

## Isofrequency Opalescence in Ferroelectrics

V. S. Gorelik<sup>a, b, \*</sup>, P. P. Sverbil<sup>a</sup>, A. I. Vodchits<sup>c</sup>, and Yu. P. Voinov<sup>a</sup>

<sup>a</sup>Lebedev Physical Institute, Russian Academy of Sciences, Moscow, 119333 Russia

<sup>b</sup>Bauman Moscow State Technical University, Moscow, 105005 Russia

<sup>c</sup>Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, 220072 Belarus

\*e-mail: gorelik@sci.lebedev.ru

**Abstract**—Isofrequency dependences of the spectral intensities of inelastic scattering in LiTaO<sub>3</sub>, Pb<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub>, BaTiO<sub>3</sub>, and KNbO<sub>3</sub> crystals are registered at a fixed frequency of the spectrometer close to that of the exciting radiation. Results from soft mode analysis are presented.

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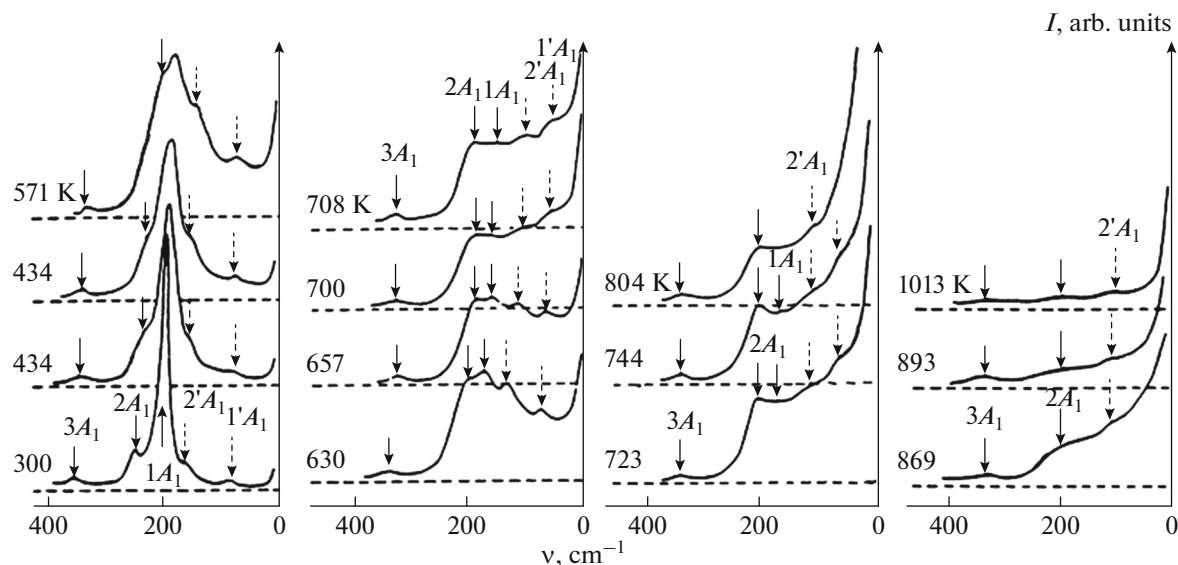
### INTRODUCTION

The effect of isofrequency opalescence is observed in the form of an abrupt increase in the spectral intensity of scattered radiation in crystals (e.g., LiTaO<sub>3</sub> and BaTiO<sub>3</sub>) at a fixed frequency of the spectrometer close to the line of excitation when approaching the temperature of a phase transition.

