

Isofrequency Temperature Anomalies of Raman Scattering Intensity in Quartz Crystals

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Abstract—Isothermal dependences of Raman scattering intensity $i(\omega')$; $T = \text{const}$) on frequency $\Omega = \omega_0 - \omega'$ and isofrequency temperature dependences of $i(\Omega = \omega_0 - \omega' = \text{const}; T)$ in quartz crystals in a wide temperature range, including the α – β phase transition point (ω_0 and ω' are the excitation and Raman frequencies, respectively) have been compared. The isofrequency temperature dependences exhibit an intensity peak (near the phase-transition point), whose spectral position and magnitude depend on the fixed frequency $\Omega = \omega_0 - \omega'$. A theory of these dependences is developed for the crystals undergoing structural phase transitions. The theory predicts a soft-mode effect in the form of Raman opalescence: an anomalous increase in the spectral intensity of the isofrequency maximum $i_0(\Omega, T)$ with a decrease in frequency Ω near the phase-transition temperature ($T \approx T_c$). Agreement is established between the experimentally observed spectral intensity anomalies and the developed theory of isofrequency temperature dependences and processes of interaction of the fundamental soft mode with a low-frequency high- Q oscillator.

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1. INTRODUCTION

When studying the structural phase transition (PT) α – β in crystalline quartz in a narrow temperature range, a sharp increase (by three to four orders of magnitude) in the scattered light intensity, similar to the occurrence of opalescence near the liquid–vapor transition, was previously revealed in the vicinity of the phase transition point ($T_c = 846$ K) [1–3]. Anomalies of material parameters (specific heat, elastic constants, etc.) in the vicinity of the phase transition in quartz were also found [4–7]. It was suggested in [8] that the opalescence observed in [1–3] is related to the formation of a large number of twin domains, arising near the incommensurate PT observed in a narrow temperature range ($\theta_i = \theta + 1.8$ K) [9–13] near the α – β transformation. Another explanation of the opalescence effect in quartz crystals is based on the increase in the Raman scattering intensity on the soft mode, whose frequency decreases, while the oscillation amplitude anomalously increases when approaching the phase-transition point.

The Raman spectra of quartz crystals have been studied by many researchers [14–30]. The tempera-

ture behavior of two A_1 -symmetry lines, having frequencies of 207 and 466 cm^{-1} at room temperature, was investigated in [14]. The 466- cm^{-1} line broadened with an increase in temperature but did not exhibit any significant variations in frequency. This line was also present in the Raman spectrum above the PT point. The 207- cm^{-1} line was strongly diffused upon crystal heating and absent above the PT point. The Raman spectrum of α -quartz in the temperature range of 77 to 888 K was investigated in [22, 24]. It was found that the Raman band having a maximum at 147 cm^{-1} (at room temperature) and low intensity at low temperatures, which was observed in the $x(zz)y$ scattering geometry, becomes significantly shifted towards the excitation line with an increase in crystal temperature. The temperature dependence of the frequency of this line below the transition temperature was approximated by the relation $\Omega_0 = a|T - T_c|^\gamma$ at $0.4 \leq \gamma \leq 0.5$. This behavior was considered to be due to the existence of a soft mode, responsible for the lattice instability at the α – β transition. When heating a crystal, a strong broadening of the Raman band under consideration and its transformation into a wide wing near the excitation line was observed in the vicinity of the α – β transition. Thus, the frequency shift of the aforementioned mode near the transition

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temperature could not be measured exactly. An analysis of the slow-neutron scattering spectra near the α - β transition in quartz crystals [31] showed that these spectra contain (in a finite range of β -phase temperatures $846 < T < 1046$ K) a central peak due to quasi-elastic scattering processes. A study of the hyper-Raman scattering (HRS) in quartz crystal [32] revealed that the HRS spectrum exhibits soft-mode opalescence in the form of a sharp increase in the HRS intensity in the low-frequency (LF) region when approaching the α - β transition temperature from the side of high temperatures and a sharp decrease in the HRS intensity in the α -phase.

