Electrogyration and Faraday rotation in pure and Cr-doped lead germanate crystals

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Abstract
We present the results of studies on the temperature dependence of the electrogyration (EG) effect, Faraday rotation and natural optical activity in $Pb_5Ge_3O_{11}$ and $Pb_5Ge_3O_{11}$:Cr crystals at the phase transition. A high EG coefficient is found for $Pb_5Ge_3O_{11}$:Cr crystals. We demonstrate how the Curie–Weiss constant, the critical exponents of the order parameter and the dielectric permittivity in $Pb_5Ge_3O_{11}$:Cr crystals, as well as the coefficients of thermodynamic potential, could be derived from the temperature dependences of optical activity and the EG coefficient. We also show that the increment of the Faraday rotation in $Pb_5Ge_3O_{11}$ and $Pb_5Ge_3O_{11}$:Cr crystals appearing at the phase transition is caused by a combined magneto-electrooptic effect induced by spontaneous polarization. It is proportional to the square of spontaneous polarization. The phenomenon revealed by us corresponds to combined effects of crystal optics, which appear due to the common action of different fields.

1. Introduction

In recent years, the electrogyration effect (EG) has been extensively studied in different materials. Nanocrystals embedded into a silica xerogel matrix [1] and chiral bent-core molecular systems [2] might be mentioned as examples. Searching for optical materials with a high EG performance is important from the point of view of their possible applications in electrically operated wireless devices for high-voltage measurement, electrooptic switches, modulators, etc. Unfortunately, EG rotation of the plane of polarization of light (often termed the EG rotatory power) has so far been found to be rather small (the reader may refer to the review papers and the monograph [3–5]), thus meaning in practice a higher energy consumption when compared with the corresponding electrooptic devices. However, the EG effect can exist in both non-centrosymmetric and centrosymmetric crystals, whereas the Pockels effect is only possible in a material without an inversion centre. Such symmetry limitations cause a notable reduction in the number of electrooptic materials that could be efficiently used. Just the well known lithium niobate and tantalate, KDP and some other crystals remain. These reasons justify the search for new efficient materials to control light electrically.

The EG effect, which consists in particular in the induction of optical rotation by a biasing field, is described by the following relations:

$$\varepsilon_{ij} = \varepsilon_{ij}^0 + i e_{ijk} g_{kl} k_1 = \varepsilon_{ij}^0 + i e_{ijk}(g_{kl}^0 + \gamma_{klm} E_m$$
$$+ \beta_{klmn} E_m E_n) k_1, \tag{1}$$

$$\Delta g_{kl} = g_{kl} - g_{kl}^0 = \gamma_{klm} E_m + \beta_{klmn} E_m E_n, \tag{2}$$

or

$$\Delta g_{kl} = \tilde{\gamma}_{klm}{}^{(s)} P_m + \tilde{\beta}{}^{(s)} P_m{}^{(s)} P_n, \tag{3}$$

$$\rho = \frac{\pi}{\lambda n} G = \frac{\pi}{\lambda n} g_{kl} l_k l_l, \tag{4}$$

in terms of spontaneous polarization. Here ε_{ij} and ε_{ij}^0 are the optical-frequency dielectric permittivities that take into account and disregard the spatial dispersion phenomena, respectively; e_{ijk} is the Levi-Civita tensor; g_{kl} and g_{kl}^0 are the second-rank axial tensors that describe total and natural optical activity, respectively; k_1 is the wavevector of light; E_m, E_n and $^{(s)}P_n$, $^{(s)}P_m$ are, respectively, the components of the electric field and the spontaneous polarization; γ_{klm}, β_{klmn} and $\tilde{\gamma}_{klm}$, $\tilde{\beta}_{klmn}$ are the third- and fourth-rank axial tensors describing the linear and quadratic EG effects expressed in terms of electric field and spontaneous polarization, respectively; G is the

pseudoscalar gyration parameter; l_k and l_l are the components of the unit wavevector in the spherical coordinate system; λ is the light wavelength; and n is the refractive index for the given propagation direction.

The EG effect is quite small in dielectric compounds, while the EG coefficients for wide-band semiconductors reach larger values, since the dispersion is strong and the bandgap wavelength is located close to the visible spectral range. The other factor that can lead to rise of the EG coefficient is a closeness of a proper ferroelectric phase transition, in the vicinity of which the EG effect manifests an anomalous temperature dependence due to the Curie–Weiss law.

Probably one of the largest EG rotations has been observed in lead germanate (LG) crystals close to the Curie temperature [6]. However, the temperature of the phase transition could be smeared or matched to the normal conditions due to substitution of the corresponding chemical elements. Such a behaviour of EG has been observed in the solid solutions $Pb_5Ge_{3x}Si_{3(1-x)}O_{11}$, $(Pb_{1-x}Bi_x)_5Ge_3O_{11}$ and $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$ [7–9]. Notice that the substitution of Pb by Bi in $(Pb_{1-x}Bi_x)_5Ge_3O_{11}$ and the substitution of Ge by Si in $Pb_5Ge_{3x}Si_{3(1-x)}O_{11}$ crystals provides a larger EG peak when compared with the pure LG crystals. Nonetheless, the opposite situation occurs in $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$ under the substitution of Pb by Ba: the EG coefficient decreases. Another common future appearing at the atomic substitutions in LG is an essential shift in the phase transition point in comparison with the pure $Pb_5Ge_3O_{11}$ crystals ($T_c = 450$ K, see, e.g., [10]).

Thus, searching for the solid solutions (or doped crystals) with high values of the optical EG rotation is still interesting from the viewpoint of applications of new EG materials for controlling optical radiation. Let us stress here that not only chemical substitution could be suspected as promising for this application, but also doping of pure crystals by some chemical elements. For example, the EG effect has been studied for LG crystals doped with Li, La [11], Eu [11, 12] and Cd, Nd [13]. The phase transition temperature for $Pb_5Ge_3O_{11}$:Nd crystals is equal to 450 K [14]. Nevertheless, doping of LG crystals with different chemical elements can lead to shifts in the phase transition temperature, too. Concerning the EG in the doped LG crystals, one can recall that the magnitude of the EG coefficient in $Pb_5Ge_3O_{11}$:Nd is an order of magnitude larger than in the pure crystals [11].

