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Frequency-angle spectrum of light scattering by polaritons and interference of susceptibilities of different orders

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We investigate the singularities of the frequency-angle spectra of spontaneous parametric scattering of light by polaritons in a number of ferroelectric crystals such as lithium niobate, potassium dihydrophosphate, lithium formiate, iodic acid, and others. It is shown that most of the observed singularities can be successfully explained within the framework of the model of interference between the background and resonant values of the first- second- and third-order susceptibilities of the medium.

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The rapid advances in laser spectroscopy of media have led to the appearance of new types of spectroscopy, in which information is provided not only by the frequency ω of the scattered or absorbed electromagnetic waves, but also by their wave vector \mathbf{k} . One can speak therefore of "two-dimensional" spectroscopy in $(\omega - \mathbf{k})$ space. One of the phenomena on whose basis a method of spectroscopy in $(\omega - \mathbf{k})$ space can already be developed to a sufficient degree is spontaneous parametric scattering of light by polaritons, LSP (see, e.g., Ref. 1). However, extensive applications of this method are impeded by the fact that the LSP has not been sufficiently well studied, particularly near the natural vibrations of the lattice.

We investigate in this paper the effect of the interference of the first-, second-, and third-order susceptibilities of the medium in the vicinity of an isolated lattice vibration [characterized by a dipole moment and a Raman-scattering (RS) tensor] on the frequency-angle distribution of the intensity of light scattering by polaritons. The singularities of the light scattering by polaritons in lithium niobate (LiNbO_3), lithium iodate (LiIO_3), potassium dihydrophosphate (KH_2PO_4), deuterated potassium dihydrophosphate ($\text{K}(\text{H}_x\text{D}_{1-x})_2\text{PO}_4$), ammonium dihydrophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), lithium formiate and deuterated lithium formiate ($\text{LiHCOO}\cdot\text{H}_2\text{O}$ and $\text{LiHCOO}\cdot\text{D}_2\text{O}$), and iodic and deuterated iodic acids ($\text{Li}_x\text{Na}_{1-x}\text{HCOO}\cdot\text{H}_2\text{O}$), ($\alpha\text{-HIO}_3$, $\alpha\text{-DIO}_3$) are explained within the framework of the interference of the background and resonant values of the susceptibilities.

The intensity of a signal wave with a frequency ω_s and a wave vector \mathbf{k}_s in a three-frequency parametric process is determined by the imaginary part of the increment $\Delta\varepsilon(\omega_s)$ added to the dielectric constant by the strong pump field (ω_L and \mathbf{k}_L). The signal wave has a maximum gain and consequently a maximum intensity if the condition of spatial synchronism

$$\mathbf{k} = \mathbf{k}_L - \mathbf{k}_s \quad (1)$$

is satisfied. Here \mathbf{k} is the wave vector of the additional (polariton) wave, whose frequency is determined by the condition

$$\omega = \omega_L - \omega_s. \quad (2)$$

The conditions (1) and (2) lead to a unique relation between the frequency-angle spectrum of the scattering, on the one hand, and the dispersion characteristics of the medium, on the other.

Knowledge of the dispersion of the medium in the transparency region, which usually contains the signal and pump frequencies, together with the LSP spectra, makes it possible to determine the dispersion of the medium at the polariton-wave frequency, which can land in the region of the natural vibrations of the lattice. In those cases when the polariton-wave frequency is far enough from the frequencies of the resonances (by several line widths), information on the scattering medium is provided by the following elements of the of the LSP spectra:

a) The tuning curve, determined from the condition

$$\left. \frac{\partial I(\omega_s)}{\partial k} \right|_{\omega = \text{const}} = 0,$$

yields information on the dispersion curve of the lattice and the function $\varepsilon'(\omega)$.

b) The angular and spectral widths of the tuning curve yield information on the absorption coefficient and the function $\varepsilon''(\omega)$.

c) The scattering intensity (integrated over the scattering angle at the given frequency, as well as the amplitude) yields information on the components of the quadratic-susceptibility tensor χ_{ijk} .

