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ELECTROGYRATION PROPERTIES OF CRYSTALS

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The article contains a brief review of works devoted to investigation of the electrogyration phenomenon in crystals, the essence of which consists in the optical activity variation or appearance under the action of an electric field. The symmetry aspects of electrogyration, its relations with accompanying electro-optical effect and thermodynamical phenomenology of electrogyration in ferroelectrics are considered. The experimental section of the review contains the data including the first experiments on electrogyration detection in dielectrics and the latest works dealing with the pseudoproper ferroelectrics. Electrogyration of certain groups of crystals is discussed in connection with their individual physical properties.

1. INTRODUCTION

In the development of Solid State Physics one can scarcely find another problem historically so complicated as that of the optical activity of crystals. As a phenomenon of spatial dispersion[1-3] it has been drawing attention of scientists and evoking disagreements among them ever since it was first observed in quartz crystals by the French scientist D. Arago as far back in 1811. It is only natural therefore that electrogyration, with its essence consisting in the appearance or variation of optical activity under the action of an external electric field, has ultimately emerged as a new physical phenomenon in the course of numerous complicated research works with their successes and failures. This may be explained by the fact that electrogyration being an effect of a higher-order smallness is often accompanied by the electro-optical effect considerably surpassing it and by light ellipticity. Therefore and because of photorefraction, electrooptical effect or errors in the geometry of experiments the polarization plane rotation was mistaken for electrogyration. A detailed analysis of the scientific and history aspects of this problem as well as the results obtained till 1983 may be found in the monograph.[4] Here we shall dwell only upon the most important points of the research history of ferroelectric crystals optical activity and of electrogyration.

The optical activity of ferroelectrics evoked an increasing interest of researchers after H. Futama and R. Pepinsky (1962)[5] found that the light polarization plane rotation changes its sign at repolarization of non-enantimorphic $LiH_3(SeO_3)_2$ crystals (point group symmetry m) by means of an electric field. The phenomenon observed was explained then by a specific domain structure. Since the symmetry plane having a spontaneous polarization vector is normal to the plane of the optical axes, the neighbouring domain axes are parallel and characterized by the opposite sign of optical activity. Therefore crystal repolarization leads to mutual replacement of the axes, i.e. to the change of optical activity sign. The problem of electrogyration did not arise at that time.

Proceeding from the relationships of tensor crystallooptics, I. Zheludev predicted (1964)[6] emergence or variation of a crystal optical activity proportional to the external electric field applied. Subsequently approximately at the same time, K. Aizu[7] developed this idea of electrogyration in proper ferroelectrics, while L. Shuvalov and N. Ivanov[8] following a symmetry approach discussed the problem of the optical activity sign change at ferroelectric switching.

The first searches for electrogyration in a number of laboratories, however, failed to yield any positive results. Thus, P. Lenzo *et al.*[9–11] mistook the photorefraction effect of $Bi_{12}SiO_{20}$ crystals, put into an electric field, for electrogyration. In the geometry of their experiments electrogyration is impossible in principle. In his paper[12] Yu. Shaldin reported on a linear electrogyration detection in centrosymmetric $CrMoO_4$ crystals, however, he made a mistake: the electrooptic effect was evidently mistaken for electrogyration. Later on (1983)[13] the author admitted his mistake and found electrogyration in the same crystals to be smaller than the previous one by two orders.

The author of these lines obtained the first reliable results pertaining to the detection first of a quadratic electrogyration in quartz crystals (1969),[14,15] and then of linear electrogyration in α-HJO_3 (1971),[16] $LiJO_3$ (1974)[17] crystals. The results concerning the linear electrogyration in quartz crystals[18] were subjected to revision and later were explained theoretically.[19] The detection of a large linear electrogyration in centrosymmetric $PbMoO_4$ crystals (1975)[20] proved to be principal and unambiguous. Our results on the quadratic electrogyration in quartz crystals were soon confirmed by V. Shamburov and N. Romanova (1976)[21] and those on the linear electrogyration in $PbMoO_4$ by M. Kostov *et al.* (1979).[22] Subsequent research works on electrogyration in linear dielectrics quickly grew in number and special mention should be made here of the papers by H. Weber and S. Haussühl (1974–1983).[23–25].

As for the detection of optical activity at the ferroelectric phase transition, it should be noted that the priority in experiments is due to the two groups of authors. One of them is K. Hermelbracht and H. Unruh (1970)[26] who detected it in TGS crystals. The other is O. Vlokh *et al.* who obtained the similar results in the same crystals simultaneously[27,28] and by analogy with the spontaneous electro-optical effect the term "spontaneous electrogyration" was suggested[27] as well as its description by a third-rank axial tensor of the initial paraelectric phase.

Important landmarks in investigating the optical activity in ferroelectric crystals were the detections of optical activity at phase transition in $NaNO_2$ (M.-J. Chern and R. Phillips, 1972),[29] $Pb_5Ge_3O_{11}$ (H. Iwasaki *et al.*, 1971)[30,31] crystals, and especially the detection of the abnormally large induced electrogyration in $Pb_5Ge_3O_{11}$ crystals and in solid solutions on their base (O. Vlokh *et al.*, 1977).[32,33] The latter were confirmed by C. Konak, J. Fousek and H. Kürsten (1978).[33] In hope to detect a large electrogyration in the Curie point region the author of these lines proceeded from the fact[17] that in case of a free crystal deformation it should be determined by a substantial contribution of piezogyration caused by piezoelectric deformation, i.e. it should possess anomalies characteristic of piezoelectric coefficient anomalies.

Thus, electrogyration has come to be extensively used as a method for investigation of ferroelectric phase transitions. Here one should mention the pioneer investigations conducted by J. Kobayashi and G. Uesu (1979)[34,35] in which the method of quadratic electrogyration was used to investigate pseudo-proper (improper, in their term) phase transition in KDP crystals. Their results were confirmed and further developed by O. Vlokh *et al.* (1985).[36,37]

The results thus accumulated have given rise to creation of a microscopic theory of electrogyration based on the lattice dynamics. I. Stasyuk and S. Kotsur (1982)[38,39] applied the method of bitemporal temperature Green's function and obtained general expressions of the electrogyration tensor components in dielectric crystals of an ion type. This kind of approach, of course, enables researchers to surpass the limits of phenomenology,[19] thermodynamics[7] or oscillatory models[40] and reveal the nature of this phenomenon in certain cyrstals.