According to the well-known soft-mode theory [33, 34], the A_1 -type LF fundamental oscillation in a quartz crystal (with a frequency of 207 cm^{-1} at room temperature) should play the role of a soft mode, responsible for the PT in this crystal. A theoretical analysis of the resonance interaction between the A_1 -type LF mode (207 cm^{-1}) and an additional LF mode at 147 cm^{-1} , which manifests itself in Raman spectra in the $x(zz)y$ scattering geometry in the α -phase of quartz, was performed in [35, 36]. Based on an analysis of the temperature changes in Raman spectra in this geometry, it was found that the A_1 -type fundamental oscillation is not, strictly speaking, a classical soft mode, because its frequency does not tend to zero when approaching the PT point. The role of the soft mode is played by an additional (non-fundamental) mode, which manifests itself at room temperature in the form of a low-intensity band peaking at 147 cm^{-1} . The question about the nature of the mode under consideration still remains open. It is difficult to measure the frequencies of A_1 -type oscillations by analyzing the isothermal dependences of Raman spectra near the transition point due to their strong damping and transition from the oscillatory to relaxation mode. In this context, it was proposed to find the soft-mode parameters by analyzing the isofrequency temperature dependences of Raman intensity [37, 38] recorded at fixed frequencies $\Omega = \omega_0 - \omega'$ near the excitation frequency ω_0 (ω' is the scattered radiation frequency; $\Omega = 0 - 100 \text{ cm}^{-1}$).

Our purpose was to compare the isothermal and isofrequency dependences of Raman intensity and determine the quantitative characteristics of temperature dependences of the soft mode in a wide temperature range, including the PT point for quartz crystals. A theory of the isofrequency dependences of Raman intensity near the PT in quartz crystals and the hybridization processes involving the soft mode and the high-Q LF oscillator, which is responsible for the occurrence of central peak and opalescence effect in quartz, is developed.

2. CHARACTERISTICS OF QUARTZ CRYSTAL STRUCTURE

Quartz (SiO_2) is a rock-forming mineral, which belongs to the silica family. Currently, 12 polymorphic modifications of crystalline SiO_2 are known, the main of which are α -quartz, β -quartz, tridymite, and cristobalite. The symmetry space group of α -quartz, $D_3^4(P3_121)$, belongs to the trigonal system. The unit-cell parameters are $a = b = 4.9137 \text{ \AA}$ and $c = 5.4047 \text{ \AA}$, and the Si—O bond length is 1.610 \AA [39–41]. The unit-cell volume is 130.4935 \AA^3 ; the unit cell contains three SiO_2 molecules, shifted relative to each other by a vector $\boldsymbol{\alpha} = 1/3(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$ in the form of a screw structure with rotation by 120° . An incommensurate phase is formed near 847 K , in a temperature range of 1.3 K [9–13]. Being heated above 847 K , the crystal acquires the structure of β -quartz with a point group $D_6^4(P6_222)$.

Table 1 contains the results of group-theoretical classification of the fundamental oscillations and the selection rules for the optical processes involving the lattice modes in α -quartz (point group D_3).

According to the data in Table 1, the optical representation in this case has the form

$$T_{\text{opt}} = (\mathbf{A}_1 + A_2 + 2\mathbf{E}) + (\mathbf{A}_1 + 2A_2 + 3\mathbf{E}) + (2\mathbf{A}_1 + A_2 + 3\mathbf{E}). \quad (1)$$

Bolded designations \mathbf{A}_1 and \mathbf{E} in (1) are used for irreducible representations, corresponding to the active optical modes in the Raman spectrum; the A_2 - and \mathbf{E} -type vibrations are allowed by selection rules in the IR spectrum. The first parentheses in (1) correspond to the translational (trans) lattice modes (translational vibrations of the SiO_2 group); the second parentheses correspond to librations (lib) or torsional (quasi-vortex) vibrations of the SiO_2 group relative to the z axis; and the third parentheses correspond to the intramolecular (internal) vibrations of the SiO_2 group.

It follows from relation (1) and Table 1 that the low-temperature α -phase contains four totally symmetric A_1 -type modes, which are active in the Raman spectrum, and eight E modes, which are active in both the Raman and IR spectra. The optical representation for the β -quartz structure, whose point symmetry is described by the D_6 group, takes the form [32]

$$T_{\text{opt}} = A_1 + 3B_1 + 2A_2 + 2B_2 + 4E_1 + 4E_2. \quad (2)$$

The role of the soft mode is played [32] by the B_1 -type vibration, which manifests itself in the HRS spectrum in the $z(xxx)y$ scattering geometry.

Table 1. Irreducible representations and characters of the point symmetry group D_3

$D_3^4(P3_121)$	E	$C_3^{\pm 1}(z)$	$3C_2$	a_i	a_{ij}
α	0; 0; 0	$\frac{1}{3}; \frac{1}{3}; \frac{1}{3}$	0; 0; 0		
A_1	1	1	1		a_{xx}, a_{yy}, a_{zz}
A_2	1	1	-1	a_z	
E	2	-1	0	a_x, a_y	$a_{xx}, a_{yy}, a_{xy}, a_{xz}, a_{yz}$
χ_V	3	0	-1		
$\chi_{\bar{V}}$	3	0	-1		
$\chi[V]^2$	6	0	2		
$\chi[V]^2 \times V$	18	0	-2		
n_0	9	0	1		
m_0	3	0	1		
χ_{opt}	24	0	0		
χ_{tr}	6	0	0		
χ_{lib}	9	0	-1		

Note. Here, α are the partial translation vectors of the space group $D_3^4(P3_121)$; n_0 and m_0 are the numbers of atoms or SiO_2 groups retaining their sites after the symmetry transformation; χ_{opt} , χ_{tr} , and χ_{lib} are the characters of optical, translational, and librational representations, respectively; and a_i and a_{ij} are, respectively, the components of Raman scattering vector \mathbf{a}_i and tensor a_{ij} [42–46].