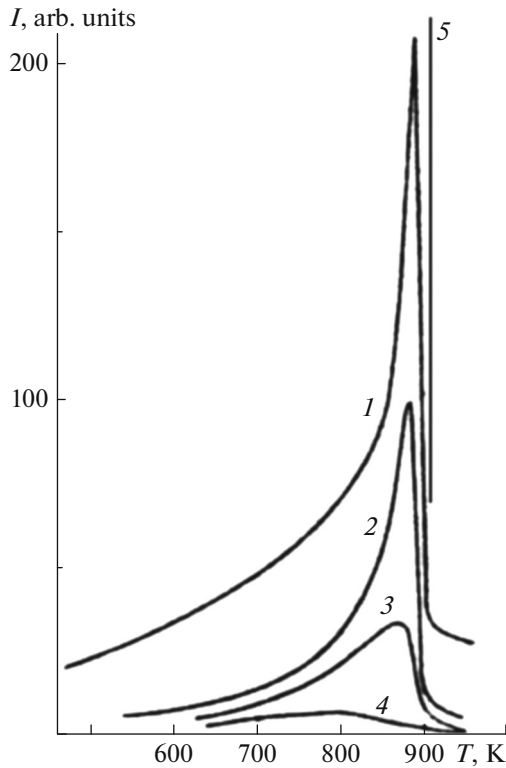
According to the dynamic theory of phase transitions in crystals [1–3], so-called soft modes should be observed in the vibration spectrum. The frequencies of

these modes tend to zero when approaching a phase transition point.

Searches for a soft mode [4–9] in Raman spectra near the points of structural phase transitions show that this effect is indeed observed for a number of ferroelectrics. However, it is difficult to observe the spectra of soft modes when analyzing isothermal dependences, due to the strong interaction between several modes and the relaxation nature of such modes. Figure 1 shows such isothermal dependences of the Raman scattering intensities characteristic of lithium tantalate crystals in a range of temperatures



**Fig. 1.** Low-frequency LiTaO<sub>3</sub> Raman spectra for  $X(ZZ)Y$  geometry at temperatures ranging from 300 to 1013 K ( $T_c = 898$  K). Solid arrows indicate the positions of the fundamental  $A_1(Z)TO$  vibrations; dashed arrows indicate the positions of additional vibrations.



**Fig. 2.** Isofrequency temperature dependences (curves 1–4) of the reduced spectral intensity of light scattering characteristic of lithium tantalate crystals for scattering geometry  $X(ZZ)Y$  in the soft mode near the phase transition point at fixed frequencies ( $\Omega = 2, 4, 16,$  and  $86 \text{ cm}^{-1}$ , respectively). Solid line (5) at  $T = T_c$  corresponds to the central peak of scattered light.

that includes a phase transition point. As we can see from Fig. 1, the soft mode was already overdamped far from the phase transition point, allowing us to measure its frequency in the required range of temperatures.

It was proposed in [10–13] that the so-called isofrequency temperature dependences of the spectral intensities for inelastically scattered radiation be registered at fixed spectrometer frequencies near that of the exciting radiation.

As our experiments showed (see Fig. 2), an effect of isofrequency opalescence is in this case observed that consists of an abrupt increase in the spectral intensity of isofrequency light scattering at frequency  $\omega'$  for low values of frequency  $\Omega$  of spectrometer detuning from exciting radiation frequency  $\omega_0$ :

$$\Omega = \omega_0 - \omega'.$$

Anomalies in the spectral intensities of the isofrequency dependences characteristic of ferroelectrics are observed for certain Raman scattering polarization geometries  $X(ZZ)Y$  corresponding to the conditions of

soft mode excitation allowed by the rules of selection—completely symmetrical vibration—in the low-temperature phase.

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

$$I(\Omega, T) = \eta_0^2(T)[m(\Omega) + 1] \text{Im} \chi(\Omega, T). \quad (1)$$

Here,  $(\eta_0)^2 = bx = b(T_c - T)$ ;  $m(\Omega, T)$  is the Bose–Einstein factor and  $\chi(\Omega, T)$  is the dielectric susceptibility corresponding to the soft mode:

$$\chi(\Omega, T) = \frac{1}{\Omega_0^2 - \Omega^2 - i\Gamma\Omega}. \quad (2)$$

At sufficiently high temperatures,

$$m(\Omega, T) = \left( \exp\left(\frac{\hbar\Omega}{kT}\right) - 1 \right)^{-1} \approx \left(\frac{kT}{\hbar\Omega}\right). \quad (3)$$

We now introduce reduced spectral intensity  $i(\Omega, x) = I(\Omega, T)/T$ . For the low-symmetry phase, we thus obtain

$$i(\Omega, x) = \frac{\Gamma bx}{[ax - \Omega^2]^2 + \Gamma^2 \Omega^2}, \quad (4)$$

where  $\Omega_0^2 = ax$ ;  $bx = b(T_c - T)$ ; and  $\Omega_0$  and  $\Gamma$  are the frequency and damping of the soft mode.