2. DESCRIPTION OF ELECTROGYRATION, SYMMETRY ASPECTS

According to the classification accepted in the non-linear optics, electrogyration may be referred to the parametric crystal-optics. But in contrast to the well-known phenomena of electro-, magneto- and piezo-optics, electrogyration is considered as a non-linear effect of the first-order space dispersion, and its description follows from the material equation including the dependence of induction D not only on the field, but also on the E field gradient of the light wave[1]

$$D_i = \varepsilon_{ij} E_j + \eta_{ijk} \frac{\partial E_j}{\partial x_k},$$

where ε_{ij} and η_{ijk} are a dielectric permitivity tensor and an antisymmetrical polar tensor, respectively. Taking into account the duality relationship the reverse relation can be written as

$$E_i = a_{ij} D_j = (a_{ij}^0 + i e_{ijk} g_{kl} k_l) D_j,$$

where a_{ij} and a_{ij}^0 are tensors of the optical polarization constants with or without spatial dispersion, respectively, e_{ijk} is a third-rank antisymmetrical unit tensor, g_{kl} is a gyration axial tensor, k_l is a wave vector.

The above effects of parametric crystallooptics can be represented by the power expansion of a_{ij}^0 tensor in the external fields of different nature. Therefore they reveal only frequency dispersion. Electrogyration can be represented by the power expansion of g_{kl} tensor in the external electric field:

$$g_{kl} = g_{kl}^0 + \gamma_{klm} E_m + \beta_{klmn} E_m E_n + \cdots,$$

where g_{kl}^0 is a gyration tensor in the absence of the field, γ_{klm} and β_{klmn} are third- and fourth-rank axial tensors describing the linear and quadratic effects, respectively.

The possiblity of electrogryration existence in different crystals is determined, first of all, by the latter ones' point symmetry, since it limits the number of independent and non-zero tensor γ_{klm} and β_{klmn} components. Since the transformation formulae for the components of polar tensors, describing the electro-optical effect, and the axial tensors, describing electrogyration, are different, the conditions of these two effects existence are different as well. In particular, while the linear electro-optical effect is possible only in 20 classes of non-centrosymmetric crystals, the linear electrogyration is possible in all the media, but the crystals with symmetry *m*3*m*, $\bar{4}3m$, 432, and vice versa, quadratic electrogyration is possible only in non-centrosymmetric crystals,[4] while the quadratic electro-optical effect—in all the media.

Thus, in a number of cases electrogyration is accompanied by electro-optical effect. Comparison of the third-order polar and axial tensors may lead to the conclusion that "pure" linear electrogyration is possible in crystals of 4, 4/*m*, $\bar{6}$, 6, 6/*m*, 3, $\bar{3}$, 23 and *m*3 classes.

In accordance with the Curie symmetry principle, electric field application to the crystal or emergence of spontaneous polarization at ferroelectric phase transition is accompanied by lowering of the crystal symmetry. Thus, the possibility of induced or spontaneous emergence of optical activity does not contradict the Neuman's principle.

3. RELATION BETWEEN ELECTROGYRATION AND ELECTRO-OPTICAL EFFECT

It is known[1–4] that the character of the waves polarization in an optically active crystal with optical linear birefringence and their interference at the crystal outlet are determined by the relation between the optical polarization constants of a_{ij} and g_{kl} gyration tensors. For this reason in the common case the normal elliptically polarized waves (with certain approximation[42]) propagate in the crystal with ellipticity of

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

where 1, 2, 3 are indices of the laboratory coordinate system in which axis 3 coincides with the wave vector direction and axes 1 and 2 with the axis of the optical indicatrix section ellipsis, $\bar{n}$ is a mean refraction index.

The polarization state of the resultant wave at the outlet of the plane-parallel crystal plate is found by various methods, i.e. by means of Jones' matrices,[43] Poincaré sphere,[44,45] the covariant[46] or coordinate[47] methods. If the initial incident wave was linearly polarized in one of the main crystal planes, it is determined by the expression:[47]

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

where χ is a polarization ellipse azimuth, $\Gamma = (2\pi/\lambda)\Delta n d$ is a phase difference of the interfering waves in the crystals, d is thickness of crystal plate, $\Delta n = n_1 - n_2$ is linear birefringence.

Interesting results are evident from the analysis of the formula (1).[47] Thus, at $|k| \ll 1$ the phase difference Γ being varied, the polarization ellipse performs the

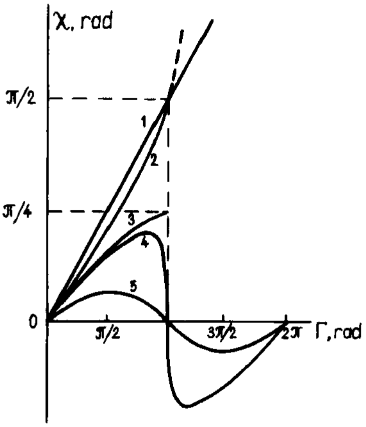

FIGURE 1 Dependences of polarization ellipse azimuth on phase differences at different parameters k.[47] 1—$k = 1$; 2—$k = 0.6$; 3—$k = 0.414$; 4—$k = 0.4$; 5—$k = 0.2$.

sine oscillations[46] $\chi \simeq k \sin \Gamma$. With k increasing, the character of the ellipse oscillations is changed (Figure 1). For $k > 0.414$ a smooth rotation of the polarization ellipse takes place with the increasing, and for $k = 1$ there appears a polarization plane rotation (the elliptically polarized wave becomes linearly polarized).

Usually χ changes with variation of the wave normal direction, wave length and sample thickness. Under the electric field action, in the common case, χ may change due to electrogyration and electro-optical effect. This results in the complicated inter-relation of these two phenomena. And being compared with the electro-optical effect and natural birefringence, the electrogyration turns out to be of a rather small value.

Here two particular cases are of interest:

1. Light propagates through a uniaxial crystal in the direction normal to the optical axis, and the electric field, beside the refractive indices and the gyration tensor components change, causes the optical indicatrix rotation around the wave normal direction through the angle ξ. Then the azimuth of the polarization ellipse big axis is determined by relation:[19]

$$\operatorname{tg} \chi = -\xi + \sqrt{\xi^2 + k^2} \sin(\Gamma + \delta),$$

where $\operatorname{tg} \delta = \xi / k$.

