

THEORY OF RAMAN SCATTERING OF LIGHT WITH FORMATION OF POLARITONS (REAL EXCITONS)

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The problem of the Raman scattering of light involving the formation of polaritons (real excitons) is discussed from the viewpoint of utilizing this method in order to obtain information about the dispersion curves when absorption and spatial dispersion are taken into account. Special attention is given to the observation of the "new" waves, and also to the scattering by surface polaritons.

THE classical method of investigating excitons is to determine the absorption spectra. Certain possibilities related to the measurement of the dispersion, i.e., the indices of refraction (for more details see [1, 2] and the references cited there), are also utilized. Finally, if one talks about optical methods, in a number of cases the dispersion curves for the excitons (the dependence of their frequencies $\omega_I(\mathbf{k})$ on the wave vector \mathbf{k}) can be obtained as a result of investigating the Raman scattering of light associated with the formation of excitons (see [1-5]). Here, of course, one touches upon the Raman scattering of x-rays ([6] and Sec. 15.1 of [1]), but in a practical scheme [7] this method still cannot compete with optical methods, due to the absence of "rasers"—the x-ray analogs of lasers. As to the use of Raman scattering in the optical region to excite different types of excitons, this is now being carried out very widely. [4, 5, 8] In this connection we call attention to the fact that by using this method it was actually possible to obtain in [8] a proof of the existence of a "new" (third) normal wave in gyrotropic crystals, [1, 9] where it has not yet been possible to observe this wave by using other methods. In addition to this question, in the present article we shall touch upon Raman scattering with the excitation of surface polaritons, and we shall also make several remarks of a general nature. The latter appears to be appropriate in connection with the fact that in the literature the question of what kind of information about the dispersion dependences can be obtained by investigating the scattering of light with absorption taken into account is still being discussed.

1. RAMAN SCATTERING OF LIGHT WITH THE FORMATION OF EXCITONS

Let us consider the process of light scattering by a crystal, when the frequency and wave vector of the incident light are equal to ω_I and \mathbf{k}_I , and the corresponding quantities for the scattered light are ω_S and \mathbf{k}_S . From the quantum point of view it is especially clear, although this is also true in the classical domain, that the scattering process is associated with the transfer of energy and momentum to the crystal, where for the case of a single incident photon and a single scattered photon the energy transfer and momentum transfer are equal to $\hbar\omega$ and $\hbar\mathbf{k}$, where

$$\omega = \omega_I - \omega_S, \mathbf{k} = \mathbf{k}_I - \mathbf{k}_S. \tag{1}$$

The momentum $\hbar\mathbf{k}$ may be entirely or partially transferred to the crystal as a whole, but it can also be transferred to one or to several excitations (excitons, phonons, etc.). This can tell something about the energy $\hbar\omega$. It is clear then, if we recall that the momentum of the incident and scattered light changes upon refraction (i.e., upon crossing the boundaries of the crystal), that in the general case the picture is extremely complicated; furthermore the incident and scattered light is generally attenuated inside the crystal, due to the fact that the vectors \mathbf{k}_I and \mathbf{k}_S are complex inside the crystal. In a number of cases, however, one can choose the frequency ω_I in such a way that the absorption at this frequency and at the frequency ω_S would be comparatively negligible. Below we shall assume that such an assumption is allowable. Then, taking \mathbf{k}_I and \mathbf{k}_S to mean the wave vectors of the light inside the crystal, one can also disregard refraction at its boundaries. In this connection it is obvious that all of the quantities in (1) are real and if the question is about the scattering of light with the formation of a single exciton, then ω and \mathbf{k} are its frequency and wave vector. But this means that the produced exciton does not decay, which is sometimes a fair approximation. The question arises, however, as to what happens upon taking attenuation into account and what kind of information about the dispersion relation $\omega_I(\mathbf{k})$ for the excitons can be obtained in this case with the aid of an investigation of the scattering of light. Ideas based on the application of perturbation theory and the neglect of attenuation suggest that the frequency ω and the wave vector \mathbf{k} (see Eq. (1)) are connected also in the presence of attenuation with a certain exciton that is produced, i.e., with an excitation that propagates in the crystal in the absence of any external influences.

