SOVIET PHYSICS JETP VOLUME 25, NUMBER 4 OCTOBER, 1967

# THEORY OF THE NONLINEAR PROPERTIES OF IONIC CRYSTALS

G. M. GENKIN, V. M. FAĬN, and É. G. YASHCHIN

Radiophysics Institute, Gorkiĭ State University; Solid State Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor May 18, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) **52**, 897-909 (April, 1967)

A semiphenomenological theory of the nonlinear properties of ionic crystals is developed. The basic assumption underlying the theory is that the adiabatic approximation is valid for the analysis of ion movement. The cross-susceptibilities $\chi_{abc}(\omega_s, \omega_l)$ and $\chi_{abcd}(\omega_s, \omega_l, \omega_r)$ are determined over the complete frequency range from the optical to the lowest frequencies. The cross-susceptibilities can be expressed in terms of coefficients defined by the electron motion at fixed ion positions. In principle these coefficients can be determined from experiment or from the microscopic theory. Corresponding estimates are made.

## 1. INTRODUCTION

INVESTIGATIONS of the nonlinear properties of crystals have become particularly timely in connection with the development of nonlinear electrodynamics and nonlinear optics. In the case of weakly nonlinear media to which we restrict our considerations here, the nonlinear electrical properties of the crystals can be characterized by the cross-susceptibilities $\chi_{abc}(\omega_s, \omega_l)$ and $\chi_{abcd}(\omega_s, \omega_l, \omega_r)$ in the expansion of the polarization $P_a$ in powers of the field (see, for example,[1,2]):

$$P_a(t) = \chi_{ab}(\omega_l)E_b(\omega_l)\exp(-i\omega_l t) + \chi_{abc}(\omega_s, \omega_l)E_b(\omega_s)E_c(\omega_l)\exp[-i(\omega_s+\omega_l)t] + \chi_{abcd}(\omega_s, \omega_l, \omega_r)E_b(\omega_s)E_c(\omega_l)E_d(\omega_r) \times\exp[-i(\omega_s+\omega_l+\omega_r)t], \tag{1}$$

where $E_b(\omega_l)$ is the Fourier component of the electric field and where the summation is over repeated indices. The majority of the nonlinear effects observed experimentally at present—second-harmonic generation, parametric transformation, stimulated Raman scattering, electro-optic effects, self-trapping, detection, etc.—are connected with the tensors $\chi_{abc}$ and $\chi_{abcd}$.

The general properties of the tensors $\chi_{abc}$ and $\chi_{abcd}$ which are not related to specific solid-state models have been explained in a number of papers (see, for instance,[1-5]). However, in order to explain the frequency dependence of these tensors, and the relations between constants appearing in different experiments, and for order-of-magnitude estimates, etc., one must take into consideration the specific properties of the solid. If one restricts oneself to the nonrelativistic approximation, then the contributions to the values of the tensors $\chi_{abc}$ and $\chi_{abcd}$ are due to the electron, phonon, and electron-phonon mechanisms. We take no account here of spatial dispersion. For the experiments mentioned above, as well as for a series of other effects in the optical region and in regions of lower frequencies, account of spatial dispersion is unimportant. This is connected with the sufficiently good fulfillment of the condition $\lambda \gg a$ (where $\lambda$ is the wavelength of the radiation and a is the lattice constant).

In this paper (Secs. 2—5) we develop a semiphenomenological theory (in the spirit of Placzek's[6] theory of polarizability) of the nonlinear properties of ionic crystals. The connection of the obtained relationships with the microscopic characteristics and mechanisms is discussed in Sec. 6.

## 2. SEMIPHENOMENOLOGICAL EXAMINATION

A basic assumption of the following examination is the applicability of the adiabatic approximation (or Placzek's approximation[6,7]). In this approximation one can write the Hamiltonian (per unit volume) of a system of ions in an external macroscopic field $E_a(t)$ in the form

$$H = \sum_j \frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 q_j^2 + \frac{1}{3}\sum_{jj'j''}\Phi(jj'j'')q_j q_{j'} q_{j''} + \frac{1}{4}\sum_{jj'j''j'''}\Phi(jj'j''j''')q_j q_{j'} q_{j''} q_{j'''} - \sum_j M_a(j)E_a q_j - \frac{1}{2}\sum_{jj'} M_a(jj')E_a q_j q_{j'} - \frac{1}{3!}\sum_{jj'j''} M_a(jj'j'')E_a q_j q_{j'} q_{j''} + \cdots$$

