Measurements of optical gyration in incommensurate $(N(CH_3)_4)_2ZnCl_4$ crystals with the universal null-polarimeter

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Abstract

Using the improved universal null-polarimetric technique, the birefringence, optical indicatrix orientation and the gyration of the (001)-plate of $(N(CH_3)_4)_2ZnCl_4$ crystals are re-studied in the temperature region close to normal-to-incommensurate phase transition. Both phases show a certain zero indicatrix rotation, while the gyration component g_{33} in the incommensurate phase is at least less than $2 \cdot 10^{-8}$. The sources of the interpretation polarimetric errors which decrease the accuracy of the universal polarimeter and the HAUP are analyzed. Possible reasons for the residual gyration are discussed.

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

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Introduction

The existence and possible physical explanations for the optical gyration effect in incommensurately modulated phases of A_2BX_4 group crystals with the inversion macroscopic symmetry concern a general problem of restrictions imposed by the inversion symmetry groups and the fundamental Neumann principle. Beginning from 1980s, the topic has attracted a permanent interest of both theoreticians and experimenters. The major experimental attention has been paid to $(N(CH_3)_4)_2ZnCl_4$ crystals abbreviated hereafter as TMAZC, whose incommensurate (IC) phase is located in the readily accessible range, the vicinity of a room temperature ($T_C \approx 7$ °C and $T_i \approx 24$ °C). After early attempts to measure the gyration of this material, many of which have proved to suffer from the experimental inaccuracies of different kinds [1-5], recently there have appeared a number of works where the polarimetric data and the corresponding errors are thoroughly analyzed [6-10]. A portion of criticism has been also addressed to the works [11,12] where the nonzero gyration component g_{33} of TMAZC is reported, with its maximum modulus reaching the values from 7×10^{-8} to 3.9×10^{-7} for different samples, contrary to the recent results [6,8-10].

We felt it important to carry out repeatedly the experimental studies on this material both from the fundamental point of view and for the reason of examining the resources of our improved universal null-polarimetric technique (see [12-14]). In the present work we report on the relevant results and careful analysis of the sources of polarimetric errors occurring within the above technique.

Experimental

TMAZC crystals were grown by means of the slow evaporation technique. We have prepared a 3.12 mm thick (001) sample using standard methods for polishing. The thickness d was chosen such that the optical retardation Δ ($\Delta = (2\pi d / \lambda)\Delta n$, with $\lambda = 632.8$ nm being the light wavelength of He-Ne laser and Δn the optical birefringence) be close to $2\pi m$, where m is an odd integer number. In order to avoid "smearing" of the retardation through the cross section of the laser beam and the corresponding "noises" in the measured Δ values (see [13]), especial care was paid to plane parallelism of the sample surfaces which was not worse than 2×10^{-4} rad. We did not observe any multiple light interference effects with this sample, although the surfaces were of a fairly well optical quality (see also [10]). The reasons are a relatively large thickness of the sample, inevitable scattering and a weak absorption in the crystal bulk, and a residual light scattering occurring in the surfaces.

Due to specific features of our temperature controlling apparatus, we studied the optical parameters of TMAZC only in the range above the room temperature. The temperature was stabilized with the accuracy of about 0.03 °C and measured with the copper-constantan thermocouple. The typical time for stabilization of each temperature point was 40 min, because it is our experience that the more accurate temperature stabilization, the more reliable the polarimetric data are (see also the discussion [8,10]). Before the experiments, the sample had been annealed for 30 h at the temperatures inside the high-temperature parent phase. This allowed to "heal" the crystal structure of the sample and greatly reduce the concentration of structural defects which are known to cause a residual gyration effect [15]. The data were obtained for the heating run.

The universal null-polarimetric technique for determining crystal optical properties is based on measuring, at each temperature, the characteristic parameters

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

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

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

The slopes of the azimuth dependences (1), the characteristic ellipticity ε_0 and the angular position θ_0' of the characteristic azimuth give the information, respectively, on the phase retardation (and so the birefringence), the normal light wave ellipticity k (and the corresponding gyration component $g_{33} = 2k\bar{n}\Delta n$, where $\bar{n}$ denotes the mean refractive index), and the rotation angle $\Delta\theta$ of the optical indicatrix axes, whenever the effective parameters p, p_0 and $\delta\chi$ are known [12-14].

