SOVIET PHYSICS JETP VOLUME 31, NUMBER 3 SEPTEMBER 1970

THEORY OF NONLINEAR LIGHT SCATTERING IN CRYSTALS

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Submitted July 18, 1969

Zh. Eksp. Teor. Fiz. 58, 929–936 (March, 1970)

A microtheory of nonlinear scattering (NS) of light by crystal vibrations is developed. In the general case of dipole-active transverse vibrations the NS intensity is determined, first, by the nature of the mechanical phonon; second, by the interaction between the phonons and transverse electromagnetic field, as a result of which the phonons change into polaritons, and third, by nonresonant processes of crystal polarization by the exciting field. Accordingly, the scattered light flux can be represented as the product of three factors—phonon, polariton, and nonresonant—which reflect the aforementioned physical causes responsible for the nature of the scattering. NS by longitudinal phonons is also considered. A close relation between the intensities of NS by transverse and longitudinal phonons and also by polaritons is established. It is shown that a very pronounced angular dependence of the scattering intensity arises for relatively small scattering angles, for which NS by mechanical phonons goes over to NS by polaritons. A relation is derived between the scattering cross section and the respective optical detection tensor, the ratio of the intensities of large-angle scattering by transverse and longitudinal phonons, and of the dispersion characteristics of the crystal is derived. The general theory is illustrated in the case of GaP, ZnSe, and ZnO crystals.

WHEN electromagnetic waves of sufficiently high intensity penetrate into a medium, they can experience spontaneous nonlinear scattering (NS) in the medium. In the elementary act of such a process, n photons of the exciting field are annihilated, in the general case, and a "Stokes" photon $\omega_s = \omega_1 \pm \omega_2 \pm \ldots \pm \omega_n - \omega_\nu$, is produced, where ω_ν is one of the frequencies of the internal motion of the particles of the medium (in particular, it is possible to have $\omega_\nu = 0$). We shall call such a process "scattering of n-th order." Experimental observation of NS of light with n = 2 was reported in[1-5].

Nonlinear scattering has been theoretically investigated earlier in a number of papers[6-9]. At the same time, there is no microscopic theory of NS of light in crystals. The development of such a theory is the main purpose of the present article. In the case of crystals there occur, naturally, a large number of specific peculiarities connected with the difference between the scattering by transverse and longitudinal phonons, scattering by polaritons[10-12], anisotropy, etc. In scattering by mechanical phonons, n + 1 photons take part in the elementary act of the process of n-th order scattering, namely, n photons of the exciting radiation and one Stokes photon ω_s. In scattering by a polariton, which is in essence a quantum of the macrofield in the vicinity of the infrared-active phonon frequency, n + 2 photons are already involved in the elementary act. As a particular case, the theory includes ordinary Raman scattering (RS), in which, for example, $\omega_s = \omega_1 - \omega_\nu$ (n = 1); a number of general results described below apply concretely to this case.

We note that scattering by a polariton at n = 1 is a particular case of parametric luminescence, and at n = 2 it is the case of scattering of light by light; a semiphenomenological description of these processes is contained in[13,14]. A microscopic theory of Raman scattering by polaritons (n = 1) has also been developed in[15-16].

The presently available experimental data on NS of light[1-5] pertain to liquids, although there are apparently no obstacles, in principle, to the observation of this effect in crystals at n = 2. As to cases with n > 2, the difficulties of registering spontaneous NS increases rapidly with increasing n. At the same time, there exist more favorable prospects for the observation of stimulated NS with n ≥ 2.[1)] The intensity and the gain g in such a scattering (in analogy with the case of stimulated Raman scattering, for which $I_{SRS} = I_{SpRS} \exp(gz)$[18], where SpRS is spontaneous Raman scattering) is determined primarily by the characteristics of the spontaneous NS. Therefore a study of stimulated NS must be preceded by an investigation of the spontaneous scattering. In addition, it is advantageous to represent the results in a form that admits of a direct comparison for the most important cases n = 1 and n = 2. In this connection, the general analysis will be carried out below without specifying n concretely.