Thus one of the aim of present paper is to study the EG effect in doped LG crystals, with a specific emphasis on the material doped with 1.20 ± 0.08 wt% of Cr ions. In addition, in present paper we will present the results of a study of the optical rotation caused by the combined action of electric (spontaneous polarization) and magnetic fields in the mentioned crystals.

In [13, 15, 16] it was experimentally shown that a rotation, which is additional to the Faraday one, can appear when a spontaneous polarization or biasing electric field is present in ferroelectric crystals. The corresponding rotation angle is proportional to both the magnetic field and the electric field (or the electric polarization). From the viewpoint of symmetry, this effect should be described by the same symmetry as the Faraday effect [17]. The possibility of the existence of such an effect was mentioned in the monograph [18].

Let us consider a polar Faraday tensor α_{kl} appearing in the relation

$$\rho_k = \frac{\pi}{\lambda n}(\alpha_{kl}H_l + \delta_{klm}H_lE_m + \Theta_{klmn}H_lE_mE_n)$$
$$= \frac{\pi}{\lambda n}(\alpha_{kl} + \delta_{klm}E_m + \Theta_{klmn}E_mE_n)H_l, \tag{5}$$

where ρ_k is the rotation of the plane of polarization of light, H_l is the magnetic field, λ is the wavelength of the light and n is the refractive index. The tensor α_{kl} can be changed under the action of an electric field on the optical medium:

$$\Delta\alpha_{kl} = \delta_{klm}E_m + \Theta_{klmn}E_mE_n, \tag{6}$$

where E_m and E_n are the electric field components and δ_{klm} and Θ_{klmn} represent third- and fourth-rank polar tensors, respectively. The phenomenon mentioned above might be also treated as a combined magneto-electrooptic rotation, which appears due to common action of the electric and magnetic fields and manifests itself as a rotation additional to the Faraday one. From this point of view, the conclusion [19] about the need for independence of this additional rotation of the optical path in the crystal seems to be unclear. Obviously, this effect should be much smaller than the Faraday one and so hard to detect experimentally. Nevertheless, this combined effect has been revealed in [16] as an increment of the Faraday rotation induced by spontaneous polarization appearing in the course of a proper ferroelectric phase transition in LG crystals. However, the authors [15, 16] have claimed observation of both linear and quadratic increments of the Faraday effect in the spontaneous polarization, while the linear one should be forbidden by the symmetry of the paraelectric (PE) phase of LG. A physically different phenomenon has been reported to be detected in [20], where the combined optical rotation due to spatial dispersion, induced by both electric and magnetic fields, is observed in magnetically non-ordered crystals ($Sr(NO_3)_2$, $Ba(NO_3)_2$, and $Pb(NO_3)_2$). Let us note that this result contradicts the Onsager principle.

The temperature changes of the Faraday coefficients $\Delta\alpha_{kl}$ below the phase transition temperature should be proportional to the square of spontaneous polarization $^sP_m^{\ s}P_n$:

$$\Delta\alpha_{kl} = \tilde{\Theta}_{klmn}{}^sP_m{}^sP_n, \tag{7}$$

where $\tilde{\Theta}_{ijkl}$ is a fourth-rank polar tensor. Since the magnetooptic rotation ρ_k is described by equation (5), the change in the optical rotatory power induced by both the magnetic field and spontaneous polarization can be presented as a result of their combined effect:

$$\Delta\rho_k = \frac{\pi}{\lambda n}\tilde{\Theta}_{klmn}H_l{}^sP_m{}^sP_n. \tag{8}$$

or

$$\Delta\rho_k = \frac{\pi}{\lambda n}\Theta_{klmn}H_lE_mE_n, \tag{9}$$

in terms of the electric field. Then the coefficients $\tilde{\Theta}_{klmn}$ could be determined from the increments of the Faraday coefficients at the proper ferroelectric phase transition and compared with the coefficients obtained experimentally (see, e.g., [13]).

Thus the present paper is also devoted to elucidation of the dependence of the increment of the Faraday rotation on

the temperature and spontaneous polarization. Furthermore, we will clarify the dependence of the combined electro-magnetooptic rotation on the optical path and estimate the tensor component describing the corresponding effect. In our experiments we have used both pure LG and $Pb_5Ge_3O_{11}$ crystals doped with 1.20 ± 0.08 wt% of Cr ions.

2. Experimental details

LG crystals undergo a second-order phase transition with the change of point symmetry group $\bar{6} \leftrightarrow 3$. The matrices of the tensors of the linear EG effect for point groups of symmetry $\bar{6}$ and 3 are respectively as follows:

$$\gamma_{klm} = \begin{array}{c|ccc} & E_1 & E_2 & E_3 \\ \hline \Delta g_1 & 0 & 0 & \gamma_{13} \\ \Delta g_2 & 0 & 0 & \gamma_{13} \\ \Delta g_3 & 0 & 0 & \gamma_{33} \\ \Delta g_4 & \gamma_{41} & \gamma_{42} & 0 \\ \Delta g_5 & \gamma_{42} & -\gamma_{41} & 0 \\ \Delta g_6 & 0 & 0 & 0 \end{array},$$

(10)

$$\gamma_{klm} = \begin{array}{c|ccc} & E_1 & E_2 & E_3 \\ \hline \Delta g_1 & \gamma_{11} & \gamma_{12} & \gamma_{13} \\ \Delta g_2 & -\gamma_{11} & -\gamma_{12} & \gamma_{13} \\ \Delta g_3 & 0 & 0 & \gamma_{33} \\ \Delta g_4 & \gamma_{41} & \gamma_{42} & 0 \\ \Delta g_5 & \gamma_{42} & -\gamma_{41} & 0 \\ \Delta g_6 & -\gamma_{12} & -\gamma_{11} & 0 \end{array}.$$

