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# Parametric crystal optics of nonmagnetic ferroics

O.G.Vlokh

Institute for Physical Optics
23 Drahomanov St., UA–290005 Lviv, Ukraine

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Proceeding from the symmetry principles of crystal physics and thermodynamics we analyze parametrical optical phenomena induced by external fields of different kind and structural phase transitions in ferroelectrics and ferroelastics. Special attention is paid to the phenomena of spatial dispersion (electro- and piezogyration). A phenomenological approach to the description of these phenomena is illustrated by the most expressive experimental results obtained for the following crystals: $KH_{2(1-x)}D_{2x}PO_4$ (KDP, DKDP), $K_2H_2AsO_4$ (CDA), $RbH_2PO_4$ (RDP), $Pb_5(Ge_{(1-x)}Si_x)_3O_{11}$, $Pb_3(PO_4)_2$, $K_2Cd_2(SO_4)_3$, $(NH_3CH_2COOH)_3H_2SO_4$ (TGS), and $NaKC_4H_4O_64H_2O$ (RS). Apart from new effects in the crystals of the $A_2BX_4$ group with incommensurately modulated structure, in particular, crystals $[N(CH_3)_4]_2ZnCl_4$, $[N(CH_3)_4]_2FeCl_4$, $K_2ZnCl_4$, $K_2ZnCl_4$, $Co^{2+}$ are considered.

**Key words:** *crystal optics, ferroelectrics, optical activity, ferroics, phase transitions*

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## 1. General remarks

### 1.1. Parametric crystal optics as a particular case of nonlinear optics

Parametric crystal optics is a particular case of nonlinear optics of high intensity light beams under the conditions that one of the interacting waves is of a low intensity, and frequencies of the others tend to zero. Nonlinear and parametric optics have a similar phenomenological description and symmetric aspects.

Such a conclusion follows from the expression that describes time averaged free energy of the unit volume [1,2]:

$$\begin{aligned} \overline{F} &= k_1 EE^* + k_2 E_0 E_0^* k_3 A_{af} A_{af}^* + \ldots \\ &+\chi_1 EEE^* + \chi_2 EE_0 E^* + \chi_3 EH_0 E^* + \ldots \end{aligned}$$

 

$$+\Theta_1 EEEE^* + \Theta_2 EE_0E_0E^* + \ldots$$

The formulas determining polarization P, magnetization M and mechanical stress X can be deduced differentiating the above expression with respect to corresponding variables ($E^*$, $H^*$, $A^*$). The terms with the third $\chi$ and the forth $\Theta$ rank tensors correspond to nonlinear optics. For example, the expression with $\chi_1$ describes the phenomena of wave generation with differential (subtractive) and summable frequencies. In particular, the phenomena of optical detection and second harmonic generation are described by the formula:

$$P^{\omega\pm\omega} = \chi_1^{\omega\pm\omega} E^{\omega} E^{\omega}$$

The expression with $\chi_2$ corresponds to the linear electrooptic effect.

### 1.2. Some tensor relations, symmetric aspects

It is known [3, 4] that optical properties of crystals are described by the material equations taking into account a spatial dispersion [2]:

$$E_i = a\prime_{ij} D_j = (a_{ij} + i\gamma_{ijl}k_l) D_j,$$

where $\gamma_{ijl} = e_{ijk}g_{kl}$ is an antisymmetric polar tensor, $g_{kl}$ is an axial gyration tensor dual to the above one, $e_{ijk}$ is a Levi-Civita tensor, $k_l$ is a wave vector, $a_{ij}$ is a tensor of the optical polarization constants without consideration of spatial dispersion ($a_{ij}$ is a reciprocal tensor with respect to $\varepsilon_{ij}$ tensor).

The parametric optical effects are determined by expanding $a_{ij}$ or $\varepsilon_{ij}$ tensors and $\gamma_{ijl}$ or $g_{kl}$ tensors into power series with respect to different fields, namely:

1. $a_{ij} = a_{ij}^0 + r_{ijk}E_k + R_{ijkl}E_kE_l + ...$ - electrooptics [5, 6]; (1)
2. $g_{ij} = g_{ij}^0 + \gamma_{ijk}E_k + \beta_{ijkl}E_kE_l + ...$ - electrogyration [2, 7-10]; (2)
3. $a_{ij} = a_{ij}^0 + \rho_{ijkl}\sigma_{kl} + ...$ - elastooptics [11]; (3)
4. $g_{ij} = g_{ij}^0 + \xi_{ijkl}\sigma_{kl} + ...$ - elastogyration [2]; (4)
5. $a_{ij} = a_{ij}^0 + q_{ijklp}\sigma_{kl}E_p$ - elasto-electrooptics;
6. $g_{ij} = g_{ij}^0 + Q_{ijklp}\sigma_{kl}E_p$ - elasto-electrogyration.

In inhomogeneous fields, gradient parametric optical effects are possible [12], for example, a torsional-gyration effect [13]:

$$\Delta g_{ij} = \eta_{ijklm}\frac{\partial \sigma_{kl}}{\partial x_m}.$$

The restrictions as to the form of polar ($a_{ij}$, $r_{ijk}$, $R_{ijkl}$, $\rho_{ijkl}$, $q_{ijklp}$) and axial ($g_{ij}^0$, $\gamma_{ijk}$, $\beta_{ijkl}$, $\xi_{ijkl}$, $Q_{ijklp}$) tensors are due to the point symmetry of crystals:

$r_{ijk} = g_{ij}^0 = \beta_{ijkl} = \xi_{ijkl} = q_{ijklp} = 0$ - in the crystals having inversion symmetry;

$a_{ij}$, $R_{ijkl}$, $\gamma_{ijk}$, $\rho_{ijkl}$, $Q_{ijklp} \neq 0$ - in acentrically and centrally symmetric crystals.

The possibility for appearing the mentioned parametric optical effects agrees with the following principles of the point symmetry:

1. The Curie principle – a superposition of the elements of the symmetry of crystals and suitable fields.

2. The Neumann principle – obedience of the symmetry of the crystal to the symmetry of the property.

The effects taking place in the magnetic field are additionally restricted not only by the symmetry of the crystal but also by that of the kinetic coefficients in non-dissipative media [14]:

1. The Onsager principle:
$a_{ij}(H) = a_{ji}(-H)$.

2. The principle of Hermitian tensor:
$a'_{ij}(H) = a'_{ji}(H)$ - for the real part of the tensor,
$a''_{ij}(H) = -a''_{ji}(H)$ - for the imaginary part of the tensor.