1. NONLINEAR SCATTERING OF LIGHT BY POLARITONS

Nonlinear scattering by polaritons is a process whose elementary act consists of annihilation of n photons of the exciting radiation (say from a laser) $(\mathbf{k}_1, \omega_1), (\mathbf{k}_2, \omega_2), \ldots, (\mathbf{k}_n, \omega_n)$ and creation of a Stokes photon $(\mathbf{k}_s, \omega_s)$ as well as of a polariton $(\mathbf{k}_p, \omega_p)$. We use here a potential gauge $\varphi = 0$; the basis states are mechanical excitons[19], and the perturbation is (in the dipole approximation) $W = -\int \mathbf{P}(\mathbf{r})\mathbf{E}(\mathbf{r})dv$, where $\mathbf{P}$ is the operator of the dipole moment, and $\mathbf{E}$, is the operator of the macro-

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[1)] Observation of stimulated NS in water at n = 2 is reported in [7].

field intensity in the medium, quantized in accordance with[20,21] 2).

The NS from a polariton, which is of interest to us, is described in the (n + 2)-d order of perturbation theory. We introduce into consideration a light beam B(Ω), scattered in a unit solid angle near the direction $\mathbf{\Omega} = \mathbf{k}_s/k_s$, for which, using the method described in[16], we obtain

$$B(\Omega) = \left(\frac{2\pi}{c}\right)^n \frac{V\hbar\omega_s{}^4\omega_p u_s u_p n_s |\chi|^2}{c^4 n_p \gamma_s\gamma_p |u_s\gamma_s - u_p\cos\psi|} \prod_{j=1}^{n}\left(\frac{J_j}{n_j\gamma_j}\right),$$
$$\chi = e_s^{i_s} e_p^{i_p} \varkappa_{i_s i_p i_1\ldots i_n}(-\mathbf{k}_p, -\omega_p; \mathbf{k}_1, \omega_1; \ldots \mathbf{k}_n, \omega_n)\prod_{\mu=1}^{n} e_\mu^{i_\mu}. \tag{1}$$

Here n_i, u_i, and J_i are respectively the refractive index, the group velocity, and the intensity of the i-th wave, ψ is the angle between the wave vector $\mathbf{k}_s$ and $\mathbf{u}_p$, γ_i is the cosine of the angle between $\mathbf{k}_i$ and $\mathbf{u}_i$, and κ is the nonlinear-susceptibility tensor of rank n + 2 and determines the generation of the sum frequency $\omega_s = -\omega_p + \omega_1 + \ldots + \omega_n$. Explicit expressions for tensors of this type are known in principle[24].

Formula (1) is valid for an arbitrary anisotropy crystal. In cubic crystals, and also in uniaxial crystals, in the case of observation along the optical axis, the expression for B must be summed over two polariton polarizations.

We denote by ω_f the frequency of an isolated dipole-active mechanical phonon, in the vicinity of which ω_p is located. The phonon in question is assumed to be also active in the scattering spectrum of the given order. In the case of odd n, particularly n = 1, this is possible only in crystals without an inversion center. The general expression that is derived from the microscopic theory for κ (without allowance for the spatial dispersion) can be split into two parts: the part κ^0 which is nonresonant with respect to ω_f, and the part $\tilde{\kappa}$, which contains resonant frequency factors $\omega_f \pm \omega_p$:

$$\varkappa_{i_s i_p i_1\ldots i_n}(-\omega_p; \omega_1\ldots\omega_n) = \varkappa_{i_p i_s i_1\ldots i_n}(-\omega_s; \omega_1\ldots\omega_n)$$
$$= \tilde{\varkappa}_{i_p i_s i_1\ldots i_n}(-\omega_s; \omega_1\ldots\omega_n) + \varkappa^0_{i_p i_s i_1\ldots i_n}(-\omega_s; \omega_1\ldots\omega_n),$$
$$\tilde{\varkappa}_{i_p i_s i_1\ldots i_n}(-\omega_s; \omega_1\ldots\omega_n) = \frac{\sqrt{N}}{\hbar}\sum_{f\nu}\frac{2\omega_f P_{f\nu}^{i_p}}{\omega_f{}^2 - \omega_p{}^2}\,\alpha^{(f\nu)}_{i_s i_1\ldots i_n}(\omega_1\ldots\omega_n), \tag{2}$$

where $\mathbf{P}_{f\nu} = v_0^{-1} d_{f\nu}$, and $d_{f\nu}$ is the dipole moment of the transition 0 → fν of one unit cell with volume v_0. The index ν numbers the mutually degenerate vibrational states with energy $\hbar\omega_f$; $N = V/v_0$.

