# Optical properties of crystals with incommensurate structure of Lifshitz's type

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## Abstract

A review of optical properties of $A_2BX_4$ group crystals with incommensurate modulated structure of Lifshitz's type a.i. crystals, which characterize nonequitranslation unit cell of high temperature and ordering - low temperature phases is done. The characteristics features of birefringence, optical activity, light absorption and the effects induced by the external influences (temperature, pressure, electric fields and mechanical stresses, *X*-ray radiation, as well as their gradients) are considered in this paper. It is shown that different types of interaction between defects or impurities and structural elements (pinning, viscous interaction, nucleation and annihilation of phase solitons or commensurate-incommensurate states (so-called discommensuration)) manifest themselves in the anomalies of optical phenomena in the incommensurate phases.

**Key words:** Incommensurate modulated structures, phase transitions, crystallooptics, birefringence, optical activity, light absorption.

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**Contents**

## 1. Introduction

Crystals with incommensurate (*IC*) phase have been of considerable interest up to date. It is well known that crystals with *IC* structure are crystals, in which modulated superstructure with non-multiple period is comparable with the period of unit cell appear in some temperature region between ordering and disordering phases. The relation of this period is surd and depends on the temperature and other external influences. The absence of *IC* translation periodicity in modulation directions define that *IC* phase can not be descripted by 230 space group of the symmetry. Hence, *IC* phase of ferroelectrics and ferroelastics may be presume intermediate state between ordering and disordering states.

A soft mode in *IC* phase has minimum in the points $k_0=k_c-k_i$ ($k_i << k_0$), placed in Brillouin zone near $k_c$, but not in the Lifshitz points, for which $k_c/a^*$=0, 1/2, 1/3,... (where $a^*=2\pi/a$ - reciprocal lattice vector). The phase transition to the *IC* phase is connected with the condensation of a soft mode near the Brillouin zone boundary, for example in the points with the wave vector $k_0=a^*(1-\delta)/2$, where $\delta=k/k_c<<1$. Then the structure with the wave vector $k_0$ differs from the structure of $k=k_c$ by a spatial modulation with the period $L=2\pi/k_i$, which is much larger than the interatomic distances. The position of the $k_o-$ point is not stable in the Brillouin zone and can depend on the temperature. When it is coincide with one of Lifshitz point, then the crystal undergo phase transmits into the ordering phase.

Among the crystals with *IC* - modulated structure there are two possible types of phase transitions [1], - especially the transition, in which unit cells in the disordering and ordering phases are equitranslation. For the description of their properties a single-component gradient invariant is added in the thermodynamical potential. The second type of the phase transitions with appearing *IC* intermediate structure corresponds to non-equitranslation unit cells of the disordering and ordering phases. Some of such crystal properties may be described by the introduction of two components of gradient Lifshitz's invariant in the thermodynamical potential [2,3]. Then, this *IC* modulated structure or crystals with such structure are called Lifshitz's crystals.

However, even such experimental facts as continuously of the phase transition, global hysteresis [4-6] and its jump-like character [7-9], partial cycles of the «parallelogram» type [7,10], non-smooth relaxation processes [9], thermodielectric [11,12], thermooptical [13] and thermoacoustic [14] memory induce one to take into account some mechanisms that are external in comparision with the phenomenological conceptions. The phase solitons interaction with defects and impurities, the introduction of the notion of soliton density [15] or regions of alternating commensurate and *IC* phases (discommensurations - *DC's*)) [16] are the examples.

The above-mentioned effects are displayed distinctly in the optical studies, for example, in the birefringence and light absorption. At the same time, the interpretation of the optical activity as well as the related effects that are induced by the external fields, their gradients in the *IC* phases are rather problematical. This report is just devoted to the above-mentioned problems. The studies have been performed on the crystals of Lifshitz's type of $A_2BX_4$ group, where A - K, Rb, Cs, $NH_4$, $N(CH_3)_4$, $NH_2(CH_3)_2$; B - Zn, Mn, Fe, Cu, Co, Be, Cd, Hg; X - Cl, Br, F.

## 2. General properties of Lifshitz's type crystals with *IC* structure.

Since crystals of $A_2BX_4$ group belong to the crystals of Lifshitz's type, the phenomenological description is based on the thermodynamical potential *F*, in which two components of the order parameter $(\eta, \xi)$ are used. According to the group theory these components of order parameter correspond to a two-dimensional irreducible representation of the high temperature symmetry group. For the $A_2BX_4$ crystals the high temperature phase is the phase of the $D_{2h}^{16}(mmm)$ group of symmetry and phase transition through *IC* phase is possible to the ferroelectric $C_{2v}^{9}(mm2)$ or ferroelastic $C_{2h}^{5}(2/m)$ phases.

Taking into account Lifshitz's invariant the free energy in this case can be written as follows [17-19]:

$$F(x)=F_0+\frac{\alpha}{2}(\eta^2+\xi^2)+\frac{\beta}{4}(\eta^4+\xi^4)+\frac{\gamma}{2}\eta^2\xi^2+\sigma\left(\xi\frac{\partial\eta}{\partial x}-\eta\frac{\partial\xi}{\partial x}\right)+\frac{h}{2}\left[\left(\frac{\partial\xi}{\partial x}\right)^2+\left(\frac{\partial\eta}{\partial x}\right)^2\right],$$

where $\alpha=\alpha_0(T-T_0)$, $\alpha$ and $h > 0$.

In the following it is suitable to use the polar coordinates ρ and φ making the changes $\eta=\rho sin\varphi$ and $\xi=\rho cos\varphi$, where $\rho$ and $\varphi$ - the amplitude and phase of the order parameter and the plane-wave model [18] at $T_c<<T<T_i$ or the constant amplitudes [20] at $T_i >>T >T_c$ can be used.