On the other hand, if the polariton frequency approaches the lattice resonant frequency, the linear and

cubic susceptibilities that characterize the given resonance begin to influence the scattering intensity and the frequency-angle spectrum. The complete formula for the LSP intensity for this case was obtained in Refs. 2 and 3. Since this formula is too complicated to use in general form for polyatomic crystals, it is not given in the present article. The analysis that follows will make use of substantial simplifications. We investigate the intensity distribution in the vicinity of an isolated resonance of frequency ω_0 . It is assumed that the first-, second-, and third-order susceptibilities are of the form

$$\begin{aligned} \varepsilon &= \frac{\varepsilon_m}{z} + \varepsilon_\infty, & \chi &= \frac{\chi_m}{z^2} + \chi_\infty, \\ \theta &= \frac{\theta_m}{z} + \theta_\infty, & z &= \frac{\omega_0 - \omega}{\Gamma} - i. \end{aligned} \quad (3)$$

Here $\varepsilon_m, \chi_m, \theta_m$ determine the contribution of the vibration, Γ is a phenomenological constant of the vibration damping, and $\varepsilon_\infty, \chi_\infty, \theta_\infty$ are the susceptibility values and are determined by the contributions of the electronic and other lattice vibrations, which are slowly varying functions.

In addition, we neglect the tensor character of the susceptibilities and the influence of the longitudinal resonant wave. Under these assumptions, χ_m, ε_m , and θ_m are connected by the condition⁴

$$\chi_m^2 = \varepsilon_m \theta_m. \quad (4)$$

The function describing the frequency-angle distribution of the scattering intensity in the resonance region assumes under the foregoing assumption the form

$$F(\omega, k) = -\frac{\chi_m^2}{\varepsilon_m} \operatorname{Im} \left[\frac{1}{z^2} + \frac{1/b + 1/z^2}{(n^2 - \varepsilon_\infty)/\varepsilon_m - 1/z^2} \right], \quad (5)$$

where

$$b = \chi_m / \chi_\infty.$$

We investigate the change of the form of $F(\omega, k)$ with changing b and Γ . The remaining parameters are fixed.

REGION WITH ZERO SCATTERING INTENSITY ON THE UPPER POLARITON BRANCH

The first explained singularity of the frequency-angle distribution was the presence of a section with zero scattering intensity (intensity dip) on the upper polariton branch (at frequencies higher than the resonant frequency of the vibrations).^{5,6} The cause of the dip was interference between the lattice and electronic parts of the quadratic susceptibility, as well as "linearization" of the crystal at a frequency close to 1400 cm^{-1} .

A dip on the upper polariton branch is easily obtained also within the framework of the considered model when the parameters b and Γ are widely varied. For example, at $b = 13$ and $\Gamma = 10 \text{ cm}^{-1}$ ($LO-TO$ splitting, in which $\omega_{||} - \omega_0 = 10 \text{ cm}^{-1}$) the distribution of the intensity on the $(\omega-k)$ plane takes the form shown in Fig. 1. A dip on the upper polariton branch is observed also in the lithium iodate crystal,⁷ where it covers the region of the one-dimensional synchronism at a frequency close to 1000 cm^{-1} .

At small Γ ($\Gamma < \omega_{||} - \omega_0$) the line has a Lorentzian an-

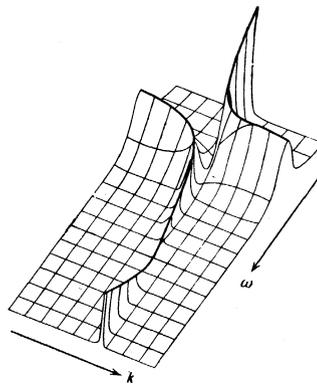


FIG. 1. Scattering-intensity distribution in $\omega-k$ space (Eq. (4) at $b = 13$, $\Gamma = 10 \text{ cm}^{-1}$, $\omega_{||} - \omega_0 = 10 \text{ cm}^{-1}$).

gular profile (Fig. 2, solid line) and does not depend on the measurement frequency. An increase of the damping constant ($\Gamma > \omega_{||} - \omega_0$) leads to a change in the scattering line shape. The corresponding cross section of the intensity with respect to angle is shown by the dashed line of Fig. 2 for the distribution obtained at $\Gamma = 30 \text{ cm}^{-1}$, $b = 6$, and $\omega_{||} - \omega_0 = 10 \text{ cm}^{-1}$ (the cross-section frequency is the same as in the preceding case). The lines are seen to have wings as well as dips at certain scattering angles at which the intensity is zero, a feature typical of the Fano antiresonance case.⁸ The crystal-linearization frequency is independent of Γ .

