Optical activity and critical exponent of the order parameter in lead germanate crystals.

1. The case of diffused phase transition in Pb$_5$Ge$_3$O$_{11}$ doped with Cu, Ba and Si ions

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Received: 22.10.2009

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$_5$Ge$_3$O$_{11}$:Cu$^{2+}$ crystals is experimentally studied. The critical exponents obtained for Pb$_5$Ge$_3$O$_{11}$:Cu$^{2+}$ and Pb$_5$(Ge$_{0.6}$Si$_{0.4}$)$_3$O$_{11}$ 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$_x$)$_5$Ge$_3$O$_{11}$ 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.

PACS: 33.55.Ad, 77.80.Bh, 64.60.Fr, 77.84Bw, 78.20Wc, 61.72.Ww

UDC: 535.56

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$_2$CH$_2$CO$_2$H)$_3$H$_2$SO$_4$ (TGS) [6], KH$_2$PO$_4$ (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$_5$Ge$_3$O$_{11}$) and in solid solutions on its basis, Pb$_5$Ge$_{3x}$Si$_{3(1-x)}$O$_{11}$, (Pb$_{1-x}$Bi$_x$)$_5$Ge$_3$O$_{11}$ and (Pb$_{1-x}$Ba$_x$)$_5$Ge$_3$O$_{11}$ [10–14]. The experimental data concerned with the studies of lead germanate crystals doped with Li$^{3+}$, La$^{3+}$, Eu$^{3+}$, Cd$^{2+}$, 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 $\gamma_{333}$ in Pb$_5$Ge$_3$O$_{11}$:Cr$^{3+}$ [16,17] measured in the vicinity of Curie point achieves the value of $(3.1\pm0.3)\times10^{-11}$ m/V, which exceeds essentially the corresponding value for the pure
lead germanate crystals. Let us remind that Pb$_5$Ge$_3$O$_{11}$ undergoes a second-order, proper ferroelectric phase transition at $T_c = 450$ 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 polarization 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 polarization plane $\rho$, which is induced by spontaneous polarization $P_3'$ in the case of proper second-order ferroelectric phase transitions, can be presented as

$$\rho = \frac{\pi g_{33}}{\lambda n_0} = \frac{\pi \gamma'_{333} P_3'}{\lambda n_0},$$  \hspace{1cm} (1)

where $g_{33}$ is the gyration tensor component, $n_0$ the ordinary refractive index, $\gamma'_{333}$ the component of the third-rank axial electrogyration tensor, and $\lambda$ the wavelength of light in vacuum. The spontaneous polarization is proportional to the specific rotation of light polarization plane,

$$P_3' - \rho = (T_c - T)^\beta,$$  \hspace{1cm} (2)

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

$$\log \rho - \beta \log(T_c - T).$$  \hspace{1cm} (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 $\beta$.

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$_5$Ge$_3$O$_{11}$:Cu$^{2+}$ crystals, and development of appropriate approach for determining the critical exponent $\beta$.

2. Experimental

The change in gyration tensor components $\Delta g_{kl}$ under the action of electric field is described by the relation

$$\Delta g_{kl} = g_{kl} - g_{kl}^0 = \gamma_{klm} E_m + \tau_{klmn} E_m E_n,$$  \hspace{1cm} (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 $\gamma_{klm}, \tau_{klmn}$ 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:

$$\Delta g_{ui} = g_{ui} - g_{ui}^0 = \gamma_{klm}^* P_{klm}^* + \tau_{klmn}^* P_{klm}^*,$$

where $P_{klm}^*$ is the spontaneous polarisation vector, and $\gamma_{klm}, \tau_{klmn}$ axial third- and fourth-rank electrogyration tensors presented in the units of reciprocal polarisation. Then the optical rotation power is given by

$$\rho = \frac{\pi}{\lambda n} G = \frac{\pi}{\lambda n} \Delta g_{ui} l_i l_j,$$

with $G$ being the scalar gyration parameter, $l_i, l_j$ 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

$$\rho = \frac{\pi}{\lambda n} \gamma_{33}^* E_3,$$

where $n_o$ is the ordinary refractive index.

The optical activity in Pb$_5$Ge$_3$O$_{11}$: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$_5$Ge$_3$O$_{11}$: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 $\Theta = 444$ K (the derivative taken at $E=0$ V/m).
The optical rotation power for Pb$_5$Ge$_3$O$_{11}$: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$_5$Ge$_3$O$_{11}$:Cu$^{2+}$ crystals at $T=300$ K is equal to 5.65 ±0.45 deg/mm, while for Pb$_5$Ge$_3$O$_{11}$ crystals it is 5.9 deg/mm [10].

