Theory of Stimulated Raman Scattering by Polaritons in Cubic and Uniaxial Crystals

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Expressions are obtained for the gain $g$ and the relative amplitudes of polariton radiation in stimulated Raman scattering by polaritons in cubic and uniaxial crystals. Two lines may appear in the scattering spectrum for cubic crystals, a polariton line and one due to scattering by a longitudinal phonon. With the increase of scattering angle $\theta$, the polariton line moves along the excited polariton dispersion curve, which is determined without taking absorption into account. When the phonon frequency is approached, the amplitude of the transverse part of the polariton wave decreases strongly as a result of growth of absorption and particularly of wave mismatch. A consequence of this is that in the region of sufficiently large $\theta$ the polariton wave excited at the mechanical (transverse Coulomb) phonon frequency becomes practically longitudinal. This anomalous longitudinal wave, which is maintained by the pumping field, can exist only in a pumped medium. In this case scattering is due to superposition of parametric polariton processes related to excitation of the above-mentioned wave and described by a quadratic polarization nonlinearity, and also of purely phonon type processes which can be described by a cubic nonlinearity and are of the same nature as in the case of nonpolar phonons. Because of the contribution of polariton processes, the expressions which determine the magnitude of $g$ and also of the cross section $\sigma$ for spontaneous Raman scattering in the region of large $\theta$, differ from those for the case of nonpolar phonons. An example of the differences which arise is the "front-back asymmetry" of the $g$ and $\sigma$ angular dependence. It is also shown that owing to deformation of the dielectric constant by the pumping field, a cubic crystal becomes anisotropic: proper polarizations and the respective eigenvalues of $g$ appear. In uniaxial crystals there exist scattering lines for ordinary, extraordinary and longitudinal polaritons centered on the corresponding dispersion curves without allowance for absorption. Expressions are obtained and analyzed which define the spectrum and angular dependence of $g$ for these lines.

INTRODUCTION

Stimulated Raman scattering (SRS) by polaritons, in crystals having no inversion center, has been attracting increasing attention of late. This phenomenon was investigated theoretically, in particular, in Refs.1–6. No complete theory has been developed for it, however, even for the case of excitation by plane monochromatic waves, and therefore a number of general physical laws remained unexplained.

The main shortcoming of the preceding studies were as follows: 1) No account was taken of the fact that the pump field, by deforming the permittivity of the medium, changes its symmetry. As a result, for example, a pumped cubic crystal becomes anisotropic. Corresponding proper polarizations set in together with corresponding eigenvalues of the gain. 2) The scattering by longitudinal phonons was not considered. 3) It was assumed that only waves with fixed transverse polarizations interact.

The latter assumption may not hold, for example, for a polariton wave in the vicinity of the phonon frequency. When the polariton line approaches (with increasing scattering angle $\theta$) to the phonon frequency, the amplitude of the transverse part of the polariton wave (at the center of the line) decreases rapidly. This is due initially to the increased absorption, and with further increase of $\theta$ it is caused by the growth of the wave mismatch, which is due to the large difference between the lengths of the wave vectors of the visible and infrared bands (if the pump frequency lies in the visible region). As a result, the amplitude of the transverse polariton wave turns out to be commensurate with, and later on much lower than the amplitude of the longitudinal polariton wave, which is less sensitive to the value of the absorption and does not depend on the wave mismatch. Therefore, at sufficiently large $\theta$, practically only longitudinal polariton waves are excited. On the other hand, if this is forbidden by the selection rules, the parametric polariton processes, which are described by the quadratic nonlinearity of the polarization, become completely unrealizable here, and the scattering is due to pure phonon processes, which are determined by the cubic nonlinearity, i.e., by processes of the same type as in the case of dipole-inactive oscillations.

It must be emphasized that we deal in this case with longitudinal waves occurring at the frequencies of the mechanical7 phonons, which determine the poles (and not the zeroes) of the dielectric constant of the medium7. Such waves are maintained by the pump field and exist only in a pumped medium. We shall therefore call them anomalous longitudinal waves, to distinguish them from the ordinary (normal) longitudinal waves that can exist also in an unpumped medium. The possibility of exciting anomalous longitudinal waves at the frequency of the mechanical phonons is the fundamental difference between scattering by dipole-active (polar) phonons and scattering by dipole-inactive (nonpolar) ones. In addition, of course, normal longitudinal waves can also be excited.