Because of these features the following magneto-optic effects are possible in the non-dissipative nonmagnetic crystals:

1. Magneto-optic change of optical birefringence (Kotton-Moutton):

$$\Delta a'_{ij} = F_{ijkl} H_k H_l. \tag{5}$$

2. Magneto-optic activity with the symmetry $\infty/m$ (Faraday), arises spontaneously in crystals with the magnetic ordering:

$$\Delta a''_{ij} = f_{ijk} H_k \equiv i e_{ijl} \varphi_{ij} H_k. \tag{6}$$

3. Irreversible addition to the phase velocity of light [15]:

$$\Delta a'_{ij} = \delta_{ijkl} H_k K_l. \tag{7}$$

4. Crossing effects of an optical activity of Faraday-type with the symmetry $\infty/m$ [16]:

$$\Delta a'_{ij} = i e_{ijk} (\delta_{lkm} H_k E_m + \eta_{lkmn} H_k E_m E_n). \tag{8}$$

5. Magnetogyration effect as an analog of the electrogyration effect with the symmetry of the axial tensor $\infty 2$ is possible [2] only in dissipative crystals or the crystals with magnetic ordering:

$$\Delta g_{ij} = \delta_{ijk} H_k. \tag{9}$$

### 1.3. Waves in gyrotropic crystals

In considering parametric optical effects in different directions of anisotropic crystals, the superposition of an ordinary (or frequency) and a spatial dispersion has to be taken into account. As a result, two waves with an orthogonal elliptic polarization propagate in the crystal. The ellipticity of the waves is [2]:

$$k = \frac{2 g_{33}}{(a_{22} - a_{11}) \pm \sqrt{(a_{22} - a_{11})^2 + 4 g_{33}^2 \overline{n}^2}},$$

where $a_{11}$, $a_{22}$, $g_{33}$ are the tensor components in the physically caused laboratory coordinate system.

The polarization state of a wave emerging off a plane-parallel plate under the condition of a linearly polarized incoming wave in one of the principal planes of the crystal is determined by the azimuth of the polarization ellipse [2,17]:

$$\tan 2\chi = \frac{2k(1+k^2)\sin\Gamma}{(1-k^2)^2+4k^2\cos\Gamma},$$

where $\Gamma = \frac{2\pi}{\lambda}\Delta n d$ is a phase retardation of interfering waves, d is the sample thickness, $\Delta n = n_2 - n_1$ is a linear birefringence.

In figure 1 the dependences of angle $\chi$ on $\Gamma$ under different values of $k$ are shown.

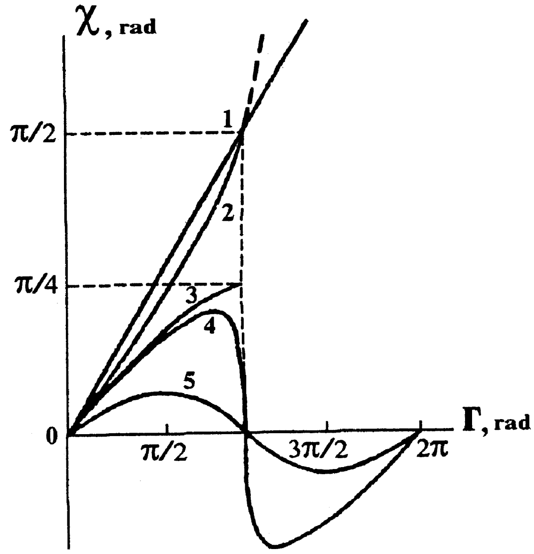


**Figure 1.** Dependences of polarization ellipse azimuth on phase differences at different parameters k [17]: 1 - k=1; 2 - k=0.6; 3 - k=0.414; 4 - k=0.4; 5 - k=0.2.

Parametric effects through the changes of $a_{ij}$ and $g_{ij}$ cause the changes of $\Gamma$ and $k$, and, hence, $\chi$ changes. Their separation is a rather complicated problem. Some results given below are a bright illustration of the current progress in the field of theoretical foundations and experimental possibilities of high-accurate polarimetry equipped with PC and lasers.

## 2. Parametric effects in proper ferroelectrics and ferroelastics

### 2.1. Electro- and piezooptics

Taking into account the facts that at phase transitions the parametric effects arise spontaneously and their character is described by the behaviour of the corresponding order parameters, it is convenient to rewrite formulas (1)-(3) in terms of polarization $P$ and mechanical stress $X$:

$$\Delta a_{ij} = r^*_{ijk}P_k + R^*_{ijkl}P_kP_l, \qquad \Delta a_{ij} = \pi_{ijkl}X_{kl}, \tag{10}$$

where $r^*_{ijk} = r_{ijk}/k_{ij}$, $R^*_{ijkl} = R_{ijkl}/k^2_{ij}$, $\pi_{ijkl} = \rho_{ijkl}/C_{klrs}$, $k_{ij}$ and $C_{klrs}$ are tensors of dielectric susceptibility and elasticity, respectively. Thus, temperature dependences of r and $\rho$ for the induced effects in the region of phase transitions are determined by k and C anomalies, i.e. these dependences are governed by the Curie-Weiss law and the law of "two". $R^*$, $r^*$ and $\pi$ coefficients at free strain and constant electric induction remain practically temperature independent. This is illustrated on the examples of KDP ($\bar{4}2m \to mm2$) and $Pb_3PO_4)_2$ ($\bar{3}m \to 2m$) crystals (figures 2, 3). That is why the behaviour of parametric effects reflects the character and the type of the transition as well as the influence of isotopic substitution $H \to D$.

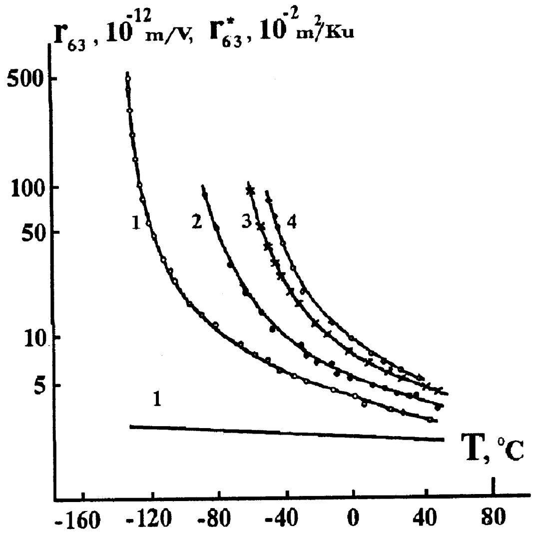


**Figure 2.** The temperature dependences of the electrooptic coefficients $r_{63}$ (1,2,3,4) and $r^*_{63}$ (1′) of $KH_{2(1-x)}D_{2x}PO_4$ crystals [18]. x: 1, 1′ - 0; 2 - 0.50; 3 - 0.82; 4 - 0.93.

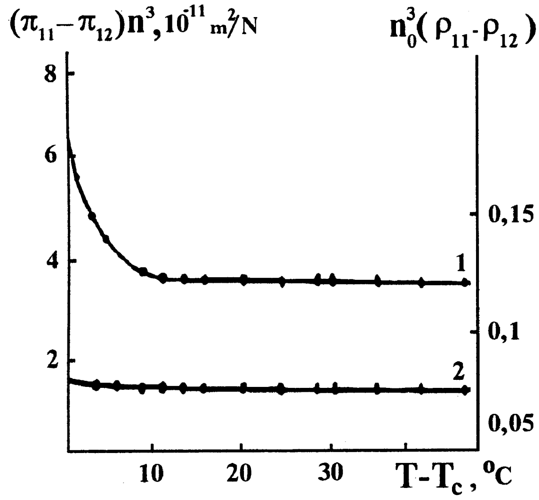


**Figure 3.** The temperature dependences of the elastooptic $\rho\prime$ (1) and piezooptic $\pi\prime$ (2) coefficients of $Pb_3(PO_4)_2$ ferroelastics [19]. $\rho\prime = n_0^3(\rho_{11}-\rho_{12})$, $\pi\prime = n_0^3(\pi_{11}-\pi_{12})$.

