Optical activity and critical exponent of the order parameter in lead germanate crystals.
1. The case of diffused phase transition in $Pb_5Ge_3O_{11}$ doped with Cu, Ba and Si ions

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Abstract

In the present paper an approach for evaluation of critical exponent of the order parameter at the diffused phase transition is developed on the basis of optical activity data. The temperature dependence of the optical activity in $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals is experimentally studied. The critical exponents obtained for $Pb_5Ge_3O_{11}:Cu^{2+}$ and $Pb_5(Ge_{0.6}Si_{0.4})_3O_{11}$ crystals are equal to 0.40 and 0.35, respectively. On the basis of the critical exponents evaluated it is shown that the solid solutions $(Pb_{(1-x)}Ba_x)_5Ge_3O_{11}$ with x = 0.05 stay quite close to tricritical point on the x,T-phase diagram ($\beta = 0.28$). The critical exponent for the pure lead germanate is also clarified.

Keywords: critical exponent, diffused phase transitions, optical activity, lead germanate crystals.

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1. Introduction

Electrogyration effect that consists in changes of optical activity of crystals under the action of biasing electric field has been well studied in a number of crystals [1–3]. Crystalline quartz [4], Rochelle salt [5], $(NH_2CH_2CO_2H)_3H_2SO_4$ (TGS) [6], KH_2PO_4 (KDP) [7, 8], alums [9] and many others belong to those crystals. One of the most convenient crystals are those belonging to lead germanate family, where the electrogyration effect can be studied without influence of any accompanying linear birefringence. The effect has been studied both in pure lead germanate crystals ($Pb_5Ge_3O_{11}$) and in solid solutions on its basis, $Pb_5Ge_{3x}Si_{3(1-x)}O_{11}$, $(Pb_{1-x}Bi_x)_5Ge_3O_{11}$ and $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$ [10–14]. The experimental data concerned with the studies of lead germanate crystals doped with Li^{3+}, La^{3+}, Eu^{3+}, Cd^{3+}, Nd^{3+} and Cr^{3+} are also available in the literature [15]. It has been found that the chemical substitution leads to shifts of the phase transition temperature, changes in the magnitude of electrogyration coefficients, as well as diffusing of the phase transition. For example, the electrogyration coefficient γ_{333} in $Pb_5Ge_3O_{11}:Cr^{3+}$ [16,17] measured in the vicinity of Curie point achieves the value of $(3.1 \pm 0.3) \times 10^{-11}$ m/V, which exceeds essentially the corresponding value for the pure lead germanate crystals. Let us remind that $Pb_5Ge_3O_{11}$ undergoes a second-order, proper ferroelectric phase transition at $T_c \simeq 450$ K, with the change of point symmetry group $\bar{6} \leftrightarrow 3$. Moreover, it has been shown in the recent papers that the temperature behaviour of electrogyration effect induced by spontaneous polarisation may be used for obtaining the data concerned with critical fluctuations occurred in the vicinity of phase transitions [18], in particular for the case of lead germanate crystals [19, 20].

The other known fact is that the temperature dependence of optical activity in the lead germanate may be used for deriving the critical exponent of temperature dependence of the order parameter. Actually, the specific rotation of polarisation plane ρ, which is induced by spontaneous polarisation P_3^s in the case of proper second-order ferroelectric phase transitions, can be presented as

$$\rho = \pi g_{33} / \lambda n_0 = \pi \gamma_{333} P_3^s / \lambda n_0 , \tag{1}$$

where g_{33} is the gyration tensor component, n_0 the ordinary refractive index, γ_{333} the component of the third-rank axial electrogyration tensor, and λ the wavelength of light in vacuum. The spontaneous polarisation is proportional to the specific rotation of light polarisation plane,

$$P_3^s \sim \rho \sim (T_c - T)^{\beta} , \tag{2}$$

where T_c is the Curie temperature and β the critical exponent of the order parameter. In case of well defined temperature T_c, determination of the critical exponent β is reduced to finding of the slope of the linear dependence

$$\log \rho \sim \beta \log(T_c - T) . \tag{3}$$

However, if the phase transition is diffused the Curie temperature cannot be correctly determined, thus leading to essential errors in determination of critical exponent β.