We shall show that these shortcomings narrow down considerably the region of applicability of the results of the earlier studies. We have therefore developed a

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1We recall that the frequencies of the mechanical phonons used by us in this paper coincide with the frequencies of the transverse Coulomb phonons, which can be introduced as a particular case of Coulomb excitons7.
theory that is free, to a considerable degree, of these shortcomings. In view of the customary large absorption of crystals in the vibrational region of the spectrum even away from the phonon resonances, primary interest attaches to the cases when the absorption coefficient at the polarization frequency greatly exceeds the gain. We have performed such an investigation. Principal attention was paid to a calculation and analysis of the gain, which determines the intensities of both stimulated (SRS) and spontaneous (SpRS) Raman scattering.

We carry out our analysis in the approximation of a given stationary pump field, which is approximated by a linearly polarized plane monochromatic wave. It is assumed that the scattering medium takes the form of a layer bounded by the planes \( z = 0 \) and \( z = l \). The pump wave

\[ E(r, t) = e_A \exp[(i(k_L - \omega_0)t) + c.c. \]  

propagates along the \( z \) axis. The subscripts \( l, s, p \) and \( p \) will henceforth denote the pump (usually laser), Stokes, and polariton wave fields; \( \omega \) are the frequencies, and \( n \) and \( k \) are the refractive indices and the wave vectors in the unpumped medium, and \( e \) are real unit vectors of polarization. The medium is assumed to be nonmagnetic and transparent at the frequencies \( \omega_1, \omega_2 \).  

1. CASE OF CUBIC CRYSTALS

We seek the Stokes and polariton fields in the form

\[ E_s(r, t) = \sum_{p=1,3} \sum_{\alpha, \beta} e_{p, \alpha}^{(\beta)} \exp[(i(k_p r - \omega_p t)) + c.c., \]  

\[ E_p(r, t) = \sum_{\alpha, \beta} e_{p, \alpha}^{(\beta)} \exp[(i(w r - \omega_p t)) + c.c., \]  

where \( k = n \) and \( w = n \omega/c \).

The longitudinal component of the Stokes wave can obviously be neglected, but this cannot be done for a polariton wave in the phonon region. As will be seen from the formulas that follow, with further advance into this region all three amplitudes \( A^{(\alpha)} \) first become comparable, after which \( A^{(1)} \) predominates, provided the excitation of the longitudinal waves is allowed by the selection rules. The phase shift of the polariton wave is determined by the vector \( w \) and not by \( k_p \)

\[ k_p = q_p \exp{\phi_p}, \quad q_p = \omega_p/c, \quad \phi_p = \epsilon_p'r + k_p'' \]  

is the dielectric constant at the frequency \( \omega_p \). When the phases are chosen as in (1), the amplitudes \( A^{(\alpha)} \) are smooth functions of \( z \), so that the method of shortened equations is applicable (see also \(^5\)).

The fields \( E_{s,p} \) are related via the nonlinear part of the polarization of the medium \( P^{NL}(r, t) \). The latter has at the frequency \( \omega_s \) the following form:\(^5\)

\[ P^{NL} = (\chi_{ijk}(\omega_p - \omega_j, \omega_s) + \chi_{ijk}(\omega_s - \omega_j, \omega_p)) A_i A_j A_k + \gamma_{ijkm}(\omega_p, \omega_j, \omega_s) A_i A_j A_k A_m \]  

Here \( \chi_{ijk} = \chi_{ijk}(\omega_p, \omega_j, \omega_s) \) and \( \gamma_{ijkm} = \gamma_{ijkm}(\omega_p, \omega_j, \omega_s) \) are the corresponding nonlinear polarizabilities of the medium \( g \). The terms quadratic in the field determine the contributions of the parametric processes, while the cubic terms determine the phonon contributions. A similar expression, with an obvious interchange of indices, holds also for the nonlinear polarization at the frequency \( \omega_p \). We note that in view of the strong absorption in the frequency region \( \omega_p \), the terms of \( P^{NL} \) containing \( \gamma_{ijkm}(\omega_p, \omega_j, \omega_s) \) are immaterial and can be omitted.\(^6\)

