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ON THE BIREFRINGENCE FLUCTUATIONS IN A_2BX_4 CRYSTALS NEAR THE NORMAL-INCOMMENSURATE PHASE TRANSITION

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A critical analysis of the literature data for temperature dependences of optical birefringence near the normal-incommensurate phase transition in Rb_2ZnCl_4, $(N(CH_3)_4)_2ZnCl_4$ and $(N(CH_3)_4)_2CuCl_4$ crystals is performed. It is shown that the correct data interpretation and determination of critical indices should involve consideration of fluctuation corrections and, in particular, a comparison of the temperature regions under study with the Ginzburg number.

Key words: birefringence, incommensurate phase transitions, fluctuations, critical exponents.

Linear optical birefringence represents a powerful tool for investigating structural phase transitions in insulating and semiconducting crystals, in particular those into incommensurately modulated phases (see, e.g., [1]). In spite of a very large number of works performed using the birefringence technique and devoted to the critical behaviour of A_2BX_4-family crystals (see [1–7] and references therein), there still exist essential discrepancies regarding the critical indices of the order parameter and manifestations of critical fluctuations near the normal-to-incommensurate phase transitions.

In this work we would like to analyze critically some of the recent results on the topic and comment on a number of important methodological points. Namely, we will find the reasons of discrepancies mentioned above and show that some of them are in fact seeming.

For the physical systems under test, spontaneous change Δn_S in the birefringence Δn occurred in the incommensurate phase due to the phase transition is proportional to the square of properly averaged order parameter, $\Delta n_S \propto \langle \eta^2 \rangle$, and so it can reflect the critical fluctuations of the latter. However, as thoroughly shown by Ivanov et al. [4], the birefringence in the temperature region of true critical behaviour (the so-called scaling region) is governed by the critical exponent α of heat capacity rather than the exponent β of the order parameter η. That is the reason why the usually exploited relation

$$\Delta n_S(\tau) \propto |\tau|^{2\beta}, \qquad (1)$$

(with $\tau = (T - T_i)/T_i$ denoting the reduced temperature and T_i the phase transition point) is invalid in this region. This restriction naturally disappears in a wider temperature region around T_i, where one can employ Landau theory with the critical index β differing from the naive value ½, and so the relation (1).

On the other hand, instead of formula (1), the authors [4] have suggested to describe the birefringence by the relation based on the first fluctuation correction to the Landau theory,

$$\Delta n_S(\tau) = 2\lambda^+ \tau^{1/2} \quad (\tau > 0),$$
$$\Delta n_S(\tau) = a^2 A T_i \,|\tau| / B + 2\lambda^- |\tau|^{1/2} \quad (\tau < 0), \tag{2}$$

where a means the optical susceptibility, A and B the temperature-independent coefficients appearing in the thermodynamic Landau expansion for the second-order phase transitions. Here the constant parameters $\lambda^\pm$ are linked as $\lambda^- / \lambda^+ = \sqrt{2}$ for the case of 3D XY-model and the indices "+" and "–" refer respectively to the regions above and below T_i. The term in (2) linear in τ corresponds in fact to the Landau behaviour $|\tau|^{2\beta}$ with $\beta = ½$, while the terms including $\lambda^\pm$ describe (relatively weak) fluctuations present in both the incommensurate and normal phases.

One can find a close relation between the approaches given by formulae (1) and (2). Obviously, the relation (2) for the incommensurate phase becomes equivalent to (1), if only we put temperature-dependent critical exponent $¼ \le \beta(\tau) \le ½$ in the latter. Such the situation should imply an (abrupt or more or less continuous) crossover in the critical behaviour, which is often observed for many systems.