Not taking into account mathematical details, only some results of this approach are shown:

1. The phase transition into the modulated phase with wave vector $k_i$ takes place at the $T=T_i=T_0+\sigma^2/\alpha_0 h$ and is a phase transition of the second order:

$$\rho^2=\alpha_0(T_i-T)/\beta$$

The components of order parameters $\eta$ and $\xi$ are sinusoidal functions of coordinates, radius-vector $\rho$ uniformly rotate on the circle and the phase of the order parameter increases linearly with the increasing of coordinates $\varphi = k_i x$, where $k_i=|\sigma|/h$. When the temperature is lowered to $T_c$ [21], then the amplitude of the order parameter rotates nonuniformly, the phase of the order parameter changes by the step-like behavior $\varphi=tg^{-1}(e^{\lambda x})$, where $\lambda=-2\rho(\beta/h)$ and the coordinate dependence of the components of the order parameter are similar to domain-like structures. The «domain boundary» are perpendicular to the modulation direction. Thus, at the

$$T_i >> T > T_c = T_0 - \frac{\pi}{2}\left[\frac{\beta+\gamma}{\beta-\gamma}\right]\frac{\sigma^2}{h\alpha_0}$$

the structure consists of the commensurate regions which are separated by boundaries and are called as phase solitons [22]. These phase solitons define main properties of crystals with the *IC* structure. The phase transition at $T=T_c$ is the phase transition of the first order. For the ferroelectrics and ferroelastics in $F(x)$ must be taken into account the additional invariants that include spontaneous polarization $P_i$ or spontaneous deformation $U_{ij}$. The period of the modulation of *IC* phase secondary parameters is twice less from the modulation period of $\eta$ and $\xi$.

2. The peculiarity of the *IC* phase consists in the fact that dependencies of $k_i$ on the temperature as well as thermodynamical potential on $k_i$ are not smooth functions [23]. At one-harmonic approximation the magnitude $k_i$ changes step-like and has only rational values relatively to the period of the high temperature phase. Thus, the temperature change of the *IC* structure period is step-like. These steps are rather inconsiderable near $T_i$ and significant near $T_c$ [21,24]. Such behavior of the structure is named as "devil's staircase"[21,24]. However, the account of the high harmonics $n_k$ significantly change the character of the phase transition from the *IC* phase to the commensurate phase and this transition becomes the continuous («lock-in») transition [13-17] contrary to the transition of the first order for a one-harmonic approaching.

For the fixed rational values $k_i$ the respective phase diagrams can exist that describe the temperature intervals of their existing in dependence from the external factors (hydrostatic or axial pressure, electric field, irradiation, etc.).

3. Soliton structure dynamics [25-28] have interesting peculiarities. Specifically, for the description of which it is necessary to introduce the conception of the soliton density $n_s=d_0/x_0$, where $d_0$ - soliton's width, $x_0$ - distance between solitons as well as the order parameter, soliton density $n_s\rightarrow 1$ with approach to $T_i$ and jump-like disappear at $T_c$. The global temperature hysteresis, the «parallelogram» type cycles, thermooptical memory, relaxation processes are caused by the existing of the soliton structure. A nucleation and annihilation of the soliton at change temperature plays the main role in dynamic of the soliton structure. Owing to the soliton nucleation the crystal passes through an intermediate metastable states that differ by the

soliton density. These states are separated by free energy barriers and the activation energy $E_c$ is necessary for the nucleation of $n$ solitons [29]. The energy $E_c$ and radius of nuclei is approximately inversely proportional to the deviation of the incommensurate parameter $|\Delta\delta|=\delta-\delta_0$ from its equilibrium state $\delta_0$. The transition to the equilibrium state through intermediate metastable states manifest itself in the time dependencies of physical characteristics at temperature stabilization in the *IC* phase, that is in relaxation processes [28].

4. The defects (impurities, dislocations) that interact with modulated structure make influence on the hysteresis and kinetic phenomena. Then three limit cases can be realized:

a) the IC modulated structure interact with the disordered fixed defects (velocity of the structure motion is much more than the velocity of defect motion ($v_s >> v_d$) [32]);

b) the interaction between the mobile defects and the static *IC* modulated structure form «defects density wave» ($v_d >> v_s$) [33,34];

c) the «viscous» interaction between the mobile defects and mobile *IC* modulated structure ($v_s \cong v_d$) [7].

The first case manifests itself in the hysteresis and kinetic phenomena, the second - in the effect of the thermal memory, that consists in the ordering of the defects in the modulated structure field at the temperature stabilization. And, at last, the third - in the step-like dependence of crystal properties in the *IC* phase on the external influences (velocity of the temperature change, dose of *X*-ray irradiation, magnitude of electric field and pressure and its gradients). Instead of the conception of the «phase soliton» is used more frequently the conception discommensuration (*DC's*), that is incommensurate regions that are separated by commensurate ones within the *IC* phase [35]. This conception has not formal character. By introducing the value ρ, which denominate ratio of *DC's* velocity $v_a$ to the diffusion coefficient D and conception of the force of defects interaction between defects and *DC's*, details of mentioned anomalies can be analyzed.

On the basis of above-mentioned facts we shall consider the most interesting optical effects, that are caused by incommensurate structure and the possibility of their using in the study of the incommensuration at example of $A_2BX_4$ group crystals. Certainly, each crystal of this group has specific peculiarities, dued by chemical structure, sequence of the phase transitions, the nature of order parameter (polarization, strain, deformation, etc.). It is impossible to analyze all these peculiarities in a short review paper. Therefore, below, the selected results of the experimental investigations of the optical properties obtained on the different crystals will be presented.

## 3. Anomalies of optical birefringence: manifestation of the defect-IC structure interaction

In general, optical birefringence in the IC phases can be described by considering the character of the optical permeability changes under the influence of spontaneous polarization $P_s$, mechanical deformation $U_{ij}$ and the order parameter components (ρ,φ). Taking into account the spontaneous polarization and mechanical deformation in the IC phase to be modulated and omitting the quadratic effects, one can derive the following linear approximation for the birefringence temperature changes in the IC phase of $A_2BX_4$ crystals [36,37]

$$\delta(\Delta n) \cong \alpha\rho^2 + \nu\rho^2\, d\varphi/dz, \qquad (1)$$

where α and ν are constants. In a plane-wave approximation we have then

$$\delta(\Delta n) \cong \rho^2 \cong (T_i - T)^{2\beta} \cong I, \qquad (2)$$

where β is a critical index, I the integral intensity of the X-ray reflexion. However, fitting the temperature dependence of the birefringence in the IC phase by formula (2) it turns out to be a good approximation only in a narrow temperature region. Obviously, this is due to the transition from the plane-wave model to the soliton regime which takes place in approaching $T_c$, and thus the gradient term in (1) cannot be neglected. The viscous interaction, the global hysteresis, the "parallelogram" type cycles, and the thermooptical memory are evidences of the mentioned effects.

