Raman opalescence near the phase transition point in lead germanate crystals

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Abstract. It was established that the nature of opalescence near the phase transition point in a lead germanate crystal is dynamic and is caused by a sharp increase in the spectral intensity of Raman scattering on a soft mode responsible for the instability of the crystal lattice near the phase transition temperature. Experimental studies of combination opalescence in a soft mode were performed using the method of constructing isofrequency temperature dependences of the spectral intensity for fixed values of the frequency shift \( \Omega \) of the scattered radiation relative to the frequency \( \omega_0 \) of the exciting radiation. It is shown that the experimentally observed anomalies of the spectral intensity agree with the dynamic theory of phase transitions in crystals, based on the concept of softening of the crystal lattice in the phase transition region.

1. Introduction and background

Lead germanate (Pb₅Ge₃O₁₁) is a uniaxial ferroelectric having a high pyroelectric effect [1, 2] and reversible (with a change in the direction of spontaneous polarization) optical activity [3]. The perspective of its use for recording holographic information, as well as in the form of films and ceramics in elements of ferroelectric memory is noted [2, 4–6].

The Raman scattering spectra (RS) of lead germanate crystals have been studied by many authors [7-20]. The temperature dependence of the Raman spectrum in the range of 115–445 K was analyzed in [7]. Three modes were detected. Mode with the lowest frequency is a soft mode. Near 270 K mode, two low-frequency modes interacted. At the same time, a soft mode of about 400 K was becoming overdamped, and it was impossible to trace its evolution above this temperature. In [8], a low-frequency Raman in a lead germanate crystal was studied in a wide temperature range. It was established that at 20 K before \( T_c \), the intensity of the central peak begins to increase sharply, reaching a maximum at \( T_c \). In this case, the authors believe that this anomaly has a static character. In [9], the Raman spectra were analyzed in the temperature range of 296–765 K. It was found that part of the lattice oscillations disappear at the phase transition temperature, and in the frequency range above 200 cm⁻¹, no changes in the Raman spectrum were observed with the exception of thermal line broadening. The temperature behavior of the \( A_{LO} \) modes was studied in [10] and the Lyddane-Sachs-Teller ratio was tested for feasibility. It was found that above \( T_c \), for some oscillations of the A-type LO-TO
splitting is non-zero. This contradicts the selection rules in the point symmetry group C_{3h}. In this connection, the authors propose to consider the symmetry of the paraelectric phase of lead germanate as pseudosymmetry. In this case, the measured temperature dependence of the A_{LO} mode obeys the Lyddane-Sachs-Teller relation. The temperature dependence of the Raman spectra of the Pb_{5-x}Ba_{x}Ge_{3}O_{11} solid solution was studied in [12, 18]. It has been established that an increase in the barium concentration leads to a blurring of the phase transition, a significant broadening of the central peak and lowers the transition temperature. The transition temperature obtained from the analysis of the Raman spectra is larger than from data based on dielectric measurements. In this case, the Curie constant is almost the same for various doping concentrations, but in a pure sample it is almost twice as large. The temperature dependence of the low-frequency Raman spectra of a Pb_{5}Ge_{3}O_{11} crystal was studied in [13]. It was found that in the temperature range of 30 K ≤ T ≤ 80 K the model of the damped harmonic oscillator is not suitable for approximating the Raman spectra. It is concluded that the existing models are not suitable for describing a strongly damping soft mode in a lead ferroelectric germanate and require further theoretical work. In [14], new measurements of the temperature dependence of the Raman spectrum of lead germinate were made. Strongly dependent on a temperature, A-type modes disappearing at the phase transition temperature were observed. It has been established that the TO-LO polar mode splitting is rather small. The article [15] is devoted to the study of the phase transition in lead germinate with pressure changes using Raman spectroscopy. It was found that at a pressure of 23 kbar, a ferroelectric-paraelectric phase transition occurs at room temperature. Gruneisen parameters were calculated for various oscillations. In this case, due to the strong elastic scattering of light, a soft mode of this crystal was not detected during the phase transition. The crystallization of amorphous Pb_{5}Ge_{3}O_{11} was studied in [16] by the Raman scattering method. It has been established that the Raman spectrum of an annealed crystal at 410 °C is different from the corresponding Raman spectrum of an annealed crystal at a higher temperature. The frequencies of the combinational satellites decrease with an increase in the annealing temperature of the crystal, which is associated with the voltage arising during the crystallization process. In [17], the soft mode of a lead germinate crystal doped with silicon is analyzed based on the approximation of the Raman spectrum by various susceptibility functions. It is established that an increase in the concentration of silicon lowers the frequency of the soft mode. This is confirmed by the results of direct dielectric measurements [21, 22]. The temperature dependence of the frequency of the soft mode obeys the Curie-Weiss law.