In some cases a procedure of searching the minimum of the temperature dependence of derivative $d\rho / dT$ is used for determining T_c. The temperature location of this minimum is taken as T_c. However, there are no proves or logical explanations of the correctness of such the approach. Let us note that solid solutions based on the lead germanate crystals reveal diffused phase transitions and so could be modelling objects for development of approach for determination of critical exponent of the order parameter.

Thus the present paper is devoted to the studies of optical activity and electrogyration effect, in particular in $Pb_5Ge_3O_{11}$:Cu^{2+} crystals, and development of appropriate approach for determining the critical exponent β.

2. Experimental

The change in gyration tensor components Δg_{kl} under the action of electric field is described by the relation

$$\Delta g_{kl} = g_{kl} - g_{kl}^0 = \gamma_{klm} E_m + \tau_{klmn} E_m E_n , \tag{4}$$

where g_{kl} and g_{kl}^0 denote the axial second-rank gyration tensors at $E_m, E_n \neq 0$ and

$E_m, E_n = 0$, respectively, while E_m, E_n are the electric field components, and γ_{klm}, τ_{klmn} are axial third- and fourth-rank tensors that describe linear and quadratic electrogyration effects, respectively. Similar relation may be written for description of the change in optical activity (gyration) in the course of proper ferroelectric phase transitions:

$$\Delta g_{kl} = g_{kl} - g_{kl}^{0} = \gamma'_{klm} P_m^s + \tau'_{klmn} P_m^s P_n^s \,, \tag{5}$$

where P_m^s is the spontaneous polarisation vector, and γ'_{klm}, τ'_{klmn} axial third- and fourth-rank electrogyration tensors presented in the units of reciprocal polarisation. Then the optical rotation power is given by

$$\rho = \frac{\pi}{\lambda n} G = \frac{\pi}{\lambda n} \Delta g_{kl} l_k l_l \,, \tag{6}$$

with G being the scalar gyration parameter, l_k, l_l the components of unit wave vector in spherical coordinate system, and n the refractive index.

For the lead germanate crystals, at the geometry of experiment ($E \parallel k \parallel Z$, with k being the wave vector of light) in both the paraelectric and ferroelectric phases the electrically induced optical rotation is defined by the relation

$$\rho = \frac{\pi}{\lambda n_o} \gamma_{333} E_3 \,, \tag{7}$$

where n_o is the ordinary refractive index.

The optical activity in $Pb_5Ge_3O_{11}$:Cu^{2+} crystal was studied for the light propagating along the optic axis and electric field applied along the same direction, with using of polarimetric set-up described in our recent paper [16]. The electric field was applied for switching domain structure and reaching a single-domain state. For the change of temperature we have used the temperature stage permitting temperature stabilisation with the accuracy not less than 0.01K. The plate of $Pb_5Ge_3O_{11}$:Cu^{2+} crystal with the faces perpendicular to the optic axis and the thickness of 5.5 mm was placed between transparent electrodes (glass plates covered by conductive tin oxide films), to which a high voltage has been applied. Lead germanate crystals used in our experiment were doped with 0.14 weight % of Cu.

3. Results and Discussion

3.1. Experimental results

The dependences of optical rotation power on the electric field for different temperatures in the vicinity of phase transition point are presented in Fig. 1. As one can see, as a result of decreasing of the coercive field at heating, the hysteresis loops become narrower with approaching the Curie temperature, whereas the slope of the linear part of field dependence of the optical rotation increases. The slope reaches its maximum at the temperature of $\Theta \simeq 444\text{ K}$ (the derivative taken at E=0 V/m).