The frequency of the dip shifts upon decrease of the quantity θ_m , which characterizes the intensity of the Raman scattering of light by the lattice vibration. If the condition $\Gamma < \omega_{||} - \omega_0$ is satisfied, then the line contour remains Lorentzian. The dip localized on the upper polariton branch near the resonant frequency is observed in the lithium-sodium formate spectrum, the first published form of which is shown in Fig. 3. The location of the dip is marked by the arrows. We note that the dip on the tuning curve is localized at angles close to the synchronism angles of the unperturbed polaritons (to the angles that the polariton would have in the absence of resonance).

In all the considered cases the dispersion curve of the scattering medium takes the form of a normal anti-crossing, i.e., of two repelling branches, of which the upper (frequency $> \omega_{||}$) tends to the longitudinal frequency of the resonance, while the second, lower (frequency lower than ω_0) approaches the transverse frequency asymptotically with increasing scattering frequency.

The optical properties of the medium are described in the course of the scattering by the dielectric constant without allowance for absorption⁹:

$$\varepsilon^+(\omega) = \varepsilon_\infty + \varepsilon_m \omega_0^2 / (\omega_0^2 - \omega^2). \quad (6)$$



FIG. 2. Angular scattering-line shape at fixed frequency: solid line— $b = 3$, $\Gamma = 10 \text{ cm}^{-1}$; dashed line— $b = 6$, $\Gamma = 30 \text{ cm}^{-1}$.

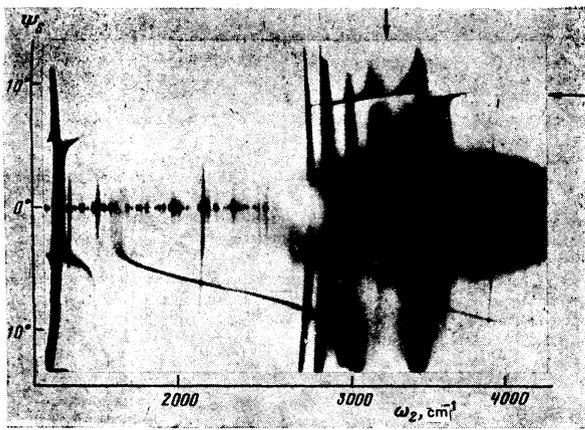


FIG. 3. LSP spectrum of lithium-sodium formate crystal at the scattering geometry $XY(Z,XY)XY + \Delta Z$. The dip of the scattering intensity is located at the intersection of the arrows (ψ_s is the scattering angle).

ASYMMETRY OF FREQUENCY-ANGLE DISTRIBUTION OF SCATTERING INTENSITY

Further decrease of the RS resonance tensor leads already to noticeable changes in the frequency-angle spectrum, namely, to the appearance of a strong asymmetry in the angular dependence of the scattering intensity on the upper and lower branches near the resonance. Asymmetry of this type manifests itself in experiment in the fact that the scattering intensity on the upper branch, at scattering angles smaller than the synchronism angles of the unperturbed polariton, is much less, by a factor of ten and more, than the scattering intensity on the lower branch, at angles larger than the synchronism angle of the unperturbed polariton, and is observed in the spectrum of potassium pentaborate at frequencies 2000–2400 cm^{-1} .¹⁰ The function (4) gives a similar distribution, for example, at $b=1$, $\Gamma=10 \text{ cm}^{-1}$, $\omega_{11}-\omega_0=10 \text{ cm}^{-1}$ (Fig. 4). The line shape remains Lorentzian in this case. In the same potassium-pentaborate spectrum there are also cases of intersection of the lattice vibration with the polarization branch, at which a vanishing of the $LO-TO$ splitting is observed and a dispersion-curve section with anomalous behavior is observed. The vanishing of the $LO-TO$ splitting is due to the increase of the damping constant.

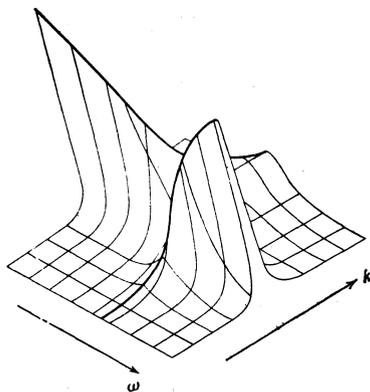


FIG. 4. Distribution of the scattering intensity in $(\omega-k)$ space [formula (4)] at $b=1$, $\Gamma=10 \text{ cm}^{-1}$, $\omega_{11}-\omega_0=10 \text{ cm}^{-1}$.

This distorts the line shape in such a way that the slope on the side of small k (small scattering angles) becomes noticeably steeper than the slope on the side of large k . The difference between the scattering intensities at small and large angles is preserved.