Let us clarify this using the simplest example, when the medium (crystal) at the frequency ω is characterized by a dielectric constant $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, that is, neither anisotropy nor spatial dispersion is taken into consideration. In such a medium the dispersion relation for the transverse electromagnetic waves (in the present case they also play the role of the excitons under consideration) has the form

$$c^2k^2/\omega^2 = (n + i\kappa)^2 = \epsilon(\omega). \tag{2}$$

From here it follows that the following relations hold in the normal waves propagating in any arbitrary direction:

$$\bar{E} = E_0 \exp \left\{ -\frac{\omega}{c} \kappa Z + i \left(\frac{\omega}{c} nZ - \omega t \right) \right\}, \quad (3)$$

$$n = \left[\frac{\epsilon'}{2} + \sqrt{\left(\frac{\epsilon'}{2} \right)^2 + \left(\frac{\epsilon''}{2} \right)^2} \right]^{1/2}, \quad \kappa = \left[-\frac{\epsilon'}{2} + \sqrt{\left(\frac{\epsilon'}{2} \right)^2 + \left(\frac{\epsilon''}{2} \right)^2} \right]^{1/2}.$$

In [10] an attempt was made to relate ω and k to the maximum of the Raman scattering line at a given angle by the relation $c^2 k^2 / \omega^2 = n^2$; in [5] the relation $c^2 k^2 / \omega^2 = \epsilon'$ is discussed. In both cases ω and k are determined from (1) and are assumed to be real, according to which attempts are made to replace the complex quantity ϵ in (2) by the real quantities n^2 or ϵ' . However, there is no known justification for such substitutions, and they do not lead to agreement with observations. In this connection, the cross section for scattering is calculated in [5] by the method of Green's functions, permitting us to regard the quantities ω and k as real, without relating them directly to the frequency and wave vector of some kind of excitation. Such an approach is correct but it is excessively complicated and, for the most part, it leaves obscure the essentially extremely simple reason for the difficulties under discussion when attempts are made to relate the scattering in a medium with attenuation and with the formation of excitons.

The whole point is that the dispersion equation (2) and, generally speaking, the dispersion equations for arbitrary normal waves in an arbitrary medium relate ω to k only for the solutions of the homogeneous field equations. In the presence of absorption the corresponding relation between ω and k is, of course, complex. Therefore, in the usual (but, of course, not compulsory) formulation of the problem in optics, the wave vector k in the normal waves (the solutions of the homogeneous problem) turns out to be complex when the frequency ω is real (see expressions (3)). In the scattering of light (just like in the problem of the radiation of charges moving in a medium) we deal, however, with the solution of the inhomogeneous field equations. Specifically, ω and k from (1) play the role of the frequency and wave vector of the driving force, and in general there is no dispersion equation relating ω and k . Upon neglecting absorption, however, the cross section for scattering has the form of a δ -function, i.e., the intensity of the scattering is large only at the exact resonance. Therefore, in the scattering line ω and k are related in the same way as for free excitons. However, in the presence of absorption and in the steady-state regime, the incident field supplies the scattered field and the forced oscillations (waves) in the medium, and the frequency ω and wave vector k of these waves, taken together, generally do not coincide and should not coincide with the frequency and wave vector of the normal waves (excitons).¹⁾

¹⁾It is curious that fallacies associated with the question of the line widths of the scattered light are extremely hard to kill. The calculation of the line width for Rayleigh scattering of light in gases may serve as an example (in this connection, see [11]).

In connection with what has been said, let us consider the evaluation and discussion of the cross section for Raman scattering of light in crystals.

The electromagnetic field equations lead to the following equation (see, for example, [11]):

$$\left\{ k^2 \delta_{ij} - k_i k_j - \frac{\omega^2}{c^2} \epsilon_{ij}(\omega, \mathbf{k}) \right\} E_j = 4\pi \frac{\omega^2}{c^2} P_{ext,i}. \quad (4)$$

Here $E_i \equiv E_i(\omega, \mathbf{k})$ and $j_{ext,i} \equiv -i\omega P_{ext,i}(\omega, \mathbf{k})$ are the Fourier components, respectively, of the electric field and of the "external" current density; furthermore, as usual the electric displacement $D_i = \epsilon_{ij} E_j$.

As in [5] we shall confine our attention to the case of cubic crystals and the propagation of transverse waves (the other simplifications also correspond to the ones made in [5]). Then one can set $\epsilon_{ij} = \epsilon_{\perp}(\omega, \mathbf{k}) \delta_{ij} \equiv \epsilon(\omega, \mathbf{k}) \delta_{ij}$ and Eq. (4) takes the form

$$\left\{ \frac{c^2 k^2}{\omega^2} - \epsilon(\omega, \mathbf{k}) \right\} E(\omega, \mathbf{k}) = 4\pi P_{ext}(\omega, \mathbf{k}). \quad (5)$$