The maximum of function  $i(\Omega, x)$  is obtained for the following values of  $i_0, x_0$ :

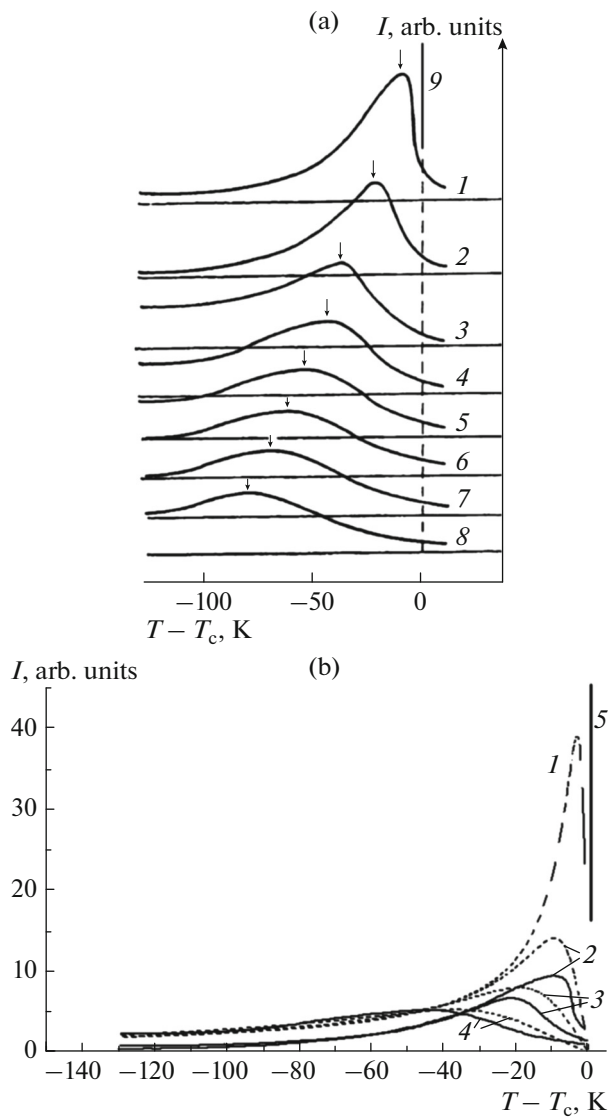
$$i_0 = \frac{\Gamma}{2\Omega(\sqrt{\Omega^2 + \Gamma^2} - \Omega)}, \quad x_0 = \frac{\Omega\sqrt{\Omega^2 + \Gamma^2}}{a}. \quad (5)$$

We investigated crystals of lead germanate  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ . Figure 3a shows the registered isofrequency temperature dependences of spectral intensity for inelastically scattered radiation in lead germanate crystals near phase transition point  $T_c = 451 \text{ K}$ . The isofrequency temperature dependences of spectral intensity for inelastically scattered radiation in lead germanate crystals approximated according to formula (4) are given in Fig. 3b.

The isofrequency temperature dependences in Raman spectra were also measured for barium titanate polycrystals (Fig. 4a) and potassium niobate (Fig. 4b) at fixed frequencies:  $\Omega = 7, 12, 24, 40 \text{ cm}^{-1}$  (curves 1–4 in Fig. 4a) and  $\Omega = 5, 10, 20, 40 \text{ cm}^{-1}$  (curves 1–4 in Fig. 4b).