The global temperature hysteresis manifests itself in the temperature dependence of physical quantities on the heating and cooling branches which are different, and not only near the point of the phase transition into the ordered phase which is of first order. The transition often becomes continuous, and the hysteresis loop includes the whole IC phase and partly the ordered phase (fig.1).

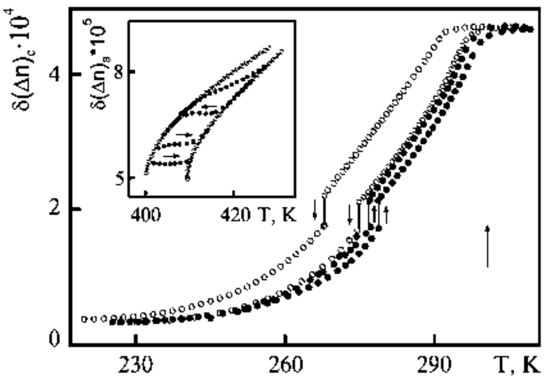

**Fig.1.** Temperature dependences of the birefringence $\delta(\Delta n)_c$ in $[N(CH_3)_4]_2ZnCl_4$: 1(●) - dT/dt=1.1 K/h, 2(o) - 0.11 K/h. Inset - partial cycles of thermal hysteresis of the birefringence $\delta(\Delta n)_a$ in $K_2ZnCl_4$:$Co^{2+}$.

Its shape depends on the sample prehistory, the thermal annealing, the impurity and defect concentration, the temperature variation rate. The "parallelogram" cycle type appears between the cooling and heating runs. Two opposite sides of the parallelogram lie on the branches of cooling and heating, the two other ones should be horizontal due to the constancy of the soliton density. This is not the case. Only by keeping the temperature for very long (≅20 h) before the transition to another branch leads to the expected result.

The observed effects are related to the pinning of the IC structure by defects (impurities) for which the mobility is much less than that of IC modulated structure ($v_s >> v_d$). It is noteworthy that the relaxation [10,15] is not smooth, and owing to the soliton nucleation, the crystal passes through a series of intermediate metastable states which differ by their soliton density.

One must take into account that the transitional metastable states are separated by the free energy barriers. The activation energy $E_c$ is necessary for the transition to another state. The time of staying in the metastable state has to be much longer than the time of passing through the barrier. Thus the metastable states represent the "energy steps" affecting the crystal during its approach towards a thermodynamical equilibrium. This is clearly seen [9] for $[N(CH_3)_4]_2FeCl_4$ crystals (fig.2).

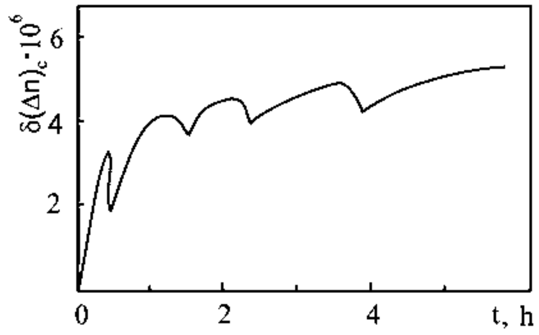

**Fig.2.** Temporal dependence $\delta(\Delta n)_c$ of $[N(CH_3)_4]_2FeCl_4$ crystals. The velocity of approaching to $T_{st}$ = 270.36 K in regime of heating is dT/dt = 5.7 K/h.

Peaks are observed in the kinetic dependence of $\delta(\Delta n)_c$ (*c* is the modulation direction), and the distances between them increase with the time. Note that the time the crystal stays in the "lower" metastable states is essentially larger than that in the "upper" ones. The sloping regions of the kinetic dependence corresponds to an invariable soliton density, and the peaks characterize the transitions from one soliton density to another (accompanied with a sharp change in the phase distribution $\varphi$ of the order parameter).

Besides the structure relaxation, an ordering of the mobile impurities and defects along with their pinning occur. This is caused by fixing the static phase solitons (since $v_d >> v_s$) and forming a "defect density wave". This is testified, in particular, by the thermo-optical memory effect which consists of defects ordering in the field of the modulated structure during the temperature stabilization, and in the localization of the wave vector k at a value corresponding to the last point of the temperature stabilization. Repeated transition through this temperature in the same run (e.g. on heating) is accompanied by the anomaly of $\delta(\Delta n)$ if the crystal is not driven into the paraphase. The anomaly on the global hysteresis is shifted in the temperature scale by the hysteresis width. The anomaly is also observed (fig.3) at the temperature which corresponds to a doubling of the modulation wave period. The shape of the anomaly depends on the temperature stabilization time, the temperature variation rate, and the external factors [7,38].

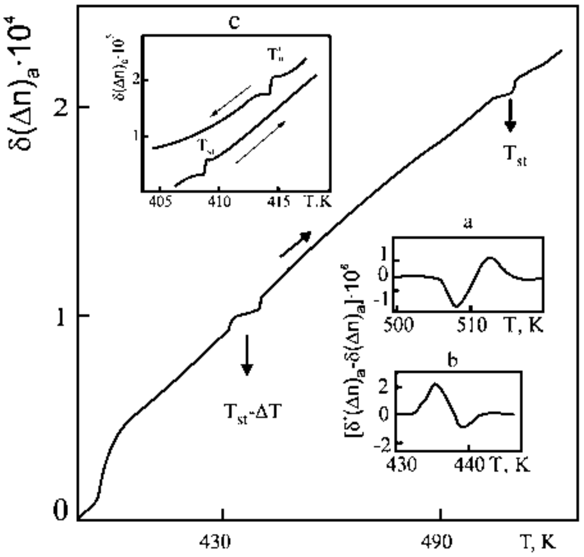

**Fig.3.** Temperature dependence of the birefringence in $K_2ZnCl_4$ crystals kept for t=26h at $T_{st}$=510.5K. Insets: a,b – the anomalys at $T_{st}$ and $T_{st}$–ΔT correspond, δ' and δ correspond to the samples kept or not at $T_{st}$; c – the anomaly shift on global hysteresis branches.