The shortened equations for the amplitudes \( A^{(\alpha)} \) are obtained from Maxwell's equations by the standard procedure\(^6\) and take the form

\[ \frac{\partial A^{(\alpha)}_{\omega_p}}{\partial z} = \frac{2iw}{\omega_p} \frac{\partial A^{(\alpha)}_{\omega_s}}{\partial \tau} - \frac{4q_p^2 \chi_{ijk}}{\omega_p} A_i A_j A_k, \]  

\[ \frac{\partial A^{(\alpha)}_{\omega_s}}{\partial z} = \frac{2iw}{\omega_s} \frac{\partial A^{(\alpha)}_{\omega_p}}{\partial \tau} - \frac{4q_p^2 \chi_{ijk}}{\omega_s} A_i A_j A_k, \]  

\[ \frac{\partial A^{(\alpha)}_{\omega_j}}{\partial z} = \frac{2iw}{\omega_j} \frac{\partial A^{(\alpha)}_{\omega_s}}{\partial \tau} - \frac{4q_p^2 \chi_{ijk}}{\omega_j} A_i A_j A_k. \]  

In deriving the system (2-4), we took into account the fact that \( \chi_{ijk}(\omega_p, \omega_j, \omega_s) = \chi_{ijk}(\omega_s, \omega_j, \omega_p) \).

In view of the strong absorption we have

\[ |\omega A^{(\alpha)}(\omega_p - \omega_j, \omega_s)| \ll |\omega^2 - k_p^2|, \]  

and we can therefore neglect in (3) and (4) the terms with the derivatives.\(^5\) after which these equations yield

\[ A_p^{(\alpha)} = \frac{4q_p^2 \chi_{ijk}}{\omega_p} A_i A_j A_k, \]  

\[ A_s^{(\alpha)} = \frac{4q_p^2 \chi_{ijk}}{\omega_s} A_i A_j A_k, \]  

\[ A_j^{(\alpha)} = \frac{4q_p^2 \chi_{ijk}}{\omega_j} A_i A_j A_k. \]  

Substituting the obtained expressions in (2), we arrive at a system of two differential equations with respect to \( A^{(\alpha)} \). We seek its solution in the form

\[ A^{(\alpha)} = B^{(\alpha)} \exp{\pm ik_s} \]  

assuming \( B^{(\alpha)} \) to be independent of \( z \). We then obtain a system of algebraic equations with respect to \( B^{(\alpha)} \). Choosing in a plane perpendicular to \( k_s \) a two-dimensional coordinate system \( \vec{x} \) with axes along the unit vector \( \gamma_{ijkm} \).\(^6\)

\(^5\)The corresponding criterion is of the form \( \epsilon_p'r > 4\pi \Im \gamma_{ijkm} |A_i|^2 \) where \( \gamma = \gamma_{ijkm} \gamma_{ijkm} \).

\(^6\)In addition to the solution that increases with \( z \), which is of interest to us, the system (2-4) has also a solution that attenuates with increasing \( z \) and the rate of attenuation is determined by the quantity \( k^2 = \Im k_s \). Assuming that \( k^2 > 1 \), we take into account only the solution that grows in space. The criterion that allows us to neglect the terms with the derivatives in (3) and (4) can be represented in the form \( g < \Im k_s/w \).
tensors $e^{jkl}_\mu$, we represent the equations for $B_{\mu}$ in the form of a tensor relation

$$\Delta_{\mu}B_{\mu} = -2\hbar^2 x B_{\mu}, \quad \mu = 1, 2, \ldots, 6,$$

where

$$\Delta_{\mu} = 4n^2_{\mu} - 4n_{\mu}^2 + 4n_{\mu}^3 = \left(\Delta_{1\mu} - \Delta_{2\mu}\right)^2 + 4\Delta_{3\mu}^2 = \left(\frac{8n}{V}\right)^2 \Delta_{\mu},$$

(6)

The quantities $\gamma^\mu_{\mu}$ and $\gamma^{\mu}_{\mu}$ are the components, in the $\sigma$ system, of the second-rank tensors $\gamma_{ijkl}$, $\gamma_{ijk}$, and $\gamma_{ijkm}$ of the dipole operators $e^{\mu}_{ijkl}$, $e^{\mu}_{ijk}$, and $e^{\mu}_{ijkm}$ of the microscopic theory in the dipole approximation. The principal values of the nonzero components of the tensor $\sigma^{\mu}_{ijkl}$ coincide with the common value of the nonzero components of the tensor $\gamma^{\mu}_{ijkl}$.