It follows from the form of these tensors that the linear EG effect really exists for the experimental geometry $k \parallel E \parallel z$ chosen by us. In this case the optical rotatory power due to the EG effect may be presented as

$$\rho = \frac{\pi}{\lambda n_o} \gamma_{33} E_3,$$

(11)

with n_o meaning the ordinary refractive index. Since the so-called second-order symmetry operations are lost at the phase transition with the symmetry change $\bar{6} \rightarrow 3$, the domains in the ferroelectric phase should be enantiomorphous. This should lead to reversal of the natural optical activity whenever the domain structure is switched over by means of the biasing field E_3. At the same time, the LG crystals should possess no natural optical activity in the paraelectric phase, due to general symmetry limitations.

Since LG crystals undergo a second-order phase transition with the change of point symmetry group $\bar{6} \leftrightarrow 3$, the Faraday tensor in both structural phases has the form

$$\alpha_{kl} = \begin{array}{c|ccc} & H_1 & H_2 & H_3 \\ \hline \rho_1 & \alpha_{11} & 0 & 0 \\ \rho_2 & 0 & \alpha_{11} & 0 \\ \rho_3 & 0 & 0 & \alpha_{33} \end{array}.$$

(12)

The Faraday rotation observed in our experimental geometry ($k \parallel H \parallel z$) is defined by the formula

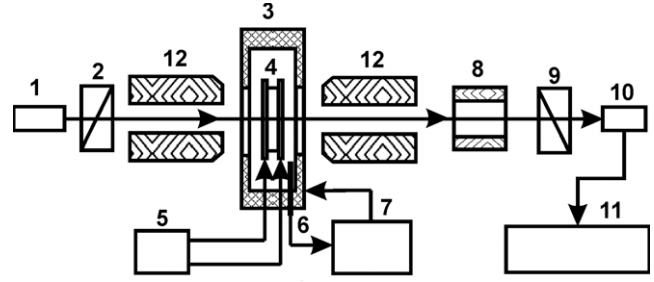$$\rho_3 = \frac{\pi}{\lambda n_o} \alpha_{33} H_3,$$

(13)

Figure 1. Experimental set-up: 1, He–Ne laser; 2, 9, polarizers with rotation stages; 3, furnace; 4, sample with transparent electrodes; 5, high-voltage source; 6, thermocouple; 7, temperature controller; 8, Faraday cell; 10, photomultiplier; 11, oscilloscope; 12, electromagnet.

whereas the total optical rotation induced by the magnetic field and the electric field (or the spontaneous polarization) may be written as

$$\rho_3 = \frac{\pi}{\lambda n} (\alpha_{33} + \Theta_{3333} E_3 E_3) H_3,$$

(14)

or

$$\rho_3 = \frac{\pi}{\lambda n} (\alpha_{33} + \tilde{\Theta}_{3333} {}^s P_3 {}^s P_3) H_3.$$

(15)

The experimental set-up is presented in figure 1.

The samples had the shape of plates, with a thickness of 5.0–6.0 mm and faces perpendicular to the optic axis. The flatness of the samples was no worse than 0.15°. The mismatch of the orientation of faces with respect to the direction perpendicular to the optic axis was less than 0.32°. The samples were placed in an optical heating stage allowing temperature stabilization with an accuracy of 0.1 K.

The electric field up to 10^6 V m^{-1} was applied along the direction $\langle 001 \rangle$ in crystals, using glass electrodes coated by a conducting tin oxide layer. Thin glass plates with a thickness of $d = 0.15$ mm were introduced between the sample and transparent electrodes to avoid the appearance of electric current. Thus, the electric voltage between the sample surfaces was lower by 5% when compared with that applied to the electrodes. In the PGO crystals, grown by the Czochralski technique, residual birefringence can exist along the z axis. However, our experimental study shows that the linear birefringence value is smaller than 10^{-6}. In such a case the electrooptic birefringence in the z direction should be a few orders of magnitude smaller than the residual one (usually electrooptically induced birefringence is three or more orders smaller than the natural one). Really, it can be caused only by a small violation of degeneration of the Pockels coefficients r_{13} and r_{23} in the ferroelectric phase and the Kerr coefficients R_{13} and R_{23} in the paraelectric phase. Thus, one can neglect the effect of electrooptic birefringence on the results of measurement of EG rotation of the polarization ellipse.

The magnetic field was applied along the same direction with the aid of an electromagnet. Note that some extra Faraday rotation (~10%) appeared in the optical windows and transparent glass electrodes because these optical elements were subjected to the magnetic field too. This additional

rotation was also taken into consideration when calculating the Faraday coefficient.

The optical activity was measured after determining the orientation of the plane of polarization of the light emerging from the sample, for the known linear polarization state of the incident light propagated along the optic axis of the crystal. When measuring the temperature dependences of optical activity, we applied the biasing field in the paraelectric phase along the $\pm z$ direction and then cooled the sample down to the ferroelectric phase, in order to reach a single-domain state. A Faraday modulator was used to increase the precision of the measurements of optical rotation.

Though the accuracy of the measurements of the orientation of the polarization was no worse than $0.1°$, the total errors were higher. For example, the magnitude of the optical activity ρ during the measurement of the temperature dependence of the natural optical rotation was determined with an error of 7% because of slight unipolarity of the crystals; the electrically induced increment of the optical rotatory power $\Delta\rho$ was measured with an error of 2–10% at temperatures lower than $\sim$460 K and the mentioned error still increased at higher temperatures up to 10–25%, since high temperatures caused damage to the film electrodes; the EG coefficient was determined with the same error as the increment of optical rotatory power. The absolute values of the Faraday coefficients were determined with an error of 12%, while the relative changes in the Faraday rotation were measured more precisely (the error did not exceed 2%).