Spontaneous effects are determined by the symmetry of the initial paraelectric phase. For example, in a TGS crystal (transition $2/m \to 2$) (figure 4) and in $Pb_5Ge_3O_{11}$ ($\overline{6} \to 3$) (figure 5) the spontaneous electrooptic effect is quadratic, though in the latter the paraphase is acentric ($r^*_{ij3} = 0$).

The spontaneous piezooptic effect is illustrated (figure 6) on the example of $K_2Cd_2(SO_4)_3$ crystals (transition $23 \to 222$), where the first-order phase transition is accompanied by a hysteresis of refractive indices. The behaviour of the refractive indices in the ferroelastic phase is similar to the behaviour of the spontaneous stress (strain). With repeating transitions, a mutual replacement of crystallographic axes can take place in the ferroelastic phase, since the spontaneous stress can occur along any of the principal directions with equal probability. Thus, the refractive index change is described by either $\pi_{12}$ or $-\pi_{13}$ component.

## 2.2. Electrogyration

In analogy with electrooptic effects, relation (2) can be written in the form:

$$\Delta g_{ij} = \gamma^*_{ijk} P_k + \beta^*_{ijkl} P_k P_l, \quad \text{where} \quad \gamma^*_{ijk} = \gamma_{ijk}/k_{ij}, \quad \beta^*_{ijkl} = \beta_{ijkl}/k^2_{ij}.$$

The description of electrogyration under ferroelectric phase transitions is also given on the basis of the paraphase symmetry. The consideration concerns only the crystals having optical activity in the ferroelectric phase (pyroelectric classes 1, 2, 3, 4, 6, m, mm2) and the crystals having the so-called "weak optical activity" with the symmetry $\infty$ mm (planar classes 3m, 4mm, 6mm).

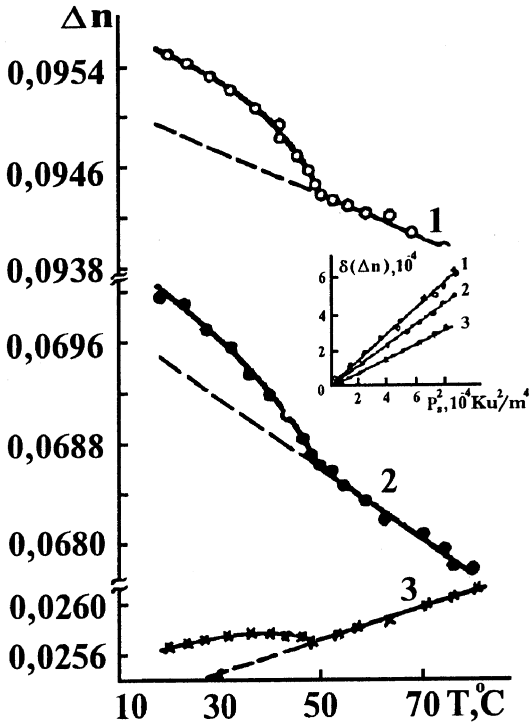


**Figure 4.** Dependences of the birefringence of TGS crystals on temperature for $\lambda$=550 nm [20]: 1 - $n_x - n_y$, 2 - $n_z - n_y$, 3 - $n_x - n_z$. On the insert: dependences of the spontaneous birefringence of TGS crystals on the square meaning of spontaneous polarization: 1,2,3 - in the z, x and y axes directions, respectively.

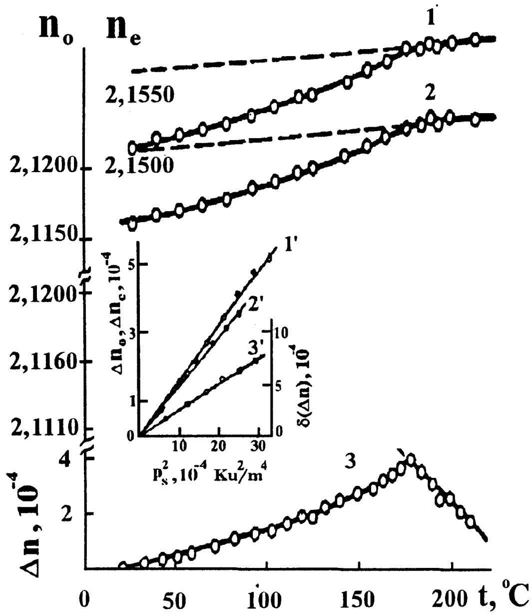


**Figure 5.** The temperature dependences of the main refraction indices (1 - $n_e$, 2 - $n_0$) and birefringence (3) in the $Pb_5Ge_3O_{11}$ ferroics [21]. On the insert – the dependences of the increasing refraction indices $\Delta n_e$ ($1\prime$), $\Delta n_0$ ($2\prime$) and birefringence ($3\prime$) on the square meaning of the spontaneous polarization.

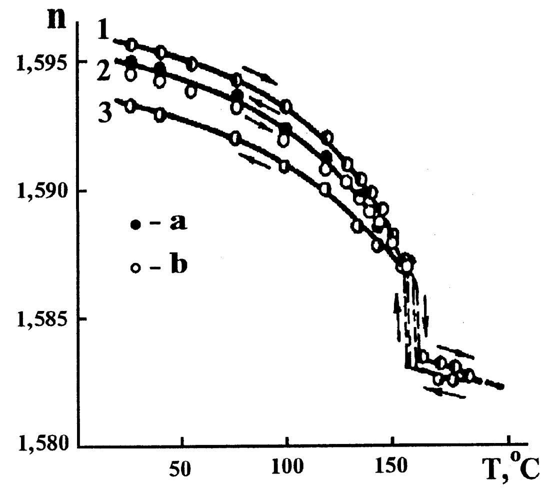


**Figure 6.** Refraction indices temperature dependences in $K_2Cd_2(SO_4)_3$ crystals for $\lambda$=546 nm [22]. 1 - $n_z$, 2 - $n_y$, 3 - $n_x$; a and b correspond to the interchanging $n_z$ and $n_y$ indices.

From this standpoint all crystals are divided into two groups [2,23]:

1. Gyroelectrics: these are ferroelectrics with a centrosymmetric paraelectric phase (they are optically inactive) and the crystals of inversion classes $\overline{6}$, $\overline{4}$, where $g_{33} = 0$, but $\gamma_{33} \neq 0$. Only linear spontaneous electrogyration can occur in these crystals, the opposite domains are enantiomorphous, the repolarization is accompanied by the electrogyration hysteresis. The temperature dependence of spontaneous electrogyration is similar to the behaviour of $P_s$:

$$G_S \sim P_S \sim (T_c - T)^{1/2}.$$

The coefficient of linearly induced electrogyration obeys the Curie-Weiss law, $\gamma \sim (T_c - T)^{-1}$, and the law of "two".