Using formulas (12) and (13), and also the relations

$$\sum_{\mu=1,2} e^{\mu}_{ijkm} = \delta_{\mu\nu} - e^{\mu}_{i\nu} e^{\mu}_{j\nu}, \quad e^{\mu}_{ijkm} e^{\mu}_{ijkm} = \delta_{\mu\nu},$$

we reduce the tensor $\Delta_{\mu}B_{\mu}$ (7) to the form

$$\Delta_{\mu}B_{\mu} = \left(\Delta_{1\mu} - \Delta_{2\mu}\right) B_{\mu} + \frac{4n^2}{3V} \frac{\hbar^2 B_{\mu}}{3V},$$

(14)

The summation in (9) and (10) is over all the dipole-active oscillations, the frequencies of which are set equal to $\omega_{1\mu} - \beta_1 \gamma_{1\mu} / 2$, where $\beta_1$ is the attenuation constant.

Thus, the pumped cubic crystal becomes anisotropy. The values of the principal axes of the tensor $\Delta_{\mu}$ are determined by the resonant regions, where the choice of the unit vectors $e^{\mu}_{ijkl}$ does not depend on the direction of the pump wave.
tropic. The anisotropy is due to the deformation of the dielectric constant by the linearly polarized pump wave.

We shall discuss henceforth in detail the case of an isolated oscillation $\omega_p$. We represent $e_p$ and $e_p'$ in the form

$$e_p' = e_p + \frac{\pi}{\beta_p} x + q', \quad e_p'' = \frac{x}{1 + q',}$$

where $e_p$ is the high-frequency limit of $e_p'$ relative to $\omega_p$. For this case, using the formulas presented above and omitting the indices $f$ and $g$, we have

$$g = G_{\Gamma} \eta_1 = \sum \left[ (\psi''')^2 \right].$$

The structure of the tensor $\alpha_{ij}^{(2)}$ is known. Using this, it is easy to verify that

$$\Lambda = \left[ e_{i}^{j} e_{j}^{k} e_{k}^{l} e_{l}^{i} + e_{k}^{j} e_{j}^{l} e_{l}^{k} e_{k}^{i} + e_{i}^{j} e_{j}^{l} e_{l}^{k} e_{k}^{i} \right]$$

$$= \left( e_{i}^{j} e_{j}^{k} e_{k}^{l} e_{l}^{i} + e_{k}^{j} e_{j}^{l} e_{l}^{k} e_{k}^{i} + e_{i}^{j} e_{j}^{l} e_{l}^{k} e_{k}^{i} \right)^2$$

(20)

Let us discuss certain properties of the gain $g (19)$. Assuming that $g_{\Gamma 1}$, $M_1$, and $\Lambda$ vary little within the limits of the scattering lines, and analyzing in analogy with\footnote{The condition $|\beta_p| \ll 1$ is determined by the condition $\sin(\theta/2) > (\omega_p^2/2\eta_2 n_2) (\eta/\beta_p)^{1/2}$ which is usually satisfied already at $\theta \sim 10 - 15$.} each of the two terms in (19), we conclude that $g$ has two maxima, corresponding to $\tau$ and $\tau_1 = \varphi^1$. The former determines the center of the polariton scattering line (cf.4,5), and the latter the lines of scattering by a longitudinal phonon, inasmuch as the condition $\tau_1 = \varphi^1$ is equivalent to $\epsilon_{\infty} + \epsilon(1 - x^2) \approx 0$. We denote these lines by $P_L$ and $P_{NL}$, respectively. The line $P_L$ is parallel to the dispersion curve of the polaritons that would be produced in the course of scattering in the absence of absorption and wave mismatch. The line $P_{NL}$ remains unchanged in position relative to $\delta$.

It is useful to note that since $M_1$ and $\Lambda$ are generally speaking of the same order, the values of the gains for the lines $P_L$ and $P_{NL}$ (which we shall denote by $g_{PL}$ and $g_{PNL}$) are also of the same order. In particular, at the center of the lines $\omega_p$ and $\omega_L$

$$g_{\omega_p} = G_{\omega_p} \left[ \eta_f 1 + A(1 - x^2) \right], \quad \Lambda = \eta_f 1 + A(1 - x^2), \quad x = \omega_p \omega_L$$

with the exception of the rare cases of very large $|\beta_p|$. We therefore have for the line $P_L$

$$g_L = G_{\omega_p} \eta_f \left[ 1 + A(1 - x^2) \right].$$

(21)