$$
\begin{aligned}
&-\frac{1}{2}\alpha_{ab}E_aE_b-\frac{1}{2}\sum_j\alpha_{ab}(j)E_aE_bq_j\\
&-\frac{1}{4}\sum_{jj'}\alpha_{ab}(jj')E_aE_bq_jq_{j'}+\ldots\\
&-\frac{1}{3}\alpha_{abc}E_aE_bE_c-\frac{1}{3}\sum_j\alpha_{abc}(j)E_aE_bE_cq_j+\ldots \qquad (2)
\end{aligned}
$$

Here $q_j$ are the normal coordinates of the ion system describing the optical vibrations with a wave vector **k** = 0, and $p_j$ are the canonically conjugate momenta; the summation over the indices j is explicitly separated, and summation over repeated indices is assumed. The second and third sums in the right-hand part of (2) are connected with the anharmonicity of the ion vibrations. The remaining terms in the right-hand part of (2) are connected with a contribution to the ion lattice energy due to the presence of the external field $E_a$. Such a contribution is of the form (see, for example,[8]).

$$dH=-P_a\,dE_a. \qquad (3)$$

Thus, the energy density (2) is equivalent to postulating the following dependence of the polarization on the field and the ion coordinates (see, for example,[7]):

$$
\begin{aligned}
P_a=-\frac{\partial H}{\partial E_a}&=\sum_j M_a(j)q_j+\frac{1}{2}\sum_{jj'}M_a(jj')q_jq_{j'}\\
&+\frac{1}{3!}\sum_{jj'j''}M_a(jj'j'')q_jq_{j'}q_{j''}+\alpha_{ab}E_b+\sum_j\alpha_{ab}(j)E_bq_j\\
&+\frac{1}{2}\sum_{jj'}\alpha_{ab}(jj')E_bq_jq_{j'}+\ldots+\alpha_{abc}E_bE_c\\
&+\sum_j\alpha_{abc}(j)E_bE_cq_j. \qquad (4)
\end{aligned}
$$

The first three terms in the right-hand side of (4) are connected with given displacements of the ions in the lattice $q_j$. For ionic crystals the term $M_a(j)q_j$ is much larger than the terms $M_a(jj') = M_a(j'j)$, and $M_a(jj'j'')$ due to the deformation of the electron cloud resulting from the electron-phonon interaction; $\alpha_{ab}$ and $\alpha_{abc}$ are the susceptibilities and cross-susceptibilities of the crystal for a given equilibrium configuration of the ions $X = X^0$. These susceptibilities are related with allowance for the electron motion only. The terms with $\alpha_{ab}(j)$, $\alpha_{ab}(jj')$, etc., can be related to an account of the electron-phonon interaction, and are determined as follows:

$$\alpha_{ab}(j)=\left(\frac{\partial\alpha_{ab}(X)}{\partial q_j}\right)_{X=X^0}$$

$$\alpha_{ab}(jj')=\left(\frac{\partial^2\alpha_{ab}(X)}{\partial q_j\,\partial q_{j'}}\right)_{X=X^0},\quad \alpha_{abc}(j)=\left(\frac{\partial\alpha_{ab}(X)}{\partial q_j}\right)_{X=X^0} \qquad (5)$$

In writing (2) an essential assumption is the absence of dispersion (frequency dependence) of the susceptibilities $\alpha_{ab}$, $\alpha_{abc}$, .... As is well known, such an assumption for the susceptibilities related to an allowance for the electron motion only is sufficiently well fulfilled in a frequency interval from the visible optical frequencies to the very lowest frequencies, since the characteristic frequencies of the electron motion occur in the ultraviolet region. This is also confirmed experimentally (see, for example,[9]).