2. Hypergyroelectrics: these are acentric crystals (they are optically active) in the paraelectric phase. The transitions are possible from 222, 32, 422, 622, 432, 23, $\overline{4}$2m classes to 2, 3, 4, 6, mm2 classes. Spontaneous electrogyration is quadratic:

$$G_s \sim P_s^2 \sim (T_c - T).$$

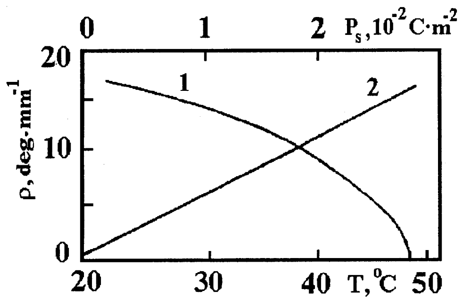


**Figure 7.** Dependence of the light polarization plane specific rotation in TGS crystals on temperature (1) and spontaneous polarization (2) [24].

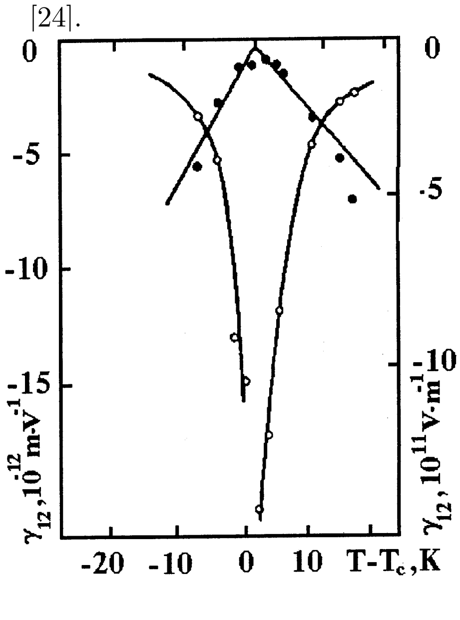


**Figure 8.** The dependences of induced electrogyration coefficient $\gamma_{12}(o)$ and its reciprocal $\gamma_{12}^{-1}(\bullet)$ value $(T - T_c)$ for (100) direction of TGS [25].

The opposite domains are non-enantiomorphous; the optical activity does not change under repolarization. The induced electrogyration is linear, $\gamma \sim (T_c - T)^{1/2}$ in the ferroelectric phase and quadratic in the paraelectric phase.

The properties inherent to gyroelectrics were first revealed [24] in TGS $NH_3(CH_2COOH)_3H_2SO_4$ crystals (transition $2/m \to 2$). Figures 7, 8, 9 confirm the conclusions of item 1.

Lead germanate crystals $Pb_5Ge_3O_{11}$ (transition $\overline{6} \to 3$) and solid solutions on their basis give an excellent example of gyroelectrics. At arising spontaneous polarization and an external field application along z-axis the electrogyration effect is not accompanied by the electrooptic effect. Spontaneous electrogyration (figure 10) has a linear character:

$$\rho = \frac{\pi}{\lambda n_0}\gamma_{33}^* P_s \sim (T_c - T)^{1/2}.$$

The repolarization is followed by an electrogyration loop (figure 11) that, unlike a quadratic electrooptic loop, is linear. The induced electrogyration (figure 12) is described as follows:

$$\frac{\Delta\rho}{E} \sim \frac{1}{4}(T_c - T)^{-1} \quad \text{at} \quad T < T_c,$$
$$\frac{\Delta\rho}{E} \sim \frac{1}{2}(T_c - T)^{-1} \quad \text{at} \quad T > T_c.$$

The properties of hypergyroelectrics can be featured on the example of the Rochelle salt (RS) $(NaKC_4H_4O_64H_2O)$ (transition $222 \to 2$) or $Ca_2Sr(C_2H_5CO_2)_6$ (transition $422 \to 4$) crystals. As it is shown in figure 13, the phase transition in the

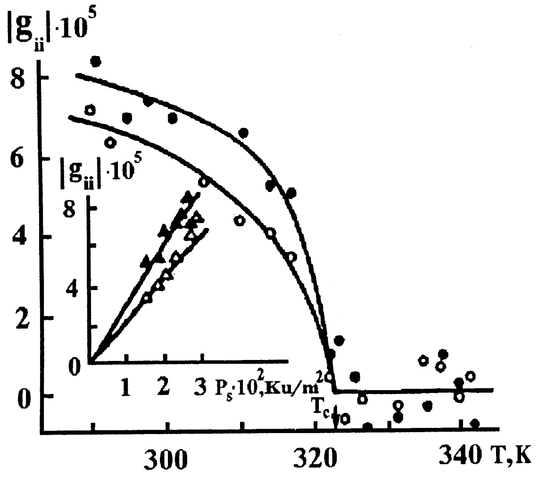


**Figure 9.** The temperature dependences of gyration component $g_{11}(o)$ and $g_{33}(\bullet)$ moduli of a single TGS. Insert - $g_{11}$ vs $P_s(\Delta)$ and $g_{33}$ vs $P_s(\triangle)$ relations in FE phase [26].

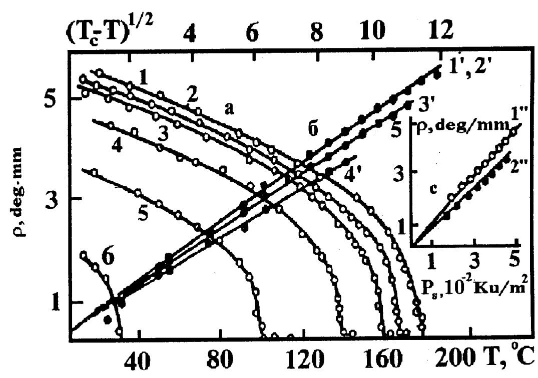


**Figure 10.** Dependences of the polarization plane specific rotation on temperature (a), on $(T_c - T)^{1/2}$ value (b) and on spontaneous polarization (c) in crystals $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ [9,10,27]. x: 1 - 0; 2, 1' - 0,03; 3, 2' - 0,05; 4, 3', 1" - 0,10; 5, 4', 2" - 0,20; 6 - 0,40.

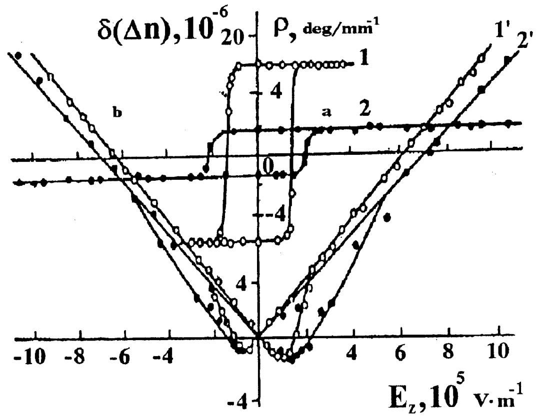


**Figure 11.** Hystereses of optocal activity (a) and birefringence increase (b) at $T = 20^0$C in crystals $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ [10,25]. x: 1, 1' - 0; 2, 2' - 0,40.