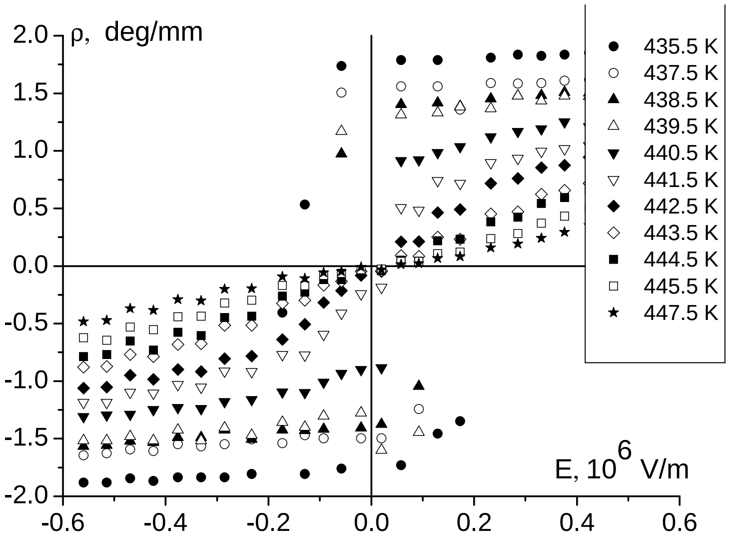

Fig. 1. Dependence of specific rotation of polarisation plane on the electric field for $Pb_5Ge_3O_{11}$:Cu^{2+} crystals in the temperature range of 435.5–447.5 K (λ = 632.8 nm).

The optical rotation power for $Pb_5Ge_3O_{11}$:Cu^{2+} crystals at the room temperature is approximately the same as for the pure lead germanate. For example, the specific optical rotation for $Pb_5Ge_3O_{11}$:Cu^{2+} crystals at T=300 K is equal to 5.65±0.45 deg/mm, while for $Pb_5Ge_3O_{11}$ crystals it is 5.9 deg/mm [10].

The thermodynamic potential for the proper second-order ferroelectric phase transition may be written as

$$F = F_0 + F_2(T - T_c)P^{2(s)} + \frac{1}{2}F_4P^{4(s)} + \frac{1}{3}F_6P^{6(s)} + \ldots, \tag{8}$$

where F_2, F_4, F_6, ... are the coefficients of thermodynamic potential, which do not depend on P^s and T.

It follows from this relation that

$$P^{2(s)} = -\frac{8\pi F_2(T - T_c)}{F_4} \tag{9}$$

and

$$\rho = \pm\frac{2\tilde{\gamma}_{333}}{\lambda n_o}\left[\frac{2\pi F_2}{F_4}(T_c - T)\right]^{0.5}, \tag{10}$$

where the critical exponent of spontaneous polarisation and optical rotation is $\beta = 0.5$.

With approaching to a tricritical point on the phase diagram this value is decreased to 0.25. As follows from the results presented in Fig. 2, the temperature dependence of optical activity in $Pb_5Ge_3O_{11}$:Cu^{2+} crystals manifests quite long “tail”, which suggests that the phase transition is diffused. If we assume the T_c temperature as being that of

