Studies of Phase Transition Sequence in $(C_3H_7NH_3)_2CuCl_4$ Crystals

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Abstract

Using the Senarmont polarimeter and the quartz dilatometer, temperature dependences of optical birefringence and thermal expansion of $(C_3H_7NH_3)_2CuCl_4$ crystals are studied. The temperature positions and characteristics of the phase transitions are discussed and the structure-defect interaction effects in incommensurate γ phase are revealed.

Key words: phase transitions, incommensurate phases, birefringence, thermal expansion.

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Introduction

Crystals exhibiting phase transformations into incommensurate (IC) phases attract a permanent interest of researchers (see, e.g., [1-4]). Propylamine tetrachlorocuprate $(C_3H_7NH_3)_2CuCl_4$ is a representative of A_2BX_4 family that belongs to particular $(C_nH_{2n+1}NH_3)_2MeCl_4$ subgroup (with n = 3 and Me = Cu) [4]. A number of structural modifications, as well as a rich variety of structural phases occurring with changing temperature, are peculiar for this group. In particular, there are two isomorphous *bis*- and *iso*- forms that differ essentially by their physical properties. The object of our interest is the *bis*-modification of $(C_3H_7NH_3)_2CuCl_4$ abbreviated hereafter as BPA-Cu. This is a layered crystal that manifests a complex sequence of phase transitions (PTs). According to [5], for the regime of crystal cooling it may be represented by the scheme

$$\xi \xleftarrow{132K} \varepsilon \xleftarrow{180K} \delta \xleftarrow{378K} \gamma \xleftarrow{423K} \beta \xleftarrow{436K} \alpha,$$

though there has been much disagreement in the data by different authors and the relevant PT points sometimes differ as much as tens of Kelvins (see [4-7]). It is certain at least that the BPA-Cu possesses several ferroelastic and IC phases, among which the IC phase γ of a "re-enter" type looks interesting since it is located between the two identical β and δ phases with the orthorhombic symmetry *Pbca* [1].

Besides of the important question of PT temperatures for BPA-Cu, the properties of such the re-entrant IC phases are still less known than those of the more common IC phases. One of particular problems is manifestations of so-called temperature "irreversible" phenomena linked with the interaction of IC structure and defects [1-2], e.g., the global thermal hysteresis, temporal relaxation of physical properties, thermal "memory", etc. The aim of the present work is to study temperature behaviours of linear optical birefringence (LB) and linear expansion of BPA-Cu in the course of PTs, determine the PT temperatures and reveal the mentioned "irreversible" effects in those crystals.

Experimental

We prepared several (001) BPA-Cu samples, using the availability of natural cleavage planes. The typical thickness (~ 0.1 mm) was chosen starting from the absorption coefficient value and the requirements of optimum polarimetric sensitivity. Especial care was taken of plane-parallelism of their surfaces, in order to ensure a minimum "smearing out" of the optical phase retardation $\Delta = 2\pi d\Delta n/\lambda$ (with d being the sample thickness, Δn the LB and λ the free-space light wavelength) due to a finite cross-section of the probing laser beam [8]. The sample was placed into thermostat enabling us to control temperature above the room one with the accuracy of about ~ 0.05 K. In some experiments we avoided using optical windows [8]. They improved temperature stabilization though imposed ill-controlled temperature-dependent stress-induced LB and so distorted the true $\Delta n(T)$ dependence. The temperature was changed in a "quasi-continuous" heating run, the variation rate being d*T*/d*t* = 2 – 25 K/h.

LB was measured with the standard Senarmont technique, with the light propagated along the principal axis *z*. Single-mode He-Ne laser LG-38 (λ = 632.8 nm, the output power 50 mW, and the light beam divergence $5\cdot 10^{-4}$ rad) was employed as a light source. The accuracy for the LB was estimated to be slightly higher than $\sim 10^{-5}$, being mainly determined by the phase retardation "noises" mentioned above, the thermooptical coefficient and the temperature stabilization tolerance. This value should be qualified as quite good in case of our objects (cf. [5-7]).