Though there are several methods for extracting those imperfection parameters from the set of experimental data, it would be much better in practice to reduce their magnitude, basing on the knowledge of their possible sources [13]. For this aim, we performed as accurate orientation of all the optical components of our PSCA polarimeter as possible, to minimize the polarimetric errors of a "purely optical" (or "beam deviation") origin [16]. A close care was taken of the compensator (the mica quarter wave plate) and the Faraday cell, whose imperfection needed to be small enough and unchangeable in the course of experiments (see a theoretical analysis [14]). Nevertheless, our p_0 parameter had mainly a conspicuous enough magnitude of approximately 0.1 deg, while the sign of the closely related polarizer's ellipticity value p was always the same. According to the relations obtained in the work [14], this means that just p contributes mainly to p_0, the rest of the latter value is being caused by the imperfections of the compensator and the Faraday cell. These facts also testify that our polarizer's prisms are not of the best quality (as a matter of fact, we often utilize the polarizers characterized with the extinction ratio 10^{-5}, while the other authors report the values of the order of 10^{-7} - see, e.g., [10]).

A sliding construction of a sample holder enabled us to move the sample out of the optical system and re-measure the calibration azimuth dependences in the PA and PCA systems immediately during the PSA or PSCA experiments. Sometimes we observed deviations in the nulling PA and PCA positions of the order of $(1\div3)\times10^{-3}$ deg, taking place after ten or twenty hours. We ascribed the effect to a drift of null-indicator (see a scheme of out optical apparatus [13,14] for a more detail). Besides the purely optical sources of the imperfection parameters, the mentioned effect represents a very dangerous factor since it may result in a dependence of angular polarimetric error $\delta\chi$ on time and, apparently, on the temperature of the sample. That is why we kept up with the effect was always less than 5×10^{-4} deg. The resulting reproducibility of all the azimuths measured directly with the polarimeter was slightly better than 10^{-3} deg.

Results

The temperature dependences of $\cos\Delta$, ε_0 and θ_0' quantities of the TMAZC crystal are depicted in Fig.1-3, respectively. If the thermal expansion of sample is not taken into account, the data of Fig.1 allow to calculate strictly the birefringence of the *z*-cut of TMAZC (see curve 2 in Fig.1). The birefringence tends to zero at $T_0 \approx 11.7$ °C, leading to a divergent temperature behaviour of the measured quantities and causing serious difficulties in extracting the crystal optical parameters of TMAZC, since the contributions of the imperfection parameters to ε_0 and θ_0' then exceed much those of the *k* and $\Delta\theta$ parameters (see formulae (2) and (3)). The normal-to-IC phase transition temperature detected on this basis is equal to $T_i \approx 23.3$ °C. This is somewhat lower than the values reported in [6,8,9] but correlates with our earlier data [12], as well as the general temperature behaviour of the birefringence does.

Supposing that the gyration is absent at least in the spatially homogeneous parent phase described by the point symmetry group *mmm* and the imperfection parameters are kept invariable during the experiment, one can determine those parameters from the linear fit of the dependence of ε_0 upon $cot(\Delta/2)$ taken for the data points within the parent phase (Fig.2, inset). A good mean square deviation (8×10^{-4} deg), which is of the order of our experimental accuracy for the angular azimuth me-