Let, for example, the scattering occur in the plane $o'$ of the face of the principal cube, and let $k_1$ make an angle $\beta_p$ with one of its edges. We consider the cases when $k_1$ lies in the $o'$ plane and is perpendicular to it. In both cases one of the eigenvectors $e_{i}^{(2)}$ lies in the $o'$ plane (cf.\footnote{We recall that the angle $\theta$ is defined inside the medium.}), and the other ($e_{i}^{(2)}$) is perpendicular to it. This is easiest to demonstrate by verifying that $\psi_{o'} = \pi/2 = 0$. In the former case ($e_{i} \parallel \sigma'$)

$$\eta_{o'} = d_1 \sin^2 (\theta + 2\beta_p), \quad M_{o'} = 1, \quad g_{o'} = \frac{G_{\omega} \sin^2 (\theta + 2\beta_p)}{1 + \varphi^2};$$

$$\approx \frac{G_{\omega} \cos^2 (\theta + 2\beta_p)}{1 + \varphi^2}.$$

(22)

Here $\theta_p$ is the angle between $w$ and $k_1$. We have taken into account the fact that at large $\theta$ we can put $\theta_p = (\pi - \theta)/2$.

In the second case ($e_{i} \parallel \sigma'$)

$$\eta_{o'} = d_1 \sin^2 (\theta - 2\beta_p), \quad g_{o'} = \frac{G_{\omega} \sin^2 (\theta - 2\beta_p)}{1 + \varphi^2};$$

$$\approx \frac{G_{\omega} \cos^2 (\theta - 2\beta_p)}{1 + \varphi^2}.$$

(23)

Let now $k_1$ be parallel to the large diagonal of the cube and let the scattering be observed in a plane $o''$ passing through $k_1$ and one of the edges, with either $e_{i} \parallel \sigma''$ or $e_{i} \parallel \sigma'$. One of the eigenvectors $e_{i}^{(2)}$ also lies in the scattering plane $o''$ ($e_{i}^{(2)}$), and the other ($e_{i}^{(2)}$) is perpendicular to it. At $e_{i} \parallel \sigma''$ we obtain

$$\eta_{o''} = d_1 \left[ \sin(\beta_1 + \varphi^1) \right], \quad M_{o''} = \frac{\sin(\beta_1 \cos \beta_1 + 3 - 3\cos \beta_1 \sin \beta_1)}{\sin(\beta_1 \cos \beta_1)}$$

$$g_{o''} = \frac{G_{\omega} \sin^2 (\beta_1)}{1 + \varphi^2};$$

(24)

$$\eta_{o''} = d_1 \sin(\beta_1), \quad M_{o''} = 1, \quad g_{o''} = \frac{G_{\omega} \sin^2 (\beta_1)}{1 + \varphi^2};$$

$$\approx \frac{G_{\omega} \cos^2 (\beta_1)}{1 + \varphi^2}.$$

(25)

Changing over at $g_{\omega} \ll 1$ to the case of spontaneous Raman scattering (SpRS) we obtain the SpRS cross section per unit solid angle, per unit spectral interval, and per unit volume:\footnote{The spectral density of the surface brightness at the exit face is, in the Stokes frequency region, $B_0 = B_0^0 (e^{a} - 1)$. $B_0^0 = k_{01} n_1^2 / \sin^2 \varphi$.}

$$a_{\omega \omega} = B_0^0 \cos \theta / I.$$
\[ \cos^2(2\theta/2) \]

where \( \cos^2 \) is symmetrical. It would be difficult to register the resultant asymmetry experimentally.

We present also a formula for the cross section of spontaneous Raman scattering by longitudinal phonons, integrated over the frequencies, for \( \varphi \gg 1 \):

\[ \alpha = a_q = \frac{\Lambda}{1 + \lambda (1 - \varphi^2) I_c} \]

where \( a_q \) is a constant, \( \Lambda \) is the optical anisotropy of the crystal, while \( \lambda \) is the factor needed to obtain results for normal polarizations of the Stokes radiation active in the optical axis of the crystal.

The result of its application differs significantly from that obtained by using formula (24) in which the given \( \epsilon \) is substituted. This difference is greater the larger \( \varphi \).

To the contrary, it vanishes when \( \varphi \ll 1 \), i.e., in the case of spontaneous Raman scattering.

Finally, let us discuss the ratio of the amplitudes of the transverse and longitudinal polariton waves. As is clear from (5), outside the phonon resonance the polariton wave is in the main transverse and (normal) longitudinal polariton waves. An example is the spectrum of spontaneous Raman scattering by longitudinal phonons, a large extra maximum at the frequency \( \omega_1 \) would appear in addition to the polariton maximum. On going over to large \( \theta \), this extra maximum would merge with the polariton maximum, which moves towards \( \omega_1 \), and the resultant value of \( \varphi \) would differ from (21) in that there would be no factor \( M \), i.e., the value of \( \varphi \) would turn out to be the same as for the nonpolar phonons.