Linear thermal expansion was studied with the aid of quartz dilatometer with the capacitive expansion sensor, ensuring the sensitivity of about 1 nm and a small enough pressure (~ 10 g.) upon the crystals sample. The sample was continuously heated with the rate d*T*/d*t* = 60 K/h. The temperature range under studies was 77 – 435 K, though the accuracy in the highest region (~ 20 K) became progressively lower due to worsening sample quality (see also below).

Results and discussion

Figure 1 shows our LB results (curve 1), along with the corresponding data derived in the work [6] (curve 2) for a comparison. The dotted lines in Figure 1 are extrapolated using close enough

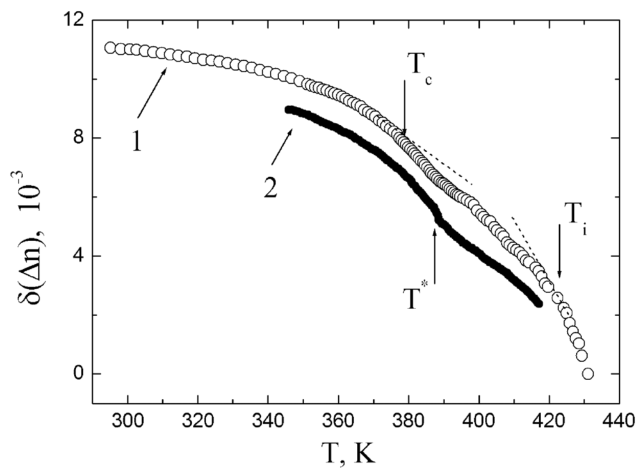

Fig. 1. Temperature dependences of the relative LB value $\delta(\Delta n)$ for BPA-Cu crystals: curve 1 – our results (heating run, d*T*/d*t* = 25 K/h), curve 2 – the data [6].

experimental points within the regions below the δ–to–γ PT point T_C and above the γ–to–β PT point T_i. Notice that the samples were gradually getting "muddy" in the open air with increasing temperature, beginning from about 400 K. Therefore we did not perform the optical experiments at $T > 430$ K for the reason of a notable accuracy reduction.

Both curves in Figure 1 change smoothly and reveal two second-order PTs. Our results for the PT points limiting the re-entrant IC phase γ are respectively T_C = 377 K and T_i = 423 K. The former value is in a fair accordance with the literature data [4-7], while the latter correlate with the results [4,5] (423 K) but not those of the studies [6,7] (410 K and 413 K, respectively). Since the temperature dependence of LB is essentially nonlinear in all the phases and the PT-led changes smooth, the accuracy for determining the Curie points is not high enough. It may be increased while using the temperature dependences of the derivative $\mathrm{d}[\delta(\Delta n)]/\mathrm{d}T$. So, the authors [6] report the values T_C = 379 K and T_i = 410 K. However, the data for $\mathrm{d}[\delta(\Delta n)]/\mathrm{d}T$ calculated with the results [6] give T_C = 381 K and T_i = 408 K. By the way, the results taken from the other sources may be also improved this way. For instance, the authors [5] state that T_C = 378 K, whereas the relevant $\mathrm{d}[\delta(\Delta n)]/\mathrm{d}T$ data yield T_C = 375 K.