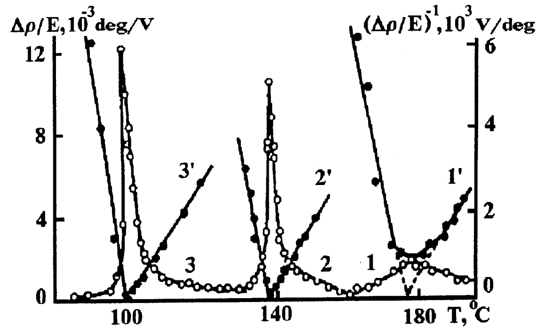


**Figure 12.** Temperature dependences of the induced electrogyration $\Delta\rho/E$ and value $(\Delta\rho/E)^{-1}$ in crystals $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ [10,25]. x: 1, 1' - 0; 2, 2 ' - 0,10; 3, 3' - 0,20.

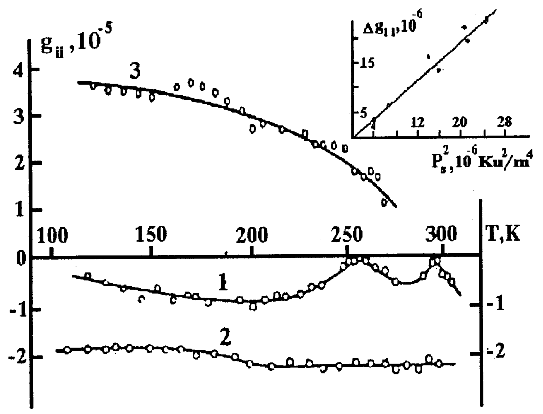


**Figure 13.** Temperature dependences of gyration $g_{ij}$ tensor components in RS crystals. $\lambda$=633 nm, 1 - $g_{11}$, 2 - $g_{22}$, 3 - $g_{33}$. On the insert - the dependence of increasing $\Delta g_{11}$ on the square meaning of spontaneous polarization $P_s^2$ [28,21,3,4].

RS crystal is accompanied by kinks in the $g_{11}$-component temperature dependence, in this case:

$$\Delta g_{11} = \beta^{*}_{11} P_x^2.$$

The induced effect is quadratic in the paraelectric phase and linear in the ferroelectric phase (figure 14). Besides, rotation of the gyration surface is proportional to $P_s$. Electrogyration properties under isotopic substitution $H \to D$ change essentially; this is completely consistent with a pseudoproper character of the ferroelectric transition (figure 15).

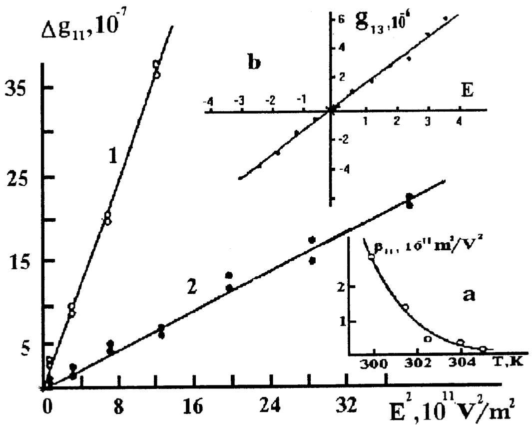


**Figure 14.** The dependence of the increasing $\Delta g_{11}$ of RS crystals on the square meaning of electric field strength $E^2$ in prototype phases [28]. 1 – $T$=300 K, 2 – $T$=250 K. On the inserts: a – the temperature dependences of square electrogyration effect coefficient $\beta_{11}$ in a prototype phase, $\lambda$=633 nm; b – the dependence of gyration component $g_{13}$ on electric field $E_2$ in a ferroelectric phase. $T$=305 K, $\lambda$=633 nm.

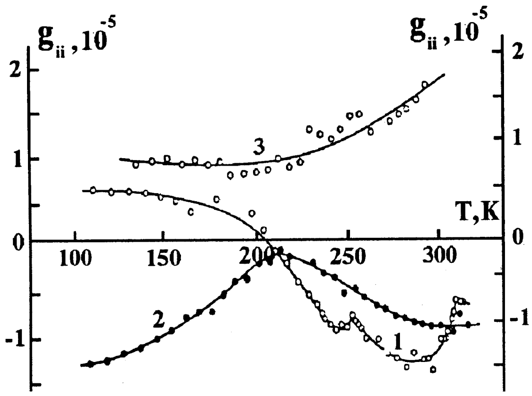


**Figure 15.** Temperature dependences of gyration $g_{ij}$ tensor components in DRS crystals [23]. $\lambda$=633 nm, 1 - $g_{11}$, 2 - $g_{22}$, 3 - $g_{33}$.

## 2.3. Piezogyration

Piezogyration properties as well as piezooptical ones are of interest as to phase transitions first of all for ferroelastic crystals. In this case expression (4) is written in the following form:

$$\Delta g_{ij} = \tau_{ijkl} X_{kl}, \tau_{ijkl} = \xi_{ijrs}/C_{klrs}.$$

Spontaneous piezogyration has the features of spontaneous quadratic electrogyration: the initial paraelectric phase has to be acentrical; these crystals are hypergyroelastics [30]. However, under deformation in crystals belonging to nonactive inverse classes and planar classes with weak activity, the rise of optical activity is possible; the above classes are gyroelastic ones. The following ferroelastic transitions correspond to such classes: $\overline{4}3m \to \overline{4}2m$, $\overline{4}3m \to 222$, $4mm \to mm2$, $4mm \to 2$, $6mm \to mm2$, $\overline{4}3m \to 3m$. The latter transition is accompanied by the rise of weak optical activity (piezogyration) with the symmetry $\infty$mm. Under other transitions, an enantiomorphous domain structure develops and switching is followed by a complicated hysteresis.

An example of the hypergyroelectrics is $K_2Cd_2(SO_4)_3$ crystals (transition $23 \to 222$) and $SiO_2$ (quartz) crystals (transition $622 \to 32$) [31]. Figure 16 presents some of the above reported conclusions if a wide interval of the incommensurate phase in quartz is ignored.

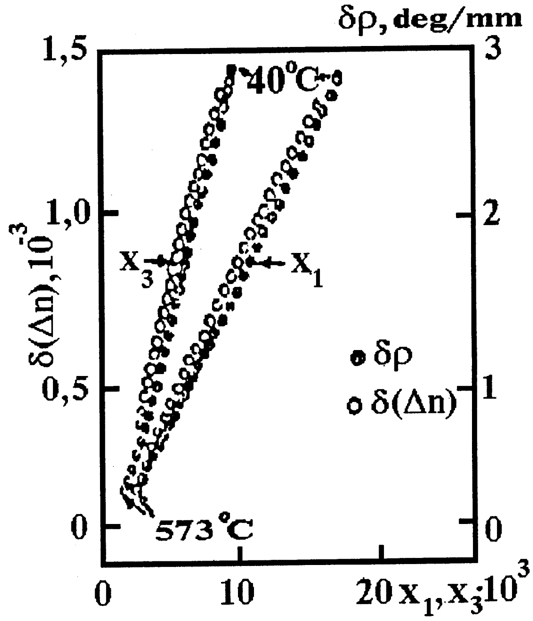


**Figure 16.** The dependence of the optical activity increase $\delta\rho$ and birefringence $\delta(\Delta n)$ on spontaneous deformations $X_1$, $X_3$ in quarz crystals [31].

