On the Theory of Parametric Scattering of Light by Polaritons

V. I. EMEL'YANOV AND YU. L. KLIMONTOVICH

Moscow State University

Submitted July 13, 1971

Zh. Eksp. Teor. Fiz. **62**, 778–788 (February, 1972)

The spontaneous parametric scattering of light in an ionic nonlinear, noncentrosymmetric crystal over the entire range of additional frequencies of the lower polariton branch (ω_2), including the resonance, is investigated on the basis of a specific model by using the method of the theory of nonequilibrium fluctuations. The medium is assumed to be transparent at the pumping frequency and at the frequency of the observed light. Formulas are derived for the linear and nonlinear (quadratic) susceptibility tensors, describing the dispersive properties of the crystal in the frequency range under consideration.

The intensity of the scattered light as a function of the frequency and direction of observation is determined by the nonequilibrium spectral function $(\delta\mathbf{P}\cdot\delta\mathbf{P})^{NL}_{\omega,\,-\mathbf{k}}$ of the nonlinear polarization, which is calculated for the regime of linear (with respect to the intensity of the pump) scattering (luminescence). The investigation is carried out by a method which permits an immediate generalization to the case of superluminescence. The obtained formula expresses the spectral function in terms of phenomenological parameters of the medium (the linear and quadratic susceptibilities) and contains three terms: 1) polariton, 2) polariton-phonon, and 3) phonon. The contribution of the cubic susceptibility to the spectral function is negligible for the regime of luminescence. The polariton contribution determines the parametric scattering in media which are transparent or weakly absorbing at ω_2, but the contribution of the remaining terms is negligible in this region; in the region of strong dispersion of the linear and nonlinear susceptibilities near the resonance $\omega_2 \approx \omega_i$, where ω_i is the frequency of a $\omega_2 = \omega_i$ and for large phonon wave vectors $k_2 \gtrsim 10^5$ cm^{-1} the parametric scattering is completely determined by the phonon term. Accordingly, the well-known results for parametric luminescence in transparent and weakly absorbing media and for Raman scattering by transverse optical phonons follow as limiting particular cases from the general formula derived for the scattered power.

INTRODUCTION

THE question of the spectral distribution of light scattered by a nonlinear crystal has been investigated in a number of articles from various points of view. The majority of these articles are devoted to an investigation of a limited region of the additional frequencies ω_2: the case of parametric luminescence in a medium which is transparent and weakly absorbing at ω_2 was investigated in the articles by Klyshko[1] and by Zel'dovich,[2] scattering by polaritons far away from the resonance was considered by Strizhevskiĭ and Obukhovskiĭ,[3] and finally the resonance case $\omega_2 = \omega_i$, where ω_i denotes the frequency of a transverse optical phonon (Raman scattering by phonons) has been treated, for example, in the article by Loudon.[4]

Macroscopic methods based on the fluctuation-dissipation theorem (FDT) for the electromagnetic field[1-3] are usually used to calculate the line shape of the scattered light associated with absorption at the frequency ω_2. Such an approach is valid if the frequency ω_2 is far from a resonance frequency of the medium. The case when the frequency ω_2 approaches and becomes equal to the resonance frequency of the medium is also of interest. In this region the nonlinear susceptibility is complex and strong dispersion is observed. Remaining within the framework of the macroscopic approach, one can obtain information about the shape of the line in the region near the resonance by enlisting the aid of the generalized FDT relations for nonlinear media, established in the article by Efremov.[5]

We note, however, that, as will be evident from what follows, even for the case of a weakly nonequilibrium medium the generalized FDT does not completely describe nonlinear scattering, since it does not take the polarization noise of second order in the pumping field into account. The generalized FDT is not, in general, applicable for a strongly nonequilibrium state. In virtue of this, another approach based on a specific model of matter and the application of the theory of nonequilibrium fluctuations to this model (as is done, for example, in the statistical theory of lasers[6] or parametric generators[7]) is of interest. Precisely such an approach is taken in the present article. In this article the scattering of light by polaritons of the lower branch is considered over the whole range of admissible frequencies $0 \leq \omega_2 \leq \omega_i$ for the case of a noncentrosymmetric medium (a crystal of the type GaP[8]). A classical model of a nonlinear medium for this case was proposed and discussed in detail in the article by Garrett.[9] (A similar model was used earlier by Akhmanov and Khokhlov[10] in order to describe Raman scattering.) A quantum model of the medium, corresponding to the classical model[9] is utilized in the present work, and on the basis of this model the line shape of the spontaneous parametric scattering is calculated. A calculation with the aid of the generalized FDT is also carried out for comparison.

1. MODEL OF A NONLINEAR MEDIUM. INITIAL EQUATIONS

Let us consider the two subsystems of a diatomic crystal. For a classical description, this system can be described by effective ionic oscillators with frequency ω_i and electronic oscillators with frequency ω_e. These subsystems interact among themselves when the anharmonic terms are taken into consideration. Each of the oscillators possesses a dipole moment; therefore both subsystems interact with the field. Such a model is considered in the article by Garrett.[9] Let us consider the corresponding quantum model. We denote the displacement of the effective ionic oscillators with eigenfrequency ω_i by $\mathbf{u}(\mathbf{R}, t)$, and the interaction energy of the ionic oscillator with the electric field is denoted by $Ze\mathbf{u}\cdot\mathbf{E}$. As the second subsystem we consider a system of effective two-level atoms; $-e\mathbf{r}\cdot\mathbf{E}$ denotes the dipole interaction of the atoms with the field. The interaction of an ionic oscillator with an atom is determined by the expression $\mathbf{C}\cdot\mathbf{u}$. The quantity C is connected with the optical deformation potential θ by the relation $C = \theta/d$, where d is the linear dimension of the cell. It depends on the electronic state of the effective atom.