Expression (4) relates the polarization with the electric field and with the normal coordinates of the ion motions. We shall only be interested in the connection between the polarization and the electric fields [as in relation (1)]. Such a connection can be obtained if it is taken into account that the $q_j$ which differ from zero appear themselves as a result of the action of the electric field[1]. Thus, for the following we must obtain a connection with the electric field. The equations of motion for $q_j$ are obtained from the relation $q = -\partial H/\partial q_j$, and according to (2) are of the form

$$
\begin{aligned}
&\ddot{q}_j+\omega_j^2q_j+\gamma_j\dot{q}_j+\sum_{j'j''}\Phi(jj'j'')q_{j'}q_{j''}\\
&\quad+\sum_{j'j''j'''}\Phi(jj'j''j''')q_{j'}q_{j''}q_{j'''}=M_a(j)E_a\\
&\quad+\sum_{j'}M_a(jj')E_aq_{j'}+\frac{1}{2}\sum_{j'j''}M_a(jj'j'')E_aq_{j'}q_{j''}+\ldots\\
&\quad+\frac{1}{2}\alpha_{ab}(j)E_aE_b+\frac{1}{2}\sum_{j'}\alpha_{ab}(jj')E_aE_bq_{j'}\\
&\quad+\frac{1}{3}\alpha_{abc}(j)E_aE_bE_c. \qquad (6)
\end{aligned}
$$

The damping constants $\gamma_j$ are introduced here phenomenologically [they do not follow from (2)]. The damping is due to the account of the interaction (due to anharmonicity) of the oscillation **k** = 0 with all the remaining oscillations with **k** ≠ 0 (see, for example,[10,11]). We shall use below the solutions of this equation with accuracy up to terms of the third order in the field $E_a$

$$q_j(t)=q_j^{(1)}+q_j^{(2)}+q_j^{(3)}+\ldots \qquad (7)$$

We shall not write here the rather cumbersome but very simply derived formulas for $q_j^{(1)}$, $q_j^{(2)}$, and $q_j^{(3)}$. We merely note that these expressions together with formulas (4) and (1) fully solve the problem of the frequency dependence of the tensors $\chi_{abc}$ and $\chi_{abcd}$ in the entire range of frequencies from the

---

[1] With the exception of ferroelectrics for which there appears spontaneous polarization below the Curie point.

optical frequencies to the very lowest frequencies. At the same time we have not taken into account spatial dispersion and have neglected the frequency dispersion of the coefficients $\alpha_{ab}$, $\alpha_{abc}$, .... Both these assumptions are sufficiently well founded in the frequency range considered, both theoretically as well as experimentally.

We shall now proceed to an analysis of the expressions for $\chi_{abc}$ and $\chi_{abcd}$.

## 3. QUADRATIC NONLINEARITY

From expression (4) it follows that terms of the second order in the field[2)] (which we shall now consider) are of the form

$$P_\alpha^{(2)} = \sum_j M_a(j) q_j^{(2)} + \sum_j \alpha_{ab}(j) q_j^{(1)} E_b + \frac{1}{2} \sum_{jj'} M_a(jj') q_j^{(1)} q_{j'}^{(1)} + \alpha_{abc} E_b E_c. \tag{8}$$

Comparing (1) with (4) and (6) with (7) we arrive at the following expressions:

$$\chi_{abc}(\omega_s, \omega_l) = \alpha_{abc} + X_{abc}(\omega_s, \omega_l) + Y_{abc}(\omega_s, \omega_l); \tag{9}$$

$$X_{abc}(\omega_s, \omega_l) = -\sum_{jj'j''} \frac{\Phi(jj'j'') M_a(j) M_b(j') M_c(j'')}{D(\omega_j, \omega_s + \omega_l) D(\omega_{j'}, \omega_s) D(\omega_{j''}, \omega_l)} + \sum_{jj'} \left[ \frac{\hat{P}_2}{2!} \frac{M_a(j) M_b(jj') M_c(j')}{D(\omega_j, \omega_s + \omega_l) D(\omega_{j'}, \omega_l)} + \frac{1}{2} \frac{M_a(jj') M_b(j) M_c(j')}{D(\omega_j, \omega_s) D(\omega_{j'}, \omega_l)} \right], \tag{10}$$

$$Y_{abc}(\omega_s, \omega_l) = \sum_j \frac{1}{2} \frac{M_a(j) \alpha_{bc}(j)}{D(\omega_j, \omega_s + \omega_l)} + \frac{\hat{P}_2}{2!} \frac{\alpha_{ab}(j) M_c(j)}{D(\omega_j, \omega_l)}, \tag{11}$$

where $D(\omega_j, \omega) = \omega_j^2 - \omega^2 - i\omega\gamma_j$. Here $\hat{P}_2$ is the operator of the sum of permutations of pairs of indices ($\omega_s$, b) and ($\omega_l$, c), and $\alpha_{abc}$ is as previously the cross-susceptibility due to an account of the electron motion only with fixed positions of the nuclei. In the region of optical frequencies and lower it is practically independent of the frequency.