3. EXPERIMENTAL DATA ON THE ISOTHERMAL AND ISOFREQUENCY DEPENDENCES OF RAMAN SPECTRA IN CRYSTALLINE QUARTZ

Figures 1(a) and 1b show the isothermal Raman spectra in a quartz single crystal in the $x(zz)y$ geometry, which were obtained by us in the digitized form. According to the selection rules (see Table 1), the soft mode responsible for the α – β phase transition should manifest itself in this geometry. The dashed lines indicate the background level in all plots.

The LF region in the Raman spectrum for the polarization geometry $x(zz)y$ (see Fig. 1) contains an additional band (indicated by an asterisk), which was not predicted by the group-theoretical analysis. When heating the crystal, the frequency corresponding to the peak intensity of this band decreases from 147 cm^{-1} at $T = 300 \text{ K}$ to 34 cm^{-1} at $T = 819 \text{ K}$. Upon further heating, this band is transformed into a low-frequency wing, and the corresponding frequency cannot be measured. The spectral intensity of this band near the excitation line sharply increases when approaching the PT point, which is interpreted by us as the effect of soft-mode Raman opalescence. Under these conditions, the positions of the Raman intensity peaks for the fundamental modes $1A_1(\text{TO})$, $2A_1(\text{TO})$, and $3A_1(\text{TO})$ change only slightly in the entire temperature range under study.

When SiO_2 groups in the α -phase undergo torsional vibrations with respect to the threefold symmetry axis, they are in a potential well with two minima of different depths. This fact explains the presence (along with the fundamental mode $1A_1$ at 207 cm^{-1}) of a weak 147-cm^{-1} band in the low-frequency region of Raman spectrum at room temperature (indicated by asterisks in Fig. 1). With an increase in temperature the difference in depth between the two potential energy minima decreases, and the intensity of the non-fundamental torsional mode in the Raman spectrum increases (Fig. 1(b)).

Figure 2 shows the isofrequency temperature dependences of Raman spectra in quartz crystals, i.e., the temperature changes in the Raman spectrum intensity at fixed spectrometer frequencies Ω ranging from 40 to 100 cm^{-1} . The solid and dashed arrows indicate, respectively, the Raman signal and the central peak (which manifests itself at the α – β transformation point). The numbers near the curves in Fig. 2 correspond to fixed spectrometer frequencies Ω (in cm^{-1}).

The dashed line indicates the background level. The isofrequency temperature dependences of Raman spectra were recorded using a DFS-24 double monochromator with a spectral resolution of 0.5 cm^{-1} . The error in measuring temperature was 0.5 K . It can be seen in Fig. 2 that the position of maximum spectral intensity of the isofrequency dependence tends to the transition temperature with