Generalizing these results of the optical birefringence studies on the incommensurate phase, we come to the conclusion that both the amplitude ρ and the phase φ of the order parameter contribute to the birefringence temperature and temporal changes in such a way that the anomalous part assigned to the φ behavior is superimposed on the smooth dependence connected to the ρ behavior.

The third case of interaction between the IC structure and defects (impurities) - the case of "viscous" interaction ($v_d \cong v_s$) - also manifests itself in the optical birefringence. Just for its analysis, the notion of DC's (i.e. the alternance of incommensurate and commensurate regions within the IC phase) is used instead of the concept of "phase soliton". According to this interpretation, the viscous interaction corresponds to the case when the DC's velocity becomes close to the diffusion velocity of defects (impurities) in crystal. Under these conditions, the global hysteresis is not smooth but step-like. The effect was observed for the first time [7] in the crystals of quartz. Similar results for $[N(CH_3)_4]_2FeCl_4$ are displayed in fig.4 [9]. One can see that the temperature dependence of the birefringence is associated to the appearance of cogs and this effect increases with the decrease of the temperature variation rate s (in the heating regime). Lowering the rate of nucleation and the mobility of new incommensurabilities increases the friction force. Of course, the difference in the $\delta(\Delta n)$ values taken for two neighbouring minima characterizes the increment of the order parameter amplitude ρ between the two neighbouring metastable states of *k* localization.

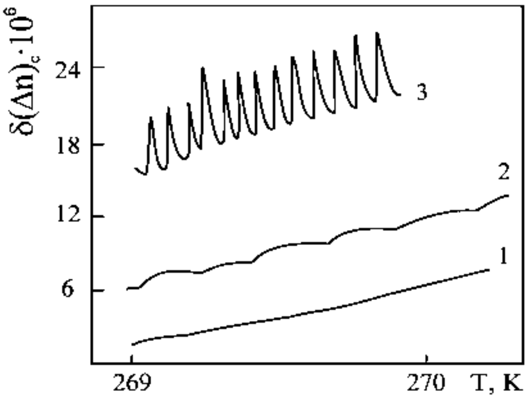

**Fig.4.** Temperature dependence of $\delta(\Delta n)_c$ for $[N(CH_3)_4]_2FeCl_4$ crystals at the temperature variation rate dT/dt=1500 mK/h (1); 300mK/h(2); 60 mK/h (3).

## 4. Influence of external factors on the interaction of IC structure with defects

Strengthening the interaction between the IC structure and impurities or defects can be achieved by increasing their concentration, e.g. owing to X-ray irradiation (fig.5), or under the influence of hydrostatic pressure, external mechanical stress, electric field or their gradients [9,39]. Simultaneously, the temperature dependence in the IC phase of the piezooptical coefficient, as the derivatives of the optical permeabilities (birefringence components) on mechanical stresses, have in many cases a peak-like shape, for example in $Cs_2CdBr_4$ and $Cs_2HgBr_4$ crystals [39].

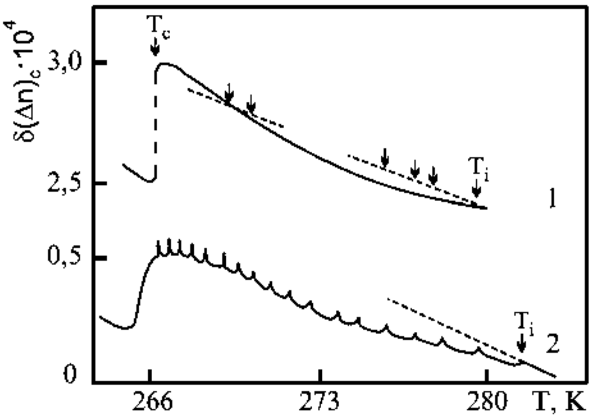

**Fig.5.** Temperature dependences of the birefringence variations in $[N(CH_3)_4]_2FeCl_4$ crystals in the heating regime (dT/dt=10K/h): 1 - non-irradiated, 2 - irradiated (during 3h) samples.

The analysis of these results testifies that the quantity of metastable states increases when the irradiation doze increases. Besides, a regular distribution of DC's infringes. Therefore the pinning of the IC structure on defects counteracts the elastic energy of the interaction between the DC's. The availability of an external mechanical stress related to a spontaneous deformation in ferroelastics, or the corresponding external electric field in ferroelectrics, induces narrowing or even the disappearance of the incommensurate phases. However, peaks are absent (fig.6) on the anomalies so that the phase term associated with the energy barrier for the transitions between the metastable states becomes negligible. A localization of the wave vector in the IC phase occurs at the pinned commensurabilities of a higher order, and smooth transitions between them take place. In these cases the crystals can be characterized by the specific phase diagrams (fig.7).

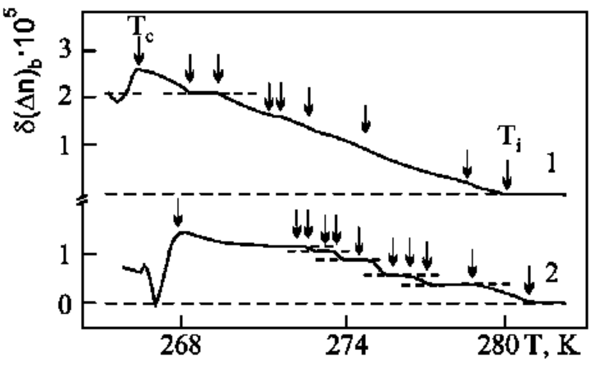

**Fig.6.** Temperature dependence of the birefringence spontaneous increment $\delta(\Delta n)_b$ of $[N(CH_3)_4]_2FeCl_4$ crystals under the influence of uniaxial mechanical stress $\sigma_3=0(1)$; $\sigma_3=1.47\times10\ N\times m^{-2}(2)$. The temperature variation rate is dT/dt=5.7 K/h.