The results of our dilatometric experiment are represented in Figure 2. It is evident that the dilatation corrections to the LB data (< 4%) are not of a primary importance and cannot distort notably the $\delta(\Delta n)$ dependence near the PT points. One can see that the sample dimensions suffer a jump-like change in the course of the low-temperature first-order ξ–to–ε PT, manifest a noticeable slope change at the ε–to–δ PT, corresponding to a second-order transformation, and then remain almost unchangeable up to the room temperature. While performing measurements in the cooling run, we have observed a clear temperature hysteresis of the

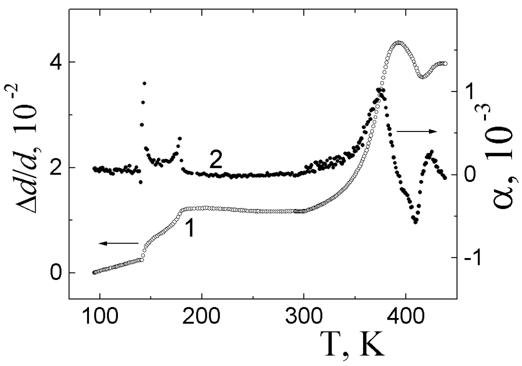

Fig. 2. Temperature dependences of the relative value of linear thermal expansion $\Delta d/d$ (curve 1) and the expansion coefficient α (curve 2) for BPA-Cu crystals (heating run, d*T*/d*t* = 60 K/h).

ξ–to–ε PT (~ 10 K). Notice that the dependence $\Delta d/d$ of Figure 2 matches qualitatively that obtained in the study [5], except for the highest-temperature region. Using the temperature dependence of the thermal expansion coefficient α, we get the following PT temperatures: $T_{\xi\to\varepsilon} = 141$ K, $T_{\varepsilon\to\delta} = 179$ K and $T_C = 377$ K. All of those results agree well with the earlier data [4-7] (e.g., $T_{\xi\to\varepsilon} = 142$ K [5] and $T_{\xi\to\varepsilon} = 141$ K [7] (both obtained in the heating run) and $T_{\varepsilon\to\delta} = 180$ K [5,7]).

There is still uncertainty regarding the Curie temperature T_i, since the two points (409 K and 423 K) are seen in Figure 2 that may be suspected as the PT temperature. Curiously, those points are very close to the T_i values reported respectively in [6,7] and [4,5] (see the discussion of the LB). Unfortunately, both our LB and dilatometric results in the region of the highest temperatures are marked somewhat by the decreased accuracy mentioned above and so further investigations are necessary in order to shed some light upon the problem of disagreement in the β–to–γ PT location. It seems also that our results support the viewpoint that at least some of the PT temperatures for BPA-Cu are sample-dependent.

According to [6], additional peculiar point T^* = 388 K exists inside the IC phase γ. It has been explained [6] as a transition from the sine spatial modulation to the multi-soliton region, despite of that the structural data for the isomorphous *bis*-$(C_3H_7NH_3)_2MnCl_4$ do not testify such the transition and, moreover, the latter is a continuous process and can hardly take place at a single temperature point. Since the results of our studies and those known from the literature [4,5,7] do not reveal this peculiarity, we conclude that the $\delta(\Delta n)$ behaviour [6] detected in the vicinity of T^* should be rather related to some experimental apparatus imperfections than the characteristics of BPA-Cu itself. One of the reasons may be internal multiple light interference effects in thin samples (see, e.g., the data presented in Figure 2a). It is worthwhile in this respect that the peculiar point T^* found in [6] for *bis*-$(C_3H_7NH_3)_2MnCl_4$ coincides, with the accuracy of ± 1 K, with the PT point T_C detected by the other authors [9,10].

Let us now analyse the temperature dependences of spontaneous LB increments $\delta_s(\Delta n)$ due to the PTs (Figure 3). This allows determining critical indices β_1 and β_2 of the PTs according to the relations

$$\delta_s(\Delta n) \sim (T - T_C)^{2\beta_1}, \quad \delta_s(\Delta n) \sim (T_i - T)^{2\beta_2}. \qquad (1)$$