Using the eigenfunctions of the effective atom, let us write down the expression for the matrix element of the Hamiltonian describing the interaction between the atom at the point $\mathbf{R}$ and the field $\mathbf{E}(\mathbf{R}, t)$ and the displacement $\mathbf{u}(\mathbf{R}, t)$ of the ionic oscillators:

$$H_{nm}^{\text{int}} = \mathbf{C}_{nm}\mathbf{u}(\mathbf{R}, t) - e(\mathbf{r}_{nm} - Z\mathbf{u}(\mathbf{R}, t)\delta_{nm})\mathbf{E}.$$

The corresponding equation for the elements of the density matrix of the atoms takes the form

$$\frac{\partial}{\partial t}\rho_{nm}(\mathbf{R}, t) + i\omega_{nm}\rho_{nm} = -\frac{i}{\hbar}\sum_k \{H_{nk}^{\text{int}}\rho_{km} - \rho_{nk}H_{km}^{\text{int}}\}. \quad (1.1)$$

Let us denote the upper level by a, and the lower level by b. In the approximation of two levels, $\rho_{aa} + \rho_{bb} = 1$. Let $D = \rho_{aa} - \rho_{bb}$ denote the difference of the populations, and let $\mathbf{r} = \mathbf{r}_{aa} - \mathbf{r}_{bb}$ denote the difference between the diagonal matrix elements of the displacement $\mathbf{r}$. Here we confine ourselves to the approximation in which the matrix describing the interaction with the lattice is diagonal, that is, $\mathbf{C}_{nm} = \delta_{nm}\mathbf{C}_{nn}$, and we introduce the notation $\mathbf{C} = \mathbf{C}_{aa} - \mathbf{C}_{bb}$. We then obtain from (1.1) the following system of equations for the functions D, ρ_{ab}, and ρ_{ba}:

$$\left(\frac{\partial}{\partial t} + \gamma_D\right) D = \frac{2ie}{\hbar}(\mathbf{r}_{ab}\rho_{ba} - \rho_{ab}\mathbf{r}_{ba})\mathbf{E}, \quad (1.2)$$

$$\left(\frac{\partial}{\partial t} + i\omega_{ab} + \gamma_{ab}\right)\rho_{ab} = -\frac{ie}{\hbar}\mathbf{r}_{ab}\mathbf{E}D + \frac{ie}{\hbar}\mathbf{r}\mathbf{E}\rho_{ab} - \frac{i}{\hbar}\mathbf{C}\mathbf{u}\rho_{ab}; \quad (1.3)$$

$$\rho_{ba} = \rho_{ab}^*. \quad (1.4)$$

The relaxation constants γ_D and γ_{ab} are introduced in these equations.

Let us supplement this system by the equations for $\mathbf{u}$ and $\mathbf{E}$:

$$\left(\frac{\partial^2 u}{\partial t^2} + \Gamma\frac{\partial u}{\partial t} + \omega_i^2 u\right) = -\frac{Ze}{M}\mathbf{e}_u\mathbf{E} - \frac{\mathbf{e}_u\mathbf{C}}{2M}D, \quad (1.5)$$

$$\frac{\partial^2 E}{\partial t^2} - c^2\Delta E = -4\pi\frac{\partial^2 \mathbf{P}}{\partial t^2}, \ \operatorname{div}\mathbf{E} = 0. \quad (1.6)$$

In these equations M denotes the mass of the ionic oscillator, Γ denotes the attenuation coefficient of the displacement, and $\mathbf{P}$ is the polarization vector:

$$\mathbf{P} = en[(\mathbf{r}_{ab}\rho_{ba} + \mathbf{r}_{ba}\rho_{ab} + {}^1/_2\mathbf{r}D) - Z\mathbf{u}]. \quad (1.7)$$

Here e denotes the effective charge of the atomic dipole, and n is the concentration of atoms.

2. THE NONLINEAR SUSCEPTIBILITY

Let us denote the frequency of the external field by ω_3, by ω_1 the frequency of the signal, and by ω_2 the frequency of the additional field: $\omega_3 = \omega_1 + \omega_2$. In order to calculate the nonlinear susceptibility at the signal frequency we assume that two average fields act on the crystal:

$$\mathbf{E}_3(\mathbf{R}, t) = \mathbf{e}_3 E_3 \exp(-i\omega_3 t + i\mathbf{k}_3\mathbf{R}) + \text{c.c.} \quad (2.1)$$

$$\mathbf{E}_2(\mathbf{R}, t) = \mathbf{e}_2 E_2 \exp(-i\omega_2 t + i\mathbf{k}_2\mathbf{R}) + \text{c.c.} \quad (2.2)$$

E_3 and E_2 are complex amplitudes; $\mathbf{e}_3$ and $\mathbf{e}_2$ are unit vectors along the directions of the field intensities. Below we shall assume that the frequencies ω_1, ω_2, and ω_3 are far away from the transition frequency ω_{ab}. In addition, $\omega_1, \omega_3 \gg \omega_i$, that is, there are no resonances at the frequencies ω_1 and ω_3; $\omega_2 \lesssim \omega_i$, therefore a resonance of the additional wave is possible at the ion frequency ω_i.

The average nonlinear polarization at the frequency ω_1 is given by

$$\langle \mathbf{P}_1\rangle^{\text{NL}} = en\langle \mathbf{r}_{ab}\rho_{ba} + \mathbf{r}_{ba}\rho_{ab} + {}^1/_2\mathbf{r}D\rangle^{\text{NL}}, \quad (2.3)$$

where ρ_{ab}^{NL} and D^{NL} are the solution of Eqs. (1.2)–(1.5) in second-order perturbation theory with respect to the parameters

$$\frac{erE}{\hbar(\omega_{ab} - \omega_{1,2,3})}, \ \frac{c}{M\omega_i\Gamma}\frac{ZeE}{\hbar(\omega_{ab} - \omega_{1,3})} \ll 1.$$

(In Eq. (2.3) we have neglected the contribution from u, which is small at the frequency $\omega_1 \gg \omega_i$.) Let us determine the nonlinear susceptibility in the usual fashion:

$$\langle P_1\rangle_\alpha^{\text{NL}} e^{i\omega_1 t} = \chi_{\alpha\beta\gamma}(\omega_2, -\omega_3) E_{2\beta} e^{-i\omega_2 t} E_{3\gamma}^* e^{i\omega_3 t}. \quad (2.4)$$