2. Light propagates in a uniaxial gyrotropic crystal along the optical axis or in the cubic crystal, in this case electrogyration is accompanied by appearance of the induced birefringence. If the latter is much less than the gyration parameter, the passed wave will remain practically linearly polarized, and additional rotation of the polarization plane on the basis of the electrogyration and electro-optical effect superposition may be determined:[47]

$$\Delta\chi = \Delta\chi_{eg} + \Delta\chi_{0g} = \frac{\pi}{\lambda n}\left(\gamma_{0j} E_j + \beta_{0j} E_j^2 + \frac{n^8 r_{0j}^2 E_j^2}{2 g_{33}}\right), \qquad (2)$$

where γ_{0j}, β_{0j}, r_{0j} are matrix components of tensors of linear and quadratic electrogyration and linear electro-optical effect, respectively.

Thus, measurement of electrogyration is not a matter of great experimental difficulty only in the case of the elliptical birefringence absence. But on the whole, separation of the interrelated phenomena of electrogyration and electro-optical effect or natural birefringence is not a simple experimental problem. A number of authors proposed particular variants for separation of gyration from birefringence based on the analysis of light interference in gyrotropic crystals,[48–50] on measurement of relative intensity of light passing through the polarization system of a crystal within crossed or parallel polarizer and analyzer,[51,52] on measurement of oscillations of the light polarization ellipse.[46] A simple and accurate method is based on the light azimuth analysis before and after its propagation through the crystal.[4,37]

4. ELECTROGYRATION PHENOMENOLOGY IN FERROELECTRICS

With ferro- an antiferroelectric phase transitions, gyration may arise spontaneously. Evidently, only those crystals should be considered, the ferroelectric phases of which belong to seven optically active classes, namely: 1, 2, 3, 4, 6, *m*, *mm*2. The crystals of 3*m*, 4*mm*, 6*mm* classes are the exceptions as those with weak activity not affected by the spontaneous polarization influence. Gyration in ferroelectrics is described by the expansion of the gyration tensor components in terms of polarization powers P:

$$\Delta g_{ij} = \gamma^*_{ijk} P_k + \beta^*_{ijkl} P_k P_l + \cdots$$

Since arising of the spontaneous polarization is equivalent to the electric field action on the crystal in the initial paraelectric phase, the character (linear or quadratic) of the gyration is determined, first of all, by the paraelectric phase symmetry. Here are two particular cases of special interest:

1. Ferroelectrics with centrosymmetric phase. Only linear electrogyration effect is possible in the paraelectric phase. Therefore, in the ferroelectric phase the neighbouring domains differ by the sign of gyration tensor components, and the crystals repolarization by the electric field results in the change of the optical activity sign according to the hysteresis loop of the usual type (e.g. crystals TGS, transition $2/m \rightarrow 2$). K. Aizu[7] calls such crystals "gyroelectric" ones.

2. Ferroelectrics with non-centrosymmetric paraelectric phase. Spontaneous gyration in the ferroelectric phase is due to linear or to quadratic electrogyration properties of the paraelectric phase. Its order is determined by the shape of the axial tensors of the initial symmetry and by the direction of the spontaneous polarization. For example, transition $\bar{6} \rightarrow 3$ ($Pb_5Ge_3O_{11}$ crystals) is accompanied by the appearance of spontaneous gyration due to the linear electrogyration in the upper phase. And at the transitions from classes 32, 422, 622 to classes 3–6 (e.g. crystals $Ca_2Sr(C_2H_5COOH)_6$, $422 \rightarrow 4$) the spontaneous gyration is due to the quadratic electrogyration in the upper phase. Hence, the domains with antiparallel directions of the spontaneous polarization belong to one enantimor-

phic modification and gyration is not changed with repolarization. In K. Aizu's term[7] such crystals may be referred to as "hypergyroelectric".

Thermodynamic approach[7] may be applied to these two cases accepting gyration to be a transition parameter and postulating its presentation similarly to the free energy ϕ. In the case

$$\phi = \phi_0 + A(T - T_0)P^2 + B_2P^4, \tag{3}$$

$$G = \alpha + \beta(T - T_0) + \gamma_1 P + \delta_2 P^2, \tag{4}$$

where α, β, γ_1, γ_2 are constants depending on the crystal symmetry and the direction of the light propagation.

In the case of linear spontaneous gyration (gyroelectrics[7]) $\alpha + \beta = \gamma_2 = 0$, $G = \gamma_1 P$. Thus, in accordance with (3), $G = \gamma_1(A/2B_2)^{1/2}(T_0 - T)^{1/2}$ with $T \leqslant T_0$ and $G = 0$ with $T \geqslant T_0$. Determining the coefficient of the induced linear electrogyration as $\gamma = (dG/dE)_{E=0}$ and taking into account the temperature dependence of dielectric susceptibility resulting from (3), we shall obtain: $\gamma = (\gamma_1/4A)(T_0 - T)^{-1}$ with $T < T_0$ and $\gamma = (\gamma_1/2A)(T_0 - T)^{-1}$ with $T > T_0$.

In case of the quadratic spontaneous gyration (hypergyroelectrics[7]) $\gamma_1 = 0$ and $G = \alpha + \beta(T - T_0) + \gamma_2 P^2$. Then $G = \alpha + (\gamma_2 A/2B_2 - \beta)$ with $T \leqslant T_0$ and $G = \alpha + \beta(T - T_0)$ with $T \geqslant T_0$. Respectively, $\gamma = \gamma_2(8AB_2)^{-1/2}(T_0 - T)^{1/2}$ with $T < T_0$ and $\gamma = 0$ with $T > T_0$.

Thus, in gyroelectrics the spontaneous gyration depends on the temperature as well as the spontaneous polarization, the induced linear electrogyration is possible on both sides of the Curie point and is submitted to the "law of doubling" (Figure 2a). In hypergyroelectrics the optical activity linearly depends on the temperature on both sides of the Curie point and it remains non-zero at $T \geqslant T_0$, the linear induced electrogyration is possible only in the ferroelectric phase (Figure 2b). It should be noted that such qualitative classification is not the