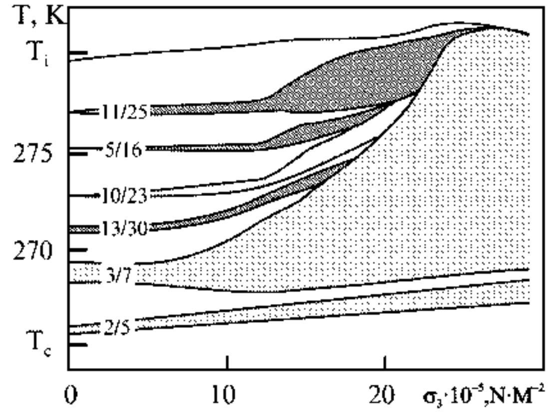

**Fig.7.** Phase diagram ($\sigma_3$,T) of $[N(CH_3)_4]_2FeCl_4$ crystals. The dashed regions correspond to the commensurate phases.

The character of interaction between the IC structure and defects manifests also itself strikingly in the crystals with gradients of concentration of X-ray defects, temperature, electric fields, mechanical stresses etc. Moreover, long-period anomalies appear on the temperature dependence of the δ(Δn) (fig.8) if the irradiation doze passing through a thick sample increases (i.e. the defect gradient increases). These anomalies are accompanied by the effect characteristic for the case of viscous interaction. Moreover, regularity of long-period anomalies do not depend on the temperature variation rate. They are observed both in the IC ferroelectrics ($[N(CH_3)_4]_2ZnCl_4$) and ferroelastics ($[N(CH_3)_4]_2CuCl_4$). Obviously, the long-period anomalies are caused by an oscillation of discommensuration density along the modulation direction under the action of gradient factors, the competition of pinning and elastic soliton-soliton interaction [40].

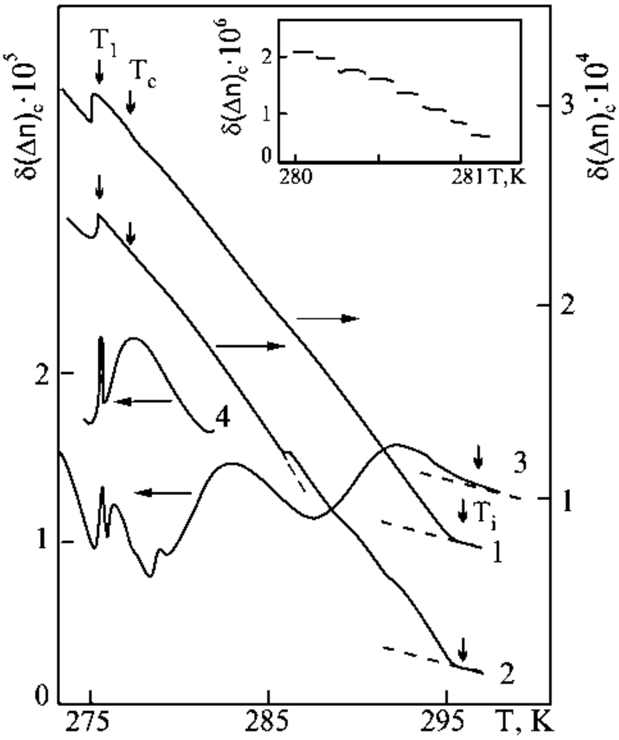

**Fig.8.** Temperature dependences of $\delta(\Delta n)_c$ in c-cut of $[N(CH_3)_4]_2ZnCl_4$ irradiated along the c axis ($l_c$=6 mm) during t= 0 (1), 3 (2), 6 (3), 6 (4) h. The temperature variation rate is equal to dT/dt=16 K/h in the heating regime (1,2,3). Inset - part of long-period curve (4) in enlarged scale at dT/dt=2 K/h and t=6.0 h.

## 5. Problem of optical activity in IC phases

The problem of the optical activity in crystals with IC structure is probably one of the most disputable in the recent crystal optical studies. The optical activity of the IC phase is forbidden from the standpoint of symmetry since the average structure is centrosymmetric. On the other side, the incommensurate modulation period is comparable with the wavelength. This is a condition for the existence of the optical activity. Various experimental results are also contradictory. The reasons for those discrepancies are caused in some cases by the lack of correct experimental methods, and also by the state of the samples under investigation. This is characteristic for crystals with IC structure.

The immediate measuring of the rotation angle ρ of the polarization plane in $K_2ZnCl_4$ and $Rb_2ZnCl_4$ crystals can be considered as the most correct and reliable. According to symmetry requirements (class mm2), the effect should take place if the light passes along one of the optical axes. No optical activity is observed at all in the IC phase of $K_2ZnCl_4$. The effect which can be considered as a linear spontaneous electrogyration is observed in the C phase, since $\rho \sim P_s$, and a characteristic hysteresis loop appears with depolarizing crystal [41]. Similar situation takes place also in $Rb_2ZnCl_4$ crystals (fig.9) [42]. Unlike $K_2ZnCl_4$, a slight optical activity (gyration component $g_{13} \cong 10^{-7}$) exists even for the multidomain sample. It remains also in a certain temperature region of the IC phase, including the transitions of the single-domain states to the IC phase. Obviously, this is caused by a partial unipolarity of the sample in the C phase which is kept in the multisoliton region of the IC phase.