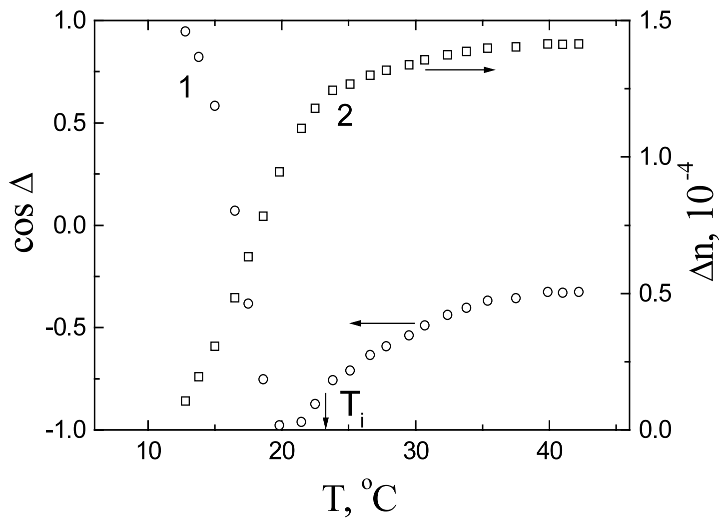

Fig.1. Temperature dependencies of $cos\,\Delta$ value (1) and the birefringence Δn (2) for TMAZC calculated without accounting for the thermal expansion effect.

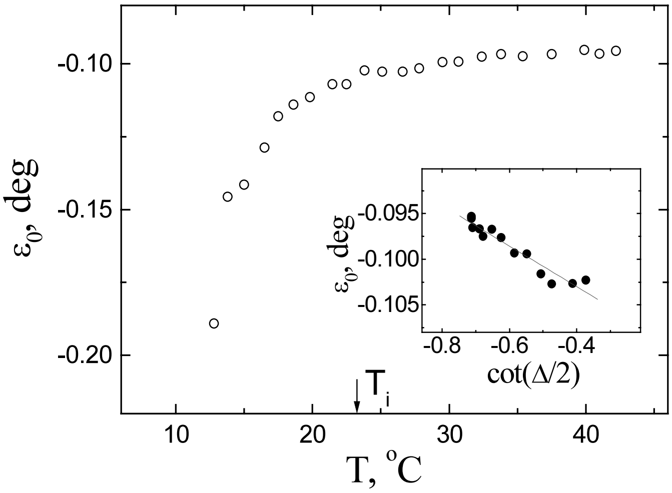

Fig.2. Temperature dependence of ε_0 for TMAZC. The inset represents a linear fit of ε_0 against $cot(\Delta/2)$ value for the parent phase.

asurements, testifies the validity of the above assumption. This gives p_0=0.112 and, $\delta\chi$=2.2×10^{-4} *deg* the latter value (~ 4×10^{-4} rad) being quite bearable. Using formula (2), one can calculate the temperature dependence of the eigenwave ellipticity *k*, which is not represented here for the reason of conciseness.

An alternative approach to the problem consists in assuming that the gyration effect is forbidden by symmetry in all the temperature range under test. Then the linear relation between ε_0 and *cot*(Δ/2) should hold for the all data points, including those in the IC phase. The corresponding fitting is less accurate (the mean square deviation is equal to 2.9×10^{-3} deg, i.e., it is worse than the initial experimental accuracy for the θ and χ quantities), whereas p_0 and $\delta\chi$ become somewhat different from the values cited above.

Our next step is to calculate the values of the effective characteristic azimuth position $\theta'_{eff} = \theta'_0 - k\,cot(\Delta/2) - \delta\chi/(1-cos\,\Delta)$.