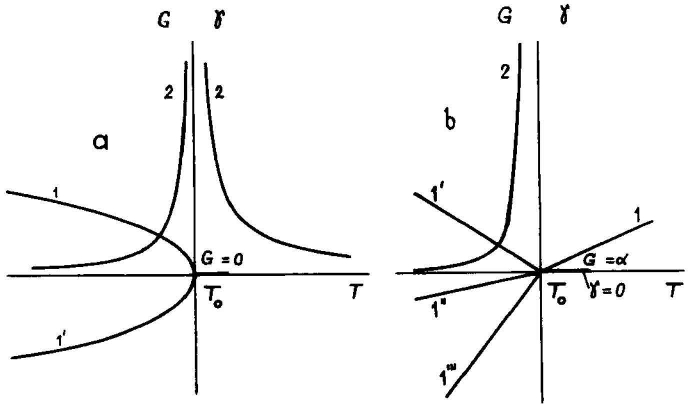

FIGURE 2 Theoretical dependences of spontaneous gryation G and electrogyration coefficient γ temperature.[7] *a*—in gyroelectrics; G—1.1′; γ—2; 1—$\gamma_1 > 0$; 1′—$\gamma_1 < 0$; 2—$\gamma_1 > 0$. Origin of coordinates $(T_0, 0)$; *b*—in hypergyroelectrics $(\beta > 0,\ \gamma_2 > 0)$. 1—$G$ in paraphase, 1′—$\gamma_2 > 2\beta\, B_2/A$, 1″—$0 < \gamma_2 < 2\beta B_2/A$, 1‴—$\gamma_2 < 0$, 1′, 1″, 1‴—$G$ in ferrophase, 2—$\gamma_2 > 0$. Origin of coordinates (T_0, α).

absolute one, finally, the shape of tensors concrete symmetry class should be taken into account. Fundamental possiblity of significant induced electrogyration was noted by the author,[17] proceeding from the fact that the effect depends on the crystal state (free or forbidden deformation), i.e. in the phase transition region it should possess the same anomalies as the piezoelectric and electrostriction effects.

5. FIRST RESULTS ON ELECTROGYRATION

For the first time electrogyration was detected and investigated[14,15] on the example of the quadratic effect in quartz crystals (class 32). The effect was revealed in the variation of polarization plane rotation for the light ($\lambda = 632.8\,\text{nm}$) propagating along the optical axis, with the electric field acting normally to the axis (components E_x and E_y). In this case linear electro-optical and quadratic electrogyration effects take place, being of significantly lower values in comparison with optical activity. The first of them leads to the negligible light ellipticity, simulating the electrogyration; the second one—to additional rotation of the polarization plane (of ellipse with big excentricity). The general effect of variation of the polarization plane $\Delta\rho$ specific rotation is expressed by the formula of the (2) type. On the basis of the experimental dependence $\Delta\rho = f(E^2)$ $\beta_{31} = (3.47 \pm 0.28) \cdot 10^{-20}\,\text{m}^2/\text{V}^2$ was found.

The linear electrogyration was obtained for the first time[16] with the light propagation along the optical axis in biaxial crystals α-HJO_3 (class 222). Here, under the field E_y action the effect value is determined by the formula

$$\Delta\rho = \frac{\pi}{\lambda n_y}\gamma_{32}E_y \sin 2\theta,$$

where $\theta = 67°$ is the angle between the optical axis and the obtuse-angle bisectrix. The effect is complicated by a number of factors caused by the piezoelectric deformation and the electro-optical effect. Taking them into account, according to the data of Figure 3, we find $\gamma_{52} = (7.1 \pm 0.5) \cdot 10^{-12}\,\text{m/V}$.

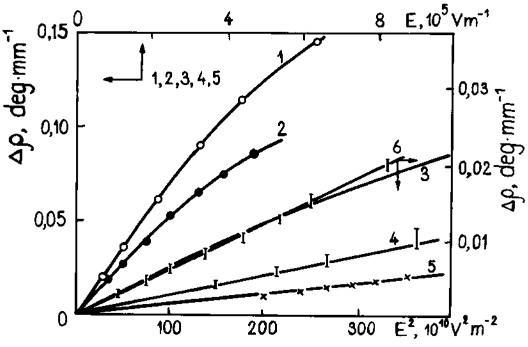

FIGURE 3 Dependences of increase of polarization plane specific rotation on electric field intensity in gyrotropic crystals. 1—$AgGaS_2$,[55] 2—$CdGa_2S_4$,[55] 3—$Bi_{12}SiO_{20}$,[57] 4—α-HJO_3,[16] 5—$LiJO_3$,[17] 6—SiO_2,[14] ($\Delta\rho \sim f(E^2)$).

More favourable conditions for observation of the linear electrogyration are present in uniaxial crystals $LiJO_3$ (class 6). In them with the light propagating and with the field acting along the optical axis the linear electrogyration is not accompanied by the electro-optical effect, and only the crystal deformation contributes ~17% to the observed[17] dependence $\Delta\rho = f(E)$ (Figure 3). Due to the ionic conductivity the investigations were conducted at −140°C. The effect is described by the formula

$$\Delta\rho_3 = \frac{\pi}{\lambda n_0}\gamma_{33}E_z, \tag{5}$$

where $\gamma_{33} = (1.57 \pm 0.30)\cdot 10^{-13}\,\mathrm{m/V}$ for $\lambda = 632.8\,\mathrm{nm}$.

Fundamental was detection of the optical activity only due to the electric field without accompanying effects in the centrosymmetric crystals. The first such reliable result was obtained[20] in crystals $PbMoO_4$ (class $4/m$) with the action of electric field and light propagation along the optical axis. It was stated, that the sign of the optical activity is changed with the change of the field sign (Figure 4). Proximity of the fundamental absorption edge allowed to observe the effect of dispersion (Figure 4). The effect was confirmed by other authors[22] and this called for a series of investigations[53,54] of scheelite type ($NaBi(MoO_4)_2$, $SrMoO_4$, $CaWO_4$—class $4/m$) crystals and apatite type ($PbSeO_4(VO_4)_2$, $PbSiO_4(VO_4)_2$, $PbGeO_4(VO_4)_2$-class $6/m$) crystals (Figure 5). The analysis of the obtained results confirms that, from the electrogyration effect value point of view, the sheelite structure is more preferable than that of the apatite one for the crystals containing lead. Lead substitution by the ions with less polarizability in the scheelite structure results in considerable effect reduction, in particular, in $SrMoO_4$ crystals it is by two orders less than in $PbMoO_4$. At the same time in the

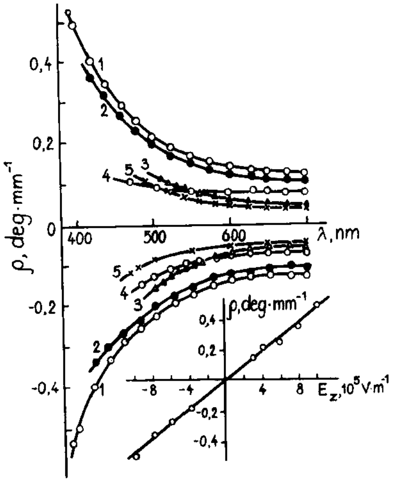

FIGURE 4 Electrogyration ρ dispersion in centrosymmetric crystals at $E = 10\,\mathrm{kV\cdot cm^{-1}}$. 1—$PbMoO_4$,[20] 2—$NaBi(MoO_4)_2$;[53,54] 3—$Pb_5SiO_4(VO_4)_2$;[22,34] 4—$Pb_5SeO_4(VO_4)_2$;[54] 5—$Pb_5GeO_4(VO_4)_2$.[22,54] On the Insert-Dependence if ρ on E value in Crystals $PbMoO_4$ ($\lambda = 400\,\mathrm{nm}$).