## CONCLUSIONS

The observed effect of isofrequency opalescence allows us to identify structural phase transitions in single crystals and in crystalline powders, and to obtain

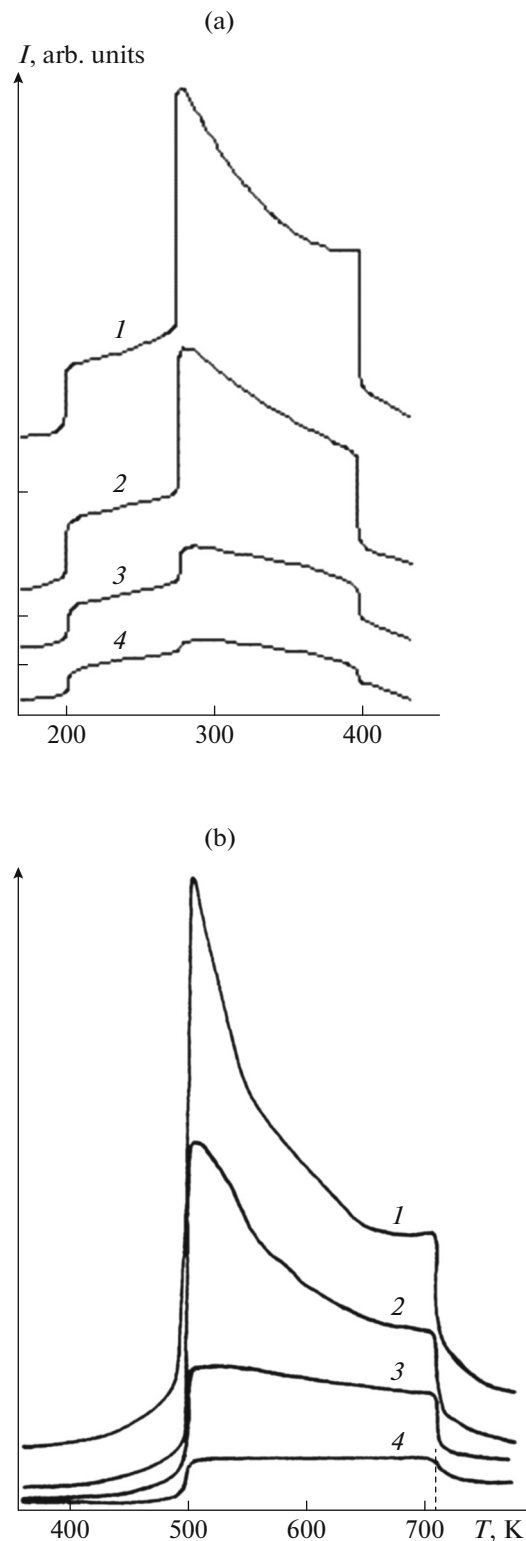


**Fig. 3.** Isofrequency temperature dependences for the spectral intensity of inelastically scattered radiation for scattering geometry  $X(ZZ)Y$  in the soft mode near the phase transition point characteristic of lead germanate crystals: (a) experimental dependences at fixed frequencies ( $\Omega = 3, 6, 8.5, 11, 13.5, 16, 18.5,$  and  $21 \text{ cm}^{-1}$ , respectively); (b) experimental isofrequency temperature dependences (solid lines, curves 2–4) for the spectral intensity of the inelastically scattered radiation characteristic of lead germanate crystals, as compared to theory (dashed lines, curves 1–4);  $\Omega = 1, 3, 6,$  and  $11 \text{ cm}^{-1}$  for curves 1–4, respectively. Solid line (5) at  $T = T_c$  corresponds to the central peak of scattered light.

quantitative information on the parameters of the soft mode.

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**Fig. 4.** Isofrequency temperature dependences of Raman spectra characteristic of (a) barium titanate and (b) potassium niobate polycrystals at fixed frequencies: (a) 7, 12, 24,  $40 \text{ cm}^{-1}$ ; (b) 5, 10, 20,  $40 \text{ cm}^{-1}$  (curves 1–4).

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