3. Results and discussion

3.1. Electrogyration

The gyration hysteresis loops for $Pb_5Ge_3O_{11}$:Cr crystals obtained at different temperatures close to the Curie point are shown in figure 2. One can see that the hysteresis loops become narrower when approaching T_c, due to the decreasing coercive field. Moreover, the slopes of the linear field dependences of the optical rotation power out of the hysteresis loops then increase. This indicates indirectly that the EG coefficient γ_{33} increases when the temperature increases up to 454 K.

One can see (figures 2(f) and (g)) that the field dependences of the optical rotation still remain nonlinear at temperatures of 454 and 455 K, while the hysteresis loop is shifted from the origin of coordinates up to $(0.3 - 0.7)$ kV mm^{-1}. Obviously, such behaviour could be explained by the fact that the application of a biasing field parallel or anti-parallel to the spontaneous polarization in the vicinity of T_c leads to additional smearing of the phase transition, shifting of T_c and induction of the ferroelectric phase and micro-domains in the whole sample volume. The electric field 0.3 kV mm^{-1} at $T = 454$ K is probably sufficient to induce the ferroelectric phase in the sample. Only when the electric field increases above this value does the domain structure begin to switch. Thus, we determine the temperature $T = 454$ K (in the cooling regime) to be a finishing point of nucleation of the ferroelectric phase in the matrix of the paraelectric phase of $Pb_5Ge_3O_{11}$:Cr crystals. This temperature is only 4 K higher

than the corresponding phase transition temperature for pure LG crystal. If we take into consideration the diffuse character of the second-order phase transition in $Pb_5Ge_3O_{11}$:Cr crystals (see figure 3), we arrive at the conclusion that the Curie temperature for the $Pb_5Ge_3O_{11}$:Cr crystals does not essentially differ from that of pure LG. It also follows from figure 3 that the processes related to the phase transition begin at $T = 457$ K in the cooling run (the temperature at which the optical activity appears) and they are completed at $T = 454$ K. Thus, the temperature region of 454–457 K might be defined as a region in which the phase transition is smeared. As one can easily see (figure 2(h)), the dependence of optical activity on the biasing field is close to linear at 457.5 K, thus implying that the crystals under study are in the paraelectric phase at this temperature. It is worth mentioning that linear dependences of optical rotation on the biasing field have been observed in the paraelectric phase up to 491.5 K (see figures 2(i)–(l)).

The natural optical activity for $Pb_5Ge_3O_{11}$:Cr crystals at room temperature is approximately the same as in pure LG. The magnitudes of the optical rotatory power for the opposite single-domain states are 5.4 and 6.2°mm^{-1} at $T = 300$ K (see figure 3). The difference in those values should be explained by the unipolarity of our samples. The mean value of the optical rotatory power for $Pb_5Ge_3O_{11}$:Cr crystals is therefore equal to $5.8 \pm 0.4°$mm^{-1} at $T = 300$ K, while, for example, for the pure $Pb_5Ge_3O_{11}$ it is $\sim$5.9°mm^{-1} [3, 4].

Let us now consider the thermodynamic potential for the proper, second-order, phase transition (for the terminology see, for example, [21]) observed in LG-type crystals:

$$F = F_0 + \alpha(T - T_c)^{(s)}P^2 + \tfrac{1}{2}\beta^{(s)}P^4 + \tfrac{1}{3}\delta^{(s)}P^6 + \cdots. \quad (16)$$

After accounting for equation (16) and the minimization conditions

$$\left(\frac{\partial F}{\partial^{(s)}P}\right) = 0, \qquad \left(\frac{\partial^2 F}{\partial^{(s)}P^2}\right) > 0, \qquad (17)$$

we obtain the solution

$$^{(s)}P^2 = \frac{\beta}{2\delta}\left(-1 \pm \sqrt{1 - \frac{4\alpha(T - T_c)\delta}{\beta^2}}\right) \qquad \text{at } T < T_c. \quad (18)$$

In SI units we have close to T_c

$$^{(s)}P^2 = -\frac{8\pi\alpha(T - T_c)}{\beta}. \quad (19)$$

Let us take equation (19) and the relations $g_3 = \gamma_{33}{}^{(s)}P_3$ and $\rho = \frac{\pi}{\lambda n_o}g_3$ into account. Then we get

$$\rho = \pm\frac{2\tilde{\gamma}_{33}}{\lambda n_o}\left[\frac{2\pi\alpha}{\beta}(T_c - T)\right]^{1/2}. \quad (20)$$