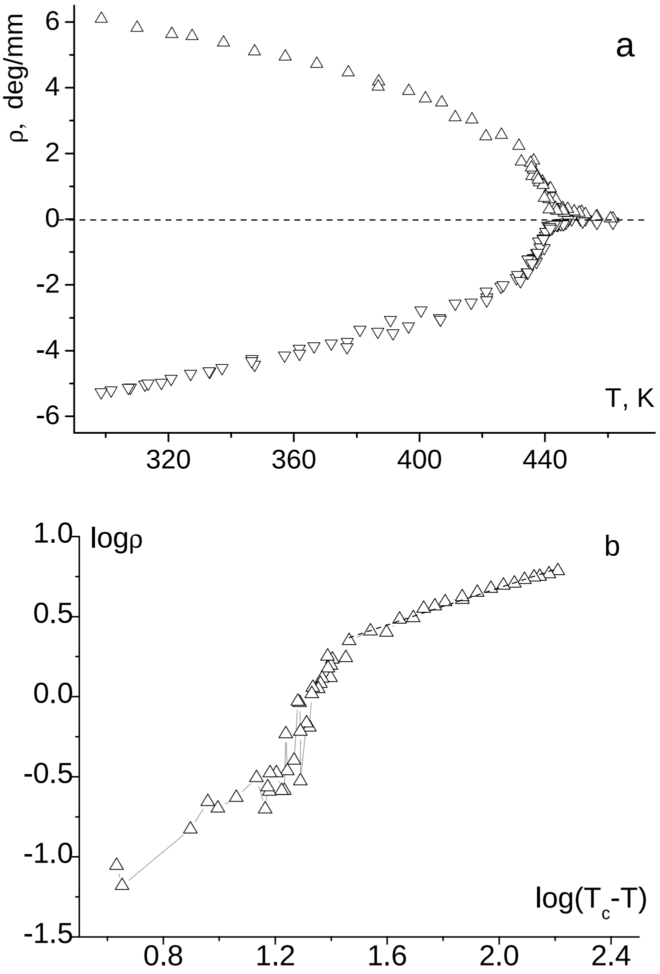

Fig. 2. (a) Temperature dependence of specific optical rotation for the opposite domains in $Pb_5Ge_3O_{11}$:Cu^{2+} crystals and for λ=632.8 nm (triangles), and (b) dependence of logarithm of specific optical rotation on logarithm of $T_c - T$.

complete disappearing of optical rotation ($460.8\,\mathrm{K}$), the critical exponent is determined as being equal to 0.58 ± 0.01 for the temperature range of $T_c - T > 30\,\mathrm{K}$. On the other hand, the temperature range $0 < T_c - T < 30\,\mathrm{K}$ may be characterised as a range of diffused phase transition, in which the dependence of optical rotation on $T_c - T$ on the log-log scale deviates from linear one and a “tail” of optical activity is observed. If one determines the T_c point as a minimum of $d\rho / dT$ derivative, it is equal to $435.7\,\mathrm{K}$. In this case the critical exponent is equal to $\beta = 0.35$ (see Fig. 3). For obtaining the temperature dependence of derivative of the optical activity, the experimental dependence has preliminary been smoothed and interpolated (see Fig. 3a).

As one can easily see, the critical exponents β determined on the basis of different criterions for choosing the Curie temperature differ essentially. Thus, it is necessary to consider peculiarities of determination of the T_c point and of the β parameter in a more detail.

3.2. Model of diffused phase transition

Let us consider a diffused phase transition caused by some scalar inhomogeneity, e.g. scalar defects which do not change the symmetry of crystalline matrix, of which existence affects distribution of the Curie temperature over a sample (this model is similar to