Solving Eqs. (1.2)–(1.5) we obtain the following result for the range of frequencies in which $\omega_1, \omega_3 \gg \omega_i$ and $\omega_2 \lesssim \omega_i$:

$$\chi_{\alpha\beta\gamma}(\omega_2, -\omega_3) = \chi^{e}_{\alpha\beta\gamma}(\omega_2, -\omega_3) + \chi^{ei}_{\alpha\beta\gamma}(\omega_2, -\omega_3), \quad (2.5)$$

where the contribution from the electronic part of the polarizability is given by

$$\chi^{e}_{\alpha\beta\gamma}(\omega_2, -\omega_3) = C_{\alpha\beta\gamma}f(\omega_1, \omega_3) + C_{\beta\alpha\gamma}f(\omega_2, \omega_3) + C_{\alpha\gamma\beta}f(\omega_1, -\omega_2),$$
$$C_{\alpha\beta\gamma} = -\hbar^{-2}ne^3 r_{ab\alpha}r_\beta r_{ab\gamma}\langle D\rangle,$$
$$f(\omega_1, \omega_3) = \frac{1}{(\omega_{ab} + \omega_1)(\omega_{ab} + \omega_3)} + \frac{1}{(\omega_{ab} - \omega_1)(\omega_{ab} - \omega_3)}, \quad (2.6)$$

where the components of the vectors $\mathbf{r}_{ab}$, $\mathbf{r}$, and subsequently $\mathbf{C}$ are denoted by the Greek letters α, β, and γ. The contribution from the electronic-ionic part of the polarizability is given by

$$\chi^{ei}_{\alpha\beta\gamma} = -\frac{Zne^3 r_{ab\alpha}C_\beta r_{ab\gamma}\langle D\rangle}{M\hbar^2}\frac{f(\omega_1, \omega_3)}{\omega_i^2 - \omega_2^2 - i\omega_2\Gamma} \quad (2.7)$$

The formula for $\chi^{e}_{\alpha\beta\gamma}$ agrees with the corresponding expression from the article by Graham and Haken[7] (in Eq. (2.6), just as in[7], it is assumed that $\mathbf{r}_{ab} = \mathbf{r}_{ba}$), and $\chi^{ei}_{\alpha\beta\gamma}$ corresponds to the classical formula of Garrett.[9] Let us note the connection of the tensor $\chi^{ei}_{\alpha\beta\gamma}$ from (2.7) with the nonlinear polarizability tensor $a_{\alpha\beta\gamma}$ due to the lattice displacements; the cross section for Raman scattering by transverse optical phonons is usually expressed in terms of this tensor (see, for example,[11]). The tensor $a_{\alpha\beta\gamma}$ is defined by the relation

$$\langle P_\alpha\rangle^{NL} e^{i\omega_1 t} = a_{\alpha\beta\gamma}(\omega_2, -\omega_3) u_\beta e^{-i\omega_2 t} E_{3\gamma}{}^* e^{i\omega_3 t}.$$

From Eqs. (2.4) and (1.5) we obtain

$$a_{\alpha\beta\gamma}(\omega_2, -\omega_3) = -\frac{Zen}{\alpha_i(0)}\left(1 - \frac{\omega_2^2}{\omega_i^2} - \frac{i\omega_2\Gamma}{\omega_i^2}\right)\chi^{ei}_{\alpha\beta\gamma}(\omega_2, -\omega_3), \tag{2.8}$$

where $\alpha_i(0) = nZ^2e^2/M\omega_i^2$ is the static ionic polarizability.

3. THE SPECTRAL FUNCTION OF THE FLUCTUATIONS OF THE NONLINEAR POLARIZATION

Now let an average pumping field $\langle \mathbf{E}_3(\mathbf{R}, t)\rangle$ act on the crystal. Let us find the power of the electromagnetic noise, scattered in a given direction $\mathbf{s}_1$, as a function of the frequency of the observed radiation. The assignment of the direction of scattering together with the synchronism conditions

$$\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2, \quad \omega_3 = \tag{3.1}$$

and the dispersion law for the signal (scattered) wave

$$\omega_1 = |\mathbf{k}_1| c / (\varepsilon_1')^{1/2} \tag{3.2}$$

determine the vector $\mathbf{k}_1 = \mathbf{s}_1|\mathbf{k}_1(\omega_2)|$ as a function of ω_2 such that a maximum will be observed in the scattered power at the frequency ω_2 (in this connection, the vector $\mathbf{k}_2$ is also uniquely determined: $\mathbf{k}_2 = \mathbf{k}_2(\omega_2)$).[1)]

The power of the electromagnetic noise, scattered at a frequency ω in the direction $\mathbf{s}_1$ per unit spectral interval $d\omega$ and angular interval $d\Omega_1$, can be expressed in terms of the spectral function of the fluctuations of the nonlinear polarization according to the formula

$$W_{\omega,s_1} = V\frac{(\varepsilon_1')^{1/2}\omega_1^4}{4\pi^2c^3}\int d\mathbf{k}\,\delta\left(\mathbf{k} - \mathbf{k}_1 - \frac{\mathbf{s}_1}{(\mathbf{v}_1)}(\omega - \omega_1)\right)(\delta\mathbf{P}\delta\mathbf{P})^{NL}_{-\omega,-\mathbf{k}}, \tag{3.3}$$

where $\delta\mathbf{P}$ denotes the negative frequency part of the fluctuations of the nonlinear polarization, and $\mathbf{v}_1 = \partial\omega_1/\partial\mathbf{k}_1$ is the group velocity. Expression (3.3) is obtained from Eq. (1.6).