Finally, the analysis within the approach [4] looks more convenient if we pass to the temperature derivatives $\xi = \mathrm{d}(\Delta n_S)/\mathrm{d}T$:

$$\xi(\tau) = \lambda^+ \tau^{-1/2} \quad (\tau > 0),$$
$$\xi(\tau) = \xi_L + \lambda^- |\tau|^{-1/2} \quad (\tau < 0), \tag{3}$$

where ξ_L is the constant "Landau step". The validity region for the Landau theory with the fluctuation corrections is given by the Levanyuk-Ginzburg criterion $G << |\tau| << G^{1/3}$ (see [4, 8, 9]), where G is the Ginzburg number, whereas the scaling region may be defined by the relations $|\tau| < G$ or $|\tau| << G$. In this respect we are to remark that the experimenters are rarely able to access the scaling region in practice, contrary to the region of relatively weak fluctuations.

As noticed above, the birefringence of A_2BX_4 crystals has been repeatedly measured by various groups of researchers. We have decided to compare the theory and the experiment on a single example of data reported in the recent study [6]. This is rather instructive example, since the authors [6] have criticized the approach [4] and concluded that their results disprove the latter. Besides, it has been inferred [6] that the birefringence data strongly support the predictions of 3D XY-model ($2\beta \approx 0,7$) but not those of the 3D Ising model ($2\beta \approx 5/16$). The temperature dependences of spontaneous birefringence for Rb_2ZnCl_4 (RZC), $(N(CH_3)_4)_2ZnCl_4$ (TMAZC) and $(N(CH_3)_4)_2CuCl_4$ (TMACC) crystals obtained in the work [6] are depicted in the main windows of fig. 1 to 3.

In the upper inserts of fig. 1 to 3 we show the calculated temperature dependences of the derivatives $\xi(\tau)$. We should note that the procedure used in [6] for locating the transition points (determining them from the best linear fit of $\log \Delta n_S$ vs. $\log(T_i - T)$) seems to be vague. As a result, our T_i's, which are clearly seen from the critical divergences of the $\xi(T)$ dependences (see formulae (3)), somewhat differ from those found in [6] (see table 1). The functions $\xi(\tau)$ manifest a peculiar behaviour in the vicinity of T_i that testifies the effect of fluctuations. Though it is known that the Ginzburg number for Rb_2ZnBr_4 is equal to $\sim 10^{-2}$ [4], the G values for the crystals under study, which define the regions of essential fluctuations, are not mentioned in the literature. We have made rough estimations basing on the $\xi(T)$ dependences and the technique proposed in [4] and obtained somewhat lower G values (see table 1).

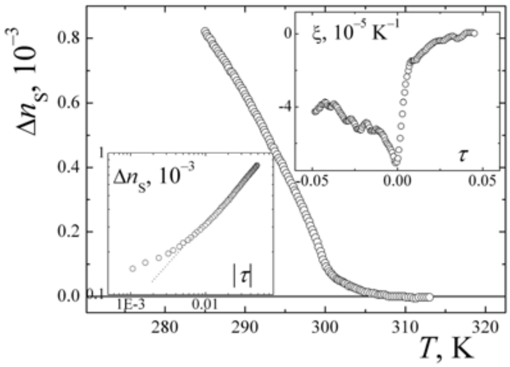

Fig. 1. Temperature dependence of spontaneous birefringence Δn_S for RZC crystals according to [6]. The inserts show the calculated dependence of derivative ξ on the reduced temperature τ and the log-log plot $\Delta n_S(\tau)$

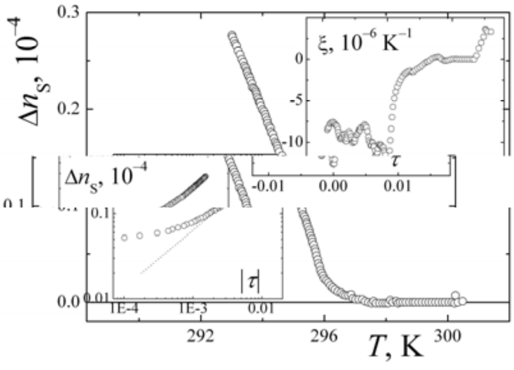

Fig. 2. Temperature dependence of spontaneous birefringence Δn_S for TMAZC crystals according to [6]. The inserts show the calculated dependence of derivative ξ on the reduced temperature τ and the log-log plot $\Delta n_S(\tau)$