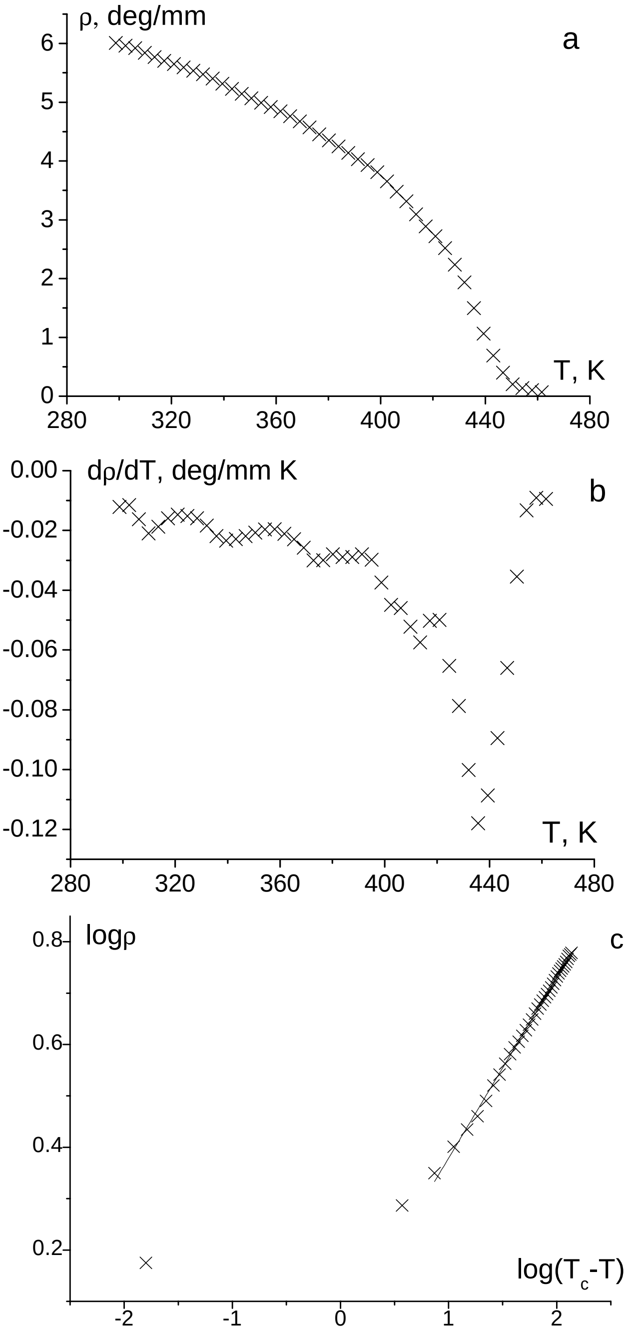

Fig. 3. Smoothed and interpolated temperature dependence of the optical activity in $Pb_5Ge_3O_{11}:Cu^{2+}$ crystals (a), its temperature derivative (b), and the dependence of the logarithm of specific optical rotation on logarithm of $T_c - T$ (c)

described in [21]). In this case the phase transition temperature should be distributed from one to the other point of crystalline sample within some temperature range $\Delta T = T_{cN} - T_{c1}$ (where T_{c1} and T_{cN} are the lowest and highest Curie temperatures).

Now let us divide the sample into N homogeneous elementary cells (in our simulation we have taken N to be $N=10^6$), the Curie temperature of each of which (the i th cell) is determined as $T_{ci}=T_{cN}-i\times\Delta T/N$. In this case the temperature dependence of the order parameter and the optical rotation may be described by the relation

$$P_3^s\sim\rho\sim g_{33}=\frac{A}{N}\sum_{i=1}^{N}(T_{cN}-i\times\Delta T/N-T)^{\beta}\,, \tag{11}$$

where A is the proportionality coefficient which is the same for all the elementary cells. After fitting the temperature dependence of optical activity presented in Fig. 3, one can determine the critical exponent. The fitting itself is presented in Fig. 4. It has been found that $\beta=0.40$ for the case of fitting parameters $A=0.75\,\mathrm{deg/mm\,K}$, $T_{cN}=460\,\mathrm{K}$ and the region of phase transition diffusing being equal to $\Delta T=30\,\mathrm{K}$. Thus, the temperature which characterises the condition when half a sample undergoes the phase transition is defined by the relation $\Theta=T_{cN}-\Delta T/2$. For the case of $Pb_5Ge_3O_{11}$:Cu^{2+} crystals this temperature is equal to $\Theta=445\,\mathrm{K}$.

Let us remind that this temperature point agrees with that experimentally obtained as a maximum of the slope of field-induced optical activity. As one can see, the fitted curve of Fig. 4 agrees well with the experimental one ($R^2=0.998$). At the same time, the point $435.7\,\mathrm{K}$ determined as a minimum of temperature dependence of the optical activity derivative differs essentially from the Θ point.