In the case n = 1, the tensor $\alpha^{(f\nu)}_{ij}$ is the usual tensor of RS in crystals[16,25], describing the scattering by mechanical phonons. The tensors $\alpha^{(f\nu)}_{i_s i_1,\ldots,i_n}$, as will be shown below, determine fully the n-th order NS by phonons, and we shall therefore call them the NS tensors. In particular, when n = 2, we have

$$\alpha^{(q)}_{ijk}(\omega_1,\omega_2) = {}^1\!/_2[\gamma^{(q)}_{ijk}(\omega_1,\omega_2) + \gamma^{(q)}_{ikj}(\omega_2,\omega_1)],$$
$$\gamma^{(q)}_{ijk}(\omega_1,\omega_2) = \frac{V^3}{\hbar^2\sqrt{N}}\sum_{m,n}\left[\frac{P_{qm}{}^i P_{mn}{}^j P_{n0}{}^k}{(\omega_m-\omega_1-\omega_2)(\omega_n-\omega_2)}\right.$$
$$\left.+\frac{P_{m0}{}^i P_{nm}{}^j P_{qn}{}^k}{(\omega_m+\omega_1+\omega_2)(\omega_n+\omega_2)} + \frac{P_{mn}{}^i P_{n0}{}^j P_{qm}{}^k}{(\omega_m+\omega_2)(\omega_n-\omega_1)}\right]. \tag{2a}$$

Here m and n number the intermediate states whose quasimomenta are equal to zero. Formulas (2) and (2a) have been obtained in the nonresonant approximation with respect to the exciting frequencies.

In the immediate vicinity of the resonance, the term (2) κ^0 is negligible, but at a sufficiently large distance from it, the role of κ^0 increases. If the vibration f lies sufficiently far, in the low-frequency side, from all the remaining actual vibrations, then κ^0 can be identified with a tensor describing the optical detection of the given order (i.e., the process of formation of the static field in nonlinear interaction of fields with frequencies $\omega_1, \ldots, \omega_n$ and $\tilde{\omega} = \sum_i^n \omega_i$), after subtracting the contribution of the considered vibration ω_f. In the particular case n = 1 we have $\kappa^0_{ijk}(-\omega_L, \omega_L) = \kappa_{jik}(0, \omega_L)$, where κ' is the tensor of the nonlinear electrooptical effect without allowance for the vibration f.

Using the following formulas, which are valid for an anisotropy crystal,

$$n^2 = \frac{e_\alpha\varepsilon_{\alpha\beta}e_\beta}{\gamma_p{}^2}, \qquad \varepsilon_{\alpha\beta} = \varepsilon_{\alpha\beta}{}^0 + \sum_{f\nu}\frac{(b^{f\nu}_{\alpha\beta})^2\omega_f{}^2}{\omega_f{}^2 - \omega_p{}^2},$$
$$(b_{\alpha\beta}{}^{f\nu})^2 = 8\pi V P_{f\nu}{}^\alpha P_{f\nu}{}^\beta(\hbar\omega_f)^{-1}, \tag{3}$$

where ϵ^0 in the vicinity of the isolated transition ω_f can be regarded as independent of ω_p, using the relation $nc(\gamma u)^{-1} = n^2 + {}^1\!/_2\,\omega\partial n^2/\partial\omega$, and neglecting the frequency dependence of γ_p and e_p, we reduce (1) to the form 3)

$$B_f^{(n)}(\Omega) = B_{0f}^{(n)}(\Omega)\Pi_f(\Omega)K_f^{(n)}(\Omega.) \tag{4}$$

Here

$$B_{0f}^{(n)} = N\left(\frac{\omega_s}{c}\right)^4\left(\frac{2\pi}{c}\right)^{n-1}\frac{n_s}{\gamma_s{}^2}\left|e_s^{i_s}\tilde{\alpha}^{(f)}_{i_s i_1\ldots i_n}e_1^{i_1}\ldots e_n^{i_n}\right|^2\prod_{j=1}^{n}\left(\frac{J_j}{n_j\gamma_j}\right),$$
$$\tilde{\alpha}^{(f)} = \tau\sum_\nu(\mathbf{e}_{f\nu}, \mathbf{e}_p)\,\alpha^{(f\nu)} - \text{effective NS tensor}$$
$$\tau^{-2} = \sum_\nu(\mathbf{e}_{f\nu}, \mathbf{e}_p)^2. \tag{5}$$