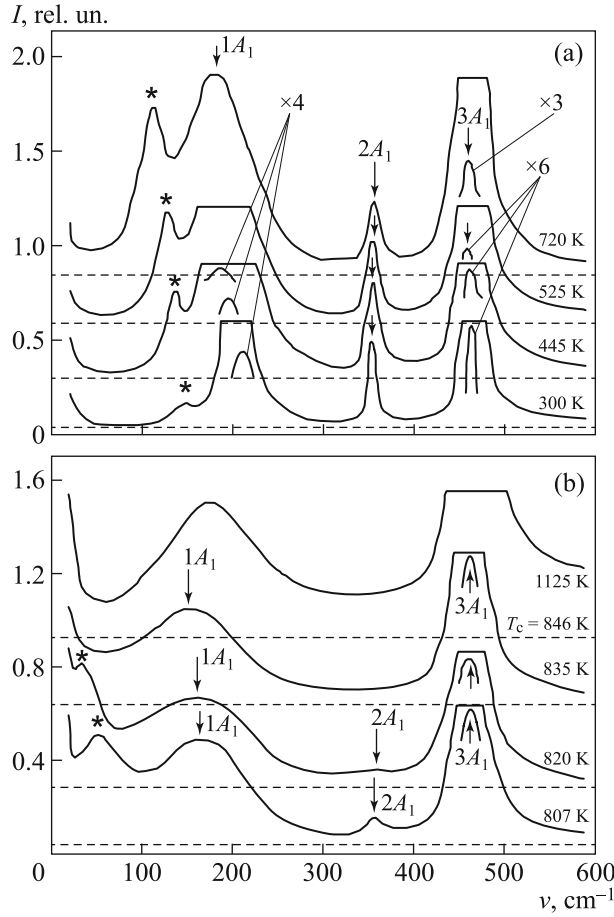


Fig. 1. Isothermal dependences of the Raman spectra of α -quartz single crystal for the $x(zz)y$ scattering geometry (the non-fundamental mode is indicated by asterisk, and fundamental oscillations of the A_1 type are shown by arrows): temperature ranges (a) from 300 to 720 K and (b) from 807 to 1125 K.

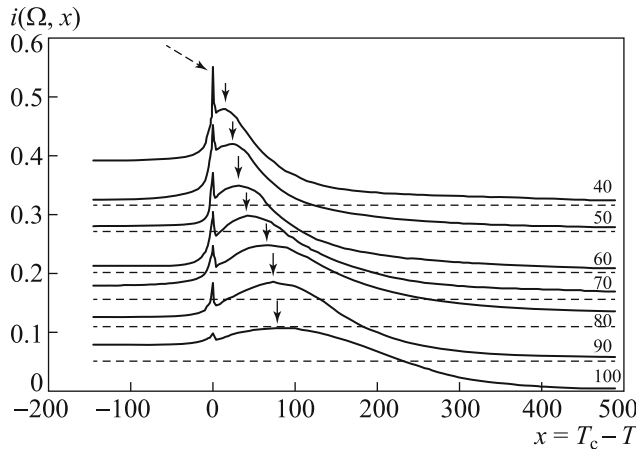


Fig. 2. Isofrequency dependences $i(\Omega, x)$ near the α - β transformation point in quartz crystals at fixed frequencies; the sharp peak on the left corresponds to quasi-static opalescence, and the maximum on the right is due to the lattice "softening".

a decrease in the fixed Raman spectrometer frequency Ω , and its intensity monotonically increases; i.e., Raman opalescence occurs. Here, two intensity peaks are observed. The first (indicated by a dashed arrow) is the manifestation of the central peak, and the second (indicated by a solid arrow) is due to the soft lattice mode.

4. THEORY OF ISOFREQUENCY TEMPERATURE DEPENDENCES OF THE SOFT-MODE RAMAN SCATTERING IN QUARTZ CRYSTALS

In accordance with the semiphenomenological Landau theory of phase transitions [47, 48], the thermodynamic potential can be expanded in a series in order parameter η :

$$\Phi = \Phi_0 + \frac{A\eta^2}{2} + \frac{B\eta^4}{4} + \frac{C\eta^6}{6} + \dots + \frac{D(\nabla\eta)^2}{2}. \quad (3)$$

The following relations hold true in equilibrium:

$$\left(\frac{\partial\Phi}{\partial\eta}\right)_{\eta=\eta_0} = 0, \quad \left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_{\eta=\eta_0} > 0. \quad (4)$$

For a second-order phase transition $B > 0$. We assume also for simplicity that $C = D = 0$. Below the PT point ($T < T_c$), we have

$$\left(\frac{\partial\Phi}{\partial\eta}\right)_{\eta=\eta_0} = A\eta_0 + B\eta_0^3 = \eta_0(A + B\eta_0^2) = 0, \quad (5)$$

$$\eta_0^2 = -A/B, \quad A < 0.$$

Above the PT point ($T > T_c$), the order parameter becomes zero ($\eta_0 = 0$) and, in correspondence with (4), $A > 0$. Thus, $A = 0$ at the PT point. The dependence $A = a|T - T_c|$ is used as the simplest approximation. Fluctuations of the order parameter $\eta = \eta_0 + \Delta\eta$ correspond to lattice vibrations $\Delta\eta$, which specify the symmetry of the low-symmetry phase. Proceeding from relation (4), we derive the equations of motion and the temperature dependence of damping oscillator frequency Ω_0 :

$$m\Delta\ddot{\eta} = -\delta\Delta\dot{\eta} - A\Delta\eta - 3B\eta_0^2\Delta\eta,$$

$$\Delta\ddot{\eta} + \Gamma\Delta\dot{\eta} + \Omega_0^2\Delta\eta = 0, \quad \Gamma = \delta/m, \quad (6)$$

$$\Omega_0^2 = -\frac{2A}{m} = a(T_c - T)(T < T_c),$$

$$\Omega_0^2 = \frac{A}{m} = \frac{a(T - T_c)}{2}(T > T_c).$$

Here m is the effective mass of the corresponding oscillator, δ is the damping constant, Γ is the reduced damping constant, and a is the constant entering the temperature dependence of the soft mode squared frequency.