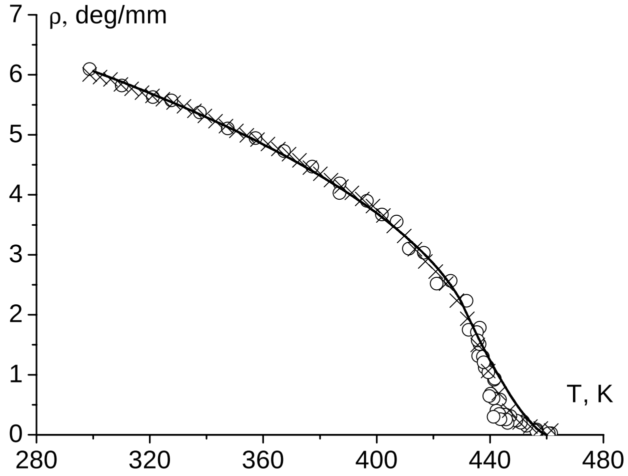

Fig. 4. Temperature dependences of optical activity in $Pb_5Ge_3O_{11}$:Cu^{2+} crystals: open circles are experimental data, crosses represent the smoothed and interpolated experimental data, and solid curve is a result of fitting with formula (11).

Now let us consider the temperature behaviour of the gyration tensor component g_{33} for $Pb_5(Ge_{0.6}Si_{0.4})_3O_{11}$ crystals [19]. As seen from Fig. 5, the fitted curve agrees well with the experimental dependence for the fitting parameters $\beta = 0.33$, $A = 0.48 \times 10^{-5}\,\mathrm{K}^{-1}$, $T_{cN} = 318\,\mathrm{K}$ and $\Delta T = 14\,\mathrm{K}$. The temperature $\Theta = 311\,\mathrm{K}$ is almost equal to the temperature determined from the derivative (310 K – see [19]), while the critical exponent obtained in [19] ($\beta = 0.35$) also agrees with that obtained in the present work. However, the range of phase transition diffusing derived from the data [19] is mach narrower than our value $\Delta T = 14\,\mathrm{K}$.

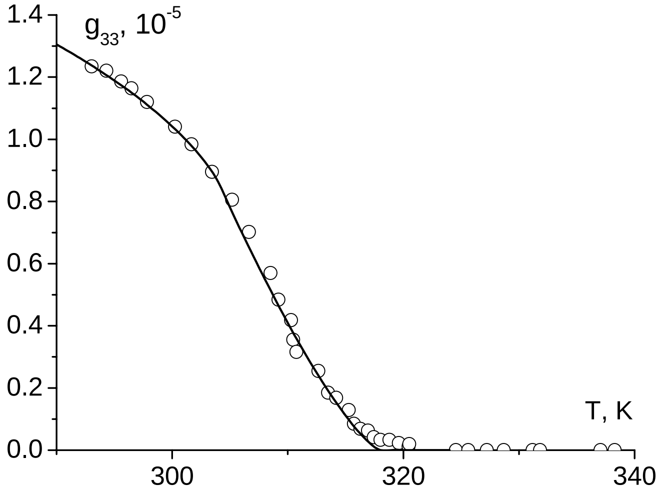

Fig. 5. Temperature behaviour of gyration tensor component g_{33} for $Pb_5(Ge_{0.6}Si_{0.4})_3O_{11}$ crystals [19] (open circles) and theoretical dependence given by formula (11) (solid curve).