According to formula (3),

$$\theta'_{eff} = \theta'_{orig} + \Delta\theta - p\,cot(\Delta/2), \qquad (4)$$

and so θ_{eff}' has to depend linearly on *cot*(Δ/2),

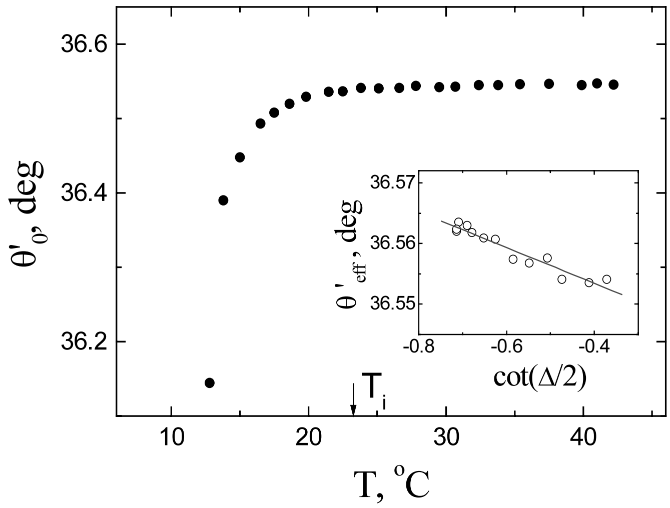

Fig.3. Temperature dependence of θ_0' for TMAZC. The inset represents a linear fit of θ_{eff}' (see text) against $cot(\Delta/2)$ for the parent phase.

whenever the optical indicatrix rotation is absent (or, more precisely, constant in the all temperature range, although the latter situation does not seem to represent a practical interest). Assuming $\Delta\theta = 0$ for the high-temperature phase only, we have the dependence θ'_{eff} versus $cot(\Delta/2)$ represented in Fig.3, inset. It is linear with the mean square deviation 1.2×10^{-3}*deg*, and we get p=2.9×10^{-2}*deg*, $\theta'_{orig} = 36.542 deg$. When we assume the absence of the indicatrix rotation in the overall temperature range, the deviation equals to 2.0×10^{-3}*deg*. Calculating the temperature dependence of $\Delta\theta$ on the basis of the θ'_0 data and formula (4) and using the two alternative assumptions yields the results presented in Fig.4. Finally, the temperature dependence of the gyration tensor component g_{33} calculated with the same alternative assumptions is depicted in Fig.5.

Discussion

In our opinion, it is rather difficult to make preference for the curves 1 or 2 in Fig.4. The first one gives a "better zero" indicatrix rotation in the parent phase, while in the IC phase it shows a sharper divergence in the vicinity of T_0. The second one has a very slight tendency to deviate from a zero level in the high-temperature phase but shows a "better zero" rotation in the IC phase. It is also hard to choose one of the curves as more reliable, because the difference in the square deviations is insignificant. The most important, the indicatrix rotation derived from both assumptions appears to be a pure result of decreasing the experimental accuracy in the vicinity of T_0, owing to slightly inaccurate $\delta\chi$ data, and can hardly be related to the phase transition. Thus, we conclude that the small apparent indicatrix rotation observed at low temperatures has nothing to do with the IC phase transition, and the effect in the IC phase is surely zero. Notice, that the latter conclusion disagrees with the earlier results [12]. It is very important for the correct choice of boundary conditions for the modulation phase used in frame of the theoretical models [17,18].

As seen from Fig.5, the data for the gyration component g_{33} derived from both assumptions mentioned above get into a very narrow range from -1×10^{-8} to 2×10^{-8}. It is almost an order of magnitude less than the values reported in [11,12]. We infer that the latter data were affected by some extra accuracy-decreasing factors, most likely, the mentioned null-indicator drift

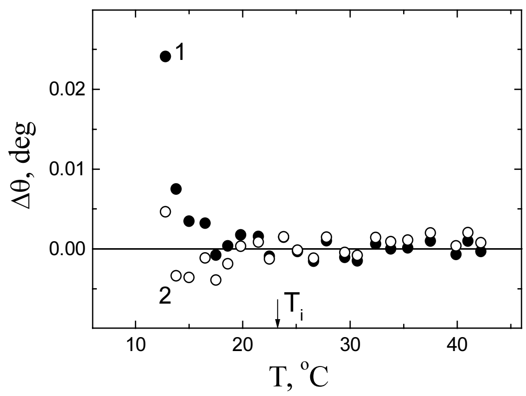

Fig.4. Temperature dependence of the indicatrix rotation $\Delta\theta$ derived by using the θ'_{eff} vs. $cot(\Delta/2)$ fit for the parent phase only (1) and for the overall temperature range (2) (see explanations in the text).