Let us calculate $(\delta\mathbf{P}\cdot\delta\mathbf{P})^{NL}_{-\omega,-\mathbf{k}}$ by using Eqs. (1.2)–(1.7). We recognize that the average pumping field produces additional (nonlinear) fluctuations in a nonlinear quadratic medium. Therefore, we represent the operators of the system in the form

$$\rho_{ab} = \langle\rho_{ab}\rangle + \delta\rho_{ab} + \delta\rho_{ab}^{NL}, \quad D = \langle D\rangle + \delta D + \delta D^{NL},$$
$$\mathbf{u} = \langle\mathbf{u}\rangle + \delta\mathbf{u} + \delta\mathbf{u}^{NL}, \quad \mathbf{E} = \langle\mathbf{E}_3\rangle + \delta\mathbf{E} + \delta\mathbf{E}_1^{NL} + \delta\mathbf{E}_2^{NL}, \tag{3.4}$$

where the spectra of the fluctuations $\delta\mathbf{E}_1^{NL}$ and $\delta\mathbf{E}$, $\delta\mathbf{E}_2^{NL}$ are concentrated, respectively, near the frequencies ω_1 and ω_2. In (3.4) the additional fluctuations satisfy the condition $\delta\rho_{ab}^{NL} = \delta D^{NL} = \delta u^{NL} = \delta\mathbf{E}_{1,2}^{NL} = 0$, provided that $\langle\mathbf{E}_3\rangle = 0$. The fluctuations of the nonlinear polarization can be expressed in terms of the nonlinear fluctuations $\delta\rho_{ab}^{NL}$ and δD^{NL}:

$$\delta\mathbf{P}^{NL} = en(\mathbf{r}_{ab}\delta\rho_{ba} + \mathbf{r}_{ab}\delta\rho_{ab} + {}^1/_2\mathbf{r}\delta D). \tag{3.5}$$

In what follows we confine our attention to an investigation of the linear scattering region, in which one can neglect the reaction of the pump-produced noise on the system. Then, in calculating δP^{NL} one can neglect δu^{NL} and $\delta\mathbf{E}_{1,2}^{NL}$ in (3.4) and regard $\delta\rho_{ab}$, $\delta\mathbf{u}$, $\delta\mathbf{E}$, and δD as the "natural" fluctuations of the medium and of the field. In this approximation we obtain from Eqs. (1.2)–(1.7) a closed system of equations for the fluctuations $\delta\rho_{ab}^{NL}$, δD^{NL}, δu, $\delta\rho_{ab}$, and δE

$$\left(\frac{\partial}{\partial t} + i\omega_{ab} + \gamma_{ab}\right)\delta\rho_{ab} = \frac{ie}{\hbar}\mathbf{r}(\langle\mathbf{E}_3\rangle\delta\rho_{ab} + \langle\rho_{ab}\rangle\delta\mathbf{E}) - \frac{iC}{\hbar}\delta\mathbf{u}\langle\rho_{ab}\rangle. \tag{3.6}$$

The first two terms on the right-hand side of Eq. (3.6) are nonresonant, but the third is a resonance term (at $\omega_2 = \omega_i$). They are of the same order of magnitude, since $C/M\omega_i\Gamma \approx r$. The term containing $\langle u\rangle$ is omitted since it is not resonant and it is Γ/φ_i times smaller,

$$\left(\frac{\partial}{\partial t} + \gamma_D\right)\delta D^{NL} = \frac{2ie}{\hbar}(\mathbf{r}_{ab}(\langle\rho_{ba}\rangle\delta\mathbf{E} + \langle\mathbf{E}_3\rangle\delta\rho_{ba})$$
$$- \mathbf{r}_{ab}(\langle\rho_{ab}\rangle\delta\mathbf{E} + \langle\mathbf{E}_3\rangle\delta\rho_{ab})), \tag{3.7}$$

$$\left(\frac{\partial^2}{\partial t^2} + \Gamma\frac{\partial}{\partial t} + \omega_i^2\right)(\delta u - \delta u^s) = -\frac{Ze}{M}(\mathbf{e}_u\delta\mathbf{E}). \tag{3.8}$$

Here it is taken into account that the contribution from the term $CD/2M$ in Eq. (1.5) is small (of the order of $(Cr/\hbar\omega_i)(er\delta E_1^{NL}/\hbar\omega_{ab})$); δu^s denotes the random source of the fluctuations δu. It is introduced in accordance with the methods expounded in[6] by one of the authors.

The equation for the linear fluctuations $\delta\rho_{ab}$ has the form

$$\left(\frac{\partial}{\partial t} + i\omega_{ab} + \gamma_{ab}\right)(\delta\rho_{ab} - \delta\rho_{ab}^s) = -\frac{ie}{\hbar}\mathbf{r}_{ab}\delta\mathbf{E}\langle D\rangle. \tag{3.9}$$

On the right hand side, only the major contribution according to perturbation theory is taken into account; $\delta\rho_{ab}^S$ denotes the corresponding source of the fluctuations $\delta\rho_{ab}$. The equation for $\delta\mathbf{E}$ has the form

$$\frac{\partial^2\delta\mathbf{E}}{\partial t^2} - c^2\Delta\delta\mathbf{E} = -4\pi\frac{\partial^2\delta\mathbf{P}}{\partial t^2}, \tag{3.10}$$

$$\delta\mathbf{P} = en(\mathbf{r}_{ab}\delta\rho_{ba} + \mathbf{r}_{ab}\delta\rho_{ab} - Z\delta\mathbf{u}). \tag{3.11}$$

The average value $\langle\rho_{ab}\rangle$ in Eqs. (3.6) and (3.7) is determined by the equation

$$\left(\frac{\partial}{\partial t} + i\omega_{ab} + \gamma_{ab}\right)\langle\rho_{ab}\rangle = -\frac{ie}{\hbar}\mathbf{r}_{ab}\langle\mathbf{E}_3\rangle\langle D\rangle. \tag{3.12}$$

In what follows we shall omit the source of the fluctuations $\delta\rho_{ab}^S$ in Eq. (3.9) since its role is negligible for the frequency region $\omega_2 \ll \omega_{ab}$ (we recall that $\omega_2 \lesssim \omega_i$).