One can see (figure 3) that the dependence of optical rotation close to T_c is well fitted by the function $(T_c - T)^\mu$, where $\mu = 0.5$. Thus, equation (20) is satisfied for $Pb_5Ge_3O_{11}$:Cr crystals in the temperature region $T_c - 40$ K $< T < T_c - 5$ K. Notice that the critical exponent for the pure LG crystals has been found to be equal to 0.35 for the temperature
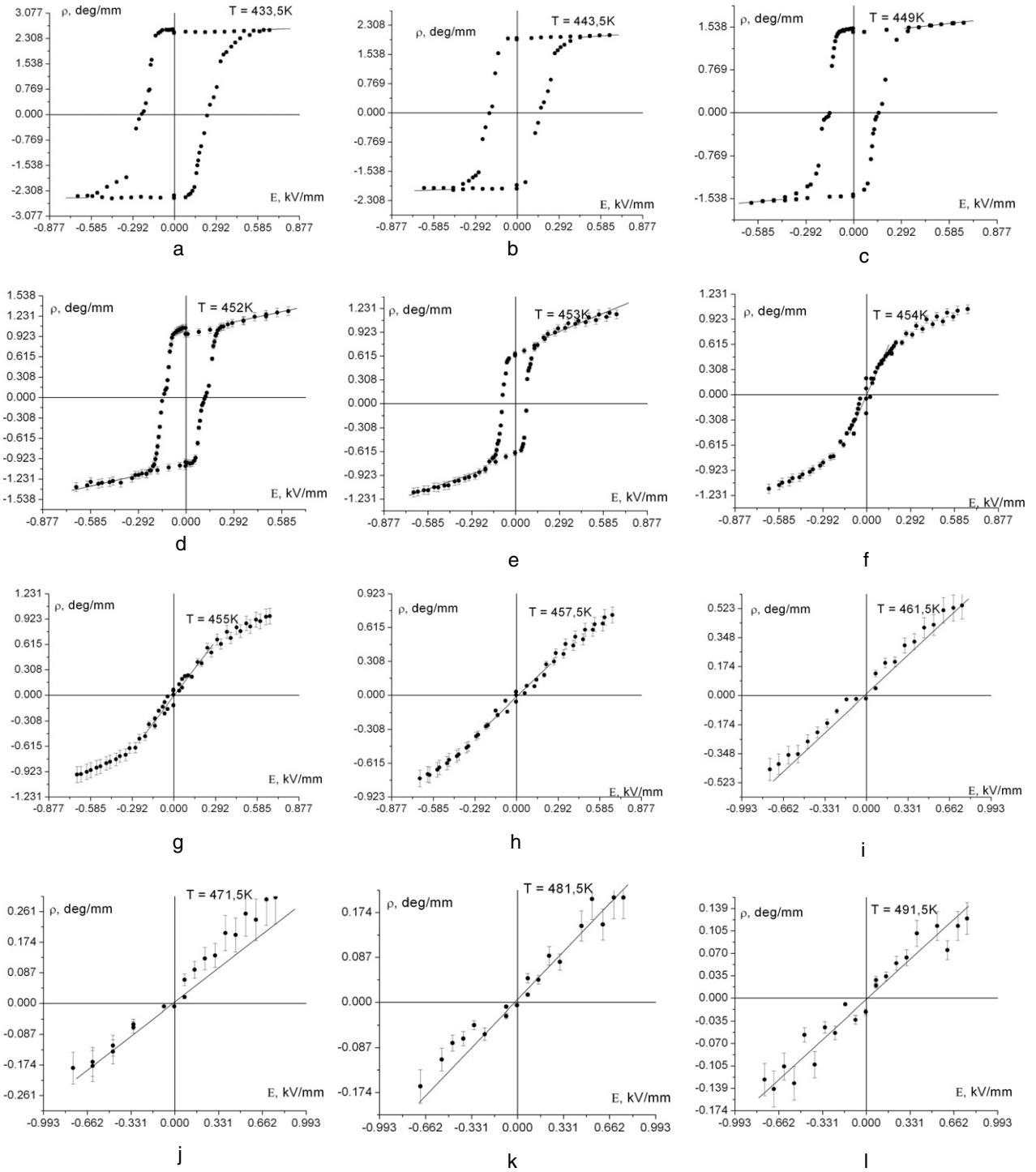
Figure 2. Dependences of the optical rotatory power for $Pb_5Ge_3O_{11}$:Cr crystals on the biasing field E_3 at different temperatures ($\lambda = 632.8$ nm). Bars show the relative errors and straight lines indicate the optical rotation increments associated with the EG.

interval between room temperature and $T = T_c - 3$ K [22]. It is interesting that we observe a tail of optical activity above $T_c - 5$ K and the dependence of optical activity on $(T_c - T)^{0.5}$ still remains linear below $T < T_c - 40$ K, though the slope is then changed. A similar behaviour was found earlier for the square of spontaneous polarization in pure LG crystals [10].

In order to calculate EG coefficient (see equation (11)), we used the data presented in figure 2 and the value of

the refractive index $n_o = 2.12$ for pure LG crystals [23]. This is reasonable, since the properties of pure and Cr-doped compounds (e.g. the values of the natural optical activity and the phase transition temperatures) are quite close. It is seen from figure 4(a) that the EG coefficient γ_{33} manifests anomalous behaviour in the vicinity of T_c. It reaches the value $\gamma_{33} = (3.1 \pm 0.3) \times 10^{-11}$ m V^{-1} at T_c. This is the largest coefficient measured so far for LG-type crystals and,
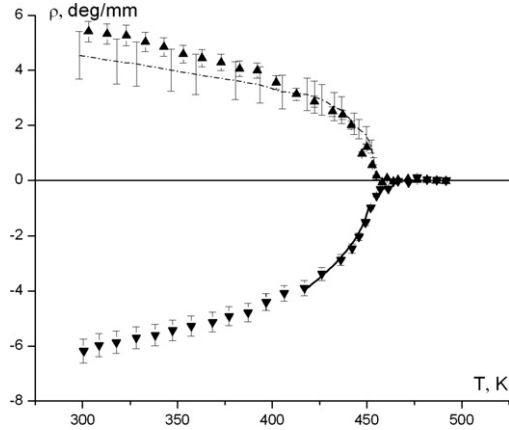
Figure 3. Temperature dependences of optical rotatory power for the opposite single-domain states (full triangles) in $Pb_5Ge_3O_{11}$:Cr crystals ($\lambda = 632.8$ nm; bars indicate the relative errors). The dashed line corresponds to the temperature dependence of optical rotatory power calculated with the spontaneous polarization data for the pure $Pb_5Ge_3O_{11}$ [10] and the relation $\rho = \frac{\pi}{\lambda n_o} \tilde{\gamma}_{klm}^{(s)} P_m$ (bars indicate the relative errors). The solid line corresponds to fitting of the temperature dependence, using the critical exponent $\mu = 0.5$.