Expressions (9)—(11) fully determine the nonlinear (quadratic) electrodynamic properties of the medium in the frequency ranges under consideration. We shall dwell in more detail on this assertion and we shall show how the components of the tensors $\chi_{abc}(\omega_s, \omega_l)$ are connected with the observed nonlinear effects and how the constants appearing in (10) and (11) can in principle be determined from experiment.

The constants $M_a(j)$ are fully determined from measurements of the linear electrodynamic characteristics. In fact, the usual susceptibility which can readily be obtained from (1), (4) and (6) is of the form

$$\chi_{ab}(\omega) = \alpha_{ab} + \sum_j \frac{M_a(j) M_b(j)}{D(\omega_j, \omega)}. \tag{12}$$

Thus the $M_a(j)$ are determined from measurements of the dielectric susceptibility of the medium $\epsilon_{ab}(\omega) = \delta_{ab} + 4\pi\chi_{ab}$, and in particular by the resonance measurements at frequencies $\omega \approx \omega_j$ for which one can approximately write

$$-i\omega_j \gamma_j \chi_{ab}(\omega_j) \approx M_a(j) M_b(j). \tag{13}$$

The constants $\alpha_{ab}(j) = \partial\alpha_{ab}/\partial q_j$ determine, as is well known,[6] the cross section for first-order Raman scattering, and can in turn be found from a series of experiments on Raman scattering by various optical lattice vibrations.

In addition to the constants $\alpha_{ab}$ and $M_a(j)$ expressions (9)—(11) contain the constants $\alpha_{abc}$, $\Phi(jj'j'')$, and $M_a(jj')$. These constants must be determined from nonlinear experiments. At frequencies $\omega_s$ and $\omega_l \gg \omega_j$ the nonlinear properties are determined by the constant $\alpha_{abc}$. At present this quantity has been determined for a whole series of substances (for details see the conclusion where the experimental values of this and other constants are given). The constants $\Phi(jj'j'')$ and $M_\alpha(jj')$ can be determined from measurements of $X_{abc}(\omega_s, \omega_l)$ in the infrared and microwave frequency range.

We now turn to consider the connection between the components $\chi_{abc}(\omega_s, \omega_l)$ and the observed nonlinear effects. We shall in turn consider various frequency ranges. As has already been noted, at frequencies $\omega_s$, $\omega_l$, and $\omega_s + \omega_l > \omega_j$ the nonlinear properties are mainly determined by $\alpha_{abc}$. However, experimentally a dependence (albeit rather weak) has been observed of the constant $\chi_{abc}(\omega, \omega)$ determining second-harmonic generation in this region on the parameters of the ion system, in particular on the masses of the ions.[12] Such a dependence can be connected in the first place with the tensor $Y_{abc}$ which in this instance makes a frequency dependent contribution to $\alpha_{abc}$

$$Y_{abc}(\omega, \omega) = -\frac{1}{2\omega^2} \sum_j \left[ \frac{1}{4} M_a(j) \alpha_{bc}(j) + \alpha_{ab}(j) M_c(j) + \alpha_{ac}(j) M_b(j) \right]. \tag{14}$$

---

[2)] We recall that for a quadratic nonlinearity to exist it is essential that the medium should not have a center of symmetry. In the entire discussion below it is assumed that there is no center of symmetry, i.e, the crystal is, generally speaking, anisotropic.

On the other hand, in general, the cross-susceptibility $Y_{abc}(\omega_s, \omega_l)$ differs appreciably from zero and together with $\alpha_{abc}$ determines effects in the case when one of the frequencies $\omega_s$, $\omega_l$, or $\omega_s + \omega_l$ lies in the infrared region of the spectrum or at lower frequencies (i.e., the frequency should be lower than the frequency $\omega_j$ which lies commonly in the infrared region of the spectrum); the other frequencies can on the other hand be located in the entire considered range of frequencies (from the optical to the very lowest ones).