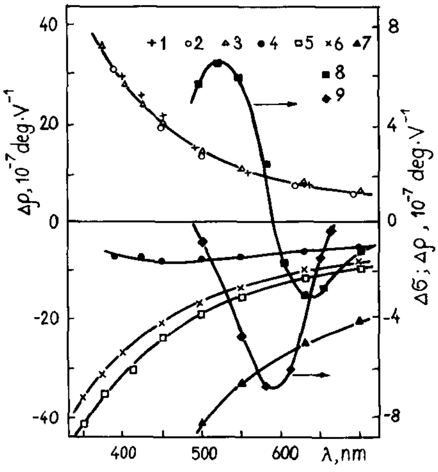

FIGURE 5 Dispersion of electrogyration $\Delta\rho^{24}$ and circular electrodichroism $\Delta\delta^{23}$ of some alum for $e_{\parallel}\langle 001\rangle$, $k_{\parallel}\langle 110\rangle$, $l = 1$ cm, $|E| = 1\ \mathrm{V\cdot cm^{-1}}$ 1—PbFeS; 2—NH_4FeS; 3—CsFeS; 4—NH_3CH_3Fe; 5—NH_3CH_3GaS; 6—NH_3CH_3AlS; 7—NH_3CH_3AlSe; 8—$K(Al, Cr)(SO_4)_2\cdot 12H_2O$; 9—$\Delta\delta$ for $K(Al, Cr)(SO_4)_2\cdot 12H_2O$; 8 and 9—for molar concentration $KCr(SO_4)_2\cdot 12H_2O$-6.22%, E, $k_{\parallel}\langle 111\rangle$.

number of α-HJO_3, $LiJO_3$, $PbMoO_4$ crystals electrogyration coefficients expressed through polarization are of the same order. These facts confirm the significance of the ions polarizability in the electrogyration.

Among the medium system crystals the semiconductive silver thiogalat (class $\bar{4}2m$) and cadmium thiogalat (class $\bar{4}$) crystals which, at a certain wavelength λ_i, are characteristic of the birefringence sign inversion are of interest. The symmetry of these crystals prohibits the optical activity in the optical axis direction, while the birefringence sign inversion allows to measure the tensor components g_{11} and g_{12} without difficulties. This fact also determines the possiblilty to measure the linear electrogyration tensor component γ_{41} describing the change of polarization plane rotation $\Delta\rho$ with the light propagating at 45° angle to the y and z axes and its electric field E_x action:

$$\Delta\rho = \frac{\pi}{n\lambda_i}\gamma_{41}E_x. \tag{6}$$

It is important that in this case the E_x field does not cause the λ_i shift since the variation of the birefringence due to the linear electro-optical effect depends on $(r_{41}E_x)^2$. On the basis of the experimental data[55] (Figure 3) the electrogyration coefficients γ_{41} are calculated and are equal to $2.03\cdot 10^{-12}$ and $1.52\cdot 10^{-12}$ m/V for $AgGaS_2$ and $CdGa_2S_4$ respectively.

Considering electrogyration in the cubic crystals, it is expedient to separate the gyrotropic (non-centrosymmetric) and non-gyrotropic (centrosymmetric) crystals, because in the first case electrogyration may be complicated by a linear electro-optical effect. The sillenite structure ($Bi_{12}SiO_{20}$, $Bi_{12}TiO_{20}$—class 23) crystals may be referred to the first group, a great number of alum structure crystals (class $m3$)—to the second group.

Crystals $Bi_{12}BiO_{20}$, $Bi_{12}GeO_{20}$ and $Bi_{12}TiO_{20}$ possess a significant sensitivity. This fact as well as incorrect experiment setting resulted[56] in the incorrect interpretation of the seeming optical activity variation under the electric field action. The real electrogyration without accompanying electro-optical effect is possible only in the direction $\langle 111 \rangle$. In the small electric fields the polarization saturation caused by the photoconductivity is not yet manifested, the real electrogyration is described by the relation of (6) type. According to the data[57] for $Bi_{12}SiO_{20}$ crystals $\gamma_{41} = 9.52 \cdot 10^{-13}\,\mathrm{m/V}$.

The alum forms a big group of centrosymmetric crystals with the general formula $AB(CO_4)_2 \cdot 12H_2O$, where A is univalent cation, B is trivalent cation, C–S or Se. Different modifications (α-, β-, γ-alum) are structurally similar, but considerably differ in their physical properties. For example, the alum in which A corresponds to $NH_3CH_3^+$ and NH_4^+—are ferroelectrics. The linear electrogyration was investigated[23,24] in more than 30 compounds with the alum structure, which allowed to discover the role of various structural units in the effect magnitude. In particular, ferroelectric methylammonium alum produces the negative effect, in Ferric (Fe^{3+}) alum it is positive, while NH_3CH_3FeS has the intermediate value (Figure 5), i.e. in the latter case the opposite sign effects are compensated. Practically, in all the α-alums the ion with the lowest symmetry and greatest polarizability increases the interrelation with the water molecules and provides for the electrogyration increase. The ion polarizability role is also manifested[58] in isomorphic crystals group of class $m3$: $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$. Electrogyration dispersion in alum is well described by the Chandrosecar's formula, but it is not submitted to the Miller's rule.[59]

In chrome activized alum $KAl(SO_4)_2 \cdot 12H_2O$ in the absorption band region the electrogyration is accompanied by anomalous dispersion and induced circular dichroism (electrodichroism) (Figure 5).[23,25]