maybe, the highest EG magnitude ever achieved. Based on the thermodynamic potential defined by equation (16), with the additional term $(-PE)$, and the condition $\varepsilon = \frac{\partial D}{\partial E}$, one readily obtains for the behaviour of dielectric permittivity:

$$\varepsilon = \frac{C}{T - T_c} \qquad \text{at } T > T_c \tag{21}$$

and

$$\varepsilon = \frac{C}{2(T_c - T)} \qquad \text{at } T < T_c, \tag{22}$$

where $C = (2\alpha)^{-1}$ is the Curie–Weiss constant. Considering the relation $\gamma_{33} = \tilde{\gamma}_{33}\varepsilon_0(\varepsilon_3 - 1) \simeq \tilde{\gamma}_{33}\varepsilon_0\varepsilon_3$ (with ε_0 being the permittivity of free-space), we have

$$\gamma_{33} = \frac{C\varepsilon_0\tilde{\gamma}_{33}}{T - T_c} \qquad \text{for } T > T_c, \tag{23}$$

and

$$\gamma_{33} = \frac{C\varepsilon_0\tilde{\gamma}_{33}}{2(T_c - T)} \qquad \text{for } T < T_c. \tag{24}$$

Hence,

$$\frac{(\gamma_{33}^{-1})_{T<T_c}}{(\gamma_{33}^{-1})_{T>T_c}} = 2. \tag{25}$$

As seen from figure 5, equation (25) is approximately satisfied in the temperature range close to T_c (the corresponding ratio is equal to ~2.4, close to the value of 3.0 found for pure LG crystals [10]). When calculating the EG coefficient $\tilde{\gamma}_{33}$, we used the temperature dependence of the dielectric permittivity for pure LG crystals presented in [10]. It is clear (see figure 4(b)) that the recalculated coefficient $\tilde{\gamma}_{33} \simeq \frac{\gamma_{33}}{\varepsilon_0\varepsilon_3}$ does not depend on temperature and is equal to $(6.0 \pm 1.0) \times 10^{-4}$ m^2 C^{-1}. Using this value, the relation $\rho = \frac{\pi}{\lambda n_o} \tilde{\gamma}_{klm}^{(s)} P_m$ and the temperature dependence of spontaneous polarization for the pure LG crystal [10], one can estimate the temperature dependence of the optical rotatory power
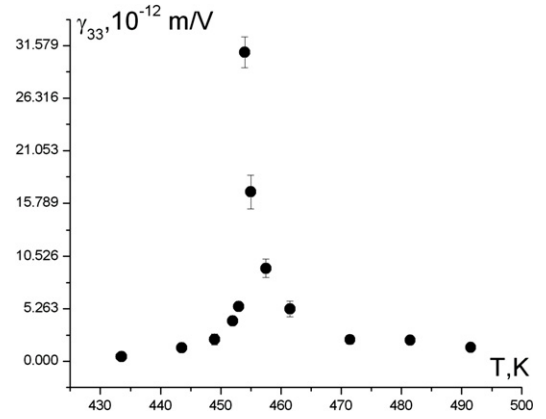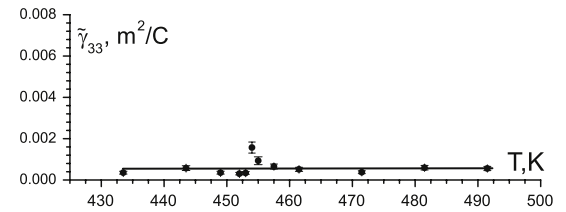
Figure 4. Temperature dependences of the EG coefficient γ_{33} for $Pb_5Ge_3O_{11}$:Cr crystals obtained experimentally (a) and the coefficient $\tilde{\gamma}_{33}$ (b) calculated with the relation $\tilde{\gamma}_{33} \simeq \frac{\gamma_{33}}{\varepsilon_0\varepsilon_3}$ ($\lambda = 632.8$ nm). Bars indicate the relative errors.
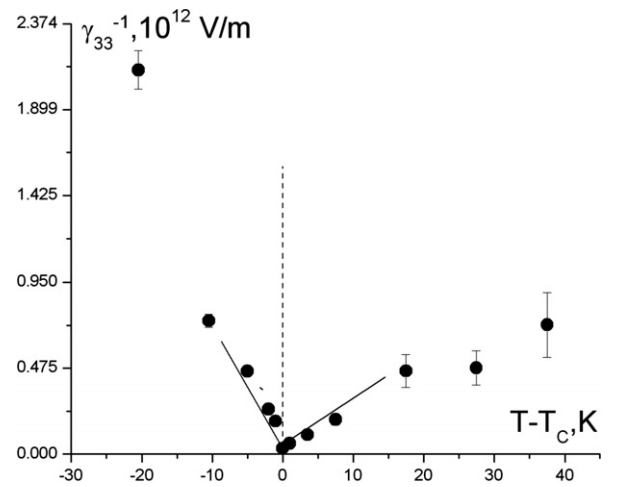

Figure 5. Dependence of the reciprocal EG coefficient on $T - T_c$ for $Pb_5Ge_3O_{11}$:Cr crystals (bars indicate the relative errors).