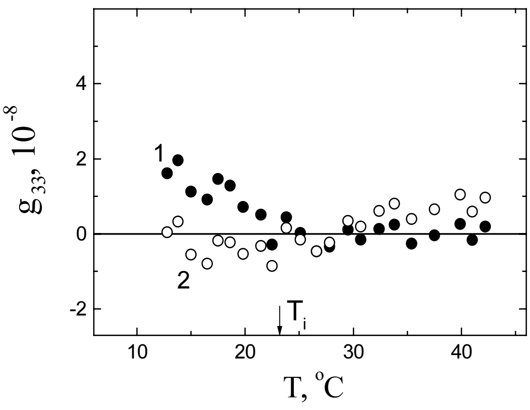

Fig.5. Temperature dependence of the gyration component g_{33} derived by using the ε_0 vs. $cot(\Delta/2)$ fit for the parent phase only (1) and for the overall temperature range (2) (see explanations in the text).

effect, and so contained errors. Another reason for their insufficient quality was that the sample was kept in the open atmosphere for too long, while the five polarimetric experiments were being performed (see [12]). This might cause worse surface quality and lead to increasing the angular imperfection parameter $\delta\chi$ and less reliable data. The maximum gyration in the study [12] was measured just in the experiment 5 performed after the sample had been X-irradiated. The latter caused additional damage of its bulk and surface. It is known that strongly irradiated samples exhibit some unusual optical phenomena (see, e.g., the results [19] for the optical birefringence). At the same time, the gyration data [12] for the annealed sample (the maximum value in the IC phase 7×10^{-8}) were not so strongly different from those reported here.

The curve 1 in Fig.5 built in the assumption of optically active IC phase seems to be more realistic than the curve 2 derived as if the optical activity were completely absent. Furthermore, the corresponding mean square deviation is more than three times less. The gyration effect may be rigorously zero in the parent phase (see curve 1) and does not have a tendency to increase at high temperature, as with the curve 2 (the maximum gyration value apparently reaches the value 10^{-8} at 40 °C). If the above assumption is indeed right, then the maximum gyration effect in the IC phase amounts $\sim 2\times10^{-8}$. On the other hand, even relatively high final precision for the gyration component ($\sim 10^{-8}$) presented here is not sufficient for categorical conclusions. As a matter of fact, the authors [6] have interpreted qualitatively similar experimental data for the g_{13} component (though derived with a lower accuracy) as testifying a totally zero optical activity. Notice also that the results of all the recent studies on the TMAZC [7-10] show a zero g_{33} within approximately the same accuracy of $\sim 10^{-8}$.

Irrespective of the data reliability aspects, it is very difficult to interpret unambiguously the gyration which manifests itself in the normal wave ellipticity of the order of 5×10^{-5} to 4×10^{-4}, as in our case. It is worth noticing that the lower limit for the k value corresponds to the magnitude of the apparent "gyration effect" detected [10] in optically inactive MgF_2 crystals and is prescribed to the residual light wave ellipticities arising from the surface roughness (and so is the sample preparation). The maximum g_{33} gyration component of the TMAZC taken from Fig.5 is equivalent to the optical rotatory power $\sim 4\times10^{-3}$ deg/mm if the (001) direction were parallel to the optical axis. It is indeed a small value which, in the opinion of the authors [6], should be regarded as zero. This agrees well with a natural assumption that the symmetry restrictions imposed on the material properties of the IC phase are governed by the inversion point group associated with the corresponding superspace group [6,7]. On the other hand, ignoring the gyration less than $\sim 10^{-8}$ might appear to be a too rough approach. So, it would be hardly correct to neglect the linear birefringence effect in a weakly anisotropic TMAZC, which is also very small (less than 10^{-4}), and to state that the crystal is optically isotropic.