2. CASE OF UNIAXIAL CRYSTALS

We proceed now to investigate SRS by polariton in uniaxial crystals. We confine ourselves to a scattering geometry in which only one of the two possible polarizations of the Stokes radiation is active (the \( o \)- or \( e \)-wave). This covers most of the chosen geometries of greatest interest. We seek the Stokes field in the form \( \mathbf{E}_{\mathbf{r}}(\mathbf{r}, t) = \epsilon_0 A_0 \exp[i(\mathbf{k}_s \cdot \mathbf{r} - \omega_1 t)] + c.c., \epsilon_0 = 1 \), and the polariton field in the same form (1) as before. We choose the unit vectors \( e^{(2)}_p \) in the following manner: \( e^{(2)}_p \) is perpendicular to the plane \( \sigma \) passing through \( \mathbf{w} \) and the optical axis \( C \) of the crystal, while \( e^{(2)}_p \) lies in the plane \( \sigma \).

The shortened equations for the amplitudes \( A_\sigma, p \) are obtained in standard fashion \([5]\), but unlike in the preceding section it is necessary to take into account the anisotropy of the dielectric tensor \( \epsilon \). We denote the principal values of \( \epsilon \) and the axes along which the dielectric anisotropy is the largest (along with \( \epsilon_1 \) and \( \epsilon_2 \)).

In particular, the result for the integral intensity is here the fact that not only \( \epsilon_1 \) and \( \epsilon_2 \) but also \( \epsilon_3 \) are independent of \( \sigma \). We write out immediately the algebraic equations satisfied by the quantities \( B \):

\[ B_{\sigma} = B_{\sigma} \cdot B_{\sigma} = 0 \]

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namely a and b along the component of w on the Σ plane and along the optical axis, respectively. We resolve $e_p^{(2)}$ and $e_p$ along the directions of a and b: $e_p^{(2)} = -a \cos ξ + b \sin ξ$, $e_p = a \sin ξ + b \cos ξ$. Using these resolutions in the expressions for $\chi_{\alpha β}$, (28), we transform g (29) into

$$g = \gamma \text{Im} \left[ \frac{X_a}{1 - e^{iθ} e^{-iθ}} \right] .$$

(30)

Here

$$x_a = e^{iθ} e^{iθ} x_{ab},$$

$$\rho_a = e^{iθ} e^{iθ} \rho_{ab},$$

$$\rho_{ao} = (e^{iθ} e^{iθ} \rho_{ao}) / \Delta,$$

$$\rho_{bo} = (e^{iθ} e^{iθ} \rho_{bo}) / \Delta.$$}

Accordingly

$$B_s = \frac{\rho_{s}(\Delta \cos ξ \rho_{s} + \rho_{c} \sin ξ \rho_{c} \rho_{s} + \rho_{s} \cos ξ \rho_{s} \rho_{s})}{\Delta (\rho_{s} - \rho_{0 s})} - B_{o s},$$

$$B_s = -\rho_{s}(\Delta \cos ξ \rho_{s} + \rho_{c} \sin ξ \rho_{c} \rho_{s} + \rho_{s} \cos ξ \rho_{s} \rho_{s}) \frac{\rho_{s}}{\Delta \rho_{s} - \rho_{0 s}} .$$

We consider further the vicinity of an isolated phonon oscillation and discuss the most important particular cases.

Let the scattering geometry be such that $\chi_{\alpha β} = 0$, $\chi_{ab} = 0$. These conditions are realized in the vicinity of a doubly degenerate dipole active oscillation; such oscillations are polarized in the Σ plane. For this case, we can represent g (30) in the form

$$g = -\gamma \text{Im} \left[ \frac{X_a}{1 - e^{iθ} e^{-iθ}} \right] .$$

(31)

We use furthermore for $\chi_{\alpha β}$ and $\gamma$ the formulas (9)-(11) of the microscopic theory, which are valid in an arbitrary anisotropic crystal. The quantity $\chi_{\alpha β}$, as is clear from (9), is proportional to $μ_1$. Adding to it the quantity $\eta_B = [\sum \alpha^{(β)} (b, e_β)]^2$, which is equal to zero (we recall that $b \perp e_β$, $μ = 1, 2)$, we use formulas (14) in which we replace $e_p^{(2)}$ and $e_p$ by the vectors b and a, respectively. As a result we get

$$g = -\gamma \text{Im} \left[ \frac{X_a}{1 - e^{iθ} e^{-iθ}} \right] .$$

(32)