Let as analyse the temperature behaviour of gyration tensor component for the solid $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$ solutions [12, 21], where x = 0, 0.02, 0.05. The critical exponent for the pure lead germanate crystals determined using the procedure of searching of the temperature location of the minimum of derivative of the gyration tensor (T = 447.9 K) is equal to $\beta = 0.37 \pm 0.01$ (see Fig. 6a, open circuits). On the other side, if we choose the temperature of the phase transition as a point where the optical activity in the heating run completely disappears (i.e., T = 452.1 K), the critical exponent is equal to $\beta = 0.44 \pm 0.01$ (see Fig. 6a, full circuits). However, if we use the procedure of fitting of the temperature dependence of gyration tensor with Eq. (11), the obtained critical exponent of the order parameter is found to be equal to $\beta = 0.40$ (see Fig. 6b), with the other fitting parameters being $A = 0.55 \times 10^{-5}\,\mathrm{K}^{-1}$, $T_{cN} = 452\,\mathrm{K}$ and $\Delta T = 7\,\mathrm{K}$. Thus, we have clarified the critical exponent for the pure lead germanate. Moreover, it follows from our fitting procedure that the phase transition in this crystal is slightly diffused. This is a reason for discrepancies concerned with the critical exponent value obtained in different works.

For the solid solutions with x = 0.02 and 0.05, the temperature dependences of the gyration tensor are presented in Fig. 7. It has been found that the best fitting of

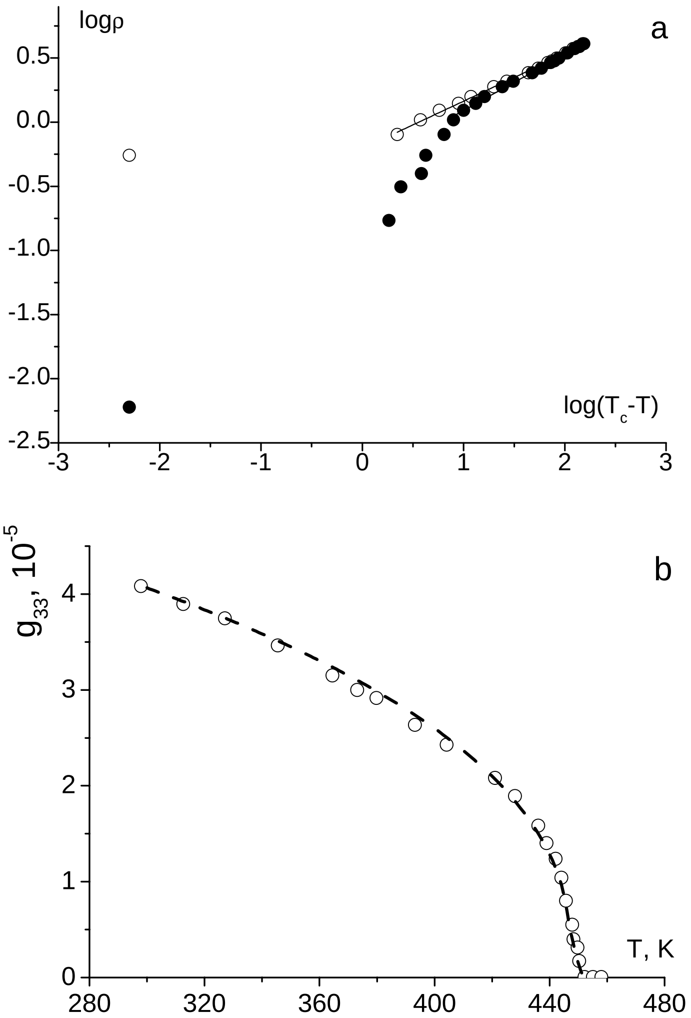

Fig. 6. Temperature dependences of logarithm of gyration tensor on logarithm of $T_c - T$ for the pure lead germanate crystals (see explanation in text) (a) and on the linear scale (b) [21].

experimental behaviour takes place with the fitting parameters equal to $\beta = 0.3$, $A = 0.87\times10^{-5}\,\mathrm{K}^{-1}$, $T_{cN} = 420\,\mathrm{K}$ and $\Delta T = 15\,\mathrm{K}$ for the solid solutions with x = 0.02, while for x = 0.05 we have $\beta = 0.28$, $A = 0.81\times10^{-5}\,\mathrm{K}^{-1}$, $T_{cN} = 366\,\mathrm{K}$ and $\Delta T = 20\,\mathrm{K}$. One can see that the critical exponent β approaches the value of 0.25 with increasing concentration of Ba ions. Thus, one concludes that the solid solutions $(Pb_{0.95}Ba_{0.05})_5Ge_3O_{11}$ are under conditions very close to tricritical point on their x,T-phase diagram. Notice that this conclusion correlates well with that obtained by us on the basis of analysing of concentration behaviour of the coefficients of thermodynamic potential for solid the solutions $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$ [22].