Thus, for example for $\omega_s \gg \omega_j$ and $\omega_l \ll \omega_j$ the tensor $Y_{abc}$ takes on the form

$$Y_{abc}(\omega, 0) = \frac{1}{2}\sum_j \frac{\alpha_{ab}(j) M_c(j)}{\omega_j^2}. \tag{15}$$

Along with the term $\alpha_{abc}$, this quantity determines in particular, as is readily seen, the contribution to the linear electro-optic effect[3]. The tensor $Y_{abc}(\omega_s, \omega_l)$ determines also the contribution to the detection effect ($\omega_s + \omega_l = 0$, $\omega_s = -\omega_l = \omega$). For $\omega \gg \omega_j$

$$Y_{abc}(\omega, -\omega) = \frac{1}{2}\sum_j \frac{M_a(j)\alpha_{bc}(j)}{\omega_j^2}. \tag{16}$$

One can readily show that the condition

$$Y_{abc}(\omega, -\omega) = Y_{cba}(\omega, 0),$$

is fulfilled; this condition is a particular case of the more general relationship which follows from the condition of transparency of the medium ([2], p. 163; see also[4]).

Let us now proceed to the case when all the frequencies $\omega_s$, $\omega_l$, and $\omega_s + \omega_l$ lie in the infrared region and at lower frequencies. The nonlinear properties are in this case determined along with $\alpha_{abc}$ and $Y_{abc}$ by the tensor $Y_{abc}(\omega_s, \omega_l)$. This tensor is determined by the anharmonicity of the vibrations of the nuclei $\Phi(jj'j'')$ and by the deformation of the electron cloud $M_a(jj')$. Although, as shown in Sec. 6, the tensors $\alpha_{abc}$, $X_{abc}$, and $Y_{abc}$ have at frequencies $\omega_s$, and $\omega_l \ll \omega_j$ according to a priori estimates the same order of magnitude, the experimental values of $X_{abc}$[13] can be larger than $\alpha_{abc}$ and $Y_{abc}$ at all frequencies $\omega_s$ and $\omega_l \lesssim \omega_j$. In this case $X_{abc}(\omega_s, \omega_l)$ fully determine the nonlinear properties of the medium in this region. The theory presented above predicts a definite frequency dependence of these properties, although it does not determine the value of the parameters $\Phi(jj'j'')$ and $M_a(jj')$. According to this theory, they can be chosen in such a way that the predicted frequency dependence should be fulfilled.

## 4. CUBIC NONLINEARITY

From expression (4) we obtain for the terms cubic in the field

$$P_a^{(3)} = \alpha_{abcd}E_bE_cE_d + \sum_j M_a(j)q_j^{(3)} + \sum_{jj'} M_a(jj')q_j^{(1)}q_{j'}^{(2)}$$
$$+ \frac{1}{3!}\sum_{jj'j''} M_\alpha(jj'j'')q_j^{(1)}q_{j'}^{(1)}q_{j''}^{(1)} + \sum_j \alpha_{ab}(j)E_bq_j^{(2)}$$
$$+ \sum_{jj'} \alpha_{ab}(jj')E_bq_j^{(1)}q_{j'}^{(1)} + \sum_j \alpha_{abc}(j)E_bE_cq_j^{(1)}, \tag{17}$$

where $\alpha_{abcd}$ is the cross-susceptibility tensor and takes into account the motion of the electrons with fixed nuclei. Using the solutions of Eq. (6) and the definitions (1), we are able to determine all the components of the tensors of the cross-susceptibility $\chi_{abcd}(\omega_s, \omega_l, \omega_r)$. Because of the lack of space we shall not write out here the rather cumbersome expressions for these tensors and will refer the reader to[14], where all these components are written for a more general case which also takes into account vibrations with $k \neq 0$. Here we shall only consider certain particular cases.

With the aid of the tensor $\chi_{abcd}(\omega_s, \omega_l, \omega_r)$ it is possible to describe, in particular, effects of frequency tripling in the optical region $\chi_{abcd}(\omega, \omega, \omega) \approx \alpha_{abcd}$, in the infrared and in the microwave frequency regions, the quadratic Kerr effect $\chi_{abcd}(\omega, 0, 0)$, the detection effect in a constant field $\chi_{abcd}(\omega, -\omega, 0)$, and a number of other effects. We shall write out explicitly the components of the tensor describing the contribution to the stimulated Raman scattering[4].

$$U_{abcd}(\omega_{1,} -\omega_1, \omega_2) = \frac{1}{6}\frac{\alpha_{ab}(j)\alpha_{cd}(j)}{\omega_j^2 - (\omega_1 - \omega_2)^2 + i(\omega_1 - \omega_2)\gamma_j}, \tag{18}$$

where $\omega_1 - \omega_2 \approx \omega_j$. The last condition deducts one term from the sum over j. The same tensor (18) with the entire sum over j determines (together with $\alpha_{abcd}$) the so-called high-frequency Kerr effect: $\chi_{abcd}(\omega, -\omega, \omega)$.