Table 2. Comparison of the calculated values of the parameters x_0 and i_0 with experimental data

Ω , cm ⁻¹	x_0 , K				i_0 , arb. un.			
	Experiment, $\Delta x_0 = 1$ K	$\gamma = 1$			Experiment, $\Delta i_0/i_0 \approx 1\%$	$\gamma = 1$		
		$\beta = 0.5$	$\beta = 0.25$	$\beta = 1/3$		$\beta = 0.5$	$\beta = 0.25$	$\beta = 1/3$
40	15	23	19	21	163	164	310	248
50	24	30	26	28	149	144	236	199
60	32	38	34	35	148	131	190	167
70	42	46	43	44	142	122	159	145
80	67	55	53	54	138	115	137	129
90	73	66	64	65	135	111	120	117
100	77	76	76	76	107	107	107	107

The normal lattice vibration specifying the symmetry of the low-temperature phase corresponds to the soft mode. According to (6), the frequency of this mode should anomalously decrease to zero when approaching the transition point.

The spectral intensity of inelastic light scattering in the one-soft-mode approximation can be written as

$$I(\Omega, T) = \eta_0^2 [n(\Omega) + 1] \text{Im} \chi(\Omega, T). \quad (7)$$

Here, $n(\Omega)$ is the Bose–Einstein factor and $\chi(\Omega, T)$ is the susceptibility corresponding to the soft mode.

The following equality is valid for the approximation in use:

$$\chi(\Omega, T) = \frac{1}{\Omega_0^2 - \Omega^2 - i\Gamma\Omega}. \quad (8)$$

We restrict ourselves to the analysis of PTs occurring at sufficiently high temperatures, when

$$n(\Omega, T) = \frac{1}{\exp(\hbar\Omega/kT) - 1} \cong \frac{kT}{\hbar\Omega}. \quad (9)$$

Let us introduce the reduced spectral intensity $i(\Omega, x) = I(\Omega, T)/T$; then we have the following relation (accurate to a constant factor) for the low-symmetry phase ($x = T_c - T$):

$$i(\Omega, x) = \frac{\Gamma\eta_0^2(x)}{[\Omega_0^2(x) - \Omega^2]^2 + \Gamma^2\Omega^2}. \quad (10)$$

For the second-order PT, we assume that $\Omega_0^2(x) = ax^\gamma$ and $\eta_0^2(x) = bx^{2\beta}$; Ω_0 and Γ are, respectively, the soft-mode frequency and damping; and β and γ are the critical indices of PT dynamics. Then expression (10) takes the form

$$i(\Omega, x) = \frac{b\Gamma x^{2\beta}}{(ax^\gamma - \Omega^2)^2 + \Gamma^2\Omega^2}. \quad (11)$$

The coordinates of the maximum of function $i(\Omega, x)$ can be written as

$$x_0^\gamma = \frac{\Omega}{2a(\gamma - \beta)} \left[\Omega(\gamma - 2\beta) + \sqrt{\Omega^2\gamma^2 + 4\beta\Gamma^2(\gamma - \beta)} \right], \quad (12)$$

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

We will use the experimental data at $\Omega = 100$ cm⁻¹ to determine the constants a and b in (12). In accordance with the shape of the isothermal spectrum near the transition temperature (see Fig. 1), we assume approximately that $\Gamma \approx 100$ cm⁻¹. The results of calculating the parameters x_0 and i_0 of isofrequency

dependences are compared with experimental data in Table 2.

Figures 3(a–c) show the obtained isofrequency dependences for different values of fixed frequency Ω , the values of functions x_0 and i_0 (calculated from formula (12)), and experimental data. The numbers