In frame of the canonical Landau theory for the second-order PTs, a usual result $2\beta_{1,2} = 1$ holds true. Plotting $\delta_s(\Delta n)$ versus the reduced temperature ($\tau_1 = (T - T_C)/(T_i - T_C)$ and $\tau_2 = (T_i - T)/(T_i - T_C)$) in a logarithmic scale, one can in principle obtain the $\beta_{1,2}$ values. However, the correct technique for determining $\beta_{1,2}$ should take into account the validity limits for the simplified Landau approach ($|\tau| << G^{1/3}$, with the relative temperature τ being equal respectively to $\tau = (T - T_C)/T_C$ for the vicinity of T_C and $\tau = (T_i - T)/T_i$ for T_i, and $G = T_C B^2 / 8\pi^2 A_T D^3$ standing for a small Ginzburg parameter defined by the coefficients A_T, B and D near the lowest-order order parameter powers in the standard thermodynamical potential for the IC PTs – see, e.g., [11]). Therefore we have taken into account only the experimental points corresponding to 378–388 K above T_C and 400–422 K below T_i (see Figure 3). Moreover, one has to account for the order parameter fluctuations. Specifically, the latter effects may be considered within the approximation of first-order fluctuation corrections in the temperature region defined by the relationships [11]

$$G << |\tau| << G^{1/3}. \qquad (2)$$

As a result, we have also excluded the experimental points that correspond to the lower

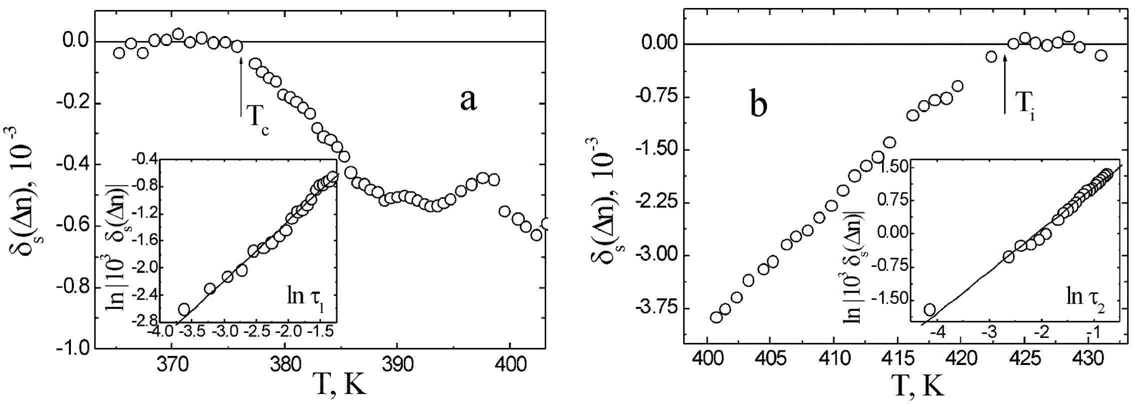

Fig. 3. Temperature dependences of the spontaneous LB increments $\delta_s(\Delta n)$ for BPA-Cu crystals in the course of PTs at T_C (a) and T_i (b). The inserts show logarithmic dependences $\delta_s(\Delta n)$ versus the reduced temperatures τ_1 and τ_2.

limit for the τ parameter in Eq. (2). Then the calculations of critical indices for the PTs at T_C and T_i (see Figure 3, inserts) have resulted respectively in the values $\beta_1 = 0.44 \pm 0.04$ and $\beta_2 = 0.48 \pm 0.05$, which turn out to be somewhat different from those found in [6].

Finally, we report on the temperature dependence of LB within the γ phase measured at different temperature scan rates. Some of the results are presented in Figure 3. As seen from Figure 4, the lower the d*T*/d*t* rate, the clearer step-like LB behaviour is observed, i.e. the temperature regions of rapid LB variations are followed by the regions where the LB remains almost invariable. When explaining those phenomena, one should consider that the LB is related to the phase of IC modulation wave and the latter could couple efficiently with point structural defects in a real crystal, under the condition of sufficiently slow temperature variations (see [2,12,13]). The temperature behaviour of the modulation wavevector **q** might therefore acquire an incomplete "devil's staircase" character at low d*T*/d*t*. The availability of regions of comparatively smooth $\delta(\Delta n)(T)$ changes in Figure 4 shows that we deal with a "border" d*T*/d*t* range separating the smooth **q**-dependence regime from the "viscous" IC structure-defect interaction regime [13].