In the problem of the scattering of light, the polarization P_{ext} arises as a result of a nonlinear interaction of the waves. In this connection, for a crystal without a center of symmetry the lowest-order term in the expression for P_{ext} is the bilinear term

$$P_{ext,i} = \chi_{lm,i} E_m^{(l)} E_m^{(s)}, \quad (6)$$

where the upper indices l and s correspond to the incident and scattered waves. For cubic crystals, to which the crystals ZnSe and ZnS considered in [5] belong, the tensor $\chi_{lm,i} = \chi_{ml,i}$ has only one independent component $\chi_{lm,i} = \chi e_{lmi}$, where e_{lmi} is the unit pseudotensor of the third rank. It is obvious that in the case (6) we have to deal with a "three-photon" process when relations (1) are valid; here the exciton wave with electric vector $E(\omega, \mathbf{k})$ which is excited during the scattering plays the role of the third "photon." The power entering into this wave in the steady-state regime is equal to the heat q which is released during its propagation. The intensity I_s of the scattered light is proportional to q :

$$\begin{aligned} I_s &= Aq = \frac{A\omega}{8\pi} \epsilon''_{ij} E_i E_j^* = \frac{A\omega}{8\pi} \epsilon'' EE^* \\ &= \frac{A\omega}{8\pi} \epsilon'' \frac{16\pi^2 |P_{ext}|^2}{(c^2 k^2 / \omega^2 - \epsilon)(c^2 k^2 / \omega^2 - \epsilon^*)} \end{aligned} \quad (7)$$

(see Eq. (5) and the standard expression for q). Now let us set

$$\begin{aligned} \epsilon(\omega, \mathbf{k}) &= \epsilon(\omega) = \epsilon' + i\epsilon'' = \epsilon_0 - \frac{\omega_0^2}{\omega^2 - \omega_r^2 + i\nu\omega} \\ &= \epsilon_0 - \frac{\omega_0^2(\omega^2 - \omega_r^2)}{(\omega^2 - \omega_r^2)^2 + \nu^2\omega^2} + i \frac{\nu\omega\omega_0^2}{(\omega^2 - \omega_r^2)^2 + \nu^2\omega^2}, \end{aligned} \quad (8)$$

which differs from the expression used in [5] only by a few symbols.

Substituting (8) into (7), we obtain after simple transformations

$$I_s = Aq = \frac{2\pi A\nu\omega_0^2 \omega^6 \epsilon_0^{-2} |P_{ext}|^2}{(\omega^2 - \omega_+^2)^2 (\omega^2 - \omega_-^2)^2 + \nu^2 \omega^2 (\omega^2 - c^2 k^2 / \epsilon_0)^2}, \quad (9)$$

where $\omega_{\pm}^2(\mathbf{k})$ are the roots of the dispersion equation in the absence of absorption, i.e., the roots of the equation

$$\frac{c^2 k^2}{\omega^2} = \epsilon = \epsilon_0 - \frac{\omega_0^2}{\omega^2 - \omega_r^2}. \quad (10)$$

It is obvious that

$$\left(\omega^2 - \frac{c^2 k^2}{\epsilon_0}\right) (\omega^2 - \omega_+^2) - \left(\frac{\omega_0^2}{\epsilon_0}\right) \omega^2 = (\omega^2 - \omega_+^2) (\omega^2 - \omega_-^2). \quad (11)$$

As $\nu \rightarrow 0$ we obtain the following result from Eq. (9):

$$I_s = \frac{\pi^2 A \omega_0^2 \omega^4 \epsilon_0^{-2} |P_{ext}|^2}{(\omega_+^2 - \omega_-^2) |\omega^2 - c^2 k^2 / \epsilon_0|} \left\{ \delta(\omega - \omega_-) - \delta(\omega + \omega_-) - \delta(\omega - \omega_+) \right. \\ \left. + \delta(\omega + \omega_+) \right\}. \quad (12)$$

On the other hand, in the absence of attenuation (for $\nu = 0$) the differential cross section, calculated by using perturbation theory, for the Raman scattering of light with the formation of excitons is given by (see, for example, [5] and Sec. 3 below)

$$\frac{d^2 \sigma}{d\Omega d\omega} = \frac{\hbar V_c \omega_i^4}{2\pi m c^4} (e_{i1} e_{s1} e_{k1} |e_{ijk}|)^2 [1 + n(\omega)] \\ \times \left[a + b \left(\frac{4\pi e^*}{V_c} \right) \frac{\omega^2}{c^2 k^2 - \epsilon_0 \omega^2} \right]^2 S(\omega) [\delta(\omega - \omega_-) - \delta(\omega + \omega_-)], \quad (13)$$

where

$$S(\omega) = \frac{\omega \omega_+ \omega_0^2 / \epsilon_0}{(\omega^2 - \omega_+^2)^2 + \omega_+^2 \omega_0^2 / \epsilon_0}. \quad (14)$$