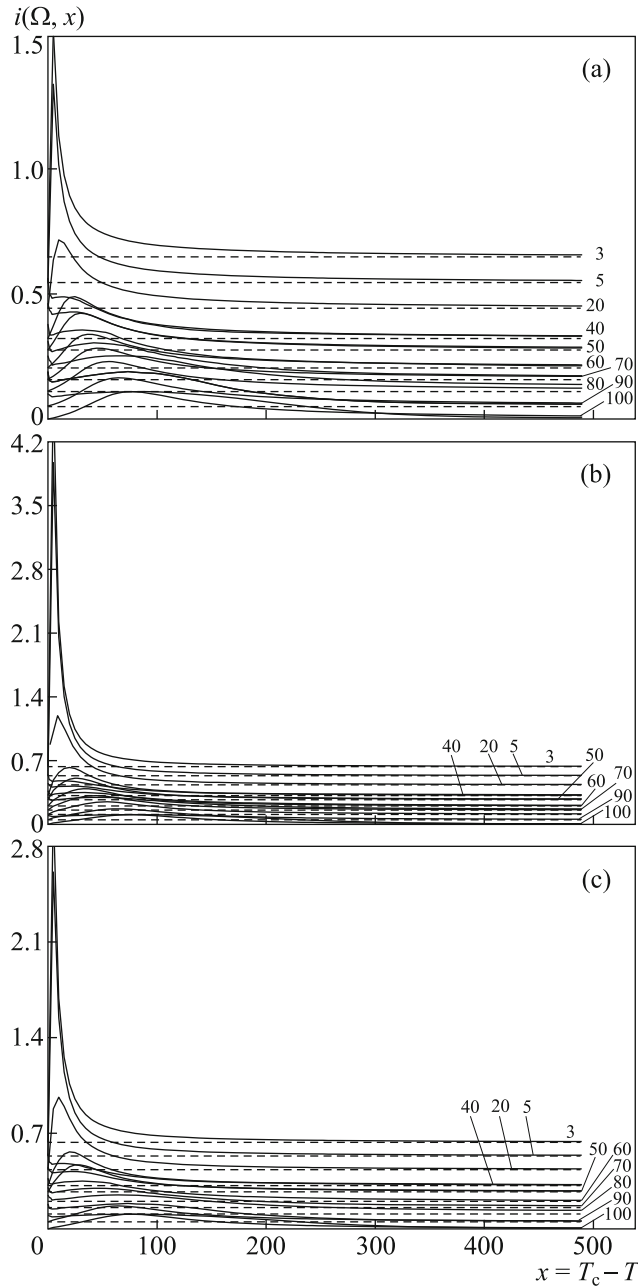


Fig. 3. Comparison of isofrequency dependences at different fixed frequencies (solid and dashed lines correspond to the theory and experiment, respectively) at different values of parameters: (a) $\gamma = 1$ and $\beta = 0.5$, (b) 1 and 0.25, and (c) 1 and $1/3$. The numbers at the curves are fixed frequencies in cm^{-1} .

at curves in Figs. 3(a–c) are fixed spectrometer frequencies Ω (in cm^{-1}). The dashed line indicates the background level. As can be seen in Table 2 and Fig. 3, the theory is in the best agreement with experiment at $\gamma = 1$ and $\beta = 0.5$, a fact indicating that the phase transition under consideration is similar to a second-order one. As can be seen in Fig. 3, the theory predicts a further sharp increase in spectral intensity

with a decrease in frequency Ω , which is consistent with the effect of soft-mode Raman opalescence.

5. ANALYSIS OF THE MODEL OF TWO COUPLED OSCILLATORS

The observation of an intense central peak at the PT temperature (see Fig. 2, dashed arrow), as well as its presence in the HRS and slow-neutron scattering spectra [31, 32], can be explained by the existence of an additional high- Q LF mode, characteristic of PTs with a complex order parameter, in particular, of incommensurate PTs. This mode resonantly interacts with the soft lattice mode, responsible for the structural PT in crystal. The equations of motion for these two coupled modes (additional mode $\xi(t)$ and torsional lattice mode $\Delta\eta(t)$) have the form

$$\begin{aligned} m_1 \frac{d^2}{dt^2} \xi &= -\gamma_1 \xi - \delta_1 \frac{d}{dt} \xi - \gamma(\xi - \Delta\eta), \\ m_2 \frac{d^2}{dt^2} (\Delta\eta) &= -\gamma_2 \Delta\eta - \delta_2 \frac{d}{dt} (\Delta\eta) - \gamma(\Delta\eta - \xi). \end{aligned} \quad (13)$$

Here γ_1 is the elastic constant of the additional mode and γ_2 is the elastic constant of the torsional lattice mode.

The solution to system (13) has the form $\xi(t) = \xi_0 \exp(i\Omega t)$ and $\Delta\xi(t) = \Delta\xi_0 \exp(i\Omega t)$. After substituting this solution into (13) and reducing similar terms, we arrive at

$$\begin{aligned} \Delta\eta_0 (m_1 \Omega^2 - \gamma_1 - \gamma - i\Omega \delta_1) + \gamma \xi_0 &= 0, \\ \Delta\eta_0 \gamma + \xi_0 (m_2 \Omega^2 - \gamma_2 - \gamma - i\Omega \delta_2) &= 0. \end{aligned} \quad (14)$$