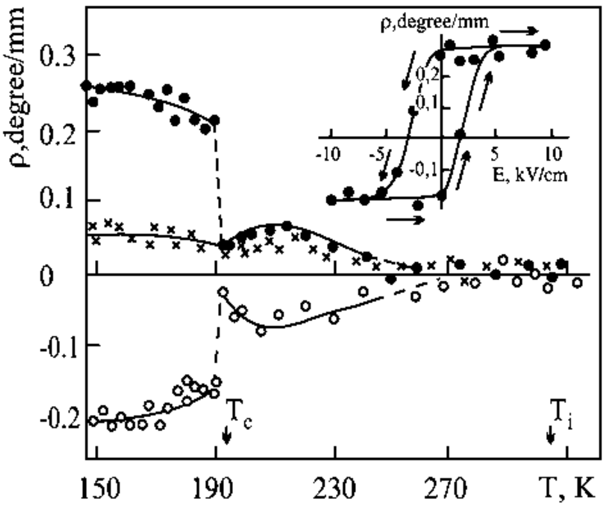

**Fig.9.** Temperature dependences of the OA in $Rb_2ZnCl_4$ on preliminary cooling (×) and subsequent heating under the action of the electric field $E_c$=5.8 kV/cm (•) and $E_c$=–5.8 kV/cm (o). Inset - hysteresis of the OA at T=150 K.

The results of studying the optical activity in $[N(CH_3)_4]_2ZnCl_4$ [43] require another explanation. In the IC phase, the temperature dependence of the component $g_{33}$ which can not appear as a result of spontaneous electrogyration in the ferroelectric phase testify that the OA is not a precursor effect of the commensurate phase. As a consequence of a precursor effect of the IC phase and defects available, the OA exists also in the paraphase and depends conspicuously on the sample state (as-grown, annealed, irradiated). Of course, the interpretation of the above results is impossible within the framework of a perfect modulated structure, the more so that the OA is accompanied by the optical indicatrix rotation and the eigenwave ellipticities changes in crystal [43-45].

On the whole, the motivation of the OA in incommensurate crystals is accessible on the basis of elaborating the Jones' models of media with the modulated dielectric parameters and accounting for the structure-defect interaction. The models should be improved for different cases [43-45]: the character of the modulation and the domain structure, ideal or unipolar states, availability of local defects or dichroism. Using the given approach, it turns out that the OA in a macroscopically centrosymmetric crystal is caused by the following reasons: inhomogeneity of (even perfect) structure; its polarization which imposes the unipolarity; local distortions of the modulation wave phase. The most essential is that the gyrotropy is not the factor of incommensurability of structural modulation but a result of a spatial inhomogeneity of the medium. Local distortions of the modulation wave are mainly affected by its pinning on the fixed defects possessing a low mobility. The magnitude of the OA in modulated phase is always less significantly than that of homogeneous acentric phase. The boundary conditions, the sample thickness and the light propagation direction [45] (along or across the modulation direction) manifest themselves in the OA of IC phases.

## 6. Peculiarities of the light absorption in IC phases

Some information regarding the phase transition character and the structure of the IC crystals can be established from the studies of the optical absorption spectra. The investigation of the temperature dependence of the energy gap $E_g$ represents here a wide – spread experimental method. The absorption coefficient is known to obey the Urbach's rule near the fundamental absorption edge [46]:

$$k=k_0\exp\{[\sigma(T)/(kT)]\times(\hbar\varpi-E_0)\},$$

where $\hbar\varpi$ is the light quantum energy, $E_0$ and $k_0$ the constants ($E_0$ corresponds to the energy gap between the upper point of the valence zone and the lower minimum of the conduction zone). $\sigma(T)$ describes the eroding of the absorption edge:

$$\sigma(T) = [\sigma_0 \cdot 2\,kT\,/\,(\hbar\varpi_0)]\tanh\{\hbar\varpi_0\,/\,kT\}.$$

Here $\sigma_0$ denotes the constant of electron-phonon interaction, $\hbar\varpi_0$ the energy of effective optical phonon which is most closely connected with the electron.

Thus, the dependence of $ln\,k$ on $\hbar\varpi$ turns out to be linear for fixed temperatures, and the lines intersect at the point ($k_0$, $E_0$). In other words, a crystal can be characterized by certain phonon eigenfrequencies. However Urbach's rule is not fulfilled in IC phases. Here $ln k \cong f(\hbar\varpi)$ does not intersect at the same point, i.e. $k_0$ and $E_0$ values, along with the electron-phonon interaction value, are not fixed. In this sense, the crystal state within the IC phase is intermediate between amorphous and ordered crystals. This conclusion is illustrated (fig.10) by the example of $[N(CH_3)_4]_2CoCl_4$ crystals [47].

A global hysteresis and a thermooptical memory can also be observed in the absorption of IC crystals [48]. Infrared absorption and reflection spectra are sensitive to the onset of IC structures, as well as the Raman spectra [49]. Thus, additional bands appear in absorption spectra which can be attributed to the influence of the ordered defect wave on the energy structure of crystals [50].

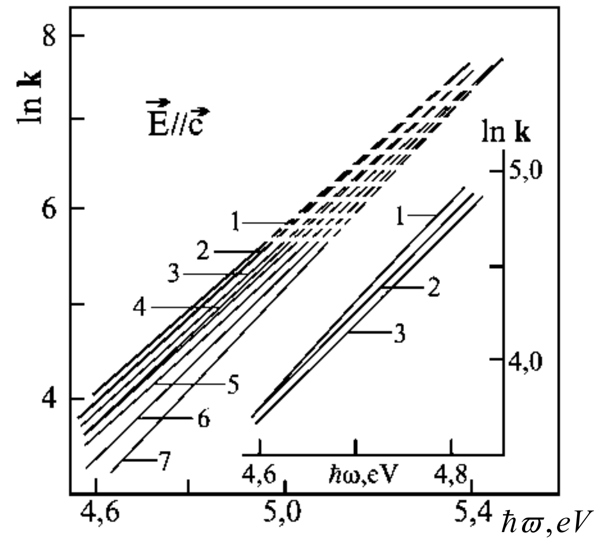

**Fig.10.** The dependence *ln* **k** = f(ħϖ) in $[N(CH_3)_4]_2CoCl_4$ at the temperatures 1 - 330, 2 - 314, 3 - 300, 4 - 284, 5 - 274, 6 - 258, 7 - 231 K. Inset - the dependence *ln* k = f(ħϖ) in the IC phase: 1 - 293, 2 - 287, 3 - 284 K.