Further

$$\Pi_f = \frac{\omega_f}{2}\frac{\partial n_p{}^2}{\partial\omega_p}\left|n_p{}^2 + \frac{\omega_p}{2}\frac{\partial n_p{}^2}{\partial\omega_p} - \frac{c}{u_s\gamma_s\gamma_p}n_p\cos\psi\right|^{-1},$$
$$K_f^{(n)} = [1 + A_f^{(n)}(1 - x_p{}^2)]^2, \qquad x_p = \frac{\omega_p}{\omega_f}, \qquad A_f^{(n)} = \frac{(\mathbf{e}_p, \varphi_n{}^0)}{(\mathbf{e}_p, \varphi_n)}. \tag{6}$$

$$\varphi_n{}^i = \frac{2\sqrt{N}}{\hbar\omega_f}\sum_\nu P^i_{f\nu}\alpha^{(f\nu)}_{i_s i_1\ldots i_n}e_s^{i_s}e_1^{i_1}\ldots e_n^{i_n};$$
$$\varphi_n^{0i} = \varkappa^0_{i i_s i_1\ldots i_n}e_s^{i_s}e_1^{i_1}\ldots e_n^{i_n}. \tag{7}$$

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2) We note that the separation of the waves into "ordinary" and purely longitudinal waves (for which the ω(k) dependence is determined by solving the Fresnel equation of crystal optics and the equation det $\epsilon_{\alpha\beta}(\mathbf{k}, \omega) = 0$, resepctively), which is employed in [21] in the quantization of the macrofield, is actually unnecessary, since the purely longitudinal waves constitute a particular case of the "ordinary" waves and are included among the latter, inasmuch as the Fresnel equation is not connected with any limitations on the character of the wave polarization. In anisotropic crystals, purely longitudinal waves can propagate only along the principal axes of the tensor $\epsilon_{\alpha\beta}$, and in arbitrary directions they are only "quasilongitudinal" [22,23], since, generally speaking, there arises a transverse part that is proportional to the degree of anisotropy. We shall henceforth confine ourselves to the approximation of purely longitudinal waves.

3) It can be verified that the explicit form of formulas (5)–(7) is conserved if one uses a Coulomb gauge for the potentials and Coulomb excitons [19] as the basis states.

As is clear from (7) and (2), A_f is practically independent of ω_p.

Thus, the scattered light flux is represented in the form of a product of three factors B_{0f}, π_f, and K_f, which we shall call respectively the phonon, polariton, and nonresonant factors. The polariton factor π_f is significant in the region where the phonon goes over into a polariton; on the other hand, as seen from (3), as ω_p approaches ω_f along the lower polariton branch in the denominator of (6), the term $\frac{1}{2}\omega_p \partial n_p^2/\partial \omega_p$ begins to dominate, and $\pi_f \rightarrow 1$. The form of expression (6) for π_f does not depend on the scattering order n, but the $\omega_p(\theta)$ and $\psi(\theta)$ dependences (θ is the scattering angle in the crystal, i.e., the angle between $\mathbf{k}_L = \sum_i^n \mathbf{k}_i$ and $\mathbf{k}_s$) is different for different n.

The factor K_f is due to the presence of a nonresonant part κ^0 in the tensor κ. In the particular case of dipole-inactive phonons $x_p = 1$ and $K_f = \pi_f = 1$. The scattering intensity is then completely described by the phonon factor of B_{0f}. The same holds true in scattering by polar phonons in the region of sufficiently large scattering angles θ, when $\omega_p \rightarrow \omega_f$. In the general case A_f can be either positive or negative.