In ferroelectrics-ferroelastics of axial classes the invariant relations exist between the coefficients describing electro-, piezooptics and electro-, piezogyration effects in a paraphase and under spontaneous effects [32]: $\gamma_{ijk}/r_{ijk} = \xi_{ijkl}/\rho_{ijkl}$ under the condition that $a_{ij}$, $g_{ij}$, $\chi_m$, $E_k$ are transformed by the same irreducible representation.

## 2.4. Magneto-optics

The analysis of magneto-optic effects under ferroelectric phase transitions is made on the example of $Pb_5Ge_3O_{11}$ crystals (figure 17).

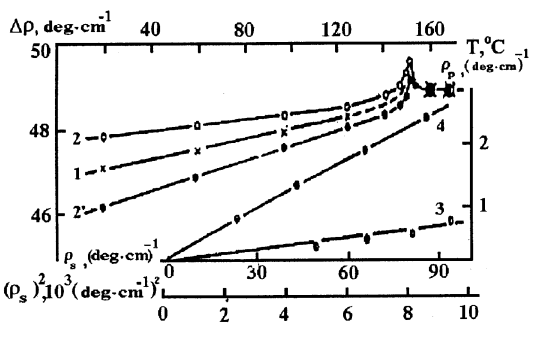


**Figure 17.** Temperature dependences of total magnetooptical activity in the polydomain (1) and monodomain states (2, 2′ - according to the opposite signs of spontaneous polarization, excluding spontaneous electrogyration) of $Pb_5Ge_3O_{11}$:$Nd^{3+}$ crystals and their approximation (3, 4 – linear and square effects regarding to $P_s$, respectively) across spontaneous electrogyration $\rho_s \sim P_s$ [9]. $H$=13.3kE, $\lambda$=514.5nm.

As it is seen from the figures (multidomain $Pb_5Ge_3O_{11}$ samples), a parabolic dependence of the magneto-optic rotation power is observed on the background of the Faraday effect. This dependence is explained by the second term in formula (8), i.e. the term corresponding to quadratic in $P$ magnetopolarization activity. However, in single domain samples, a sign of optical activity changes under repolarization, i.e., it is bilinear with respect to $P$ and $H$. The observed effect cannot be treated as a spontaneous magneto-polarization activity (the first term in (8)), since in the initial phase $\delta_{333} = 0$. Moreover, the induced effect proportional to EH is absent in the paraelectric phase; it arises only in the ferroelectric phase, where $\delta_{333} \neq 0$. Hence, it is possible to assume [34] that in single domain crystals $Pb_5Ge_3O_{11}$ there exist two effects: a Faraday-type magneto-polarization activity induced by electric and magnetic fields and a magneto-gyration effect under the condition of dissipation and accompanied by a spontaneous polarization: $\Delta g_{ij} = \gamma_{ijkl} P_k H_l$ - in the paraphase $\delta_{3333} \neq 0$.

# 3. Pseudoproper ferroelectrics and crystals with the incommensurate structure

## 3.1. Electrogyration as a tool to study pseudoproper ferroelectrics

Let now proceed to clarify this thesis on the example of quadratic electrogyration in the KDP-type crystals. It is common knowledge that the phase transition in these crystals is induced by the proton ordering on hydrogen bonds. While such an ordering is not an immediate cause of the spontaneous polarization it, nevertheless, is defined as the order parameter being of the same transformation properties as $P_s$.

The pseudoproper features of these crystals are apparent from the behaviour of the tensor component $g_{11}$ under the phase transition (figure 18) and $\beta_{13}$ coefficient of quadratic electrogyration in the paraphase (figure 19).

In particular, the temperature anomalies of $\beta_{13}$ coefficient in KDP, DKDP and CDA crystals are accompained by a change of the sign; they seem not to be referred to the anomalies of $k_{33}$. Coefficient $\beta^*_{13} = \beta_{13}/k^2_{33}$ depends on the temperature as well. The explanation of the above peculiarities has come about via introducing the following terms, besides polarization $P_s$, in the expression for the thermodynamical potential: $\theta_3$ is the order parameter; $X_i$ is mechanical stress; $T_\theta$ is the transition temperature of the proton system under the condition that it does not interact with the lattice.

Then one has [35]:

$$
\begin{aligned}
A \;=\; & A_0 + \frac{1}{2}\beta(T-T_0)\theta_3^2 + \frac{1}{2}\gamma\theta_4^4 + \frac{1}{6}\delta\theta_3^6 + \frac{1}{2}\omega P_3^2 - \\
& -\frac{1}{2}S_{ij}X_iX_j - \frac{1}{2}b_{3i}X_iP_3 - Q_{3i}X_iP_3^2 - \frac{1}{2}h_{3i}X_i\theta_3 - \\
& -R_{3i}X_i\theta_3^2 - W_{3i}X_iP_3\theta_3 + fP_3q_3.
\end{aligned}
$$

From where

$$\Delta g_{11} = \beta_{13}^{*Q} P_3^2 + \beta_{13}^{*R} \theta_3^2 + \beta^{*W} 13 P_3 \theta_3 \cong (\beta_{13}^{*Q} \chi_P^2 + \beta_{13}^{*R} \chi_\theta^2 + \beta_{13}^{*W} \chi_P \chi_\theta) E_3^2 \qquad (11)$$

hence,

$$\beta_{13}^* = \beta_{13}^{*Q} - \beta_{13}^{*W} (-f/\beta)(T - T_0')(T - T_\theta)^{-2},$$

where

$$T_0' = T_\theta - (\beta_{13}^{*R}/\beta_{13}^{*W})(-f/\beta).$$

The approximation of temperature dependence of $\beta_{13}^*$ coefficient by this formula agrees well with the experimental data (figure 19) for KDP, DKDP and CDA crystals. The pseudoproper character of the ferroelectric transition is conditioned by the coupling strength between the order parameter and the spontaneous polarization $P$. The value of $\Delta T = T_c - T_\theta = f^2/\beta\omega$ approximately equals $\Delta T$-value derived from the proton-lattice interaction, where $\Delta T = F^2/k\Omega^2$ (F is the interaction constant, $k$ is the Boltzmann constant, $\Omega_0$ is the frequency of the proton-lattice interaction). The substitution ($H \to D$) results in a strong shift of $T_c$ and $T_\theta$, but does not affect the $\Delta T$=55 K value, i.e. the strength of the proton-lattice interaction. This interaction is essentially dependent on the anion substitution of $PO_4^{3-}$ by $AsO_4^{3-}$. Then $\Delta T$=65 K. The substitution of cations $K^+$ by $Rb^+$ brings about such a pronounced increase of the proton-lattice strength that the electrogyration effect in KDP crystals does not differ from the respective properties of proper ferroelectrics.