According to the well-known theory of soft modes [23, 24] the low-frequency fundamental vibration of the A type of a lead germinate crystal (with frequency of 31 cm^{-1} at room temperature) should play the role of a soft mode responsible for the phase transition in this crystal. The obtained isotherm dependencies of RS spectra near the phase transition point show that the frequency of the soft mode is difficult to measure at temperatures close to T_{c} due to the large attenuation of this mode. Therefore, recording the isothermal spectra of Raman scattering at various fixed temperatures, close to the phase transition temperature, is not enough to compare the experimental data with the theory of the soft mode and establish the nature of opalescence. Therefore, to analyze the characteristics of the soft mode in this crystal, we propose a method of isofrequency temperature dependences [25, 26] recorded at fixed frequencies Ω near the frequency ω_{0} of the exciting line (Ω = 0-100 cm^{-1}).

The purpose of this paper was to quantitatively analyze the anomalies of the Raman intensity in the soft mode of a lead germinate crystal according to the investigation of the isofrequency temperature
dependences of the Raman spectra in this crystal in order to establish the characteristics of the effective soft mode over a wide temperature range, including the phase transition point. To clarify these dependencies, we compared them with the data on the isotemperature Raman spectra in $x(zz)y$ geometry.

2. Characteristic of lead germanate crystal structure

The crystal structure of lead germanate refers to the trigonal system with space group $C_{3h} (P3)$ and in the elementary cell there are 3 molecules. The elementary cell has the following parameters: $a=1.0251$ nm, $c=1.0685$ nm [27-29]. At temperature $T_c=451$ K in this crystal the second-kind ferroelectric phase transition of the type of displacement to the paraelectric phase occurs. Spatial group of the paraelectric phase in this crystal is $P6_3/m$. Lead germanate has a complex crystal structure. It consists of alternating layers of GeO$_4$ tetrahedra and double tetrahedra Ge$_2$O$_7$ located along the ferroelectric axis. Moreover, its structure contains empty channels running along the edges of the unit cell, parallel to the optical axis [27-29].

Table 1 shows the results of the group-theoretical classification of fundamental vibrations and the selection rules for the optical processes of the lead germanate lattice modes (point group-$C_3$) [30-33]. Here $\alpha$ are the vectors of partial translations of the spatial group $C_{3h} (P3)$; $n_0$ and $m_0$ are the numbers of atoms or molecular groups remaining in place during the symmetry transformation; $\chi_v$, $\chi_{v'}$, $\chi_{v''}$, $\chi_{v'''}$ are the characters of the vector, pseudovector, Raman and hyper Raman representations, respectively; $\chi_{opt}$, $\chi_{tr}$ and $\chi_{lib}$ are the characters of the optical, translational and librational representations, respectively; $a_i$ and $a_{ij}$ are the components of the vector $a_i$ and the tensor $a_{ij}$ of the Raman scattering, respectively, where $i$, $j$ and $k$ correspond to the Cartesian coordinate system.

According to the Table 1, we see that the optical representation in this case has the form:

$$T_{opt}=56A+56E$$ (1)

From the relation (1) and Table 1, it follows that in the low-temperature phase of lead germanate there are modes of the A and E type active in the Raman spectra and IR spectra.

| $C_{3h}$ | E | C$_3$ | $C_{3h}$ | $a_i$ | $a_{ij}$ |
|----------|---|-------|---------|-------|-------|
| $\alpha$ | 0;0;0 | 0;0;0 | 0;0;0 | $a_x$ | $a_{xx}$, $a_{yy}$, $a_{zz}$ |
| A | 1 | 1 | 1 | $e^{2\pi i/3}$ | $e^{2\pi i/3}$ |
| E | 1 | $e^{2\pi i/3}$ | $e^{2\pi i/3}$ | $a_x$, $a_y$ | $a_{xx}$, $a_{yy}$, $a_{xy}$, $a_{xz}$, $a_{yz}$ |
| $\chi_v$ | 3 | 0 | 0 | $e^{2\pi i/3}$ | $e^{2\pi i/3}$ |
| $\chi_{v'}$ | 3 | 0 | 0 | $e^{2\pi i/3}$ | $e^{2\pi i/3}$ |
| $\chi_{v''}$ | 9 | 0 | 0 | $e^{2\pi i/3}$ | $e^{2\pi i/3}$ |
| $\chi_{v'''}$ | 6 | 0 | 0 | $e^{2\pi i/3}$ | $e^{2\pi i/3}$ |
| $\chi_{v''''}$ | 3 | 0 | 0 | $e^{2\pi i/3}$ | $e^{2\pi i/3}$ |
| $\chi_{v'''''}$ | 18 | 0 | 0 | $e^{2\pi i/3}$ | $e^{2\pi i/3}$ |
3. Experimental data on the isotemperature and isofrequency dependences of the Raman spectra in crystalline lead germanate