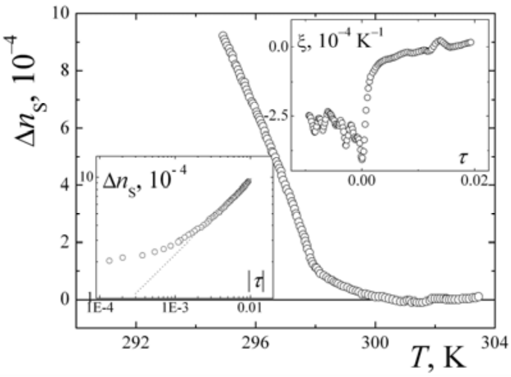

Fig. 3. Temperature dependence of spontaneous birefringence Δn_S for TMACC crystals according to [6]. The inserts show the calculated dependence of derivative ξ on the reduced temperature τ and the log-log plot $\Delta n_S(\tau)$

Table 1

Characteristics of normal-incommensurate phase transition for A_2BX_4 crystals and some additional parameters following from the data [6] and our calculations on their basis

Parameter	Crystal		
	RZC	TMAZC	TMACC
T_i [6]	300,7	296,1	298,1
T_i according to our calculations	299,5	295,8	297,7
The highest temperature τ_{max}	0,05	0,017	0,017
The temperature τ_0 closest to the phase transition point (under analysis [6])	–0,003	–0,001	–0,001
Crossover temperature τ_c	–0,1	–0,006	–
Ratio $\lambda^- / (\sqrt{2}\lambda^+)$	1,4	0,8	0,5
Ginzburg number G	0,007	0,002	0,002
Critical exponent 2β [6]	0,75	0,73	0,75
Critical exponent $2\beta_c$ after crossover [6]	0,99	0,88	–
The highest 2β value according to our calculations (temperature region)	0,63 (–0,05––0,04)	0,73 (–0,01––0,006)	0,68 (–0,01––0,006)

The fluctuations (or “birefringence tails”, in terms of [6]) occurred in the parent phase are also obvious from the $\Delta n_S(T)$ data themselves. However, we doubt that overlooking the “tails” while finding the birefringence “background” might be a real source of errors in many recent works, e.g., in [4], since the subject matter has been well known long ago and, in particular, it has been strictly pointed out in the review [1]. Moreover, since the highest temperatures τ_{max} measured in [6] are only $\sim(7–8)G$ (see table 1), it is still unclear whether the region where the fluctuations are completely absent is reached (see, e.g., the results for deuterated triglycine sulfate crystals [10] and the conclusions [1] concerning the data by Regis et al. for TMAZC). If this is not the case, the $\Delta n_S(T)$ data themselves may contain inaccuracies of interpretation.

We have quantitatively processed the data $\xi(\tau)$ for the regions of moderately weak fluctuations and made sure that the birefringence follows fairly well the main predictions of the theory [4] (the ratios $\lambda^-/(\sqrt{2}\lambda^+)$ gathered in Table 1 are close to the theoretical unit value). The authors [6] criticize the approach [4] issuing from the fact that their results $\Delta n_S(\tau)$ cannot be described by the corresponding relations valid for the scaling region (see formula (3b) in [4]). However, simple comparison of the Ginzburg numbers for RZC, TMAZC and TMACC with the temperatures τ_0 inside the incommensurate phase, which are closest to the transition point and have been subjected to the scaling analysis (see table 1), testifies that the scaling region in fact has not been analyzed in the study [6]. According to our rough estimations, the true critical behaviour of the mentioned crystals should be expected within the region defined by the limits $|\tau| < 10^{-3}$. Hence, the results [6] should not be in general regarded as though contradicting the first fluctuation approximation to the Landau theory.