Here e_I , e_S , and e denote the polarization vectors of the corresponding waves, in thermal equilibrium $n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$, V_c is the volume of the elementary cell, and the tensor χ_{lm} , $i = \chi e_{lmi}$ is written in such a form that

$$\left[a + b \left(\frac{4\pi e^*}{V_c} \right) \frac{\omega^2}{c^2 k^2 - \epsilon_0 \omega^2} \right]^2 = \frac{4\pi e^*}{V_c} \frac{\omega^4}{(c^2 k^2 - \epsilon_0 \omega^2)^2} \chi^2.$$

In the foreign literature the function S is usually called (see, for example, [4]) the "phonon strength function"; this same function has also been considered in [12, 13, 2].

Expressions (12) and (13) have an identical structure provided that it is possible to omit the delta functions containing ω_+ —since in the absence of absorption it is impossible to create the polaritons corresponding to the branch $\omega_+(\mathbf{k})$. Thus, by equating (12) and (13) one can determine the factor A in Eq. (9) or, more precisely, the factor A (as $\nu \rightarrow 0$). As a result we obtain the following expression for the scattering cross section with absorption taken into account:

$$\frac{d^2 \sigma}{d\Omega d\omega} = \frac{\hbar V_c \omega_i^4}{2\pi m c^4} (e_{i1} e_{s1} e_{k1} |e_{ijk}|)^2 (1 + n(\omega)) \\ \times \left[a + b \left(\frac{4\pi e^*}{V_c} \right) \frac{\omega^2}{c^2 k^2 - \epsilon_0 \omega^2} \right]^2 \\ \times \frac{\nu \omega (\omega^2 - c^2 k^2 / \epsilon_0)^2}{(\omega^2 - \omega_+^2)^2 (\omega^2 - \omega_-^2)^2 + \nu^2 \omega^2 (\omega^2 - c^2 k^2 / \epsilon_0)^2}. \quad (15)$$

Relation (15) differs from formula (23) obtained in [5] only by the fact that in (15) the quantity $\nu \equiv 2\Gamma$ may depend on the frequency and it appears here multiplied by ω , and not by ω_r as in [5]. This difference is associated with the fact that in [5] the attenuation was calculated using first-order perturbation theory, whereas in (9) and in what follows a more exact approximation is actually used. The method used to take account of the absorption may also be applied to the theory of other nonlinear effects. As a result of numerical calculations, Benson and Mills [5] called attention to the following property: the maximum in frequency (the center) of the scattering line for a given scattering angle (i.e., for a given \mathbf{k}) is determined with a high degree of accuracy

(even in the presence of significant absorption of excitons) as a function of this angle by a dispersion relation for the excitons with total neglect of absorption. In other words, the $\omega(\mathbf{k})$ dependence determined with respect to the center of the scattering line corresponds to one of the dispersion curves $\omega_l(\mathbf{k})$ and, specifically, it corresponds to the curve $\omega_-(\mathbf{k})$ obtained as the result of solving the dispersion equation in the absence of absorption (see Eq. (10)). Such a result is quite obvious from formulas (9) or (15), since the maximum of the intensity is actually determined by the condition $dU(\omega, \mathbf{k})/d\omega = 0$, where U is the denominator in (9) or (15). For the branch $\omega_-(\mathbf{k})$ of interest to us, we obtain over a wide range of frequencies the result $\omega = \omega_- \{1 + 0(\nu^2/\omega_-^2)\}$ for the maximum of the intensity. Since according to [5] $\nu = 2\Gamma = 15 \text{ cm}^{-1}$ and $\omega_- \sim \omega_r \sim 200 \text{ cm}^{-1}$ for ZnSe, it is obvious that at the center of the line $\omega = \omega_-(\mathbf{k})$ to within an accuracy of the order of a percent.²⁾ Thus, even in the presence of rather strong absorption of real excitons (normal waves), from the data concerning Raman scattering one can immediately obtain a dispersion relation for the excitons which would be propagated in the given medium, but in the absence of absorption. A more general and exact conclusion reduces to the fact that Raman scattering, just like other methods (absorption, dispersion) enables us to reconstruct the dielectric permittivity tensor $\epsilon_{ij}(\omega, \mathbf{k})$ within known limits. If this tensor is known, then one can find essentially all of the dispersion curves by solving the dispersion equation

$$\left| k^2 \delta_{ij} - k_i k_j - \frac{\omega^2}{c^2} \epsilon_{ij}(\omega, \mathbf{k}) \right| = 0$$

