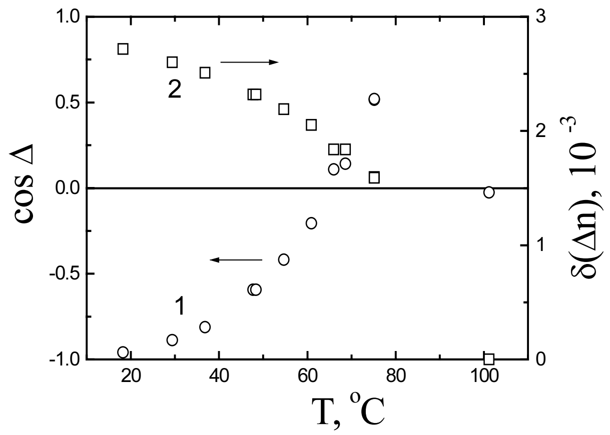


**Fig.4.** Temperature dependencies of cos$\Delta$ value (1) and the birefringence changes $\delta(\Delta n)$ (2) for *bis*-PACC crystal obtained in the experiment C2.

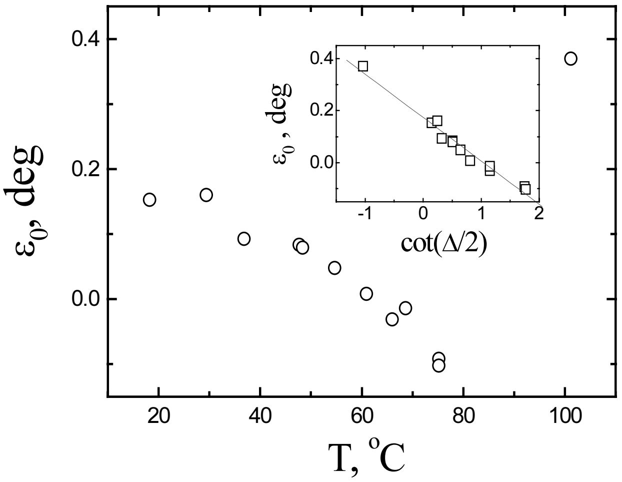


**Fig.5.** Temperature dependence of the characteristic ellipticity $\varepsilon_0$ of *bis*-PACC crystal obtained in the experiment C2. The inset represents a linear fit of $\varepsilon_0$ against $cot(\Delta/2)$ (see text).

(curve 2 in Fig.4). The results agree with those derived with the Senarmont technique fairly well (see Fig.3).

Fig.5, inset represents a linear fit of the characteristic ellipticity $\varepsilon_0$ against $cot(\Delta/2)$ for the overall temperature range, including the δ and γ phases. Since the corresponding mean square deviation is of the order of our accuracy (0.010 deg), we infer on the basis of formula (2) that the gyration effect is zero within the experimental accuracy ($k \approx 0$), while the ellipticity angles related to the imperfection parameters are equal $p_0$ = -0.173 deg and $\delta\chi$ = -0.166 deg. It is worthwhile to notice that the accuracies achieved in the present experiments C2, C3 and C4 turn out to be about ten times lower than those typical to our polarimeter (see [9,10]). We explain this fact by a comparatively low quality of samples. The latter imposes the conditions under which the imperfection parameters are not kept sufficiently invariable in the course of the experiments.

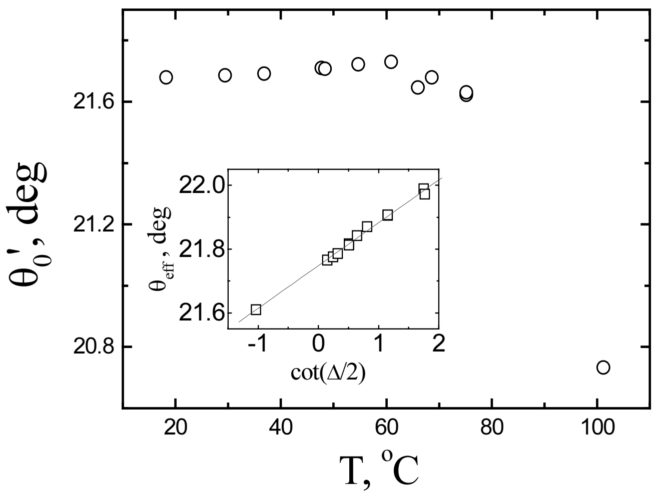


**Fig.6.** Temperature dependence of the polarizer scale reading $\theta_0'$ related to the invariant azimuth of *bis*-PACC crystal obtained in the experiment C2. The inset represents a linear fit of $\theta_{eff}$ against $cot(\Delta/2)$ (see text).