While discussing a possible gyration effect in the IC phase of TMAZC on the whole (see also the results [8,9]), we should mention the following reasons. First, a residual effect may be caused by defects available in the crystal structure [15]. It is important in this respect that single crystals grown with the slow evaporation technique are less perfect than those grown with the thermal convection [9] or the slow cooling techniques [8], and indirect methods based, for example, on analyzing the T_i data confirm this fact. Secondly, the small gyration may be a result of pinning the modulation wave at the commensurate value (2/5)**c*** (see [20]). Third, it cannot be excluded that the gyration component g_{33} does exist in the perfect, defect-free IC phases because it is not in general forbidden by the superspace symmetry [21]. A phenomenological theory [22] just predicts an apparent optical gyration originated from a new type of spatial dispersion in the spatially inhomogeneous IC structure. The effect should be weak enough, with a magnitude at least essentially less than that typical for the acentric crystals and, perhaps, less than the experimental accuracy accessible for the HAUP and the present technique.

In this respect, the TMAZC is not the best experimental object, since it is weakly optically anisotropic (and so weakly optically active, if any) and, moreover, manifests a zero-crossing birefringence point. The other A_2BX_4 representatives may be more suitable in order to arrive at decisive conclusions regarding the existence and magnitude of the gyration effect in the IC phases. Furthermore, it would be desirable to solve a serious problem of increasing the experimental accuracy. One of the particular hindering points here is that the surfaces of hygroscopic crystals are mainly of a lower optical quality, with the methodical consequences discussed above.

Finally, the main results of the present study demonstrate that the universal null–polarimeter may compete with the HAUP technique and provide a reliable tool for determining optical parameters of crystals, despite its standard, relatively simple construction and the absence of the apparatus for measuring the absolute values of light intensity.

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References

1. Kobayashi J. and Uesu Y. Ferroelectrics **64** (1985) 115-122
2. Kobayashi J., Kumomi H. and Saito K. J. Appl. Cryst. **19** (1986) 377-381
3. Dijkstra E. and Janner A. Ferroelectrics **105** (1990) 113-118
4. Dijkstra E., Meekes H. and Kremers M. J. Phys. D: Appl. Phys. **24** (1991) 1861-1868
5. Dijkstra E., Kremers M. and Meekes H. J. Phys.: Condens. Matter **4** (1992) 715-726
6. Folcia C.L., Ortega J., Etxebarria J. and Breczewski T. Phys. Rev. B **48** (1993) 695-700
7. Etxebarria J. Proc. Internat. Confer. on Aperiodic Crystals. World Scientific Publishing (1994), 219-228
8. Kobayashi J., Saito K., Takahashi N. and Kamiya I. Phys. Rev. B **48** (1993) 10038-10046
9. Kremers M., Dijkstra E. and Meekes H. Phys. Rev. B **54** (1996) 3125-3135
10. Simon J., Weber J. and Unruh H.-G. Ferroelectrics **183** (1996) 161-170
11. Kushnir O.S., Shopa Y.I. and Vlokh O.G. Europhys. Lett. **22** (1993) 389-393
12. Kushnir O.S., Shopa Y.I., Vlokh O.G., Polovinko I.I. and Sveleba S.A. J. Phys.: Condens. Matter **5** (1993) 4759-4766
13. Vlokh O.G. and Kushnir O.S. Pribory i Tekhnika Eksperim. **1** (1996) 119-124
14. Kushnir O.S. and Vlokh O.G. Proc. SPIE **3094** (1997) 88-99 (in Russian)
15. Kushnir O.S. and Vlokh O.G. J. Phys.: Condens. Matter **5** (1993) 7017-7032
16. Kushnir O.S. and Vlokh O.G. Ferroelectrics **192** (1997) 243-248
17. Kushnir O.S. J. Phys.: Condens. Matter **9** (1997) 9259-9273
18. Kushnir O.S., Lokot L.O. and Polovinko I.I. J. Phys.: Condens. Matter **12** (2000) 8321-8330
19. Kapustianik V.B., Polovinko I.I., Sveleba S.A., Vlokh O.G. and Zhmurko V.S. Europhys. Lett. **19** (1992) 429-432
20. Cummins H.Z. Phys. Rep. **185** (1990) 211-409
21. Meekes H. and Janner A. Phys. Rev. B **38** (1988) 8075-8087
22. Kushnir O.S. J. Phys. Studies (2001) submitted.