(see figure 3). The dependence obtained experimentally is in a good agreement with the theoretical one. This means that the phase transition in $Pb_5Ge_3O_{11}$:Cr crystals is indeed a proper ferroelectric one and the changes in the physical properties in the course of this transition (the optical activity in our case) are described in terms of the appearance of spontaneous electrical polarization. It is interesting to note that the Curie–Weiss constant for $Pb_5Ge_3O_{11}$:Cr crystals calculated on the basis of the temperature dependence of the EG coefficient is equal to
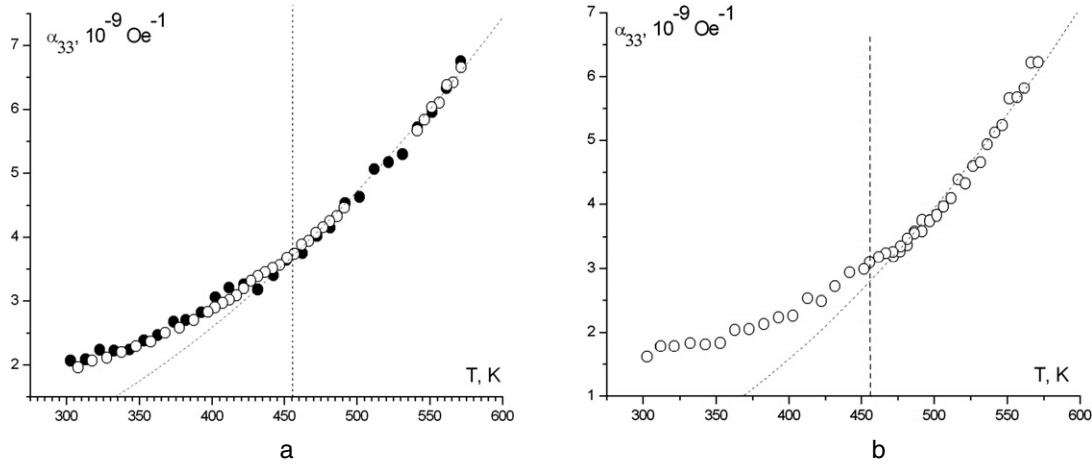
Figure 6. Temperature dependences of the Faraday coefficients for $Pb_5Ge_3O_{11}$ (a) and $Pb_5Ge_3O_{11}$:Cr (b) crystals at $\lambda = 632.8$ nm. The dashed line represents extrapolation of the temperature curve for the Faraday coefficients from the PE phase into the ferroelectric one. Open and full circles in (a) correspond to the sample thicknesses $d = 8.92$ mm and $d = 5.52$ mm, respectively.

$C = (0.4 \pm 0.1) \times 10^4$ K, while for the pure crystals it is $C \approx 1.04 \times 10^4$ K [10]. Finally, we have calculated the coefficients of thermodynamic potential ($\alpha \simeq 1.25 \times 10^{-4}$ K^{-1} and $\beta \approx 5$ m^4 C^{-2}), using the temperature dependence of optical rotatory power (figure 3), equation (20) and the Curie–Weiss constant.

3.2. Faraday rotation

The temperature dependences of the Faraday coefficients for $Pb_5Ge_3O_{11}$ and $Pb_5Ge_3O_{11}$:Cr crystals are presented in figure 6. As one can see, the Faraday coefficients change their behaviour in the vicinity of the phase transition. The temperature dependence in the PE phase has been fitted by a power function $\Delta\alpha_{33} = AT + BT^2$ and then approximated into the range of the ferroelectric phase. The difference between the approximating curve and the temperature dependence experimentally obtained for the ferroelectric phase corresponds to the increment of the Faraday coefficient caused by spontaneous polarization.

The fitting coefficients are equal to $A = -0.005\,36 \times 10^{-9}$ (Oe K)$^{-1}$ and $B = 2.96 \times 10^{-14}$ (Oe K^2)$^{-1}$ for pure LG crystals, while for $Pb_5Ge_3O_{11}$:Cr crystals the corresponding values are $A = -0.01 \times 10^{-9}$ (Oe K)$^{-1}$ and $B = 3.92 \times 10^{-14}$ (Oe K^2)$^{-1}$. The dependences of the increments of the Faraday coefficients on the spontaneous polarization are presented in figure 7 (notice that we have used the spontaneous polarization data for pure LG for both crystals studied here; see [10]). As seen from figure 7, these dependences are well fitted by a quadratic function (see equation (7)).

On the basis of equation (7) we have calculated the coefficients of the combined electro-magnetooptic effect for the PE phase. The coefficient is equal to $\tilde{\Theta}_{3333} = 2.9 \times 10^{-7}$ m^4 Oe^{-1} C^{-2} for pure LG crystals, while for $Pb_5Ge_3O_{11}$:Cr crystals it is larger, $\tilde{\Theta}_{3333} = 6.6 \times 10^{-7}$ m^4 Oe^{-1} C^{-2}. Using the relation

$$\Theta_{3333} = \tilde{\Theta}_{3333}\varepsilon_0^2(\varepsilon_{33} - 1)^2 \simeq \tilde{\Theta}_{3333}\varepsilon_0^2\varepsilon_{33}^2, \qquad (26)$$

with ε_{33} being the dielectric permittivity of pure LG crystals [10] and ε_0 the free-space dielectric permittivity, we have calculated the temperature dependences of the coefficients Θ_{3333} in the PE phase for both crystals (see figure 8) and the specific optical rotation referred to the electric and magnetic fields $E = 10^6$ V m^{-1} and $H = 13.3$ kOe, respectively (notice that just these values of the electric and magnetic fields have been used in [13] in the studies of magneto-electrooptic rotation). We recall here that, according to [13], magneto-electrooptic rotation in the PE phase, being proportional to the square of the electric field, has been nearly zero for $Pb_5Ge_3O_{11}$:Gd and equal to 0.3 $^\circ$cm^{-1} for $Pb_5Ge_3O_{11}$:Nd crystals in the vicinity of T_c. The bilinearity of the effect in both fields ($\rho \sim EH$) has been revealed in the ferroelectric phase close to T_c. As one can see (figure 8), the magneto-electrooptic rotation in the PE phase exceeds the experimental error and so can be detected experimentally.

The electric and magnetic fields used in our present experiments ($E = 0.3 \times 10^6$ V m^{-1} and $H = 3$ kOe at $d = 5.74$ mm) are smaller than those dealt with in [13]. According to the estimations, the optical rotation for such a field and sample thickness values should be about $\sim 3'$, which could hardly be carefully measured in our experiment. In fact, we have not observed any additional rotation induced by the common action of electric and magnetic fields in the overall temperature interval under study. Ill-defined changes in the Faraday rotation in the electric field have been detected only in the vicinity of T_c. They are probably caused by a shift in the phase transition temperature induced by the biasing field.