Let us determine δP^{NL}. In order to do this, we substitute $\delta\rho_{ab}^{NL}$ and δD^{NL}, found with the aid of Eqs. (3.6)–(3.9), into expression (3.5). As a result we obtain

$$\delta P^{NL}(-\omega, -\mathbf{k}) = \chi(\Omega, -\omega_3)E_3{}^*\delta E(\Omega, \mathbf{q})$$
$$- \frac{e(\mathbf{r}_{ab}\mathbf{e}_1)(\mathbf{C}\mathbf{e}_2)(\mathbf{r}_{ab}\mathbf{e}_3)\langle D\rangle}{Z\hbar^2}E_3{}^* f(\omega, \omega_3)\delta P^s(\Omega, \mathbf{q}), \tag{3.13}$$

where

$$\delta P^s(\Omega, \mathbf{q}) = -Zen\delta u^s(\Omega, \mathbf{q}), \tag{3.14}$$

$\Omega = \omega_3 - \omega$, $\mathbf{q} = \mathbf{k}_3 - \mathbf{k}$ denote, respectively, the changes of the frequency and wave vector of the photon upon scattering;

$$\chi(\Omega, -\omega_3) = \chi_{\alpha\beta\gamma}(\Omega, -\omega_3)e_{1\alpha}e_{2\beta}e_{3\gamma},$$

1)We note that the fulfilment of the dispersion relation $\omega_2 = \omega_2(|\mathbf{k}_2|)$ for the polaritons is not assumed beforehand; this dispersion relation is not valid in the resonance region $\omega_2 \leq \omega_i$.

e_1 and e_2 are unit vectors along δP_1^{NL} and δE.

Let us also express $\delta E(\Omega, q)$ in terms of $\delta P^S(\Omega, q)$:

$$\delta E(\Omega, q) = -\frac{4\pi\Omega^2}{\Omega^2\varepsilon(\Omega) - q^2c^2}\delta P^s(\Omega, q), \qquad (3.15)$$

where $\epsilon(\Omega) = \epsilon_{\alpha\beta}(\Omega)e_{2\alpha}e_{2\beta}$, and $\epsilon_{\alpha\beta}(\Omega)$ is the dielectric constant tensor of the electron-ion system, determining the dispersion law of the polarizations:[8]

$$\varepsilon_{\alpha\beta}(\Omega) = \delta_{\alpha\beta} + 4\pi\alpha_{\alpha\beta}{}^i(\Omega) + 4\pi\alpha_{\alpha\beta}{}^e(\Omega),$$
$$\alpha_{\alpha\beta}{}^i(\Omega) = \frac{nZ^2e^2}{M}\frac{e_{u\alpha}e_{u\beta}}{\omega_i^2 - \Omega^2 - i\Omega\Gamma}, \qquad (3.16)$$
$$\alpha_{\alpha\beta}{}^e(\Omega) = -\frac{2ne^2\omega_{ab}r_{ab\alpha}r_{ab\beta}\langle D\rangle}{\hbar(\omega_{ab}{}^2 - \Omega^2)},$$

where $\alpha^i_{\alpha\beta}(\Omega)$ and $\alpha^e_{\alpha\beta}(\Omega)$ denote the linear polarizabilities of the ions and electrons, respectively. From Eqs. (3.13) and (3.15) it follows that $(\delta P\delta P)^{NL}_{\omega,-k}$ is determined by the spectral function $(\delta P\delta P)^S_{\Omega,q}$.

We obtain an equation for the double-time correlation function $\langle \delta P(t)\delta P(t')\rangle_{\tau,q} \equiv \langle \delta P\delta P\rangle_{\tau,q}$ from Eqs. (3.8) and (3.14):

$$\left(\frac{\partial^2}{\partial t^2} + \Gamma\frac{\partial}{\partial t} + \omega_i^2\right)\langle\delta P\delta P\rangle^s_{\tau,q} = 0. \qquad (3.17)$$

Let us solve this equation for the initial condition which corresponds to taking only the Stokes component into account:[2)]

$$\langle\delta P\,\delta P\rangle^s_{\tau=0,q} = \frac{\hbar Z^2e^2n}{M\omega_i}(n_q + 1), \qquad (3.18)$$

where n_q denotes the occupation number of the phonon state with wave vector q. Formula (3.18) is obtained with the aid of Eq. (3.14) if we change from $\delta u(R, t)$ to the annihilation operators of the transverse phonons:

$$\delta u(R, t) = \left(\frac{\hbar}{2N\omega_i M}\right)^{1/2}\sum_{q,\lambda=1,2} e_{q\lambda}a_{q\lambda}e^{iqR}$$

(here, just as in the initial equation (1.5), we neglect the dispersion of the long-wavelength phonons). From (3.17) and (3.18) we obtain

$$(\delta P\delta P)^s_{\Omega,q} = \frac{\hbar\varepsilon''(\Omega)}{2\pi}(n_q + 1), \qquad (3.19)$$

where $\epsilon''(\Omega)$ is the imaginary part of the dielectric constant tensor given in (3.16). By using (3.19), we obtain the spectral function $(\delta P\cdot\delta P)^{NL}_{-\omega,-k}$ of the fluctuations of the nonlinear polarization from Eqs. (3.13) and (3.15).

It is convenient to present the final result in the following form:

$$(\delta P\delta P)^{NL}_{-\omega,-k} = (\delta P\delta P)^{ind}_{-\omega,-k} + (\delta P\delta P)^{ind\text{-}s}_{-\omega,-k} + (\delta P\delta P)^s_{-\omega,-k}. \qquad (3.20)$$

The induced (polariton) part is defined by the expression

$$(\delta P\delta P)^{ind}_{-\omega,-k} = |\chi(\Omega, -\omega_3)|^2|E_3|^2(\delta E\delta E)_{\Omega q}, \qquad (3.21)$$

where the spectral function of the polaritons is given by

$$(\delta E\delta E)_{\Omega,q} = \frac{8\pi\hbar\varepsilon''(\Omega)\Omega^4}{|\Omega^2\varepsilon(\Omega) - q^2c^2|^2}(n_q + 1). \qquad (3.22)$$

The crossed polariton-phonon part has the form

$$(\delta P\delta P)^{ind\text{-}s}_{-\omega,-k} = -2\chi''^2(\Omega, -\omega_3)|E_3|^2(\delta E\delta E)_{\Omega,q} \times\left(1 + \frac{\chi'(\Omega, -\omega_3)}{\chi''(\Omega, -\omega_3)}\frac{\Omega^2\varepsilon'(\Omega) - q^2c^2}{\Omega^2\varepsilon''(\Omega)}\right). \qquad (3.23)$$

The contribution from the phonon source of fluctuations is given by the formula

$$(\delta P\delta P)^s_{-\omega,-k} = 8\pi\hbar\frac{\chi''^2(\Omega, -\omega_3)|E_3|^2}{\varepsilon''(\Omega)}(n_q + 1). \qquad (3.24)$$

The notation $\Omega = \omega_3 - \omega$, $q = k_3 - k$ is used in Eqs. (3.20)–(3.24).