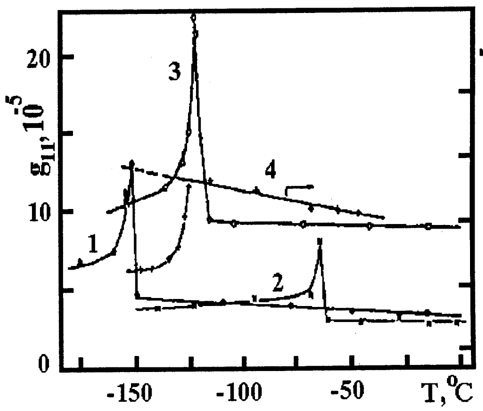


**Figure 18.** Temperature dependences of the gyration $g_{11}$ tensor component in crystals KDP (1), DKDP (2), CDA (3) and RDP (4) [2, 36].

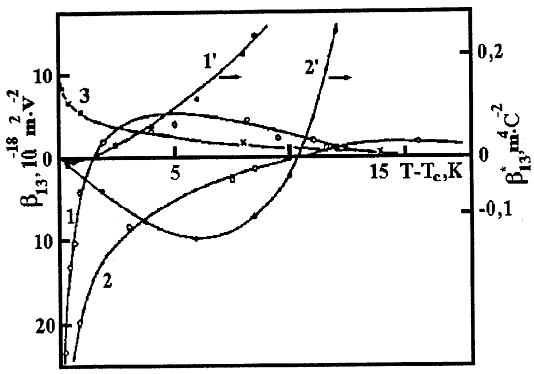


**Figure 19.** Temperature dependences of the quadratic electrogyration coefficient $\beta_{13}$ (1, 2, 3) and $\beta_{13}^*$ (1', 2') of crystals DKDP (1, 1'), CDA (2, 2') and RDP (3) [2, 36].

### 3.2. Parametric optical effects in crystals with the incommensurate structure

The effects of parametric crystal optics are especially sensitive to the incommensurate structures. In particular, the character of the optical birefringence changes clearly demonstrates the global hysteresis and its jump-like behaviour along with the particular "parallelogram" - type cycles, non-smooth relaxation processes (the kinetics), thermo-optical memory, etc. [37]. These effects are explained (without consideration of the zone-model) by adding the gradient terms, a two-component gradient Lifshitz invariant among others, to the thermodynamic potential. The invariant is as follows [38]:

$$\xi\frac{\partial\eta}{\partial x}-\eta\frac{\partial\xi}{\partial x},$$

where $\eta=\rho\sin\varphi$ , $\xi=\rho\cos\varphi$ , $\rho$ and $\varphi$ are an amplitude and a phase of the order parameter, respectively. Changing $T_i$ to $T_c$ requires transition from the plane-wave model to the model of phase solitons and the model of commensurate and incommensurate phase coexistence.

On this basis and taking into account the fact that the linear effects caused by spontaneous polarization and spontaneous deformation are absent in the modulated incommensurate phase, the temperature changes of the birefringence are described by the relationship [39, 40]: $\delta(\Delta n)\cong\alpha\rho^2+\nu\rho^2 d\varphi/dz$ - ($\alpha$, $\nu$ - constants) or in the plane-wave model $\delta(\Delta n)\cong\alpha\rho^2\cong(T_i-T)^{2\beta}\cong I$, with a critical index $\beta$ and intensity of the incommensurate X-ray reflex $I$.

However, the above approach is not aimed to explain the nontrivial effects in the incommensurate phase. An essential role is played by the interaction of the defects (impurities) and phase solitons. This interaction depends on the ratio between the mobilities of the defects $V_d$ and solitons $V_s$ [41, 42]. So, the three boundary cases can arise:

1. $V_s\gg V_d$ – the attachement (pinning) of the incommensurate structure to the defects (impurities);

2. $V_s\ll V_d$ – the attachement (pinning) of the defects (impurities) to the incommensurate structures coupled with the creation of a "soliton density wave".

3. $V_s\cong V_d$ – a "viscous" interaction of the incommensurate structure with the defects (impurities).

Let us illustrate the conditions for these three cases realization on the example of the optical birefringence study in the $A_2BX_4$ group crystals containing both incommensurate ferroelectrics (phase transition $mmm\to 2mm$) and ferroelastics ($mmm\to 2/m$).

1. An example of the global hysteresis in the $[N(CH_3)_4]_2ZnCl_4$ crystal, the "paralelogram"-type cycle in the $K_2ZnCl_4{:}Co^{2+}$ crystal and the optical birefringence relaxation in $[N(CH_3)_4]_2FeCl_4$ are presented in figures 20, 21.

These effects manifest themselves under the condition of $V_s\gg V_d$, i.e., the condition of the incommensurate structure pinning on the defects or the constant soliton density at the transition between different temperature regimes.

During the relaxation process because of the soliton nucleation, the crystal passes through some intermediate metastable states that differ in the soliton density. The states are separated by a free-energy barrier. The gently sloping parts of the birefringence kinetics dependence are related to the fixed soliton density.

As to the peaks, they are coupled with the transitions from one soliton density to another (a sharp change takes place in the orderparameter phase, the wave vector $k$).

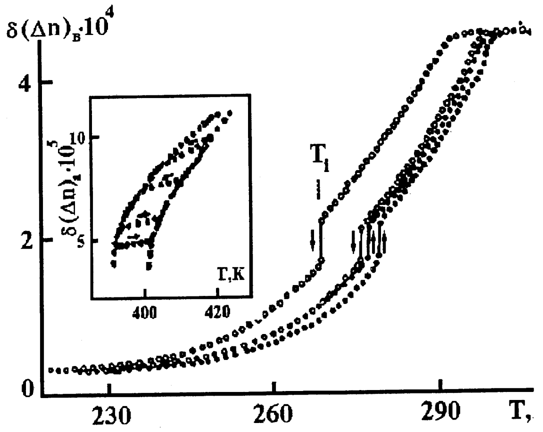

**Figure 20.** Temperature dependences of the birefringence $\delta(\Delta n)_b$ in $[N(CH_3)_4]_2ZnCl_4$:1(•) - d$T$/d$t$=1.1 K/h; 2(o) - 0.11 K/h. Insert - partial cycles of thermal hysteresis of the birefringence $\delta(\Delta n)_a$ in $K_2ZnCl_4:Co^{2+}$ [37].

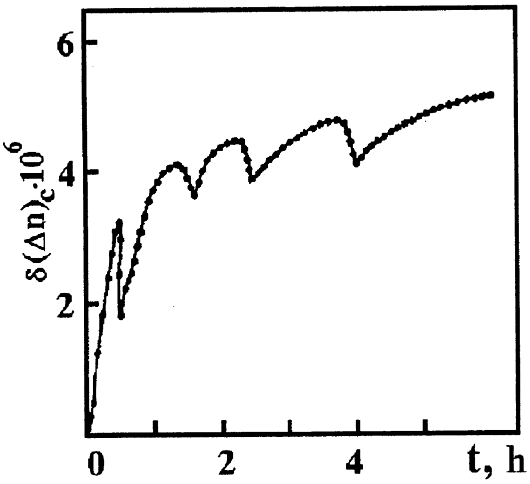

**Figure 21.** Temperature dependence $\delta(\Delta n)_c$ of $[N(CH_3)_4]_2FeCl_4$ crystals. The velocity of approaching to $T_{st}$=270,36 K in the regime of heating is d$T$/d$t$=5,7 K/h [37].