In the present study we have also measured the temperature dependence of the Faraday coefficient for pure LG crystals, using samples with different thicknesses (see figure 6(a)). It has been found that the increment of the Faraday rotation caused by spontaneous polarization differs for samples with different thicknesses, thus being evidently dependent on the optical path. As a consequence, the prediction of [19] concerning the independence of the magneto-polarization (or magneto-electric) phase difference on the optical path is questionable.
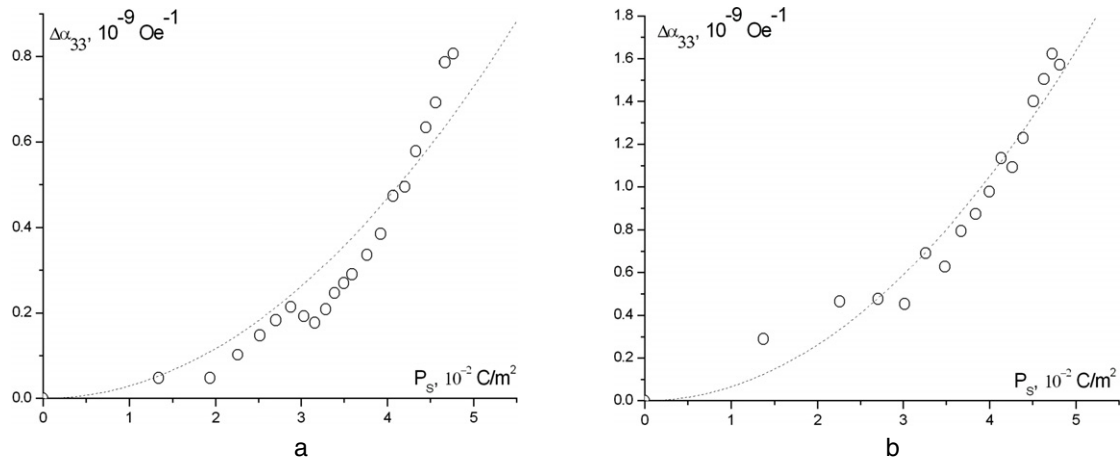
Figure 7. Dependences of increments of the Faraday coefficients on the spontaneous polarization for $Pb_5Ge_3O_{11}$ (a) and $Pb_5Ge_3O_{11}$:Cr (b) crystals at $\lambda = 632.8$ nm. Open circles correspond to the experimental data and dashed curves to the fitting by a quadratic function.
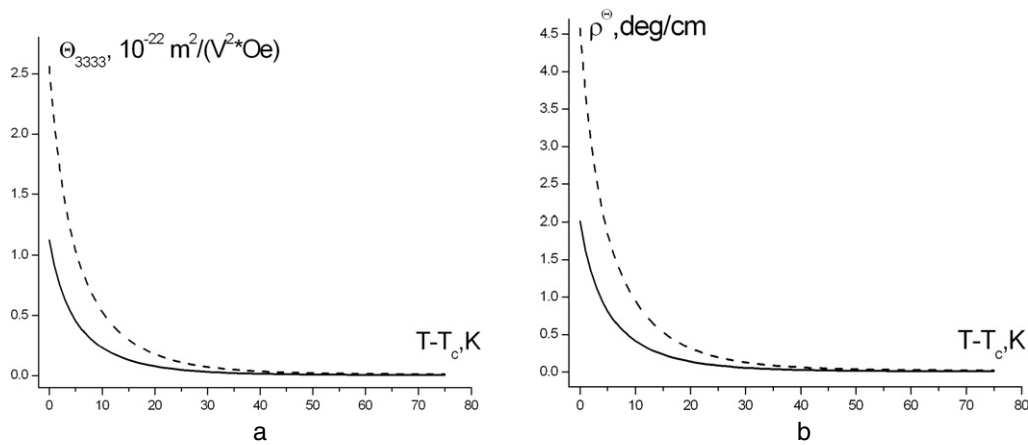

Figure 8. Calculated temperature dependences of the coefficient Θ_{3333} (a) and the specific optical rotation (b) induced by common action of the electric ($E = 10^6$ V m^{-1}) and magnetic ($H = 13.3$ kOe) fields for $Pb_5Ge_3O_{11}$ (solid curve) and $Pb_5Ge_3O_{11}$:Cr (dashed curve) crystals. The light wavelength is $\lambda = 632.8$ nm.

4. Conclusions

We have studied the EG effect in $Pb_5Ge_3O_{11}$:Cr crystals, induced by an external biasing field and spontaneous polarization in the vicinity of phase transition. It has been found that the EG coefficient reaches an extremely large value ($\gamma_{33} = (3.1 \pm 0.3) \times 10^{-11}$ m V^{-1} at T_c). This is probably the highest among the EG coefficients for all known materials. On the basis of the temperature dependences of the optical rotatory power and the EG coefficient it is shown that the phase transition in $Pb_5Ge_3O_{11}$:Cr crystals is a proper second-order ferroelectric one. The Curie–Weiss constant, the critical exponent for the order parameter, the dielectric permittivity and the coefficients of the thermodynamic potential in $Pb_5Ge_3O_{11}$:Cr crystals have been calculated following from the temperature dependences of optical activity and the EG coefficient.

We have revealed magneto-electrooptic rotation induced by the external magnetic field and spontaneous polarization in $Pb_5Ge_3O_{11}$ and $Pb_5Ge_3O_{11}$:Cr crystals. However, we have not detected the corresponding effect induced by the biasing electric field, because it is too small to be detected with the electric fields at our disposal. The value of the magneto-electrooptic coefficient estimated for the PE phase is equal to $\tilde{\Theta}_{3333} = 2.9 \times 10^{-7}$ m^4 Oe^{-1} C^{-2} in the case of $Pb_5Ge_3O_{11}$ and $\tilde{\Theta}_{3333} = 6.6 \times 10^{-7}$ m^4 Oe^{-1} C^{-2} for $Pb_5Ge_3O_{11}$:Cr crystals. It has been shown that the phase difference responsible for the magneto-electrooptic rotation and induced by the common action of electric and magnetic fields depends on the optical path.

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