## 7. Studies of phase diagrams by optical methods

Below we shall illustrate a possibility of the optical methods to study phase diagrams. In fig.11, isobaric temperature dependences of the birefringence increments σ(Δn) are represented, along with the (P,T) phase diagram of $[N(CH_3)_4]_2ZnCl_4$, based on birefringence measurements [51]. The dependence δ(Δn)=f(T) at atmospheric pressure are characterized by anomalies displayed at the phase transitions: 0'-1'($T_i$), 1'-2' ($T_c$), 2'-3' ($T_L$). The jamps and breakings correspond to transitions of the first and second order, respectively. The phase transitions are shifted toward higher temperatures under the pressure, the jumps at $T_l$ decrease, and the anomalies at $T_c$ erode. The phase transition lines intersect at triple points. An additional weak anomaly appears at $T_l$ under the pressures 50≤P≤100 MPa. It corresponds to transitions from the ferroelastic phase 2 into the IC phase with the wave vector k=2/5a*(l-δ). From the example above, the following important conclusions can be deduced. It is associated with crystals of the $[N(CH_3)_4]_2XCl_4$ type. In particular the δ(Δn) dependence on the order parameter amplitude is quadratic in the IC phase; the birefringence increments in the IC phase (and therefore, the order parameter) is independent of pressure; the baric coefficient of shift of the phase transition is positive, i.e. the transition is of the "order-disorder" type. Similar studies also were carried out for other $A_2BX_4$ crystals [52,53]. Specifically, $Cs_2HgBr_4$, $Cs_2CdBr_4$ and $Cs_2HgCl_4$ are of interest in this respect. Finally, we note that the studies of the phase diagrams with the optical methods were supplemented by ultrasonic methods [54,55].

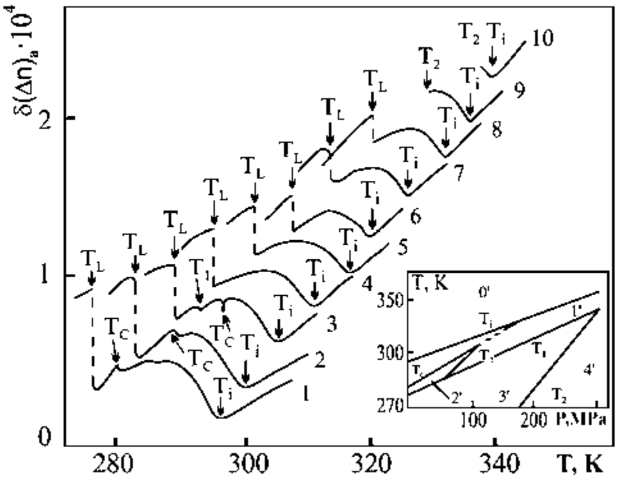

**Fig.11.** Isobaric temperature dependences of the birefringence increment in c-cut of $[N(CH_3)_4]_2ZnCl_4$: 1 - 0.1, 2 - 40, 3 - 80, 4 - 120, 5 - 160, 6 - 200, 7 - 240, 8 - 285, 9 - 320, 10 - 345 MPa. Inset - phase (P,T) diagram.

## 8. Conclusion

Studies of birefringent, gyrotropic and absorbing properties of crystals with the IC structure, as well as the related effects imposed by the action of external fields or irradiation, supplement essentially the ideas in the domain of phase transitions and the anomalies observed in IC phases. Such phenomena as global hysteresis, the complete cycles, step-like temperature anomalies, kinetics, and the memory of the optical characteristics are caused by interaction of defects with the modulated IC structure. Although the macroscopic symmetry group of the IC phases includes an inversion center, the effects forbidden by symmetry conditions are observed here (optical activity, linear electrooptical effect). However, they are not caused from the same origin as the IC state, but from defects and degree of structural unipolarity. Studies of the phase diagrams with the birefringence method reveal not only simplicity, but sufficiently high sensitivity and accuracy. This enables to find out polycritical points, in particular the Lifshitz's points in different types of ferroics. Furthermore, these methods are also sensitive to the effects of external factors and the external fields gradients. One can study in this way the DC's dynamics, their nucleation and annihilation. The Urbach's rule does not hold in the IC phase. This proves that the notion of the phonon energy is, as a matter of fact, not defined here, and the IC phase represents, to a certain degree, a quasi amorphous state.