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

$$ F = F_0 + F_2 (T - T_c) P^{2(s)} + \frac{1}{2} F_4 P^{4(s)} + \frac{1}{3} F_6 P^{6(s)} + ..., $$

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

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

and

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

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$_5$Ge$_3$O$_{11}$: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...
complete disappearing of optical rotation (460.8 K), the critical exponent is determined as being equal to 0.58 ± 0.01 for the temperature range of $T_c - T > 30$ K. On the other hand, the temperature range $0 < T_c - T < 30$ 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 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 $\beta$ 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 $\beta$ 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
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 \( T_i = T_{ci} - i \times \Delta T / N \). In this case the temperature dependence of the order parameter and the optical rotation may be described by the relation

\[
P_{33}^g = \rho - g_{33} = A \sum_{i=1}^{N} \left( T_{ci} - i \times \Delta T / N - T \right)^\beta,
\]

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 \( A = 0.75 \text{deg/mmK} \), \( T_{ci} = 460 \text{K} \) and the region of phase transition diffusing being equal to \( \Delta T = 30 \text{K} \). Thus, the temperature which characterises the condition when half a sample undergoes the phase transition is defined by the relation \( \Theta = T_{ci} - \Delta T / 2 \). For the case of PbGEO\(_{11}\):Cu\(^{2+}\) crystals this temperature is equal to \( \Theta = 445 \text{K} \).

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 K determined as a minimum of temperature dependence of the optical activity derivative differs essentially from the \( \Theta \) point.

![Fig. 4. Temperature dependences of optical activity in Pb5Ge3O11: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).](image)

Now let us consider the temperature behaviour of the gyration tensor component \( g_{33} \) for Pb5(Ge0.6Si0.4)3O11 crystals [19]. As seen from Fig. 5, the fitted curve agrees well with
the experimental dependence for the fitting parameters $\beta = 0.33$, $A = 0.48 \times 10^{-5} \text{K}^{-1}$, $T_\text{c} = 318 \text{K}$ and $\Delta T = 14 \text{K}$. The temperature $\Theta = 311 \text{K}$ 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 much narrower than our value $\Delta T = 14 \text{K}$.

Let us analyse the temperature behaviour of gyration tensor component $g_{33}$ for $\text{Pb}_5(\text{Ge}_{0.8}\text{Si}_{0.2})_3\text{O}_{11}$ crystals [19] (open circles) and theoretical dependence given by formula (11) (solid curve).

Let us analyse the temperature behaviour of gyration tensor component for the solid $\text{Pb}_{1-x}\text{Ba}_x\text{Ge}_3\text{O}_{11}$ 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 ($T = 447.9 \text{K}$) 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., $T = 452.1 \text{K}$), 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 $A = 0.55 \times 10^{-5} \text{K}^{-1}$, $T_\text{c} = 452 \text{K}$ and $\Delta T = 7 \text{K}$. 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
experimental behaviour takes place with the fitting parameters equal to $\beta = 0.3$, $A = 0.87 \times 10^{-3}$ K$^{-1}$, $T_{cN} = 420$ K and $\Delta T = 15$ K for the solid solutions with $x = 0.02$, while for $x = 0.05$ we have $\beta = 0.28$, $A = 0.81 \times 10^{-3}$ K$^{-1}$, $T_{cN} = 366$ K and $\Delta T = 20$ K. One can see that the critical exponent $\beta$ approaches the value of 0.25 with increasing concentration of Ba ions. Thus, one concludes that the solid solutions $(Pb_{0.95}Ba_{0.05})_5Ge_2O_{11}$ 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 solutions $(Pb_{1-x}Ba_x)_5Ge_2O_{11}$ [22].

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].
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 $\Delta T = 30\,\text{K}$ for $\text{Pb}_3\text{Ge}_2\text{O}_{11}:\text{Cu}^{2+}$ crystals, while for $\text{Pb}_3(\text{Ge}_{0.6}\text{Si}_{0.4})_2\text{O}_{11}$ we have $\Delta T = 14\,\text{K}$. It has been shown that the critical exponent $\beta$ decreases from the value 0.40 for the pure lead germanate down to 0.28 for $(\text{Pb}_{0.96}\text{Ba}_{0.04})_3\text{Ge}_2\text{O}_{11}$ solid solutions, thus suggesting a closeness of tricritical point on the concentration-temperature phase diagram for the compound mentioned.

References


Optical activity


Анотація. В даній роботі розроблено підхід для отримання значення критичного індексу параметру порядку при розмитих фазових переходах на основі даних про температурну поведінку оптичної активності. Експериментально досліджено температурну поведінку оптичної активності в кристалах Pb₅Ge₃O₁₁:Cu²⁺. Отримані значення критичних індексів для кристалів Pb₅Ge₃O₁₁:Cu²⁺ і Pb₅(Ge₀,₆Si₀,₄)₃O₁₁, які дорівнюють 0,40 та 0,35, відповідно. На основі отриманих значень критичних індексів показано, що тверді розчини (Pb₁₋ₓBaₓ)₅Ge₃O₁₁ з х = 0,05 знаходяться близько до трикритичної точки на х.T- фазової діаграми (β=0,28). Уточнене, також, значення критичного індексу для чистих кристалів германату свинцю.