Here

$$\Phi_s = \frac{1}{e^{iθ} e^{-iθ}} \left( \frac{\Phi_{s} + \Phi_{s}^*}{1 + e^{-iθ} e^{iθ}} \right).$$

and a similar formula, with $e_p^{(1)}$ replaced by a, holds for $A_β$. The quantities $β$ and $x$ are defined in accordance with (13), and $g_0$ in accordance with (19), with allowance for the fact that the index $n$ runs in this case through two rather than three values, since the oscillations $ω_{1β}$ is doubly degenerate. Further,

$$τ_{a} = \frac{μ_1 - μ_s}{μ_1}, \quad τ_{b} = \frac{μ_1 - μ_s}{μ_1}, \quad M = \frac{μ_1}{μ_1} = 1 - A, \quad \Lambda = \frac{μ_1}{μ_1},$$

$$\eta_β = \left[ \sum \alpha^{(β)} (a, e_β) \right] .$$

The analysis of (32) is similar to that used in the preceding section for formula (19). The first term describes a line whose frequency position at fixed $θ$ corresponds to the condition $τ = ω_{1β}$. This condition defines, in the coordinates $(k_ρ, \varphi_β)$ or $(\varphi_β, \varphi_β)$, the dispersion curve of the $α$-polarizations that might be produced in the scattering process in the absence of scattering and wave mismatch. We denote this curve by $Γ_α$, and the line itself by $p_{α}$. For this line $B_{1α} = 0$ and $B_{2α} = 0$.

The maxima of $g$, corresponding to the second term of (32), are located, generally speaking, in the nonresonant region and correspond to the condition $τ = ω_{1β}$. Here

$$B_{1α} = \frac{\rho_{s}(\Delta \cos ξ \rho_{s} + \rho_{c} \sin ξ \rho_{c} \rho_{s} + \rho_{s} \cos ξ \rho_{s} \rho_{s})}{\Delta (\rho_{s} - \rho_{0 s})} - B_{o s},$$

$$B_{1α} = -\rho_{s}(\Delta \cos ξ \rho_{s} + \rho_{c} \sin ξ \rho_{c} \rho_{s} + \rho_{s} \cos ξ \rho_{s} \rho_{s}) \frac{\rho_{s}}{\Delta \rho_{s} - \rho_{0 s}} .$$

We finally, the line $p_{α}$ vanishes at $ξ = 90°$, for in this case we have simultaneously with $Δ = 0$ also $Δ_β = 0 = \mu_1^2 - \mu_1^2 \sin^2 ξ = 0$. At $ξ = 90°$ the line $p_{α}$ vanishes at $ξ = 90°$, i.e., $ε_1 = 0$, thus defining the line $p_{α}$. In the case $0 ≤ ξ ≤ 90°$ at $Δ = 0$, we have the product $Δ_β(Δ_β - \mu_1^2 \sin^2 ξ) = 0$. Therefore, in particular, the line $p_{α}$ is inactive. The line $p_{α}$ exists, for example, in the case of scattering in the Σ plane, and for it we have $B_{1α}, 0$ and $B_{2α} ≠ 0$.

Finally, the line $p_{α}$ vanishes at $ξ = 90°$, for in this case we have simultaneously with $Δ = 0$ also $Δ_β = 0 = \mu_1^2 - \mu_1^2 \sin^2 ξ = 0$. At $ξ = 90°$ the line $p_{α}$ merges with $p_{β}$. In the region of intermediate $ξ$ at sufficiently large $θ$, when $μ$ increases appreciably, the line $p_{α}$ is transformed into the line for scattering by 'quasilongitudinal' phonons, and its position is then determined approximately by the condition $Δ = 0$. The latter follows from the relation $Δ_β(Δ_β - \mu_1^2 \sin^2 ξ) = 0$, if $μ_1^2 \sin^2 ξ ≥ |ε_1|$.

Thus, in accordance with the presence of three independent components of the amplitude of the polariton wave $A^{(1)}$, three types of scattering line are produced in general: for ordinary, extraordinary, and longitudinal polaritons. As to the latter, we can have, just as in cubic crystals, excitation of normal longitudinal polariton waves (i.e., ordinary longitudinal phonons), and anomalous longitudinal waves maintained by the pump field near the frequencies of the mechanical phonons.