Finally, we bring the rather simple formula

---

[3] The linear electro-optic effect is determined by the dependence of the dielectric permittivity on the constant ($\omega_l = 0$) electric field

$$\chi_{ab}(\omega, E_c) = \frac{\varepsilon_{ab}(\omega, E_c) - 1}{4\pi} = \frac{\varepsilon_{ab}(\omega, 0) - 1}{4\pi} + 2\chi_{abc}(\omega, 0)E_c.$$

[4] For a description of the stimulated Raman effect with the aid of the tensor $\chi_{abcd}$ see [1,2].

governing the second-harmonic generation in the presence of a constant field (at an optical frequency $\omega > \omega_j$):

$$\chi_{abcd}(\omega, \omega, 0) \approx \alpha_{abcd} + \frac{1}{3} \sum_j \frac{\alpha_{abc}(j) M_d(j)}{\omega_j^2}. \tag{19}$$

We note that it is possible to determine the quantity $\alpha_{abc}(j)$ (which also determines other effects) experimentally from measurements of the doubling of the optical frequency in a field of infrared frequency $\omega_1 \approx \omega_j$. The tensor determining such a process is of the form

$$\chi_{abcd}(\omega, \omega, \omega_j) \approx \frac{1}{3} \frac{\alpha_{abc}(j) M_d(j)}{-i\omega_j \gamma_j}. \tag{20}$$

Hence one can determine $\alpha_{abc}(j)$ experimentally from measurements of $\chi_{abcd}(\omega, \omega, \omega_j)$.

The formulas giving $\chi_{abcd}(\omega_s, \omega_l, \omega_r)$ in terms of the parameters $M_a(j)$, $\alpha_{ab}(j)$, $\omega_j$, $\Phi(jj'j'')$ etc., are in the general case rather cumbersome. However, for certain symmetry classes of a crystal these formulas can be appreciably simplified. Thus, for cubic crystals of the NaCl type the tensor which governs the nonlinear properties of a crystal in the frequency range in which at least one of the frequencies $\omega_s$, $\omega_l$, and $\omega_r$ is larger than the infrared eigenfrequency, is of the form

$$\chi_{abcd}(\omega_s, \omega_l, \omega_r) = \alpha_{abcd} + \frac{\hat{P}_3}{3!} \frac{1}{2} \sum_{jj'} \frac{\alpha_{ab}(jj') M_c(j) M_d(j')}{D(\omega_j, \omega_l) D(\omega_{j'}, \omega_r)}$$

$$+ \frac{\hat{P}_3}{3!} \sum_j \frac{\alpha_{abc}(j) M_d(j)}{D(\omega_j, \omega_s)}. \tag{21}$$

In the case of NaCl there is one doubly degenerate optically active (transverse) branch of lattice vibrations $\omega_j = \omega_0$, i.e., in the coefficient $M_a(j)$ the indices j and j′ take on two values. In this case the quantities $\alpha_{ab}(j)$, $\Phi(jj'j'')$, and $M_a(jj')$ vanish[5]. As regards the quantity $\alpha_{ab}(jj')$, it can be determined experimentally from intensity measurements of the second-order Raman effect [see, for example,[7] where the quantity $\alpha_{ab}(jj')$ is denoted by $P_{ab}(jj')$].

## 5. TEMPERATURE EFFECTS

The expressions obtained for the cross-susceptibility do not depend on the temperature explicitly. The temperature dependence can appear in these expressions when the temperature dependence of the coefficients $M_a(jj')$, and $\alpha_{ab}(j)$, etc. is taken into account. However, these coefficients determined by the electron motion depend very weakly on the temperature within a rather broad range (from 0°K up to the degeneracy temperature). An appreciable temperature dependence appears near the ferroelectric transition point. At this point $T_c$ one of the characteristic frequencies of optical phonons vanishes as[15]

$$\omega_j^2 = A(T - T_c) \qquad (T \geqslant T_c) \tag{22}$$

and the main temperature dependence may in all the expressions derived above be connected with this.