Figure 1 shows the isotemperature RS spectra of lead germanate crystal with scattering geometry \( x(zz)y \). With this geometry, according to the selection rules (see Table 1), a soft mode responsible for the phase transition should manifest itself. The dashed line indicates the background level.

From Figure 1 we can see observe four vibrational modes in low-frequency region. The oscillation with the lowest frequency has the behavior predicted by the theory of a soft mode. When the crystal is heated, it shifts in frequency from 32 cm\(^{-1}\) at a temperature of 311 K to 22 cm\(^{-1}\) at a temperature of 388 K. In less than 73 K to the temperature of the phase transition, it becomes overdamped and disappears with further heating of the crystal. The spectral position of the other maxima remains virtually unchanged.

Figure 2 shows the isofrequency temperature dependences of the Raman spectra in lead germanate crystals, i.e. the temperature variations of the Raman spectral intensity for fixed frequencies of the
spectrometer $\Omega$, for frequencies in the 3-21 cm$^{-1}$ range. In this figure, the solid arrow corresponds to the Raman signal, and the dashed arrow corresponds to the central peak, which appears at the phase transition point. The numbers in the curves in Figure 2 correspond to the fixed frequencies of the spectrometer at frequencies $\Omega$ in cm$^{-1}$. The dashed line indicates the background level. The isofrequency temperature dependences of the Raman spectra were obtained on a double DFS-24-type monochromator with a spectral resolution of 0.5 cm$^{-1}$. At the same time, the accuracy of the temperature measurement was 0.5 K.

Figure 2. Isofrequency dependences $i(\Omega,t)$ near the point of phase transition in lead germanate crystals at fixed frequency values; the sharp peak on the left corresponds to quasistatic opalescence; the maximum on the right is due to the "softening" of the crystal lattice.

From Figure 2, it follows that when the fixed frequency $\Omega$ of a Raman spectrometer decreases, the position of the maximum of the spectral intensity of the isofrequency dependence on the temperature scale tends to the transition temperature, and its intensity increases monotonically, that is, Raman opalescence is observed. Two intensity maxima are detected: the first maximum (marked by a dashed arrow) is due to the manifestation of a central peak; the second one (marked by a solid arrow) is a manifestation of the soft lattice mode.

4. The theory of the isofrequency temperature dependences of the Raman scattering on a soft mode in lead germanate crystals.

In accordance with the semi-phenomenological theory of Landau phase transitions [34-36] we encounter the following expansion problem with respect to the parameter $\eta$ of the thermodynamic potential:

$$
\Phi = \Phi_0 + \frac{A\eta^2}{2} + \frac{B\eta^4}{4} + \frac{C\eta^6}{6} + \ldots + \frac{D(\nabla\eta)^2}{2}
$$

In equilibrium conditions the following formula takes:

$$
\left. \frac{\partial \Phi}{\partial \eta} \right|_{\eta_0} = 0; \quad \left. \frac{\partial^2 \Phi}{\partial \eta^2} \right|_{\eta_0} > 0
$$
For the second-order phase transitions $B>0$. For simplicity, we also assume that $C=D=0$. Below the phase transition point ($T<T_\text{c}$), we obtain:

\[
\eta_0^2 = \frac{A}{B} A < 0
\]

Above the transition point ($T>T_\text{c}$), the order parameter vanishes ($\eta_0 = 0$) and, in accordance with (3), $A>0$. Thus, we come to the conclusion that at the phase transition point $A = 0$. The simplest approximation is the dependence: $A = a | T-T_\text{c} |$. Fluctuations of the order parameter $\eta = \eta_0 + \Delta \eta$ correspond to the vibrations $\Delta \eta$ of the crystal lattice, which determine the symmetry of the low-symmetry phase. From the relation (3) we obtain the equations of motion and the temperature dependence of the frequency $\Omega$ of the corresponding damped oscillator:

\[
m \Delta \ddot{\eta} = -3 \Delta \dot{\eta} + 3 B \eta_0^2 \dot{\eta} + \Omega_0^2 \eta_0^2 = 0; \Gamma = \frac{\delta}{m},
\]

\[
\Omega_0^2 = \frac{2 A}{m} \left( \frac{2a(T - T_\text{c})}{m} (T < T_\text{c}), \Omega_0^2 = \frac{A}{m} \left( \frac{a(T - T_\text{c})}{m} (T > T_\text{c}).
\]

The normal vibration of the crystal lattice, which determines the symmetry of the low-temperature phase, corresponds to the soft mode. The frequency of this mode, in accordance with (5), should decrease anomalously as the transition temperature is approached and vanish at the phase transition point.