(for more details, see [1]). What has been said does not prevent us from identifying Raman scattering in the appropriate cases, with scattering with the formation of excitons or, for short, scattering by excitons. It is only necessary to keep in mind that, where absorption is taken into account, these excitons do not coincide with the normal waves (the real excitons, according to the terminology adopted in [1]). We note, finally, that polaritons are now customarily referred to in the literature as real excitons—that is, the normal waves corresponding to the exact solutions (with retardation taken into account) of the homogeneous field equations. In contrast to real excitons or polaritons, the solutions of the homogeneous equations of the Coulomb problem (i.e., the solutions of the field equations neglecting the transverse field and retardation) are called Coulomb excitons. For large values of \mathbf{k} the real excitons (polaritons) practically coincide with the Coulomb excitons. It is therefore actually necessary to deal with scattering by polaritons only in the case of small-angle scattering.

2. RAMAN SCATTERING AND THE "NEW" WAVE IN GYROTROPIC CRYSTALS

When using the expressions for ϵ_{ij} above, spatial dispersion was not taken into account. In addition, the crystals of the type ZnS under consideration belong to

²⁾When the frequency dependence of the numerator in formula (15) is taken into account, the coincidence of the maximum of the intensity with the frequency ω_- becomes in certain cases even more exact.

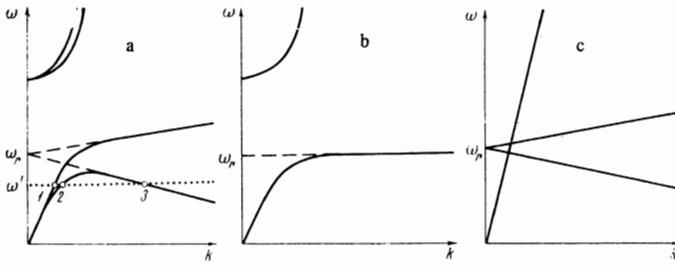


FIG. 1

the class $T_d \equiv \bar{4}3m$, for which no gyrotropy exists, notwithstanding the absence of a center of symmetry (see ^[11]). However, for crystals of lower symmetry the question arises of the influence of spatial dispersion, and primarily gyrotropy, on Raman scattering by polaritons (i.e., with formation of polaritons). Precisely such a case is discussed in ^[8] in regard to quartz. We do not know of any other experimental or theoretical investigations of Raman scattering by polaritons in gyrotropic crystals. Meanwhile, one can hope to use the method of Raman scattering to observe the "new electromagnetic wave (polariton) which should be present in gyrotropic crystals, but which has still not been observed by other methods (see ^[1, 2, 9]). The study of Raman scattering in gyrotropic medium with the appearance of the "new" waves taken into consideration is also of interest in connection with the problem of the construction of tunable lasers (under the appropriate conditions the change in the frequency of a scattered photon depends in a specific way on the angle of scattering; see Fig. 1 below).

Let us consider, for simplicity, the case of a cubic gyrotropic crystal. Then, taking spatial dispersion into account, it is necessary to write down instead of Eq. (8) (see ^[11])

$$\epsilon_{ij}^{-1}(\omega, k) = \epsilon_{ij}^{-1}(\omega)\delta_{ij} + i\delta(\omega)e_{ijk}, \quad (16)$$

where $\epsilon(\omega)$ is determined near resonance according to (8) and $\delta(\omega)$ is a certain function of ω . Below we shall assume that absorption is absent ($\nu = 0$). Under such conditions the dispersion equation for the transverse waves has the form (see ^[1, 9])

$$\left(\frac{1}{\epsilon(\omega)} - \frac{\omega^2}{c^2k^2}\right)^2 = \delta^2k^2, \quad \epsilon(\omega) = \epsilon_0 - \frac{\omega_0^2}{\omega^2 - \omega_r^2}. \quad (17)$$