As seen from the lower inserts in fig. 1 to 3, the slopes of the log-log $\Delta n_S(\tau)$ dependences vary continuously with temperature. In spirit of the Landau phenomenology, we have determined the critical indices β of the order parameter only for the lowest temperatures inside the incommensurate phase, where the fluctuations are weakest (see the lower inserts in fig. 1 to 3 and table 1, where the corresponding τ regions are also indicated). The indices are slightly different from those derived in [6] and they indeed differ from the predictions of mean-field theory. This is readily understood with the relations (2) and the *G* values, since the term proportional to λ^- still does not become negligible in the regions under analysis. With the experimental data points of fig. 1 to 3 deepest in the incommensurate phase, we have not been able to observe crossover to the plain Landau behaviour (cf. with the β_c values for the RZC and TMAZC crystals derived in [6] shown in table 1). Furthermore, the ratio τ_c / G (with τ_c being the crossover temperature) found from table 1 for RZC is notably larger than that for TMAZC. This explains why the exponent β_c for the RZC is closer to ½ (see table 1). It is not unlikely that the overall incommensurate phase in TMACC crystals lies inside the fluctuation region and so no crossover is observed. The more exact conclusions may be drawn only after obtaining more reliable *G* values.

Finally, the choice [6] between the 3D XY-model and the Ising model seems to be not so simple (see table 1). One has to consider natural experimental errors in the initial $\Delta n(T)$ data (the evaluation $\sim 10^{-7}$ [6] is hardly reliable – see real scattering of the data points in fig. 1, 2 in [6] and the accuracy analysis for the Senarmont technique [11]) and a number of weak spots in the corresponding analysis mentioned above.

Another factor that would hinder one from categorical conclusions is a quite possible effect of structural defects on the critical phenomena [12, 13], which has been completely disregarded above. We remind that the properties of degenerate systems with a “continuous symmetry” of the order parameter, including the incommensurate ones, cannot be understood without taking the defects into account [12]. This is the more so since many optical characteristics of A_2BX_4 crystals are known to be highly sensitive to interactions between the incommensurate structure and defects (see, e.g., [1, 14, 15]).

It is worthwhile in this respect that the method of slow evaporation used in [6] usually produces single crystals of lower quality, when compare to the other methods. The latter may be evidenced indirectly, e.g., by a relationship between the T_i value and crystal perfection found for TMAZC crystals [14, 16].

The birefringence results [6] for the A_2BX_4 crystals fit in general into the fluctuation correction approach [4] and so the corresponding criticism [6] seems to be misunderstanding related to interpretation in terms of different model. Moreover, there are some links between the approaches expressed by formulae (1) and (2). When interpreting the experimental data, one has to know, with a sufficient accuracy, the Ginzburg number that defines importance of the fluctuation effects. According to our approximate estimations, almost all of the temperature regions under test appear to lie in the range of non-negligible fluctuations, especially in the case of TMACC crystals.

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1. *Fousek J.* Birefringence studies of A_2BX_4 compounds with incommensurate phases // Phase Transitions. 1991. Vol. 36. P. 165–189.
2. *Maikrzak C.F., Axe J.D., Bruce A.D.* Critical behaviour at the incommensurate structural phase transition in K_2SeO_4 // Phys. Rev. B. 1980. Vol. 22. P. 5278–5283.
3. *Minteguia R.C., Tello M.J., Perez-Mato J.M.* et al. Commensurate and incommensurate phase transitions in bis-propylammonium manganese chloride crystals // Solid State Commun. 1984. Vol. 50. P. 501–503.
4. *Ivanov N.R., Levanyuk A.P., Minyukov S.A.* et al. The critical temperature dependence of birefringence near the normal-incommensurate phase transition in Rb_2ZnBr_4 // J. Phys.: Condens. Matter. 1990. Vol. 2. P. 5777–5786.
5. *Kobayashi J., Saito K., Takahashi N.* et al. Optical activity and birefringence of the incommensurate phase of Rb_2ZnCl_4 // Phys. Rev. B. 1994. Vol. 50. P. 2766–2774.
6. *Dal-Young Kim, Sook-Il Kwun, Jong-Gul Yoon.* Linear birefringence behavior of ritical behaviour at the incommensurate structural phase transition in A_2BX_4 ferroic crystals in the normal-incommensurate phase transition // Phys. Rev. B. 1998. Vol. 57. P. 11173–11177.
7. *Sveleba S., Katerynchuk I., Semotyuk O.* et al. Correlated movement of T-groups in the initial phase of $[N(CH_3)_4]_2CuCl_4$ crystals // Visnyk Lviv. Univ. 2006. N 39. P. 76–81 (in Ukrainian).
8. *Strukov B.A., Levanyuk A.P.* Physical fundamentals of ferroelectric phenomena. Moscow: Nauka, 1983 (in Russian).
9. *Lines M.E., Glass A.M.* Principles and application of ferroelectrics and related materials. Oxford: Clarendon Press, 1977.
10. *Kushnir O.S., Shopa R.Y., Polovynko I.I.* Optical studies of ferroelectric phase transition in deuterated triglycine sulfate crystals // Phase Transitions. 2007. Vol. 80. P. 89–94.
11. *Kushnir O.S., Burak Y.V., Bevz O.A., Polovinko I.I.* Crystal optical properties of lithium tetraborate // J. Phys.: Condens. Matter. 1999. Vol. 11. P. 8313–8327.
12. *Levanyuk A.P., Sigov A.S.* Influence of defects on the properties of ferroelectrics and related materials near second-order phase transition point // Izv. AN SSSR, Ser. Fiz. 1981. Vol. 45. P. 1640–1645 (in Russian).
13. *Levanyuk A.P., Sigov A.S.* Defects and structural phase transitions. New York: Gordon and Breach, 1988.