The spectral intensity of inelastic light scattering in one soft mode approximation can be represented in the form:

\[
I(\Omega, T) = n(\Omega) + 1 \ln \chi(\Omega, T)
\]

Here $n(\omega)$ is the known Bose-Einstein factor, and $\chi(\omega, T)$ is the susceptibility corresponding to the soft mode. For the approximation used the following formula takes place:

\[
\chi(\Omega, T) = \frac{1}{\Omega_0^2 - \Omega^2 - i\Gamma\Omega}
\]

We confine ourselves to the analysis of the phase transitions occurring at sufficiently high temperatures when

\[
n(\Omega, T) = \frac{1}{\exp \frac{kT}{\hbar\Omega} - 1} = \frac{kT}{\hbar\Omega}
\]

Let us introduce the so-called reduced spectral intensity $i(\omega, x) = I(\omega, T)/T$; in the case of a low-symmetry phase ($x=\Theta-T=\Theta-T_\text{c}$) accurate to a constant factor, we obtain:

\[
i(\Omega, x) = \frac{\Gamma \eta_0^2(x)}{[\Omega_0^2(x) - \Omega^2] + \Gamma^2\Omega^2}
\]

For the second-order phase transitions, we assume that \( \Omega_0^2(x) = ax^\gamma \) and \( \eta_0^2(x) = bx^{2\beta} \), \( \Omega_0, \Gamma \) is the frequency and damping of the soft mode, $\beta$ and $\gamma$ are the critical indices characterizing the dynamics of the phase transition. Then expression (9) takes the form:

\[
i(\Omega, x) = \frac{b\Gamma x^{2\beta}}{(ax^\gamma - \Omega^2)^2 + \Gamma^2\Omega^2}
\]

The coordinates of the maximum of the function $i(\Omega, x)$ accordingly take the form:
\[
x^0_0 = \frac{\Omega}{2a(y-\beta)} \left[ \Omega(y-2\beta) + \sqrt{\Omega^2 y^2 + 4\beta \Gamma^2 (y-\beta)} \right]
\]

\[
i_0 = \frac{b\Gamma}{2a(y-\beta)} \left( \frac{\Omega(y-2\beta) + \sqrt{\Omega^2 y^2 + 4\beta \Gamma^2 (y-\beta)}}{\Omega(y-2\beta) + \sqrt{\Omega^2 y^2 + 4\beta \Gamma^2 (y-\beta)}} \right)^{2/\gamma}
\]

(11)

(12)

In particular, for \( \gamma = 1 \) and \( \beta = 0.5 \) (the mean field approximation for a second-order phase transition), we obtain:

\[
i(\Omega, x) = \frac{b\Gamma x}{(ax-\Omega^2)^2 + \Gamma^2 \Omega^2}, \quad x_0 = \frac{\Omega \sqrt{\Omega^2 + \Gamma^2}}{a}, \quad i_0 = \frac{b\Gamma}{2a\Omega \sqrt{\Omega^2 + \Gamma^2 - \Omega}}
\]

(13)

when \( \gamma = 1 \) and \( \beta = 0.25 \) (a transition close to the tricritical point) takes place the following:

\[
i(\Omega, x) = \frac{b\Gamma x}{(ax-\Omega^2)^2 + \Gamma^2 \Omega^2}, \quad x_0 = \frac{\Omega (\Omega + \sqrt{4\Omega^2 + 3\Gamma^2})}{3a} - \frac{3b\Gamma \sqrt{3\Omega \left[ \Omega + \sqrt{4\Omega^2 + 3\Gamma^2} \right]}}{\Omega^2 \sqrt{a} \left[ \sqrt{4\Omega^2 + 3\Gamma^2} - 5\Omega \right] + 9 \left( \Omega^2 + \Gamma^2 \right)}
\]