We have considered above a light flux that is integral in the frequencies, with scattering of arbitrary order from polariton or phonon excitations of the crystal. It is also of interest to consider the line shape of polariton scattering, which we shall now discuss briefly (in the isotropic approximation). It is convenient to investigate this problem within the framework of the fluctuation-dissipation method, in analogy with[13]. The expression for the scattered light flux can be represented in the form

$$B^{(n)}(\Omega)=\int_0 B^{(n)}(\Omega,\omega)\,d\omega=B_0^{(n)}(\Omega)K^{(n)}(\Omega)\int_0^\infty \Pi(\Omega,\omega)\,d\omega, \tag{8}$$

where the "spectral density of the polariton factor" $\pi(\Omega, \omega)$ is defined by the relation

$$\Pi(\Omega,\omega)=\frac{\omega_f}{\pi\omega}\frac{\partial\varepsilon'(\omega)}{\partial\omega}\frac{\varepsilon''(\omega)}{[n_p'^2-\varepsilon'(\omega)]^2+[\varepsilon''(\omega)]^2},$$
$$n_p'^2=\frac{\left|\sum_i \mathbf{k}_i-\mathbf{k}_s\right|^2 c^2}{\omega_p^2}, \tag{9}$$

ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant in the region of polariton frequencies.

Formulas (8) and (9) are valid if the distance from the polariton scattering line to the phonon line greatly exceeds the half-width of the latter. In this region, the tensor κ can be regarded as real. In addition, we disregard the frequency dispersion of the quantities B_0 and K, which are taken at the center of the line, since it is usually narrow. Indeed, owing to the fact that ϵ'' is small in the region under consideration, $\pi(\Omega, \omega)$ differs essentially from zero only in the vicinity of the point $\omega = \omega_p(\theta)$, which is the root of the equation[4)] $n_p'^2 - \epsilon'(\omega) = 0$. Here

$$\Pi(\Omega,\omega)=\frac{\omega_f\beta}{\pi\omega_p\varepsilon_p''}\frac{\alpha_p^2}{(\omega-\omega_p)^2+\alpha_p^2},\qquad \beta=\frac{\partial\varepsilon_p'}{\partial\omega_p},$$
$$\alpha_p=\frac{u_p u_s\omega_p\varepsilon_p''}{2cn_p|u_s-u_p\cos\psi|}.$$

The index p denotes that the quantities that depend on ω are taken at $\omega = \omega_p$. We see that the line has a Lorentz shape with half-width $2\alpha_p$ and a peak value $\omega_j\beta(\pi\omega_p\epsilon_p'')^{-1}$.

2. SCATTERING BY LONGITUDINAL PHONONS. CONCRETE EXAMPLES

The results obtained in Sec. 1, which pertain to scattering by polaritons, can be directly transferred to the case of longitudinal optical phonons. To this end it is sufficient to replace ω_p by $\omega_f^{\parallel}$ and $\mathbf{e}_p$ by the unit vector $\mathbf{s}_L$ of polarization of the longitudinal wave, and to set $n_p \approx 0$. Then $\pi_f = \omega_f/\omega_f^{\parallel}$, and we obtain for the integral intensity of the scattering line, in lieu of (4),

$$B_f^{\parallel}(\Omega)=B_{0f}^{\parallel}(\Omega)K_f^{\parallel}(\Omega)x_{\parallel}^{-1},\qquad x_{\parallel}=\omega_f^{\parallel}/\omega_f,$$
$$K_f^{\parallel}=[1+A_f^{\parallel}(1-x_{\parallel}^2)]^2,\qquad A_f^{\parallel}=(\mathbf{s}_L\cdot\varphi^0)(\mathbf{s}_L,\varphi)^{-1}. \tag{10}$$

The quantity $B_{0f}^{\parallel}$ is defined by formula (5), in which $\tilde{\alpha}(f)$ must be replaced by the effective tensor $\tilde{\alpha}(f^{\parallel})$ of Raman scattering by longitudinal optical phonons. The quantity $A_f^{\parallel}$, generally speaking, differs from A_f in (7). In many cases of practical importance, however, these quantities coincide (or differ only by a certain geometric factor). Equality takes place if, for example, the tensors $\tilde{\alpha}^{(f)}$ and $\tilde{\alpha}^{(f\parallel)}$ are expressed only in terms of a single nonzero component of the tensor $\alpha^{(f\nu)}$ and the unit vectors $\mathbf{e}_s$ and $\mathbf{e}_L$ are identical for both cases. This circumstance can be used for an experimental determination of A_f. It suffices to measure the ratio of the intensities of scattering by the corresponding longitudinal and transverse phonons (in the region of large scattering angles), after which, using the fact that $B_{0f}^{\perp}$ and $B_{0f}^{\parallel}$ differ only by a certain geometric factor, we can obtain

$$A_f=\frac{1\pm z}{x_{\parallel}^2-1},\qquad z=\left[x_{\parallel}\frac{B_f^{\parallel}}{B_{0f}^{\parallel}}\right]^{1/2}. \tag{11}$$

To eliminate the ambiguity connected with the choice of the sign in the numerator, it is necessary to use, for example, a different set of exciting frequencies, or else to measure additionally A_f at least at one value of θ in the region of small scattering angles, or else to make use of additional auxiliary considerations.