Formulas (3.3), (3.20)–(3.24), simultaneously with the expressions for χ given by Eqs. (2.3)–(2.5) and formula (3.16) for ϵ, give the solution to the problem of determining the power of the noise, scattered in a given direction, as a function of the frequency of the observed radiation over the entire range of the lower branch of the polariton frequencies: $0 < \Omega \leq \omega_i$. In this connection, the position of the maximum of the power scattered in a given direction (that is, the frequency ω_1) and also $|k_1|$ in the general case are determined from Eqs. (3.1) and (3.2), where by ω_2 one should understand the value of the frequency Ω which maximizes the expression for $(\delta P\cdot\delta P)^{NL}_{\omega,-k}$ obtained from Eqs. (3.20)–(3.24).

In calculating δP^{NL} we have neglected the back effect on the system of the electromagnetic noise created by the pump. By a similar method one can give a more accurate description and systematically take the effect of the nonequilibrium nature of the medium on parametric scattering into account. We note that in the assumed approximation the crossed polariton-phonon part—given by expression (3.23)—in macroscopic approach can be obtained from the generalized FDT for nonlinear media (see the Appendix). The contribution $(\delta P\cdot\delta P)^S_{-\omega,-k}$ is not determined by this theorem.

Formulas (3.20)–(3.24) take into account the contributions to $(\delta P\cdot\delta P)^{NL}_{-\omega,-k}$ determined by the quadratic susceptibility tensor χ. Consideration of the cubic nonlinearities of the polarization gives an additional contribution. In this case one can represent $(\delta P\cdot\delta P)^{NL}_{-\omega,-k}$ in the form

$$(\delta P\delta P)^{NL}_{-\omega,-k} = (\delta P\delta P)^{(\chi)}_{-\omega,-k} + (\delta P\delta P)^{(\gamma)}_{-\omega,-k},$$

where $(\delta P\cdot\delta P)^{(\chi)}_{-\omega,-k}$ is given by Eqs. (3.20). In this connection it turns out that

$$(\delta P\delta P)^{(\gamma)}_{-\omega,-k} = 4\hbar\gamma''|E_3|^2 n_{-k_1}, \qquad (3.25)$$

where $\gamma = \gamma_{\alpha\beta\gamma\sigma}(\omega_3, -\omega_3, -\omega_1)e_{1\alpha}e_{3\beta}e_{3\gamma}e_{1\sigma}$, $\gamma_{\alpha\beta\gamma\sigma}$ is the cubic susceptibility tensor, n_{-k_1} is the number of thermal phonons in the state $-k_1$. By using the methods of Sec. 2 of the present article, one can obtain an explicit expression for γ. In this connection one finds that

$$\gamma'' \approx (ne^4r^4/\hbar^4\omega_{ab}{}^4)(C^2/M\omega_i\Gamma).$$

By using this estimate, from (3.25) and (3.24) we have

$$(\delta P\delta P)^{(\gamma)}_{-\omega,-k} \sim n_{-k_1}(\delta P\delta P)^{(\chi)}_{-\omega,-k},$$

that is, the contribution from γ is negligible in the

[2)]Here δP denotes the positive frequency part of the fluctuations of the linear polarization.

luminescence mode, when

$$n_{-\mathbf{k}_1} = [\exp(\hbar\omega_1/\varkappa T) - 1]^{-1} \ll 1.$$

In concluding this section we note that for certain applications another way of writing $(\delta\mathbf{P}\cdot\delta\mathbf{P})^{\mathrm{NL}}_{-\omega,-\mathbf{k}}$ is more convenient. By combining Eqs. (3.21) and (3.23) we obtain

$$(\delta\mathbf{P}\delta\mathbf{P})^{\mathrm{NL}}_{-\omega,-\mathbf{k}} = (\delta\mathbf{E}\delta\mathbf{E})_{\Omega,\mathbf{q}}|E_3|^2\Big\{\operatorname{Re}\chi^2(\Omega,-\omega_3) + \operatorname{Im}\chi^2(\Omega,-\omega_3)\frac{q^2c^2-\varepsilon'(\Omega)\Omega^2}{\varepsilon''(\Omega)\Omega^2}\Big\} + 8\pi\hbar\frac{\chi''^2(\Omega,-\omega_3)}{\varepsilon''(\Omega)}|E_3|^2(n_{\mathbf{q}}+1). \quad (3.26)$$

4. ANALYSIS OF THE GENERAL FORMULA FOR $(\delta\mathbf{P}\cdot\delta\mathbf{P})^{\mathrm{NL}}_{-\omega,-\mathbf{k}}$. CERTAIN SPECIAL CASES