The matrix A_{ij} corresponding to (14) can be written as

$$A_{ij} = \begin{pmatrix} m_1 \Omega^2 - \gamma_1 - \gamma - i\Omega \delta_1 & \gamma \\ \gamma & m_2 \Omega^2 - \gamma_2 - \gamma - i\Omega \delta_2 \end{pmatrix} \quad (15)$$

and the tensor of the Green's function is

$$G_{ij} = \frac{1}{\Delta} \begin{pmatrix} m_2 \Omega^2 - \gamma_2 - \gamma - i\Omega \delta_2 & -\gamma \\ -\gamma & m_1 \Omega^2 - \gamma_1 - \gamma - i\Omega \delta_1 \end{pmatrix}, \quad (16)$$

where

$$\begin{aligned} \Delta &= (m_1 \Omega^2 - \gamma_1 - \gamma - i\Omega \delta_1) \\ &\quad \times (m_2 \Omega^2 - \gamma_2 - \gamma - i\Omega \delta_2) - \gamma^2. \end{aligned}$$

According to the Nyquist theorem [33, 34, 49], which specifies in our case the spectrum of two coupled oscillators, we obtain the following relation for the Raman spectrum intensity:

$$I(\Omega, T) = A \frac{kT}{\hbar \Omega} \eta_0^2 \text{Im} \sum_{i,j=1,2} p_i p_j G_{ij}. \quad (17)$$

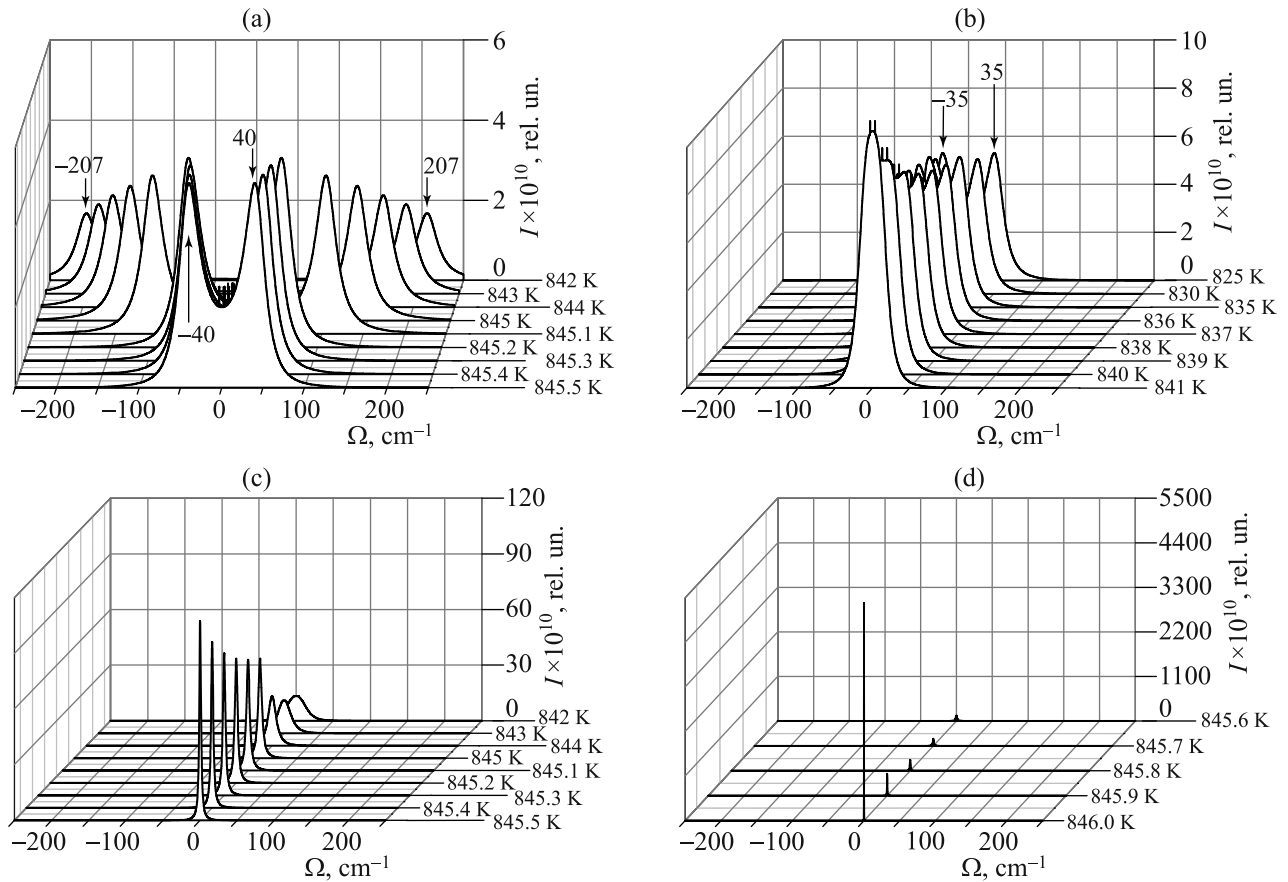


Fig. 4. Evolution of the spectral intensity $I(\Omega, T)$ in different temperature ranges: (a) 300–820 K, (b) 825–841 K, (c) 842–845.5 K, and (d) 845.6–846.0 K.