6. ELECTROGYRATION IN PROPER FERROELECTRICS

The triglycine sulphate $(NH_3CH_2COO)_3 \cdot H_2SO_4$ (TGS)[26–28] and Rochelle salt $NaKC_4H_4O_6 \cdot 4H_2O$ (RS)[60] crystal investigations interpreted as spontaneous gyration may be referred to the first investigations of the optical activity in ferroelectrics. Weak optical activity anomalies in the phase transition region in the Rochelle salt crystals was reported in the paper,[26] but they were not interpreted respectively. In TGS crystals (transition $2/m \rightarrow 2$) the optical activity was measured according to the polarization plane rotation in monodomain crystals with light propagation along the optical axis. In this case the temperature variation of the optical axis direction caused by the thermal deformation and spontaneous electro-optical effect was taken into consideration. The polarization plane specific rotation ρ dependence on the spontaneous polarization P (Figure 6) is described by the relation

$$\rho = \frac{\pi}{\lambda n_z} G = \frac{\pi}{\lambda n_z} (\gamma_{12}^* \cos^2 \varphi + \gamma_{22}^* \sin^2 \varphi) \cdot P$$

where φ is angle between the optical axis and axis X ($\varphi = 58.9°$ for $\lambda = 632.8\,\mathrm{nm}$),

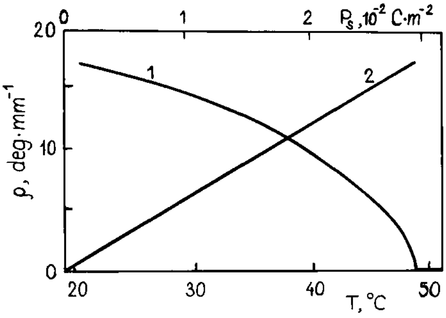

FIGURE 6 Dependence of light polarization plane specific rotation in TGS crystals on temperature (1) and spontaneous polarization (2).[28]

n_2 is refraction index of the wave propagating along the optical axis. On the basis of the obtained results it was found $0.26\gamma_{12}^{*} + 0.74\gamma_{22}^{*} = (1.51 \pm 0.20) \cdot 10^{-5}\ \mathrm{m^2/C}$. Further in the phase transition region[61] the induced linear electrogyration coefficient γ_{22} anomaly characteristic of gyroelectric crystals with the second-order transition, and the optical activity hysteresis[62] caused by the domains enantimorphism were found. Earlier the optical activity hysteresis was observed[5,63] in crystals $LiH_3(SeO_4)_2$ (transition $2m \rightarrow m$). But its nature is not connected with the enantimorphism of domains, it is caused by rearrangement of the optical axes along which the opposite sign polarization plane rotation occurs.

In recent views, to the number of the first hypergyroelectrics may be referred $Ca_2Sr(CH_5CO_2)_6$-DSP and $Ca_2Pb(CH_5CO_2)_6$-DPP crystals which undergo the second-order transition (422→4) at the temperatures of 8.5 and 60°C respectively. The phase transition should be accompanied by spontaneous gyration due to quadratic electrogyration in the paraelectric phase, the domains with anti-parallel directions of spontaneous polarization should belong to one enantimorphic modification. The experimental investigations[64,65] prove these suppositions on the whole, but they do not give complete explanation from the standpoint of the proper ferroelectricity.

The Rochelle salt crystals could turn out to be the representatives of hypergyroelectrics, since both in ferro- and paraphase (transition 222→2) they possess the optical activity. But the detected[60] distinctions of the spontaneous gyration do not allow to refer them to pure hypergyroelectrics. In the linear approximation spontaneous gyration[60] is the gyration surface rotation in the plane (yz) at an angle ξ_1 the value of which is determined by the relation

$$\mathrm{tg}\, 2\xi_1^{eg} = 2\gamma_{41}^{*} P_x / (g_{22} - g_{33}).$$

Hence, with the crystal repolarization by the external electric field, the gyration surface rotation direction is changed without variation of the enantimorphism sign. So the optical activity hysteresis (Figure 7a) observed with the light propagating along the bisectrix of the angle between the optical axes of the neighbour domains, is a derivative from the dielectric hysteresis loop. The gyration surface is rotated synchronously with the spontaneous optical indicatrix rotation

$$\mathrm{tg}\, 2\xi_1^{eo} = 2m_{41} n_y^2 n_z^2 P_x / (n_z^2 - n_y^2).$$

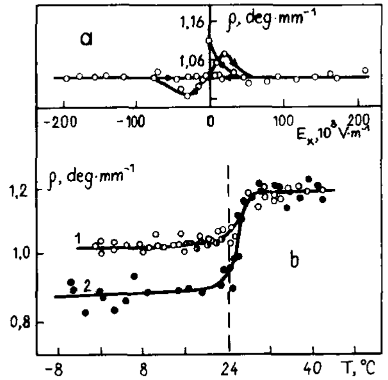

FIGURE 7 Dependences of Rochelle salt crystals polarization plane specific rotation on electric field E_x intensity (a) and temperature with different E_x (b).[60,82] 1—$E_x = 2.4 \cdot 10^5\,\mathrm{V \cdot m^{-1}}$; 2—$E_x = 25.7 \cdot 10^3\,\mathrm{V \cdot m^{-1}}$.

Considering that $\xi_1^{eo} = \xi_1^{eg}$ and using the data of the electro-optical coefficient m_{41} and the gyration tensor components g_{22} and g_{33}[60] we find $\gamma_{41}^{*} = (8.2 \pm 2.1) \cdot 10^{-5}\,\mathrm{m^2/C}$ for $\lambda = 561.6$ nm. Synchronous rotation of the optical indicatrix and gyration surface explains independence of the polarization plane specific rotation ρ on the temperature, and the hysteresis specific character explains the ρ leap value in phase transition (Figure 7b). But the leap is not explained within the phenomenological approach and, probably, is of the structural-molecular origin.