The quantity A_f may also be connected with the cross section for scattering by infrared-active phonons. This connection can be easily found by using a relation that follows from (7),

$$A_f=(\mathbf{e}_p,\varphi)^{-1}\mu-1,\quad \mu=\mu_{i_p i_s\ldots i_n}e_p^{i_p}e_s^{i_s}\ldots e_n^{i_n},$$

where $\mu_{jk\ldots l}$ is the corresponding optical-detection tensor. The differential cross section for the capture of the i-th exciting quantum in the presence of the remaining exciting fields with formation of the quanta $\hbar\omega_s$ and $\hbar\omega_f$, when calculated for a single cell, is of the form

$$\frac{d\sigma_i^{(n)}}{d\Omega}=\frac{B^{(n)}(\Omega)}{J_i}=\left(\frac{\omega_s}{c}\right)^4\left(\frac{2\pi}{c}\right)^{n-1}\frac{2\pi v_0\hbar\omega_f n_s\mu^2}{n_i\gamma_i\gamma_s^2 b_f^2[A_f^{(n)}+1]^2}\prod_{j\neq i}\left(\frac{J_j}{n_j\gamma_j}\right), \tag{12}$$

[4)] This equation represents the quasimomentum conservation law, in which, as we can see, it is necessary to take into account the real part of the refractive index $n_p \approx \sqrt{\epsilon'(\omega_p)}$ at the polariton frequency.

where the constant b_f is determined by expression (3) and can be found from dispersion measurements. In the most important case when $n = 1$

$$\frac{d\sigma^{(1)}}{d\Omega} = \left(\frac{\omega_s}{c}\right)^4 \frac{2\pi v_0 \hbar \omega_f n_s}{n_L \gamma_L \gamma_s{}^2 b_f{}^2 [A_f + 1]^2} (e_p{}^i e_s{}^j e_L{}^k \Delta_{jik})^2, \qquad (13)$$

Δ_{ijk} is the tensor of the nonlinear electrooptical effect. Formulas (13) and (12), can be used for an indirect determination of the scattering cross sections, and this may be necessary, for example, for the determination of the gain of the stimulated NS.

Let us illustrate the foregoing general results by means of several concrete examples. We consider first a cubic crystal with $n = 1$, assuming the tensors κ_{ijk} and κ^0_{ijk} to be symmetrical in the second and third indices. Let, for example, the scattering by a polariton and by longitudinal and transverse phonons be registered at the following geometry of the experiment: 1) polariton: $k_L \parallel [111]$, $e_L \perp e_s$ (in accordance with the experiments of[10]); 2) longitudinal and transverse phonons: $k_L \parallel x$, e_L, $k_s \parallel y$, $e_s \parallel z$ (the axes x, y, and z are parallel to the edges of the unit cube). In this case, as can be readily verified, $A_f = A^{\parallel}_f$.

Further, for each of the triply-degenerate states $f\nu$ ($\nu = x, y, z$) the tensor $\alpha^{(f\nu)}$ contains only one nonzero component that is independent of ν[22]. Assuming that e_{p_1} lies in the xy plane and that $e_{p_2} \parallel z$, we obtain $B^{\perp}_{0f} = B^{\parallel}_{0f}$, so that $z = [x_{\parallel} B^{\parallel}_f / B^{\perp}_{0f}]^{1/2}$. In the case of GaP ($\lambda_L = 6328$ Å), it follows from the results of[26] that $A_f = -1.89$. In the case of ZnSe we get from the results of[27], where the angular dependence of the intensity of scattering by polaritons was investigated, that $A_f \approx -3$. The corresponding values of the scattering cross sections are: $d\sigma^{(1)}/d\Omega = 1.7 \cdot 10^{-28}$ cm^2 (GaP, $\omega_f = 365$ cm^{-1}), $d\sigma^{(1)}/d\Omega = 4.1 \cdot 10^{-28}$ cm^2 (ZnSe, $\omega_f = 205$ cm^{-1}).