(14)

when \( \gamma = 1 \) and \( \beta = 1/3 \) we obtain:

\[
i(\Omega, x) = \frac{b\Gamma x^{2/3}}{(ax-\Omega^2)^2 + \Gamma^2 \Omega^2}, \quad x_0 = \frac{\Omega (\Omega + \sqrt{9\Omega^2 + 8\Gamma^2})}{4a} - \frac{16b\Gamma \left[ \Omega (\Omega + \sqrt{9\Omega^2 + 8\Gamma^2}) \right]^{2/3}}{\sqrt{16a^2 \Omega^2 \left[ \Omega + \sqrt{9\Omega^2 + 8\Gamma^2} \right] \left[ \sqrt{9\Omega^2 + 8\Gamma^2} - 7\Omega \right] + 16 \left( \Omega^2 + \Gamma^2 \right)}}
\]

(15)

We use the experimental data for \( \Omega = 21 \) cm\(^{-1} \) to determine the constants \( a \) and \( b \) in (13-15). In accordance with the form of the isothermal spectrum near the transition temperature (see Figure 1), we approximately assume that \( \Gamma \approx 24 \) cm\(^{-1} \). Table 2 compares the results of calculating the parameters \( x_0 \) and \( i_0 \) of the isofrequency dependences with the experimental data.

**Table 2.** Comparison of the calculation data of the parameters \( x_0 \) and \( i_0 \) with the experiment.

| \( \Omega \) (cm\(^{-1} \)) | \( x_0 \) (K) | \( \gamma=1 \) | \( \gamma=1 \) | \( \gamma=1 \) | \( \gamma=1 \) | \( \gamma=1 \) | \( \gamma=1 \) | \( \gamma=1 \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( \Delta x_0 = 1 \) K | \( \Delta i_0 = 1 \% \) | \( \Delta i_0 = 1 \% \) | \( \Delta i_0 = 1 \% \) | \( \Delta i_0 = 1 \% \) | \( \Delta i_0 = 1 \% \) | \( \Delta i_0 = 1 \% \) | \( \Delta i_0 = 1 \% \) | \( \Delta i_0 = 1 \% \) |
| 3 | 9 | 9 | 7 | 7 | 185 | 307 | 1001 | 664 |
| 6 | 22 | 18 | 14 | 15 | 133 | 174 | 389 | 294 |
| 8.5 | 37 | 26 | 22 | 23 | 121 | 135 | 249 | 201 |
| 11 | 43 | 35 | 31 | 32 | 105 | 115 | 181 | 154 |
| 13.5 | 55 | 45 | 41 | 42 | 99 | 103 | 141 | 126 |
| 16 | 62 | 55 | 52 | 53 | 94 | 95 | 116 | 108 |
Figure 3 (a-c) illustrate the obtained isofrequency dependences for different values of the fixed frequencies $\Omega$, and the values of the corresponding functions $x_0$ and $i_0$ calculated from the formulae (13-15), and experimental data. The numbers in the curves in Figure 3 (a-c) correspond to the fixed frequencies $\Omega$ (in cm$^{-1}$) of the spectrometer. The dashed line indicates the background level.
Figure 3. Comparison of isofrequency dependences for different values of fixed frequencies (blue lines - theory, green lines - experiment) for several values of the parameters: a- $\gamma = 1$ and $\beta = 0.5$, b- $\gamma = 1$ and $\beta = 0.25$, c- $\gamma = 1$ and $\beta = 1/3$. The numbers in the curves are fixed frequencies in cm$^{-1}$.

As it can be seen from the Table 2 and Figure 3 (a-c), the best agreement between the theory and experiment corresponds to the values $\gamma = 1$ and $\beta = 0.5$, which corresponds to the closeness of the investigated transition in lead germanate to the second-order phase transition. As can be seen from Figure 3 (a-c), the theory predicts a further sharp increase in the spectral intensity with decreasing frequency $\Omega$, which corresponds to the soft-mode Raman opalescence effect.

5. Conclusions

Thus, the analysis of the isotemperature Raman spectra at various temperatures in lead germanate has shown that in the low-frequency region of the spectrum for the polarization geometry $x(zz)y$ the fundamental lattice soft mode, classified by the type of symmetry A, becomes overdamped and for less than 73 K its position is not possible to determine in the Raman scattering spectra.

On the basis of the isofrequency temperature dependences method, it was found that there are two intensity maxima on these dependences: the first maximum corresponds to a narrow central peak. The second maximum is related to the fundamental soft mode responsible for the softening of the crystal lattice. Using the oscillator model, the theoretical isofrequency dependences were compared with the experimental data, and it was established that the best fit is the mean field approximation corresponding to a second-order phase transition.

The observed regularities are of a general nature, and can become apparent for other crystals undergoing a structural phase transition with a soft tilting mode such as strontium titanate [37].

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