The most thorough electrogyration investigations[31–33,66–74] were done in the ferroelectric crystals of lead germanate $Pb_5Ge_3O_{11}$ and solid solution on its basis. These crystals are very convenient since both spontaneous and induced electrogyrations in the both phases are not complicated by the accompanying effects. The axial tensors shape allows the linear electrogyration in both phases, besides, the high paraelectric phase symmetry excludes the natural optical activity. It is convenient to illustrate some laws of this crystals group electrogyration[79] on solid solutions of $Pb_5(Ge_{1-x}Si_x)_3O_{11}$. As is seen in Figure 8, spontaneous gyration has

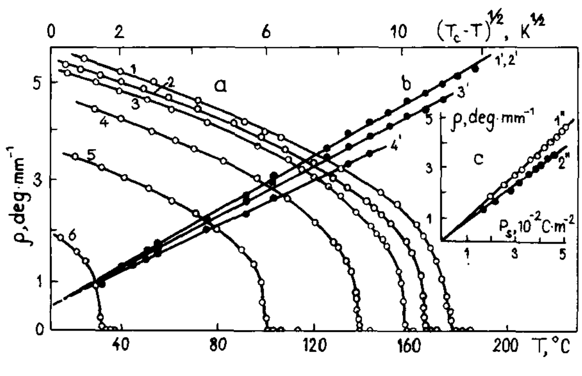

FIGURE 8 Dependences of polarization plane specific rotation on temperature (a), on $(T_0 - T)^{1/2}$ value (b) and on spontaneous polarization (c) in crystals $Pb_5(Ge_{1-x}Si_x)_3O_{11}$[73,74] 1—$x = 0$; 2,1′—$x = 0.03$; 3,2′—$x = 0.05$; 4,3′,1″—$x = 0.10$; 5,4′,2″—$x = 0.20$; 6—$x = 0.40$.

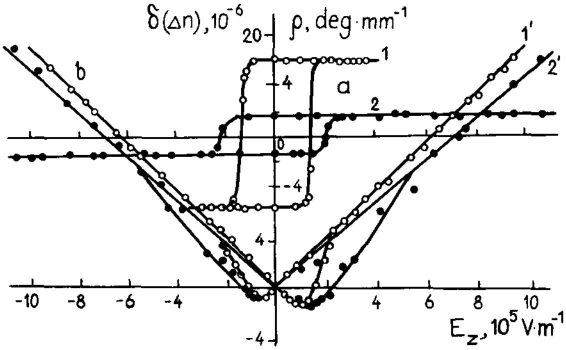

FIGURE 9 Hystereses of optical activity (a) and birefringence increase (b) at $T = 20°$ in crystals $Pb_5(Ge_{1-x}Si_x)_3O_{11}$,[73,74] 1,1'—$x = 0$; 2,2'—$x = 0.40$.

the linear character:

$$\rho = \frac{\pi}{\lambda n_0} \gamma_{33}^{*} P$$

and depends on the temperature as well as the spontaneous polarization $\rho \sim (T_0 - T)^{1/2}$ in the whole temperature region excluding the phase transition neighbourhood. The latter is evidently caused by non-coincidence of T_0 determined by spontaneous polarization and gyration. With the Si concentration increased, temperature T_0 is essentially shifted, while the effect value is reduced. According to the ρ data the phase transition does not manifest the diffusion features unlike the P value data, i.e. spontaneous gyration more definitely reflects the transition character, since it is measured with the external field absent on the crystal. The crystal repolarization is accompanied by the gyration loop which differs from the birefringence loop (Figure 8) in accordance with the character of these two effects (spontaneous electro-optical effect is a quadratic one). For the first time in the phase transition region the anomally great linear induced electrogyration (Figure 10) which on the whole agrees with the thermodynamical theory laws was detected:[32] $\Delta P/E \sim (T - T_0)$ on the both sides of the phase transition and sufficiently well fulfils the "law of doubling".

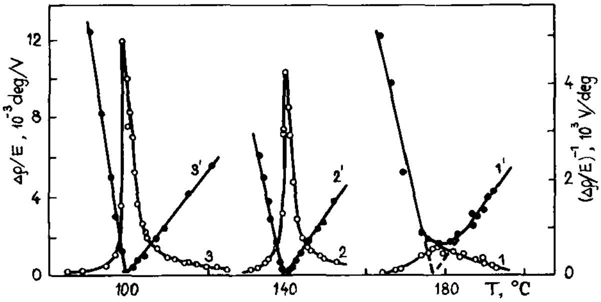

FIGURE 10 Temperature dependences of induces electrogyration $\Delta\rho/E$ and value $(\Delta\rho/E)^{-1}$ in crystals $Pb(Ge_{1-x}Si_x)_3O_{11}$[71] 1,1'—$x = 0$; 2,2'—$x = 0.10$; 3,3'—$x = 0.20$.

7. PSEUDOPROPER FERROELECTRICS

We shall now proceed to illustrate the possibilities of applying electrogyration to the investigation of pseudoproper ferroelectrics of KDP type crystals. By many macroscopic properties they show features of the displacement type ferroelectrics. At the same time the phase transition is induced by the protons ordering on the H-bonds, and their ordering does not initiate the spontaneous polarization directly. From this point of view they may be referred to as pseudoproper (they are called "improper" in Reference 34) ferroelectrics in which the protons ordering degree, which is of the same transformational properties as the spontaneous polarization, is considered as the ordering parameter. The electrogyration methods turn out to be the most sensitive ones.[34–37,75–78]

The pseudoproperness features of the KDP type crystals group (except for RDP) follow from the behaviour of the gyration tensor g_{11} component with phase transition (Figure 11). Presence of sharp peaks[75,36] in KDP, DKDP, CDA crystals cannot be explained by the gyration expected here on the basis of crystal-physics and thermodynamical approaches to the proper ferroelectrics. But the spontaneous gyration in the RDP crystals completely corresponds to these expectations (Figure 11).

Results of the quadratic electrogyration investigations[34,61] in the paraelectric phase, presented by temperature dependences of the coefficient β_{13} (Figure 12), especially definitely express the distinctive features of this crystals group. Thus, in the DKDP and CDA crystals the temperature β_{13} anomalies are accompanied by the sign change at a definite temperature. These anomalies cannot be explained by the anomalies of the dielectric constant ε_{33}. Coefficient β_{13}^* calculated according to the ε_{33} data also depends on the temperature (Figure 12). But the β_{13} temperature dependence for RDP crystals corresponds to ε_{33} anomalies.