Here, p_1 and p_2 are the strengths (effective contributions to the interaction) of the first and second oscillators, respectively.

The Raman spectra were calculated based on relation (17) for different values of coupled-oscillator parameters. As a result, satisfactory agreement with the Raman spectra recorded at different temperatures (see Fig. 1) was obtained for the following values of parameters: $\delta_1 = 0.1$, $\delta_2 = 30$, $\gamma_1 = 1$, $\gamma_2 = 78.7(T_c - T) - \gamma$, $\gamma = 10$, $p_1 = 0.0001$, $p_2 = 1$, and $m_1 = m_2 = 1$. Figures 4(a–d) show a temperature dependence of the spectral intensity of Stokes and anti-Stokes (disregarding the Bose factor) components $I(\Omega, T)$ for the model of two coupled oscillators in a wide temperature range.

As can be seen in Fig. 4(a), the fundamental lattice mode with a frequency of 207 cm^{-1} manifests itself far from the transition point. The central peak is absent. When the crystal is heated (Fig. 4(b)), the non-fundamental torsional mode plays the role of soft mode, whose frequency anomalously decreases when approaching the transition temperature. The central peak arises near the transition temperature (Figs. 4(c, d)); its maximum is at the frequency $\Omega = 0$

(i.e., $\omega' = \omega_0$). The spectral width of the central peak sharply decreases when approaching the transition point, whereas its spectral intensity anomalously increases, which is consistent with the observed opalescence effect at the transition point. These regularities are in agreement with the experimental data on isothermal Raman spectra (see Fig. 1) and isofrequency temperature dependences (see Fig. 2), as well as with the slow-neutron scattering data [31]. The central-peak intensity increases by more than two orders of magnitude in the vicinity ($\Delta T = \pm 1 \text{ K}$) of the phase transition (see Fig. 4(d)).

6. CONCLUSIONS

Thus, using the method of isofrequency temperature dependences, we showed that quartz crystals exhibit a sharp increase in the maximum Raman spectrum intensity $i_0(\Omega, T)$ when approaching the PT temperature, and with a decrease in the frequency Ω at a fixed temperature in the vicinity of PT. Raman opalescence is observed at $\Omega \approx 0$, which is caused by the anomalous increase in the soft-mode oscillation amplitude with approaching the PT point.

An analysis of the model of two coupled oscillators, corresponding to the fundamental lattice mode of the A_1 type and the low-frequency non-fundamental torsional oscillation, showed the occurrence of an intense narrow central peak in the vicinity of PT in quartz, whose intensity exceeds the spectral intensity of lattice Raman scattering by several orders of magnitude. The frequency of the A_1 -type fundamental mode does not undergo any significant changes when approaching the transition temperature, but its intensity sharply decreases.

Apparently, the observed regularities may manifest themselves in other crystals undergoing soft-mode structural PTs, for example, in strontium titanate[50], lead germinate, etc. The high- Q LF mode “central peak”, observed in a narrow vicinity of PT, is of interest for further studies with interferometers operating in different scattering geometries, aimed at supplementing the well-known light scattering from acoustic waves in condensed media. The low frequency and high- Q factor of this peak are convenient for implementing low-threshold induced light scattering on the mode under consideration. It is also of interest to study the soft-mode HRS near the PT point. Since the HRS tensor for quartz crystals does not change much with a change in the order parameter η in the vicinity of PT, the reduced soft-mode HRS intensity can be written as (see relation (10))

$$i(\Omega, x) = \frac{\Gamma}{[\Omega_0^2(x) - \Omega^2]^2 + \Gamma^2\Omega^2}. \quad (18)$$

At low frequencies Ω near the PT point, when $\Omega_0^2(x)$ tends to zero, the HRS spectral intensity should anomalously increase. An intense central peak of hyper-Rayleigh scattering should manifest itself at the PT temperature for the second-harmonic frequency ($\omega' = 2\omega_0$); i.e., hyper-opalescence is expected to occur. Since the refractive index at the second-harmonic frequency $\omega' = 2\omega_0$ differs significantly from that at $\omega' = \omega_0$, one would expect an anomalous increase in the hyper-Rayleigh scattering intensity in both forward and backward scattering geometries. Hyper-opalescence near the structural PT point can also be observed in other crystals, characterized by the presence of a soft mode at the PT point, in particular, in strontium titanate, lead germanate, potassium niobate, barium titanate, and others.

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