At the same time there is a series of effects which are essentially connected with an account of the temperature motion (or of zero-point fluctuations). First we obtain an expression for the cross-susceptibility tensor that determines the second-order stimulated Raman effect for definite vibrations $q_j(\mathbf{k})$ and $q_{j'}(-\mathbf{k})$.

We note that, unlike previously, in order to investigate the second-order Raman effect one must consider the normal coordinates of the lattice $q_j(\mathbf{k})$ also for $\mathbf{k} \neq 0$ (see, for example,[7]). The second-order Raman scattering is given, as is well known,[7] by

$$\alpha_{ab}\begin{pmatrix} \mathbf{k} & -\mathbf{k} \\ j & j' \end{pmatrix} = \left( \frac{\partial^2 \alpha_{ab}(X)}{\partial q_j(\mathbf{k}) \partial q_{j'}(-\mathbf{k})} \right)_{X=X^0}.$$

Therefore, to obtain the sought tensor we separate from (2), (4), and (6) the terms connected with $\alpha_{ab}$:

$$P_a = \frac{1}{2} \sum_{\mathbf{k}jj'} \alpha_{ab}\begin{pmatrix} \mathbf{k} & -\mathbf{k} \\ j & j' \end{pmatrix} \langle q_j(\mathbf{k}) q_{j'}(-\mathbf{k}) \rangle E_b, \tag{23}$$

$$\langle \ddot{q}_j(\mathbf{k}) \rangle + \omega_j^2(\mathbf{k}) \langle q_j(\mathbf{k}) \rangle + \gamma_j(\mathbf{k}) \langle \dot{q}_j(\mathbf{k}) \rangle$$

$$= \frac{1}{2} \sum_{\mathbf{k}j'} \alpha_{cd}\begin{pmatrix} \mathbf{k} & -\mathbf{k} \\ j & j' \end{pmatrix} \langle q_{j'}(\mathbf{k}) \rangle E_c E_d. \tag{24}$$

Here we consider the problem with the aid of quantum theory. In this case the quantities entering in (2) (except for the given fields) are understood to be operators, and mean values of these operators $\langle q_j \rangle$ and $\langle q_j^2 \rangle$ enter in (4) and (6).

We shall further assume (and this corresponds to the second-order Raman effect) that $E_c E_d$ contains a harmonic component with a frequency close to $\omega_j(\mathbf{k}) + \omega_{j'}(\mathbf{k})$. Let

$$E_b = E_b^0 \cos \omega_1 t, \qquad E_c = E_c^0 \cos \omega_1 t, \qquad E_d = E_d^0 \cos \omega_2 t,$$

$$\omega_1 - \omega_2 \approx \omega_j(\mathbf{k}) + \omega_{j'}(\mathbf{k}) \tag{25}$$

We shall assume that this condition is fulfilled only

---

[5] We note that although the NaCl crystal has a center of symmetry, the quantity $\alpha_{abc}(j)$, unlike $\alpha_{abc}$, does not vanish if the index j refers to the optical branches of the spectrum of lattice vibrations. It should be noted in general that the symmetry properties of $\alpha_{abc}(j)$, $\alpha_{ab}(jj')$, etc. are respectively determined both by the symmetry of the initial tensors $\alpha_{abc}$ and $\alpha_{ab}$ and by the symmetry of $q_j$ and $q_i q_j{}'$.

for one pair of branches j and j′, i.e., we shall not consider the degenerate case.

Equation (24) describes the parametric excitation $\langle q_j \rangle$ and if the fields $E_c$ and $E_d$ are small (below the excitation threshold), then $\langle q_j \rangle = 0$. However, at the same time $\langle q_j(\mathbf{k}) q_{j'}(-\mathbf{k}) \rangle$ differs from zero and has a part which is connected with the fields $E_c$ and $E_d$.

To determine $\langle q_j(\mathbf{k}) q_{j'}(-\mathbf{k}) \rangle$, we shall start with the Hamiltonian

$$H = \sum_{\mathbf{k}j} \hbar\omega(\mathbf{k}_j) n_j(\mathbf{k}) - \frac{1}{4} \sum_{\mathbf{k}jj'} \alpha_{cd} \begin{pmatrix} \mathbf{k} & -\mathbf{k} \\ j & j' \end{pmatrix} \times E_c E_d q_j(\mathbf{k}) q_{j'}(-\mathbf{k}). \tag{26}$$