14. *Kushnir O.S., Shopa Y.I., Vlokh O.G., Polovinko I.I.* et al. The influence of annealing and X-irradiation on the optical anisotropy in incommensurate $(N(CH_3)_4)_2ZnCl_4$ // J. Phys.: Condens. Matter. 1993. Vol. 5. P. 4759–4766.
15. *Kushnir O.S., Vlokh O.G.* Peculiar properties of crystal optics in real modulated phases // J. Phys.: Condens. Matter. 1993. Vol. 5. P. 7017–7032.
16. *Kushnir O.S., Lutsiv-Shumski L.P., Polovinko I.I.* et al. Measurements of optical gyration in incommensurate $(N(CH_3)_4)_2ZnCl_4$ crystals with the universal null-polarimeter // Ukr. J. Phys. Opt. 2001. Vol. 2. P. 126–132.

ПРО ФЛУКТУАЦІЇ ДВОПРОМЕНЕЗАЛОМЛЕННЯ В КРИСТАЛАХ A_2BX_4 ПОБЛИЗУ ФАЗОВОГО ПЕРЕХОДУ НОРМАЛЬНА-НЕСУМІРНА ФАЗИ

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Проведено критичний аналіз відомих з літератури даних для температурної залежності оптичного двопроменезаломлення в околі фазового переходу нормальна-несумірна фази у кристалах Rb_2ZnCl_4, $(N(CH_3)_4)_2ZnCl_4$ і $(N(CH_3)_4)_2CuCl_4$. Показано, що для правильної інтерпретації даних і визначення критичних індексів параметра порядку треба зважати на флуктуаційні поправки, порівнюючи досліджений температурний діапазон з числом Гінзбурга.

Ключові слова: двопроменезаломлення, несумірні фазові переходи, флуктуації, критичні індекси.

О ФЛУКТУАЦИЯХ ДВУХЛУЧЕПРЕЛОМЛЕНИЯ В КРИСТАЛЛАХ A_2BX_4 ВБЛИЗИ ФАЗОВОГО ПЕРЕХОДА НОРМАЛЬНАЯ–НЕСОРАЗМЕРНАЯ ФАЗЫ

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Проведен критический анализ известных из литературы данных для температурной зависимости оптического двухлучепреломления в окрестности фазового перехода нормальная-несоразмерная фазы в кристаллах Rb_2ZnC_{l4}, $(N(CH3)_4)_2ZnCl_4$ и $(N(CH3)_4)_2CuCl_4$. Показано, что для правильной интерпретации данных и определения критических индексов параметра порядка нужно учитывать

флуктуационные поправки, сравнивая исследованный температурный диапазон с числом Гинзбурга.

Ключевые слова: двухлучепреломления, несоразмерные фазовые переходы, флуктуации, критические индексы.

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