## References

1. Bruce A.D. and Cowley R.A., J. Phys. C: Solid State Phys. **11** (1978) 3577-3630.
2. Lifshitz E.M., Zhurn. Eksper. Teor. Fiz. **11** (1941) 255-268 (in Russian)
3. Levanyuk A.P. and Sannikov D.G., Fiz. Tverd. Tela. **18** (1976) 423-426 (in Russian)
4. Hamano K., Hishinuma T. and K. Ema, J. Phys. Soc. Japan **50** (1981) 2666-2671
5. Vlokh O.G., Kaminsky B.V., Polovinko I.I. and Sveleba S.A., Fiz. Tverd. Tela. **28** (1986) 2911-2914 (in Russian)
6. Vlokh O.G., Kaminsky B.V., Polovinko I.I. and Sveleba S.A., Ukrain. Fiz. Zhurn. **31** (1986) 1389-1391 (in Russian)
7. Mogeon F., Dolino G. and Vallade M. Phys. Rev. Lett. **62** (1989) 179-182
8. Bzionet M., Almairac R. and Saint-Gregoire P. J. Phys. C: Solid State Phys. **20** (1987) 2635-2645
9. Vlokh O., Polovinko I, Sveleba S., Zhmurko V. and Kapustianik V. Ferroelectrics **132** (1992) 289-291
10. Unruh H.G. J. Phys. C: Solid State Phys. **16** (1883) 3245-3255
11. Jamet J.P. and Lederer P. J. Physique Lett. **44** (1983) 1257-1264
12. Lederer P., Montambax G., Jamet J.P., Chauvin M., J. Physique Lett. (France) **45**, (1984) L 627-L 637
13. Vlokh O.G., Kityk A.V., Kaminsky B.V. and Polovinko I.I. Fiz. Tverd. Tela **27** (1985) 3436-3438 (in Russian)
14. Vlokh O.G., Kityk A.V., Mokry O.M., Grybyk V.G. Fiz. Tverd. Tela **33** (1991) 312-315 (in Russian)
15. Blinc R., Prelovsek P., Levstic A. and Filipic C. Phys. Rev. B.: **29** (1984) 1508-1510
16. Srolovitz D.G., Eykholt R., Вактett D.M. and Hirth J.P. Phys. Rev. B.: **35** (1957) 6107-6121
17. Blinc R. Levanyuk A.P. Incommensurate phases in dielectrics. Part 1, Fundamentals. Part 2, Theory. North Holland. 1986.
18. Levanyuk A.P. and Sannikov D.G. Fiz. Tverd. Tela **18** (1976) 423-427 (in Russian)
19. Ishibashi I. Ferroelectrics **20** (1978) 103-108
20. Mc. Millan W.L. Phys. Rev. B. **14** (1976) 1496-1502
21. Bac P., Bachm J. Phys. Rev B. **52** (1980) 2526-2533
22. Blinc R. Physics Report. **76** (1981) 331-398
23. Dzyaloshinskii I.E. Zhurn. Eksper. Teor. Fiz. **46** (1964) 1420-1497 (in Russian)
24. Sannikov D.G. Zhurn. Eksper. Teor. Fiz. 26 (1989) 2198-2208 (in Russian)
25. Janovec V., Gadefroy G., Gadefroy L.R. Ferroelectrics. **53** (1984) 333-336
26. Prelovsek R. Ferroelectrics. **54** (1984) 29-32
27. Strukov V., Uesk I., Arutjunova V.M. Pis'ma v JTEF, **35** (1982) 424-427 (in Russian)
28. Nettermann T. J. Phys. C: Solid State Phys. **18** (1985) 5683-5696
29. Kawasaki K. J. Phys. C: Solid State Phys. **16** (1983) 6911-6920
30. Hiroyuki M., Hiroyuki K. Jap. J. Appl. Phys. **24** (1985) 802-804
31. Prelovsek P. and Blinc R. J. Phys. C: Solid State Phys. **17** (1984) 577-588

32. Villain J. J. Phys. Lett. **43** (1982) L.551-558
33. Jamet J.P. Phase Transitions. **11** (1988) 335-371
34. Lederer P. and Montambaux G., Jamet J.P. J. Phys. Lett. **45** (1984) L 627-L 638
35. Kowasaki K. and Jamanaka S. Phys. Rev. B.: **34** (1986) 7986-7987
36. J. Fousek, Ferroelectrics **20** (1978) 11; Phase Transitions **36** (1991) 165.
37. C. Kon'ak, Phys.Status Solidi (a). **54** (1979) 99.
38. O.G. Vlokh, B.V. Kaminsky, A.V. Kityk, I.I. Polovinko and S.A. Sveleba, Fiz. Tverd. Tela. **29** (1987) 2215-2217. (in Russian)
39. O.G. Vlokh, V.S. Zhmurko, I.I. Polovinko and S.A. Sveleba, Ukrain. Fiz. Zhurn. **36** (1991) 1040; (in Russian) Fiz.Tverd.Tela. **33** (1991) 3109-3112. (in Russian)
40. A.V. Kapustianik, I.I. Polovinko, S.A. Sveleba, O.G. Vlokh and V.S. Zhmurko, Europhys. Lett. **19** (1992) 429- 432.
41. O.G. Vlokh, A.V. Kityk and I.I. Polovinko, Krystallogr. **30** (1985) 1194-1196; Fiz. Tverd. Tela. **27** (1985) 1581-1583. (in Russian)
42. O.G. Vlokh, A.V. Kityk and I.I. Polovinko, Krystallogr. **32** (1987) 140-142. (in Russian)
43. O.G. Vlokh, O.S Kushnir and Y.I. Shopa, Ukrain.Fiz. Zhurn. **38** (1993) 862-871. (in Russian)
44. O.S. Kushnir, Y.I. Shopa and O.G. Vlokh, Europhys. Lett. **22** (1993) 389-393.
45. O.S. Kushnir and O.G. Vlokh, J. Phys.: Condens. Matter. **5** (1993) 7017-7032.
46. M.I. Fridkin. Ferroelectrics-semiconductors. 1976, p.408. (in Russian)
47. O.G. Vlokh, I.I. Polovinko and S.A. Sveleba, Ukrain. Fiz. Zhurn. **34** (1989) 673-677. (in Russian)
48. O.G. Vlokh, V.I. Mokry, I.I. Polovinko and S.A. Sveleba, Krystallogr. **36** (1991) 919-924. (in Russian)
49. Th. Rezing, P. Wyder, A. Janner and T. Janssen, Phys.Rev.B, **25** (1982) 7504-7519.
50. O.G. Vlokh, I.I. Polovinko and S.A. Sveleba, Fiz.Tverd.Tela. **31** (1989) 277-280. (in Russian)
51. O.G. Vlokh, A.V. Kityk and I.I. Polovinko, Fiz.Tverd.Tela. **27** (1985) 1581-1583. (in Russian)
52. O.G. Vlokh, I.I. Polovinko, S.A. Sveleba, A.V. Kityk, O.M. Mokry and V.G. Gribyk, Ukrain.Fiz. Zhurn. **35** (1990) 520-525. (in Russian)
53. A.V. Kityk, V.P. Soprunyuk and O.G. Vlokh, J. Phys.: Condens.Matter. **5** (1993) 235-246.
54. A.V. Kityk, O.M. Mokry, V.P. Sopronyuk and O.G. Vlokh, J. Phys. Condens. Matter. **5** (1993) 5189-5200.
55. O.G. Vlokh, A.V. Kityk and V.P. Soprunyuk, Fiz.Tverd. Tela. **34** (1992) 513 (in Russian); Phys. Stat.Sol.(a) **138** (1993) 119-131.