These experimental facts may be well explained on the basis of the pseudoproper ferroelectrics thermodynamical potential:[34,78]

$$\begin{aligned} A = {} & A_0 + \tfrac{1}{2}\beta(T - T_\theta)\theta_3^2 + \tfrac{1}{4}\gamma\theta_3^4 + \tfrac{1}{6}\delta\theta_3^6 + \tfrac{1}{2}\omega P_3^2 \\ & - \tfrac{1}{2}s_{ij}x_ix_j - \tfrac{1}{2}b_{3i}x_iP_3 - \theta_{3i}x_iP_3^2 - \tfrac{1}{2}n_{3i}x_i\theta_3 - R_{3i}x_i\theta_3^2 \\ & - W_{3i}x_iP_3\theta_3 + fP_3\theta_3, \end{aligned}$$

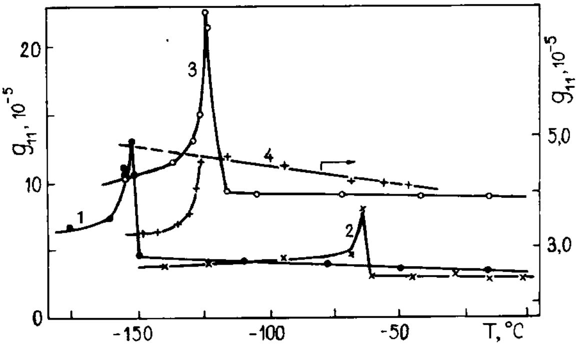

FIGURE 11 Temperature dependences of gryation g_{11} tensor component in crystals KDP (1), DKDP (2), CDA (3) and RDP (4)[37,83]

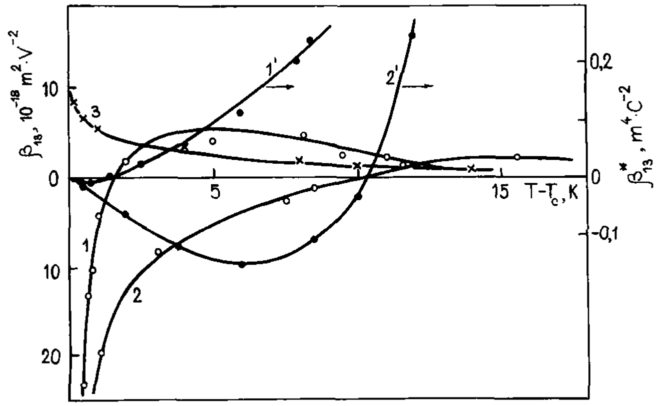

FIGURE 12 Temperature dependences of quadratic electrogyration coefficient β_{13} (1,2,3) and β^*_{13} (1′,2′) of crystals DKDP (1,1′), CDA (2,2′) and RDP (3).[37]

where θ_3 is order parameter component, x_i is mechanical tension, f is negative constant, T_θ is phase transition temperature for the proton system not interacting with the lattice. On the basis of this, the optical activity variation under the electric field action may be explained by the relation:

$$\Delta g_{11} = \beta^{*\theta}_{13} P^2_3 + \beta^{*R}_{13}\theta^2_3 + \beta^{*W}_{13} P_3\theta_3 = (\beta^{*\theta}_{13}æ^2_p + \beta^{*R}_{13}æ^2_\theta + \beta^{*W}_{13}æ_p æ_\theta)E^2_z.$$

From this expression similarly with the electrostriction and quadratic electro-optical effect we shall obtain the β_{13} coefficient temperature dependence in the paraelectric phase

$$\beta^*_{13} = \beta^{*\theta}_{13} - \beta^{*W}_{13}(-f/\beta)(T - T'_0)(T - T_\theta)^{-2}, \tag{7}$$

where designation

$$T'_0 = T_\theta - (\beta^{*R}_{13}/\beta^{*W}_{13})(-f/\beta)$$

is introduced.

Results of the β^*_{13} temperature dependences approximation by the relation (7) well conform to the experimental results (Figure 12) for DKDP, KDP and CDA crystals, i.e. these crystals really possess the pseudoproper ferroelectricity determined by the force of the order parameter connection with spontaneous polarization. In this case $\Delta T = T_0 - T_\theta = f^2/\beta\omega$ which approximately equals ΔT determined[79] from the model of the proton-lattice interaction, in which

$$\Delta T = \frac{F^2}{k\Omega^2_0}$$

where F is proton–photon interaction constant, k is Boltzmann's constant, Ω_0 is proton–phonon mode frequency.

Thus, thermodynamical parameters obtained by the quadratic electrogyration methods for KDP crystals allow to discover new specific features of their phase transition. So, H-D substitution in the KDP crystals, much changing the T_0 and T_θ values, practically does not influence the $\Delta T = 55$ K value, i.e. the force of the proton–ion interaction (feature of the phase transition improperness). More considerable in this process is the anion and, especially, cation substitution. For example, the anion PO_4^{3-} group substitution for AsO_4^{3-} group considerably changes the order parameter and spontaneous polarization connection force manifested in the change of the $\Delta T = 65$ K value, while cations K+ for Rb+ substitution increases this connection force so much that RDP crystal properties do not differ from the respective properties of proper ferroelectrics.

The improper ferroelectrics investigation may be performed effectively by the linear electrogyration methods. For instance, in methylammonium alum (transition $m3 \rightarrow 3$) the properties of improper ferroelectrics were found[80] in the γ_{41} temperature and dispersion dependences in centrosymmetric phase. The phase transition mechanism is connected with the SO_4^{2-} anion tetrahedron ordering and the shift of the H_2O molecules which are connected by the complicated system of hydrogen bonds.

8. CONCLUSION

It should be noted in conclusion that the material presented in this review is mainly concerned with the experimental results on electrogyration. Their interpretation is within the limits of phenomenological theory that does not reveal the microscopic nature of the phenomenon. Rather limited are also the possibilities of oscillatory models. Therefore, for understanding the electrogyration mechanism in certain crystals a theory is required that would take into account a real crystal structure, lattice dynamics and a complicated system of electrons energy states. Such a theory has been worked out[38,39,81] for ion dielectric crystals on the basis of Green's function method. Unfortunately, even a concise exposition of this theory is impossible because of the limited volume of this review. It should only be mentioned that the expressions obtained there for the linear electrogyration tensor components enable the researchers to analyze their dispersions and temperature dependence as well as to single out three components of the phenomenon mechanism—the ion, crystal and mixed components. For example, in $PbMoO_4$ crystals the electrogyration is accounted for by decompensation of the ions sublattice gyrotropy. The microscopic approach implies that parameter a/λ, characterizing the value of spatial dispersion effects, in the case of electrogyration, is determined by the distance considerably surpassing the lattice constant or the atom radius. This determines possible existence of a large electrogyration effect in certain crystals and inconsistency of Miller's relation for electrogyration.

In a brief review like this it is impossible to cover and discuss all the papers devoted to the problem. The author, therefore, feels obliged to offer his apology to the scientists whose papers did not find here the expression they deserve.

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