Let us divide the admissible range of the additional (polariton) frequencies $0 < \Omega \le \omega_i$ into three characteristic regions: a) the region of transparency: $\epsilon''(\Omega) \to 0$ and $\chi''(\Omega, -\omega_3) \to 0$; b) the region of weak absorption and weak dispersion of $\epsilon(\Omega)$, $\chi(\Omega, -\omega_3)$; and c) the region of strong absorption and strong dispersion near the resonance. For cases a) and b) one can neglect the contributions (3.23)—(3.24) to $(\delta\mathbf{P}\cdot\delta\mathbf{P})^{\mathrm{NL}}_{-\omega,-\mathbf{k}}$, and also one can simplify (3.22) by making use of the narrow-band nature of $(\delta\mathbf{E}\cdot\delta\mathbf{E})_{\Omega,\mathbf{q}}$ in these regions. The dispersion relation $\omega_2 = |\mathbf{k}_2|c/(\epsilon_2')^{1/2}$ follows from (3.22) as $\epsilon''(\Omega) \to 0$; this dispersion relation together with Eqs. (3.1) and (3.2) uniquely determines $\mathbf{k}_2$, ω_2 and $\mathbf{k}_1$, ω_1 for a given $\mathbf{s}_1$. Therefore in (3.22) we set

$$\Omega = \omega_3 - \omega = \omega_2 + \omega_3 - \omega - \omega_2 \equiv \omega_2 + \Delta\omega,$$
$$|\mathbf{q}| = |\mathbf{k}_3 - \mathbf{k}| = |\mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k} - \mathbf{k}_2| \equiv |\mathbf{k}_2 + \Delta\mathbf{k}|$$

and expand in powers of $\Delta\omega$ and $\Delta\mathbf{k}$. Then we obtain

$$(\delta\mathbf{E}\delta\mathbf{E})_{\Omega,\mathbf{q}} = \frac{4\pi\hbar\omega_2 v_2(n_{\mathbf{k}_2}+1)\gamma_2}{c(\varepsilon_2')^{1/2}[(\omega-\omega_1-\mathbf{v}_2(\mathbf{k}-\mathbf{k}_1))^2+\gamma_2^2]}, \quad (4.1)$$

where

$$\gamma_2 = \omega_2^2\varepsilon_2'' \Big/ \frac{\partial\omega_2^2\varepsilon_2'}{\partial\omega_2}, \qquad v_2 = \frac{k_2c^2}{\omega_2}\Big/\Big(\varepsilon_2' + \frac{1}{2}\omega_2\frac{\partial\varepsilon_2'}{\partial\omega_2}\Big)$$

are, respectively, the damping constant and the group velocity of the polariton.

The parametric scattering due to the induced part—given by Eqs. (3.21)—was calculated in[1,2] on the basis of the macroscopic theory. Expressions are obtained from (3.3) with the aid of (3.21) and (4.1) which agree with the results given in[1,2]. In the article by Burstein et al.[11] (see also[12])[3)] a calculation of the parametric scattering by polaritons is carried out for $\Gamma = 0$, that is, without taking the damping of the phonons into account. In this case we have $\chi''(\Omega, -\omega_3) = 0$ for $\Omega < \omega_i$; therefore expressions (3.23) and (3.24) vanish and only the induced contribution remains. In this approximation, by using (2.8) we have

$$\chi(\Omega,-\omega_3) = \chi^e - \frac{Ze}{M}\frac{a}{\omega_i^2-\Omega^2}.$$

Substituting expression (3.21) into formula (3.3) and using the expression for the spectral density of the fluctuations of the field in the region of transparency (formula (4.1), where $\gamma_2 \to 0$), we obtain

$$W_{\omega,\mathbf{s}_1} = V\frac{\hbar\omega_1^4(\varepsilon_1')^{1/2}}{4\pi c^3 n\omega_i M}S_i\Big(a - \frac{(\omega_i^2-\omega_2^2)M}{Ze}\chi^e\Big)^2|E_3|^2 \times \Big|\frac{\mathbf{v}_1}{\mathbf{s}_1(\mathbf{v}_1-\mathbf{v}_2)}\Big|(n_{\mathbf{k}_2}+1)\delta(\omega-\omega_1), \quad (4.2)$$
$$S_i = \frac{4\pi nZ^2e^2\omega_i\omega_2 v_2}{M(\varepsilon_2')^{1/2}c(\omega_i^2-\omega_2^2)^2}.$$

This expression differs from the result cited in[11,12] by the presence of the factor $|\mathbf{v}_1/\mathbf{s}_1\cdot(\mathbf{v}_1-\mathbf{v}_2)|$. The presence of this factor is due to the fact that $\mathbf{v}_2$—the group velocity of the scattered oscillation (polariton)—does not vanish, and parametric scattering differs from Raman scattering, for which $\mathbf{v}_2 = 0$ (see[2]).

In the region near the resonance it is necessary to take all the terms in (3.20) into account. Let us consider the limiting case of large $q \gtrsim 10^5\ \mathrm{cm}^{-1}$ in more detail. From (3.16) we obtain $\epsilon''(\omega_i) = 4\pi\alpha_i(0)\omega_i/\Gamma$. For GaP, for example, $\omega_i/\Gamma \approx 88$ and $\alpha_i(0) \approx 1.4 \times 10^{-1}$.[9] Then from (3.26) and (3.22) we obtain the result that the contribution proportional to $(\delta\mathbf{E}\cdot\delta\mathbf{E})_{\Omega,\mathbf{q}}$ is negligible and of the order of $\omega_i^2\epsilon_i''/q^2c^2 < 10^{-1}$ of the contribution from the phonon source. In this case from (3.3) and (3.26) we have

$$W_{\omega,\mathbf{s}_1} = V\frac{2\hbar(\varepsilon_1')^{1/2}\omega_1^4}{\pi c^3}\frac{\chi''^2(\Omega,-\omega_3)|E_3|^2}{\varepsilon''(\Omega)}(n_{\mathbf{k}_2}+1). \quad (4.3)$$

Let us proceed in (4.3) to the nonlinear susceptibility due to the displacement of the lattice—that is, the quantity a (given by formula (2.8)), and we use the explicit expression for $\epsilon''(\Omega)$ given in (3.16). Then we obtain

$$W_{\omega,\mathbf{s}_1} = V\frac{\hbar(\varepsilon_1')^{1/2}\omega_1^4}{2\pi^2c^3Mn}a^2|E_3|^2\frac{\Omega\Gamma}{(\Omega^2-\omega_i^2)^2+\Omega^2\Gamma^2}(n_{\mathbf{k}_2}+1),$$

which agrees with the usual expression for the power of Raman scattering by transverse optical phonons (see, for example,[12]). Thus, the general formula obtained for $(\delta\mathbf{P}\cdot\delta\mathbf{P})^{\mathrm{NL}}_{-\omega,-\mathbf{k}}$ with increasing Ω and q describes a gradual transition from cases of parametric luminescence in transparent and weakly absorbing media to the case of Raman scattering by transverse optical phonons.