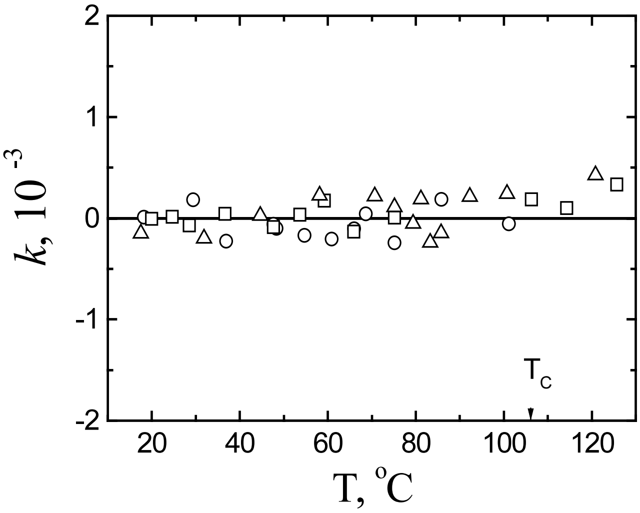


**Fig.7.** Temperature dependence of the normal wave ellipticity for *bis*-PACC crystal obtained in the experiments C2 (□), C3 (○) and C4 (Δ).

Let us now calculate the parameter related to the characteristic azimuth position, $\theta_{eff} = \theta_0' - k\,cot(\Delta/2) - \delta\chi/(1-cos\,\Delta)$.

According to formula (3),

$$\theta_{eff} = \theta_{orig} + \Delta\theta - p\,cot(\Delta/2)\,. \tag{4}$$

If the optical indicatrix rotation is assumed to be absent ($\Delta\theta = 0$), then the $\theta_{eff}$ parameter should depend linearly on $cot(\Delta/2)$. The dependence $\theta_{eff}$ versus $cot(\Delta/2)$ is shown in Fig.6, inset. It is indeed linear with the mean square deviation of 0.007 deg, and so we derive $p$ = -0.134 deg and $\theta_{orig}$ = 21.748 deg. Similar results were also obtained in the experiments C3 and C4 and the accuracy was always not worse than 0.01 deg. As a result, we conclude that the effect of the optical indicatrix rotation in *bis*-PACC is zero or, at least, less than 0.01 deg, in accordance with simple symmetry considerations for the orthorhombic structure of *bis*-PACC.

Finally, using the data of all the experiments C2, C3 and C4, we have calculated the normal wave ellipticity *k* in a way described above. The results are brought together in Fig.7. The average *k* value observed in the δ phase is certainly zero ($<k_\delta> \approx 0$), with the mean square deviation of $[<k^2_\delta>]^{1/2} = 1.4\cdot10^{-4}$. The average normal wave ellipticity slightly deviates from zero in the incommensurate γ phase ($<k_\gamma> = 2.6\cdot10^{-4}$) but there are few data points there and, moreover, the $<k_\gamma>$ value is too close to the experimental accuracy. Therefore, we infer that the optical activity effect is in general zero or less than ~ $2\cdot10^{-4}$.

In conclusion, the findings of the present study associated with the optical indicatrix rotation and the gyration effect in the *bis*-PACC crystals agree with the inversion, orthorhombic symmetry of the δ phase and the macroscopically "averaged" inversion symmetry of the γ phase. On the other hand, recent theoretical studies [12] demonstrate that (relatively weak) optical activity can still exist in a macroscopically centrosymmetric, spatially inhomogeneous incommensurate structure. With our experimental accuracy, we might possibly miss such a weak effect, if any. In order to reach decisive conclusions concerning this point, more extensive studies are necessary. This requires a number of technical improvements of the polarimetric apparatus.

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