The conditions $χ_{1α} ≠ 0$ and $χ_{β} = 0$, at a suitable scattering geometry, can be satisfied in an arbitrary uniaxial crystal without an inversion center. Since $χ_{1α} ∼ η_β$, this calls for $η_β = 0$. For example, in crystals of class $C_{4h}$ in a scattering geometry wherein $k_ρ$ lies in the Σ plane, the scattering takes place in the plane passing through $k_ρ$ and the C axis, $e_ρ$ defines the e-wave, and $e_β$ defines the o-wave, we get $η_β = d^2 \sin^2 θ β_0$, where $β_0$ is the angle between $k_ρ$ and the x axis chosen in accordance with [14] and $d$ is the value of the nonzero component of the tensor $a^{(β)}$. In this case $M = \cos^2 2θ β_0$.

If the scattering takes place in the Σ plane and $e_ρ$ corresponds before to the e-wave and $e_β$ to the o-wave, then $η_β = d^2 \sin^2 (θ - θ β_0)$ and $M = \cos^2 (θ - θ β_0)$. At large $θ$, when $θ β_0 \approx (π - θ) / 2$, we have $M = \sin^2 (θ / 2)$. As a result we get the characteristic front-back

1[The analogous dispersion curve of the e-polarizations will be designated $π_ρ$ and the corresponding scattering line $p_β$. In scattering by e-polaritons in the Σ plane, when $n_ρ = 0$, we use the notation $π_β$. Finally, the lines for scattering by longitudinal phonons, whose positions are determined by the $ε_1 = 0$ and $ε_1 = 0$, will be designated $p_β$ and $p_β$, respectively.]

1[An exception is the line $p_β$ at $ξ = 0$ (see below).]
asymmetry of the phonon scattering, due to the dipole activity of the phonons.

We consider now a geometry in which $\chi_{\perp, \Delta} = 0$ but $\chi_{\parallel} \neq 0$. These conditions can be realized in the vicinity of nondegenerate dipole active oscillations polarized along the C axis. In this case

$$g = -g \text{Im} \left( \frac{4ny^3}{\tau_0 - \epsilon_1} \right),$$

where $\xi_{\parallel}$ is defined by the same formula (31) as $\xi_{\Delta}$, except that $\epsilon_1$ and $\epsilon_\perp$ are replaced by $\xi$ and $\tau - \xi$. In analogy with (32), we also obtain

$$g = -g \text{Im} \left( \frac{\xi_{\parallel}}{1 + \tau_0} \right),$$

$$A_\perp = \frac{\xi_{\parallel}}{\tau_0} \left( \frac{2n_0 y_0 \omega_0}{\omega} \right)^{1/2},$$

$$A_\parallel = \frac{\xi_{\parallel}}{\tau_0} \left( \frac{2n_0 y_0 \omega_0}{\omega} \right)^{1/2}.$$

The maxima of $g$ are determined by the condition $\tau_{\parallel} = \varphi^{-1}$.

The analysis of the scattering spectrum is similar to the preceding one; we therefore confine ourselves to brief remarks in the discussion of the present case. In the nonresonant region, the condition that determines the maximum of the scattering line is approximately equivalent to $\Delta_\parallel (\epsilon_\perp - \mu^2 \cos^2 \xi) = 0$. The result is the line $p_\parallel$, which corresponds to the condition $\Delta_\parallel = 0$, and in the case of $\xi = 0$ we get the line $p_{\perp \parallel}$, which corresponds to $\Delta = 0$, i.e., $\epsilon_\parallel = 0$. For the line $p_{\perp \parallel}$ we have $B_1 = 0$, $B_2 = 0$, and $B_3 \neq 0$. There is no $p_\parallel$ line at $\xi = 0$, and in the case of scattering in the $\Sigma$ plane ($\xi = 90^\circ$) the $p_\perp$ line goes over into $p_\parallel$. The behavior of the latter is equivalent to the behavior of the line $p_1$. At large $\varphi$ we have for this line $g = g_0 (1 + \varphi^2)^{-1}$.

Cases of excitation of purely transverse polaritons in anisotropic crystals were considered in [12]. It follows from the present results that such cases are realized in the vicinity of the phonon frequencies if the phonon oscillation is nondegenerate; for degenerate oscillations this is realized at geometries satisfying the condition $\eta_{\parallel} = \eta$, i.e., $M = 1$ and $\Lambda = 0$. The results obtained in [4] are therefore applicable in the resonant region only in these cases. In the nonresonant region, these limitations do not exist, since no longitudinal polaritons are excited here, with the exception of the region of the lines $p_{\perp \parallel}$.

The results obtained in this section, which pertain to uniaxial crystals, can be easily generalized also to the case of biaxial crystals.

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