In the recent work [3] we have shown that the inversion symmetry of the IC γ phase leads to disappearing optical gyration, similarly to the IC phases in the other A_2BX_4 crystals. Furthermore, the hysteresis, kinetics and the "optical memory" effects have been earlier observed [6] in BPA-Cu crystals, quite similarly to the other IC systems. This certifies that the IC structure-defect interactions in the re-entrant phases should be similar with those in the other types of the IC phases. Nevertheless, we think that the results [6], concerned with observations of δ-like peaks in the temperature dependences of LB at d*T*/d*t* = 0.22 K/h, should be a subject for further verification and careful analysis. Such the behaviour is not simple to adjust with both general thermodynamical considerations and the character of temperature variations of the IC modulation wavevector. In particular, it could not be excluded that small optical indicatrix rotations arise at the **q**(*T*) break points under low d*T*/d*t*, imposing systematic LB errors in frame of the Senarmont technique (see [8]).

Conclusions

In the present work we have studied the temperature dependences of optical LB and thermal expansion coefficient for the principal direction <001> in the ferroic BPA-Cu crystals, using polarimetric and dilatometric techniques. Both the optical and mechanical parameters are demonstrated to behave nonlinearly in all the structural phases, making it difficult to determine the Curie points and derive the

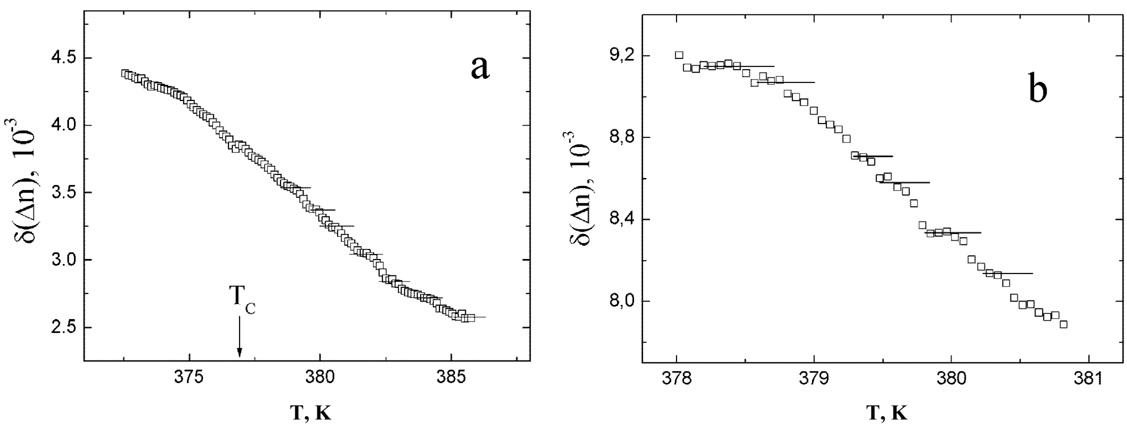

Fig. 4. Temperature behaviour of the relative LB value $\delta(\Delta n)$ for BPA-Cu crystals within the IC phase γ in case of d*T*/d*t* = 7.0 (a) and 2.3 K/h (b).

appropriate spontaneous changes linked with the PTs. The results obtained for the temperature derivative of the LB and the dependence of linear expansion have allowed us specifying the points of the PTs and some their thermodynamical features, yet the long-standing controversy about the exact T_i location still awaits it solving. A step-like temperature behaviour of the LB revealed inside the re-entrant IC γ phase at moderately low scan rates d*T*/d*t* should be tentatively related to interaction of the IC structure with defects. Together with some results known from the literature, this proves that the properties of the re-entrant IC phase are similar to those characteristic of IC phases of the other types.

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