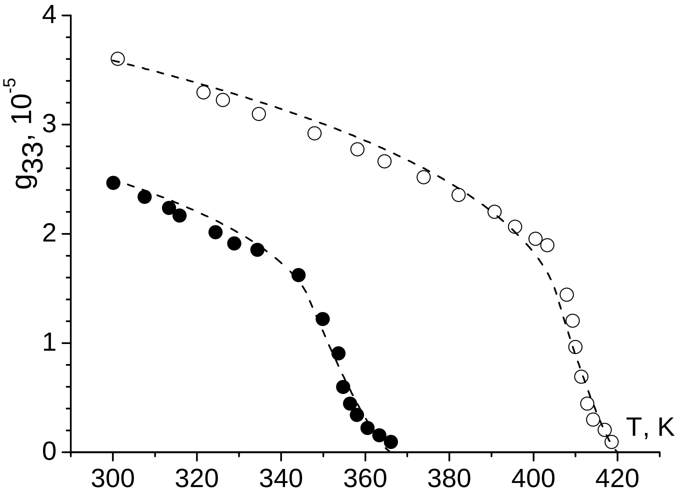

Fig. 7. Temperature dependences of gyration tensor component g_{33} for the solid solutions $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$ at x = 0.02 (open circuits) and x = 0.05 (full circuits) [12, 22]. The dashed curves correspond to fitting with formula (11).

4. Conclusions

In this paper we have shown that the critical exponent of order parameter in case of diffused phase transitions can be determined on the basis of optical activity data using the approach dividing a sample into a number of homogeneous cells with their own Curie temperatures. The corresponding relations allowing to determine the critical exponent have been derived. It has been shown that the critical exponent for the order parameter of lead germanate crystals doped with cuprum ions is equal to 0.40 while for the lead germanate with 40% substitution of Ge ions with Si ones is lower ($\beta = 0.35$). The temperature range where the phase transition is diffused can also be obtained. It has been shown that this range amounts to $\Delta T = 30\,\mathrm{K}$ for $Pb_5Ge_3O_{11}$:Cu^{2+} crystals, while for $Pb_5(Ge_{0.6}Si_{0.4})_3O_{11}$ we have $\Delta T = 14\,\mathrm{K}$. It has been shown that the critical exponent β decreases from the value 0.40 for the pure lead germanate down to 0.28 for $(Pb_{0.95}Ba_{0.05})_5Ge_3O_{11}$ solid solutions, thus suggesting a closeness of tricritical point on the concentration-temperature phase diagram for the compound mentioned.

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Анотація. *В даній роботі розвинуто підхід для отримання значення критичного індексу параметру порядку при розмитих фазових переходах на основі даних про температурну поведінку оптичної активності. Експериментально досліджена температурна поведінка оптичної активності в кристалах* $Pb_5Ge_3O_{11}:Cu^{2+}$. *Отримані значення критичних індексів для кристалів* $Pb_5Ge_3O_{11}:Cu^{2+}$ *і* $Pb_5(Ge_{0,6}Si_{0,4})_3O_{11}$, *які дорівнюють 0,40 та 0,35, відповідно. На основі отриманих значень критичних індексів показано, що тверді розчини* $(Pb_{(1-x)}Ba_x)_5Ge_3O_{11}$ *з* $x = 0,05$ *знаходяться близько до трикритичної точки на* x,T*- фазовій діаграмі (* $\beta=0.28$ *). Уточнене, також, значення критичного індексу для чистих кристалів германату свинцю.*