The dependence of ω on k , according to Eq. (17), is schematically shown in Fig. 1a. The same polariton branches are shown in Fig. 1b, but for the case $\delta = 0$, when a two-fold polarization degeneracy of each branch exists. The Coulomb excitons formally correspond to the limit $c \rightarrow \infty$ and for them, therefore, one finds

$$\frac{1}{\epsilon(\omega)} = \pm|\delta|k, \quad \omega_{\pm}^{(c)}(k) \approx \omega_r \pm ak, \quad (18)$$

$$\alpha = \frac{\omega_0^2}{2\omega_r}|\delta|.$$

The branches $\omega_{\pm}^{(c)}$ are shown on Fig. 1c, where the straight line $\omega_{\pm} = ck/\sqrt{\epsilon_0}$, corresponding to the solution of Eq. (17) for $\delta = 0$ and $\epsilon(\omega) = \epsilon_0$ (i.e., for $\omega \gg \omega_r$, $\omega \gg \omega_0$), is also given. From Fig. 1a it is clear that a number of the frequencies (for example, the frequency ω' indicated in the figure) correspond to three values of k . This is equivalent to the existence of three solu-

tions for $n^2(\omega)$ for a given value of ω , where the solution $n_3^2(\omega)$, corresponding to point 3 on Fig. 1a, is exactly what is called the "new" wave (compare with ^[11]). As has already been indicated, up till now it has not been possible to observe this wave, but in ^[8] precisely this wave was found in quartz by using the method of Raman scattering. Specifically, what was observed in ^[8] was a linear dependence of both frequencies ω_{\pm} on k , in agreement with (18), with $\alpha \approx 10^5$ cm/sec. The possibility of using in the present case the investigation given above for cubic crystals is associated with the fact that only waves (incident, scattered, and polariton waves) propagating along the optical axis were considered in ^[8]. Of course, the coefficient α is proportional to δ and can be calculated beforehand from the formula $\alpha = (\omega_0^2/2\omega_r)\delta(\omega_r)$, if the parameters ω_0 , ω_r , and $\delta(\omega_r)$ are known.

We note that what has been said with regard to formula (18) was stressed a long time ago (see ^[14] and also ^[1, 2]) and it was formulated again in ^[8] by using the microscopic theory of lattice vibrations. Meanwhile, the linear dependence of $\omega_{\pm}(k)$ on k for Coulomb excitons and the relation of the coefficient α with the rotary power of crystals (or with the coefficient δ) do not depend on the model and can therefore also be used, for example, in the region of electronic dipole transitions.³⁾

The question of the intensity of the scattering when spatial dispersion is taken into account is, of course, important. A calculation by the method of perturbation theory gives, naturally, a result similar to formula (13). The only difference consists in the fact that all of the frequencies $\omega_l(k)$ play the role of the frequency $\omega_-(k)$, where the subscript $l = 1, 2, 3$ corresponds to the normal wave in the appropriate gyrotropic crystal. In cubic crystals or upon propagation along the optical axis these normal waves are circularly polarized. In this connection, if $\delta > 0$, two of the waves are circularly polarized to the left and one to the right; however if $\delta < 0$, then the direction of rotation of the wave is reversed. By virtue of what has been said, one can assume a formula of the type (13), from which it follows that near the maximum on the lower curve in Fig. 1a the intensities of the waves associated with the formation of polaritons 1, 2, 3 (we refer to the values of $\omega_l(k)$ at the points 1, 2, and 3 shown on Fig. 1a) are roughly the same. The role of attenuation associated with the utilization of Raman scattering is, as indicated, less important than in the experiments involving absorption or dispersion, which are discussed in ^[1]. Therefore it is clear why it was precisely the method of Raman scattering which led to the first successes with respect to the "new" wave. Possibly the method of Raman scattering will also turn out to be applicable to the investigation of polaritons in liquid crystals; the latter are of very great interest, particularly in virtue of their unusually large (in certain cases) rotary power.

3. RAMAN SCATTERING OF LIGHT BY SURFACE POLARITONS

Although the problem of surface electromagnetic waves (Coulomb excitons, polaritons) in condensed me-

³⁾A related question is that of the gyrotropy of acoustic waves [^{15, 16}].

dia has been discussed for a long time, up to this time their experimental investigation has mainly been confined to the analysis of the energy lost by fast electrons passing through thin films of metals, semiconductors, etc. In this connection losses corresponding to the excitation of surface plasma oscillations were actually observed. More recently the radiative decay of surface plasmons has also been observed. However, on the whole, the study of surface waves in crystals is just beginning. At the same time interest in this circle of problems is increasing in connection with the wide utilization, both in devices and in physics experiments, of thin crystalline and amorphous films. In connection with this, let us discuss the possibility of an analysis of surface polaritons with the aid of experiments involving the Raman scattering of light.