The authors express their gratitude to D. N. Klyshko for reading the manuscript and making a number of comments, and to G. F. Efremov for helpful discussions of certain questions pertaining to the present work.

APPENDIX

SCATTERING IN NONLINEAR MEDIA AND A GENERALIZED FDT

Let us calculate the contribution to the spectral function $(\delta\mathbf{P}\cdot\delta\mathbf{P})^{\mathrm{NL}}_{-\omega,-\mathbf{k}}$ (see (3.20)) described by a generalized FDT for nonlinear media.[5] The nonlinear polarization $\langle \mathbf{P}\rangle^{\mathrm{NL}}$ is related to the average field by the relationship

$$\langle P(\mathbf{R},t)\rangle^{\mathrm{NL}} = \int\chi(\mathbf{R}-\mathbf{R}',t-t';\mathbf{R}-\mathbf{R}'',t-t'') \times \langle E(\mathbf{R}',t')\rangle\langle E(\mathbf{R}'',t'')\rangle\,d\mathbf{R}'d\mathbf{R}''dt'dt''. \quad (A.1)$$

Let an average field specified by (2.1) act on the sys-

[3)]In the article by Benson and Mills,[12] the analysis is carried out with the damping of the phonons taken into consideration.

tem. Let us represent the fluctuation δP^{NL} in the form

$$\delta P^{NL}(R, t) = \delta\tilde{P} \exp [i(\omega_3 t - k_3 R)] + c.c. \quad (A.2)$$

From (A.2) we have

$$(\delta P \delta P)^{NL}_{-\omega,-k} = (\delta\tilde{P}\delta\tilde{P})_{\Omega,q}, \quad (A.3)$$

where $\Omega = \omega_3 - \omega$ and $q = k_3 - k$.

From (A.1) (neglecting the spatial dispersion of χ), by changing to random deflections and introducing a source of the fluctuations, we obtain an equation analogous to (3.13) for $\delta\tilde{P}(\Omega, q)$:

$$\delta\tilde{P}(\Omega, q) = \chi(\Omega, -\omega_3) E_3^* \delta E(\Omega, q) + \delta\tilde{P}^{s}(\Omega, q). \quad (A.4)$$

From (A.4) we obtain

$$(\delta\tilde{P}\delta\tilde{P})_{\Omega,q} = |\chi(\Omega, -\omega_3)|^2 |E_3|^2 (\delta E \delta E)_{\Omega,q} + \chi^*(\Omega, -\omega_3) E_3 (\delta\tilde{P}^{s} \delta E)_{\Omega,q} + c.c. + (\delta\tilde{P}\delta\tilde{P})^{s}_{\Omega,q}. \quad (A.5)$$

Using Maxwell's equation, let us express $\delta E(\Omega, q)$ in terms of the source:

$$\delta E(\Omega, q) = -\frac{4\pi\Omega^2}{\Omega^2\varepsilon(\Omega) - q^2c^2} \delta P^{s}(\Omega, q). \quad (A.6)$$

Now the problem reduces to the calculation of the spectral function $(\delta\tilde{P} \cdot \delta P)^{S}_{\Omega, q}$, and it is expressed in terms of a fluctuation function of first order in the pumping field from the work by Efremov.[5] We have

$$(\delta\tilde{P}\delta P)^{s}_{\Omega,q} = 2\hbar\chi''(\Omega, -\omega_3) E_3^* (n_q + 1). \quad (A.7)$$

(In (A.7) it has been taken into account that, in comparison with[5], here twice as large a value of χ is used.)

Using (A.7), (A.6), and (A.5) we obtain formulas for $(\delta P \cdot \delta P)$ and $(\delta P \cdot \delta P)^{ind-s}_{-\omega,-k}$ which are in agreement with (3.23) and (3.21). As is clear from this consideration, the contribution $(\delta\tilde{P} \cdot \delta\tilde{P})^{S}_{\Omega,q} = (\delta P \cdot \delta P)^{S}_{-\omega,-k}$ (the polarization noise of second order in the pumping field), which is responsible for Raman scattering by transverse phonons, remains indeterminate upon using the generalized FDT.

[1]D. N. Klyshko, Zh. Eksp. Teor. Fiz. **55**, 1006 (1968) [Sov. Phys. JETP **28**, 522 (1969)].

[2]B. Ya. Zel'dovich, Zh. Eksp. Teor. Fiz. **58**, 1348 (1970) [Sov. Phys. JETP **31**, 723 (1970)].

[3]V. L. Strizhevskiĭ and V. V. Obukhovskiĭ, Zh. Eksp. Teor. Fiz. **58**, 929 (1970) [Sov. Phys. JETP **31**, 500 (1970)].

[4]R. Loudon, Proc. R. Soc. A **275**, 218 (1963).

[5]G. F. Efremov, Zh. Eksp. Teor. Fiz. **55**, 2322 (1968) [Sov. Phys. JETP **28**, 1232 (1969)].

[6]Yu. L. Klimontovich, Usp. Fiz. Nauk **101**, 577 (1970) [Sov. Phys. Usp. **13**, 480 (1971)].

[7]R. Graham and H. Haken, Z. Phys. **210**, 216 (1968).

[8]C. H. Henry and J. J. Hopfield, Phys. Rev. Lett. **15**, 964 (1965).

[9]C. G. Garrett, IEEE J. Quantum Electron. 4 (3), 70 (1968).

[10]S. A. Akhmanov and R. V. Khokhlov, Problemy nelineĭnoĭ optiki (Problems of Nonlinear Optics), Gostekhizdat, 1954.

[11]E. Burstein, S. Ushioda, A. Pinzuk, and J. Scott, in Light Scattering Spectra of Solids, edited by George B. Wright, Springer-Verlag, 1969, pp. 43–56.

[12]H. J. Benson and D. L. Mills, Phys. Rev. B **1**, 4835 (1970).

Translated by H. H. Nickle
92