2. The case of $V_s \ll V_d$ is depicted in figure 22. It is realized in the thermooptic memory effect. The effect consists in ordering the defects in the modulated structure field at the stabilized temperature. Retracing this temperature point along the same branch without going into the paraelectric phase is followed by the appearance of an anomaly. The anomaly on the global hysteresis is shifted by the hysteresis width along the temperature scale. The anomaly is also observed at the temperature at which the modulation period is doubled.

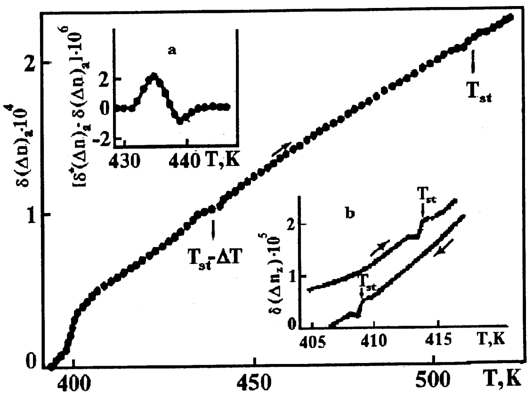

**Figure 22.** Temperature dependence of the birefringence $\delta(\Delta n)_a$ in $K_2ZnCl_4$ crystals kept for $t$=26h at $T_{st}$=510,5 K [37,43]. Inserts: a - the anomaly form at $T_{st}-\Delta T$; b - the anomaly shift on global hysteresis branches.

The temperature and temporal changes of the optical birefringence in the incommensurate phase depend on amplitude $\rho$ and phase $\varphi$ of the order parameter. The smooth dependence governed by $\rho$ is superimposed on the anomaly part coupled with the $\varphi$ behaviour.

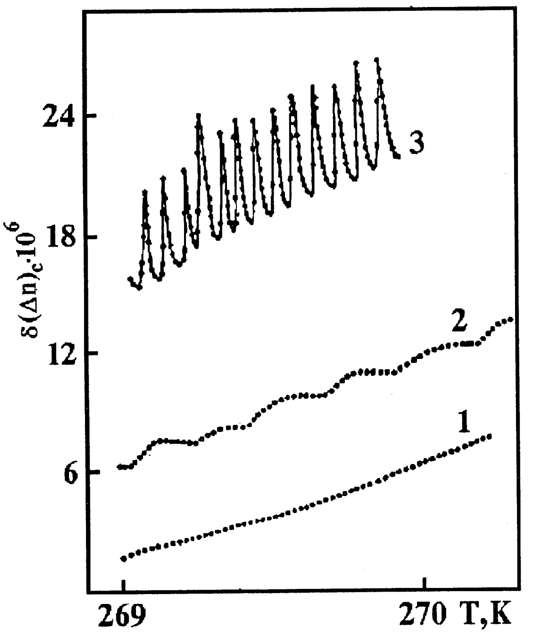


**Figure 23.** Temperature dependence of $\delta(\Delta n)_c$ for $[N(CH_3)_4]_2FeCl_4$ crystals at the temperature variation rate $dT/dt$=1500 mK/h (2); 60 mK/h (3) [37].

3. The case of $V_s \cong V_d$ "viscous" interaction. The velocity of the solitons (or DC) movement is of the same order as the velocity of the defects (impurities) diffusion. Then, the temperature curve of the birefringence under the condition of decreasing velocity of the temperature variation in the course of experiment is greater, if followed by the appearance of the steps (tooths) (figure 23). The rate of new DC nucleation and their mobility decrease because of the increase of the friction force. The difference of $\delta(\Delta n)$ values at two neighbouring minimum points is a characteristic of the increase in the order parameter amplitude $\rho$ between the two metastable states for k-localization.

Enhancing the effects can be achieved with X-ray irradiation or the influence of hydrostatic pressure, the application of an external electric field, mechanical stress or their gradients. At the same time the above factors can be accompanied by vanishing the peaks (phase factor) and appearing the steps on the $\delta(\Delta n)$ temperature dependences. The steps correspond to the high-order commensurations between which smooth transitions take place.

## 4. Summary

From the brief review of the effects of parametric crystallooptics in the phenomenological approach which is based on the investigations conducted by the author and his fellow-workers it may seem that the main problem is solved. However, it is not so, and not all the possible effects based on the phenomenological approach have been determined. This, first of all, concerns magnetic crystals and cross and gradient effects. The microscopic theory of these effects has been insufficiently worked out, especially their determination on the structural level. The exclusions are papers [44-47], which are devoted to ferroics with the hydrogenium (deuterium) bond, particularly the KDP group crystals and electrogyration in the $PbMoO_4$ and $Pb_5Ge_3O_{11}$ type crystals [48-50].

From this approach the prognosis in searching for highly effective crystals, practically useful in various elements of quantum and optoelectronics is left open. Besides, on the examples of crystals with a non-corresponding structure the physical reality in parametric crystallooptics is broader than it appears on the basis of the symmetrical aspects and phenomenological approach. In this respect a thorough research in this field is far from being completed.

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## Параметрична кристалооптика немагнітних фероїків

О.Г.Влох

Інститут фізичної оптики,
290005 м. Львів-5, вул. Драгоманова, 23

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Виходячи з симетрійних принципів кристалофізики і термодинаміки, проведено аналіз параметричних оптичних явищ, індукованих зовнішніми полями різного типу, структурними фазовими переходами в сегнетоелектриках і сегнетоеластиках. Особлива увага звертається на явища просторової дисперсії (електро- і п'єзогірація). Феноменологічний підхід до опису цих явищ ілюструється найбільш виразними експериментальними результатами, одержаними для кристалів: $KH_{2(1-x)}D_{2x}PO_4$ (KDP, DKDP), $K_2H_2AsO_4$ (CDA), $RbH_2PO_4$ (RDP), $Pb_5(Ge_{(1-x)}Si_x)_3O_{11}$, $Pb_3(PO_4)_2$, $K_2Cd_2(SO_4)_3$, а також для $(NH_3CH_2COOH)_3H_2SO_4$ (TGS), $NaKC_4H_4O_6 4H_2O$ (RS). Окремо розглядаються нові ефекти в кристалах групи $A_2BX_4$ з неспівмірно модульованою структурою, зокрема у кристалах $[N(CH_3)_4]_2ZnCl_4$, $[N(CH_3)_4]_2FeCl_4$, $K_2ZnCl_4$, $K_2ZnCl_4$ $Co^{2+}$.

**Ключові слова:** *кристалооптика, сегнетоелектрики, оптична активність, фероїки, фазові переходи*

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