Let us consider also scattering in ZnO (class C_{6v}) at the geometry used in[11]: a) scattering by polariton: $k_L \parallel x$, $e_L \parallel y$, k_s lies in the xz plane, e_s is almost parallel to the optical axis z; b) scattering by longitudinal and transverse (symmetry type E) phonons; $k_L \parallel e_s \parallel x$, $e_L \parallel z$, $k_s \parallel y$ (or $k_L \parallel x$, $e_L \parallel k_s \parallel y$, $e_s \parallel z$). Using the known data on the structure of the tensor κ_{ijk} in the approximation of symmetry in the second and third indices, we obtain $A_f = A^{\parallel}_f$, $B^{\perp}_{0f} = B^{\parallel}_{0f}$. On the basis of the experimental results of[23] we get $A_f \approx 1.8$ or $A_f \approx 0.2$. The choice between these values within the framework of the existing data is difficult at the present time.

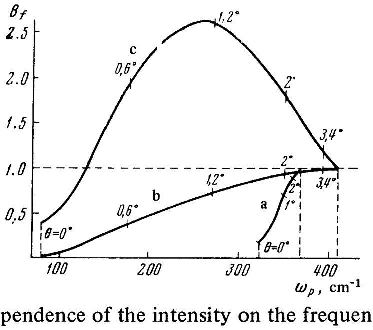

FIG. 1. Dependence of the intensity on the frequency in a crystal: a–GaP: $n = 1$, $\omega_f = 367$ cm^{-1}, $\lambda_L = 6328$ Å, $A_f = 1.89$; b–ZnO: $n = 1$, $\omega_f = 407$ cm^{-1}, $\lambda_L = 4880$ Å, $A_f = 1.8$; c–ZnO: $n = 1$, $\lambda_L = 4880$ Å, $A_f = 0.2$.

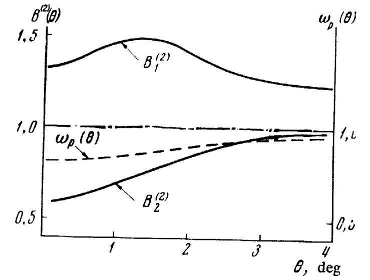

FIG. 2. Angular dependence of the intensity and frequency shifts of nonlinear scattering of second order in a ZnO crystal ($\omega_f = 407$ cm^{-1}, $\lambda_L = 1.06\,\mu$, $A_f(1) = 0.2$, $A_f(2) = 1.8$). Two ordinary photons decay into extraordinary ones (2o → e + e).

Knowledge of A_f and of the dispersion characteristics makes it possible to plot B and ω_p as functions of θ in the cases of scattering by polaritons. Figures 1 and 2 show this dependence in relative units for the crystals ZnO ($n = 1$, $\omega_s = \omega_L - \omega_p$ and $n = 2$, $\omega_s = 2\omega_L - \omega_p$) and GaP ($n = 1$). In the former case, two variants are indicated, corresponding to two possible values of A_f, it being assumed that $A_f^{(1)} \approx A_f^{(2)}$. The experimental data needed for a reliable quantitative comparison of theory with experiment are still missing[5]. In[16] we performed a numerical calculation of the nonresonant factor, i.e., actually for the polariton factor. We note that with increasing n, the interval of angles in which the polariton effects can be observed becomes narrower, roughly speaking, by a factor n. However, nonlinear scattering has the advantage that the appreciable difference between the frequencies ω_s, on the one hand, and $\omega_1, \omega_2, \ldots$, on the other hand, facilitates the separation of the scattered light from the incident light.

The authors thank D. N. Klyshko and I. I. Kondilenko for useful discussions, and J. F. Scott for the opportunity of reading his papers prior to publication.

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[5] The case $n = 1$, under certain particular limitations, was considered in [15]. Our results differ, however, in the fact that in [15] account was taken only of the influence exerted by the polariton character of the excitations on the scattering tensor, and its influence on the density of the final states, which can greatly change when polaritons are excited, was not taken into consideration.

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Translated by J. G. Adashko
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