Further increase of Γ causes the scattering intensity to decrease also at large angles, at $\omega \approx \omega_0$. It should be noted that the scattering amplitude at the line center decreases, and at a given frequency the intensity integrated over all the scattering angles remains unchanged. The scattered light retains a noticeable intensity only near the synchronism angles of the unperturbed polariton. The curve section with the anomalous dispersion becomes weakly pronounced.

This frequency-angle intensity distribution is illustrated by sections of the spectra of the crystals KDP, ADP, and DKDP in the vicinities of the vibrations of the OH and OD groups.¹¹ In all the considered cases the dispersion curve can no longer be described by the function (6), and the absorption must be taken into account.

ANOMALOUS BRANCH OF THE SCATTERING

One of the most interesting singularities observed in the spectra is the appearance of a scattering branch with anomalous dispersion within the $LO-TO$ splitting. In the distribution given by condition (4), the anomalous branch appears if $b \leq 0.01$ and $\Gamma \leq \omega_{11} - \omega_0$. An anomalous branch in the $LO-TO$ gap is observed in experiment in the biphonon region at the frequency 4180 cm^{-1} in the spectra of lithium formiate and of deuterated lithium formiate and of deuterated lithium formulate.¹²

Figure 5 shows spectrum densitograms obtained at given frequencies with variation of the scattering angle. The cross sections 1 and 2 lie on the lower polariton branch, and 6 and 5 on the upper. The sections 3 and 4 are drawn within the region of the $LO-TO$ splitting, which in this case is equal to 20 cm^{-1} . The same figure shows the curve joining the intensity maxima determined from the obtained cross sections. Thus curve depicts uniquely the dispersion curve of the crystal in the investigated section of the spectrum, a curve described no longer by Eq. (6) but by the expression⁴

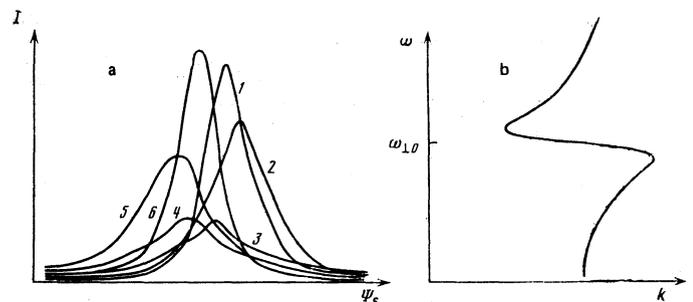


FIG. 5. a) Densitogram of the LSP spectrum of lithium formiate in the vicinity of the second-order vibration ($\omega_0=4180 \text{ cm}^{-1}$) at the following frequencies: 1—4100, 2—4160 (lower branch), 3—4185, 4—4190 (within the $LO-TO$ gap), 5—4210, 6—4250 (upper branch). b) Line of maxima, determined from the densitogram.

$$\epsilon'(\omega) = \text{Re} [\epsilon_\infty + \epsilon_m \omega_0^2 / (\omega_0^2 - \omega^2 - i\omega\Gamma)].$$

The ratios of the intensities outside and inside the region $LO-TO$ splitting, measured in the lithium-formiate spectrum and calculated from (4) under the assumption $\Gamma = 10 \text{ cm}^{-1}$, $\omega_{||} - \omega_0 = 10 \text{ cm}^{-1}$, turned out to be close.

The simplified model used in this paper for the interference between the susceptibilities of different orders has made it possible to explain qualitatively a number of the observed singularities, and has shown that in the case of a large number of lattice vibrations that are close to one another the form of the spectrum can be too complicated to interpret. Thus, when the LSP method is used for spectroscopic investigation of ferroelectrics, an attempt should be made to use only "pure" orientations, such that the plane of the wave-vector triangles and the electric vectors of the waves lie either in characteristic planes of the lattice or are directed along crystallographic axes. Thus, it is impossible to explain the singularities observed in the spectra of $\alpha\text{-HIO}_3$ and $\alpha\text{-DIO}_3$ in the vicinities of the vibrations of the OH and OD bonds at the frequencies 2900, 2200, and 1160 cm^{-1} . In all probability, "triple" Fermi resonances¹³ take place in this case between the bands of the noncoupled multiparticle states, polaritons, and weak first-order oscillations. This is quite feasible, in view of the rich phonon spectrum of the crystals and the strong anharmonicity of the vibrations of the OH and OD groups.

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