Surface polaritons possess a two-dimensional (surface) wave vector $\mathbf{k}(k_x, k_y)$. Therefore, in Raman scattering of a photon by a surface polariton, the laws of momentum and energy conservation have the following form:

$$\begin{aligned} \hbar ck_I - \hbar ck_s &= \hbar \omega(\mathbf{k}), \quad k_{I,x} - k_{s,x} = k_x, \\ k_{I,y} - k_{s,y} &= k_y, \end{aligned} \quad (19)$$

where \mathbf{k}_I and \mathbf{k}_S are the wave vectors of the incident and scattered photons (we assume that these photons are propagating in vacuum, in virtue of which $\omega_I = ck_I$ and $\omega_S = ck_S$), and $\hbar \omega(\mathbf{k})$ denotes the energy of a surface polariton with wave vector \mathbf{k} . If the vectors \mathbf{k}_I , \mathbf{k}_S , and the normal to the surface lie in one plane (for example, the plane $k_y = 0$), then relations (19) can be rewritten in the form

$$ck_{I,x}\sqrt{1+\alpha^2} - ck_{s,x}\sqrt{1+\alpha^2} = \omega(k_{I,x} - k_{s,x}), \quad (20)$$

where $\alpha_I = |k_{I,z}|/k_{I,x} = \cot \theta_I$, $\alpha_S = k_{S,z}/k_{S,x} = \cot \theta_S$, and θ_I and θ_S denote the angles of incidence and reflection (see Fig. 2). For given values of α_I and α_S , experiment enables us to determine the energy $\hbar \omega_S = \hbar ck_{S,x}\sqrt{1+\alpha_S^2}$ of the scattered quantum and, therefore, the value of $k_{S,x}$. Knowledge of this quantity, used with relation (20), enables us to determine the value of the surface polariton's energy $\hbar \omega$ for $k = k_{I,x} - k_{S,x}$. By changing the angle of incidence or the angle of reflection one can, therefore, at least in principle reconstruct the spectrum $\omega(\mathbf{k})$ of the surface polaritons over a wide range of values of \mathbf{k} .

The basic difficulty, which arises in connection with attempts to observe Raman scattering of light by surface polaritons, lies in the low probability of the process. The latter is due to the fact that in experiments on reflection, the photon traverses a relatively small path in the medium. Since, however, the cross section of the process per unit path length of the light in the medium in the region of localization of the surface polariton

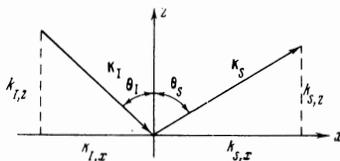


FIG. 2

turns out to be of the order of the cross section for Raman scattering by volume polaritons, the intensity of spontaneous scattering by surface polaritons can probably be increased for $\theta \rightarrow \pi/2$ (grazing incidence) and (or) by passing to the range of frequencies ω_I and ω_S corresponding to resonant Raman scattering of light.

Now let us go on to the question of calculating the cross section for Raman scattering by surface polaritons whose depth of localization is large in comparison with the lattice constant. Such polaritons can be treated within the framework of the macroscopic theory, and for them the operators representing the polarization per unit volume $\mathbf{P}(\mathbf{r})$, and the electric field intensity, $\mathbf{E}(\mathbf{r})$, can be represented in the following form (see [2]):

$$\mathbf{P}(\mathbf{r}) = \sum_{\mathbf{k}} \frac{a(\mathbf{k})}{\sqrt{N_1 N_2}} \mathbf{P}(\mathbf{k}) \xi(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}} + \text{h.c.} \quad (21)$$

$$\mathbf{E}(\mathbf{r}) = \sum_{\mathbf{k}} \frac{a(\mathbf{k})}{\sqrt{N_1 N_2}} \mathbf{E}(\mathbf{k}) \xi(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}} + \text{h.c.} \quad (22)$$

In these relations $\mathbf{P}(\mathbf{k})$ and $\mathbf{E}(\mathbf{k})$ denote the amplitudes of the polarization and of the electric field intensity in the surface polariton with wave vector $\mathbf{k}(k_x, k_y)$, $\mathbf{K} \equiv (k_x, k_y, ik_z)$, $k_z = k_z' + ik_z''$, $k_z' > 0$, $a(\mathbf{k})$ is a normalization constant, $\xi(\mathbf{k})$ and $\xi^*(\mathbf{k})$ are the operators for the annihilation and creation of the \mathbf{k} -th polariton, and $N_1 N_2$ is the number of elementary surface cells on the boundary $z = 0$ of the surface under consideration. The quantity $a(\mathbf{k})$ is determined from the condition

$$\sum_{\mathbf{n}} |a|^2 \left| \frac{e^{i\mathbf{k}\mathbf{n}}}{\sqrt{N_1 N_2}} \right|^2 = 1,$$

where the summation is carried out over all sites of the semi-infinite crystal, so that

$$|a|^2 = \left\{ \sum_{n_3=0}^{\infty} e^{-2k_z' n_3 d_3} \right\}^{-1} = (1 - e^{-2k_z' d_3})^{-1} \approx 2k_z' d_3 \equiv \frac{d_3}{\Lambda},$$

where $\Lambda = 1/2k_z'$ denotes the depth of localization of the surface polariton.

The possibility of using relations (21) and (22) makes the calculation of the cross section for Raman scattering by surface polaritons quite analogous to the corresponding calculation of the cross section for scattering by volume polaritons (see, for example, [4, 5]). The resultant scattering cross section per unit frequency interval and solid-angle interval and per unit path length, for the entire crystal without taking absorption into account, has the form

$$\begin{aligned} \frac{d^2 \sigma}{d\Omega d\omega} &= \frac{\hbar V_c \omega^4}{2mc^3} |e_{I,\alpha} e_{s,\beta} e_{\mathbf{k}} | e_{i\mathbf{k}\beta} |^2 (1 + n(\omega)) \\ &\times \left| a + b \frac{4\pi e^*}{V_c} \frac{1}{\epsilon(\omega) - \epsilon_0} \right|^2 S(\omega) \delta[\omega_I - \omega_s - \omega(\mathbf{k})]. \end{aligned} \quad (23)$$

$$\times \Delta(k_{I,x} - k_{s,x} - k_x) \Delta(k_{I,y} - k_{s,y} - k_y) L(k_{I,z} - k_{s,z} - k_z'', k_z'),$$

where $\Delta(\mathbf{x})$ is the Kronecker symbol ($\Delta(\mathbf{x}) = 1$ for $\mathbf{x} = 0$ and $\Delta(\mathbf{x}) = 0$ for $\mathbf{x} \neq 0$), $\epsilon(\omega)$ is the dielectric constant of the crystal (see, for example, Eqs. (10) and (17)) and

$$\begin{aligned} &L(k_{I,z} - k_{s,z} - k_z'', k_z') \\ &= \frac{2\pi}{N_3 d_3} \frac{k_z' / \pi}{[(k_{I,x} - k_{s,x} - k_z'')^2 + (k_z')^2]} \end{aligned} \quad (24)$$

where $N_3 d_3$ is the thickness of the crystal. We recall that $\epsilon(\omega) = -1$ for Coulomb surface excitons with a nonvanishing electric field intensity (see ^[1, 2]).

The cross section (23) is quite analogous to the cross section (13) and the same notation and assumptions are used in it. The basic difference consists in the fact that in the case of scattering by surface polaritons the component of the wave vector which is normal to the surface is conserved in the scattering process only to within an accuracy of the order of $1/\Lambda$. As $\Lambda = 1/2k'_z \rightarrow \infty$, i.e., on going to scattering by volume polaritons, the function $L(k)$ (see Eq. (24)) goes over into $\Delta(k)$ and $\epsilon(\omega) = c^2 k^2 / \omega^2$, so that Eq. (23) goes over into (13) where the symbols Δ are omitted. Since, as is evident from Eq. (24), the quantity L for $|k_{I,z} - k_{S,z} - k'_z| \lesssim k'_z$ is of the order of the ratio $\Lambda/N_3 d_3$, the intensity for the scattering by surface polaritons differs from the intensity for scattering by volume polaritons by the ratio of the localization depth Λ of a surface polariton to the crystal thickness. Usually $\Lambda \sim 10^{-3}$ to 10^{-6} cm, so that the intensity of the Raman scattering by surface excitons can apparently be quite sufficient for measurements. The investigation of scattering by surface polaritons can be especially interesting for crystals which absorb in the range of frequencies $\omega \sim \omega_I, \omega_S$, when the volume scattering is suppressed. In addition, in the transition to the regime of stimulated scattering the relative smallness of the intensity of spontaneous scattering by surface polaritons is not so important. One can carry out a calculation of the absorption associated with the scattering by surface polaritons by using a method similar to the one described in Sec. 1 (a calculation of the influence of absorption on the shape of the lines for Raman scattering of light near phase transition points of the second kind is carried out in ^[17]).

We finally note that the problem of surface excitons (in particular, polaritons) appears to us to be of interest also for the study of certain mechanisms of superconductivity, ^[18] as well as from the point of view of studying collective exciton effects (phenomena related to Bose-Einstein condensation, etc.).

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