Introducing further the creation and annihilation operators $\overset{+}{a}_j(\mathbf{k})$ and $a_j(\mathbf{k})$, we have

$$\begin{gathered} n_j(\mathbf{k}) = a_j^+(\mathbf{k}) a_j(\mathbf{k}), \\ q_j(\mathbf{k}) q_{j'}(-\mathbf{k}) = {}^1\!/_2 \hbar [\omega_j(\mathbf{k}) \omega_{j'}(\mathbf{k})]^{-1/2} [a_j^+(-\mathbf{k}) a_{j'}^+(\mathbf{k}) \\ + a_j(\mathbf{k}) a_{j'}(-\mathbf{k}) + a_j(\mathbf{k}) a_{j'}^+(\mathbf{k}) + a_j^+(-\mathbf{k}) a_{j'}(-\mathbf{k})]. \end{gathered} \tag{27}$$

From the Hamiltonian (26) one can readily write the equations for the mean-square quantities with account of dissipative processes[6]; we do not cite these here because they are cumbersome. After introducing the notation

$$\langle a_j(\mathbf{k}) a_{j'}(-\mathbf{k}) \rangle = A_{\mathbf{k}}^{jj'} \exp[-i(\omega_1 - \omega_2)t], \tag{28a}$$

$$R = \frac{1}{2} \eta_{jj'} \alpha_{cd} \begin{pmatrix} \mathbf{k} & -\mathbf{k} \\ j' & j \end{pmatrix} \frac{E_c(\omega_1) E_d(-\omega_2)}{\sqrt{\omega_j \omega_{j'}}},$$

$$\eta_{jj'} = \frac{\gamma_j(\mathbf{k}) + \gamma_{j'}(\mathbf{k})}{\sqrt{\gamma_j(\mathbf{k}) \gamma_{j'}(\mathbf{k})}}, \tag{28b}$$

one can obtain solutions of the system of equations for the mean-square quantities

$$\langle n_j(\mathbf{k}) \rangle + \langle n_{j'}(\mathbf{k}) \rangle + 1 = (\langle n_j^0(\mathbf{k}) \rangle + \langle n_{j'}^0(\mathbf{k}) \rangle + 1) \times \frac{[\omega_j + \omega_{j'} - (\omega_1 - \omega_2)]^2 + [\gamma_j + \gamma_{j'}]^2}{[\omega_j + \omega_{j'} - (\omega_1 - \omega_2)]^2 + [\gamma_j + \gamma_{j'}]^2 - R^2}, \tag{29}$$

$$A_k^{jj'} = R(\langle n_j^0(\mathbf{k}) \rangle + \langle n_{j'}^0(\mathbf{k}) \rangle + 1)(\eta_{jj'})^{-1} \times \frac{\omega_j + \omega_{j'} - (\omega_1 - \omega_2) + i[\gamma_j + \gamma_{j'}]}{[\omega_j + \omega_{j'} - (\omega_1 - \omega_2)]^2 + [\gamma_j + \gamma_{j'}]^2 - R^2}. \tag{30}$$

Here we have discarded nonresonant terms and taken the resonance condition (25) into account;

$$\langle n_j^0(\mathbf{k}) \rangle = \left( \exp \frac{\hbar\omega_j}{kT} - 1 \right)^{-1}$$

is the average number of photons in a state of thermodynamic equilibrium. In Eqs. (28)—(30) and everywhere below in this Section the argument **k** of the functions $\omega_j(\mathbf{k})$, $\omega_{j'}(\mathbf{k})$, $\gamma_j(\mathbf{k})$ and $\gamma_{j'}(\mathbf{k})$ has been left out for brevity.

We note that the fact that the denominators in expressions (29) and (30) vanish corresponds to the condition of parametric excitation of the excitations $q_j(\mathbf{k})$ and $q_{j'}(\mathbf{k})$. Using (23), (27), (28), (30), and definition (1), we obtain an expression for the cross-susceptibility tensor giving the second-order stimulated Raman effect

$$\chi_{abcd}(\omega_1, -\omega_1, \omega_2) = \sum_{\mathbf{k}} \frac{\hbar\alpha_{ab} \begin{pmatrix} \mathbf{k} & -\mathbf{k} \\ j & j' \end{pmatrix} \overset{*}{\alpha}_{cd} \begin{pmatrix} \mathbf{k} & -\mathbf{k} \\ j' & j \end{pmatrix} [\omega_j + \omega_{j'} - (\omega_1 - \omega_2) - i(\gamma_j + \gamma_{j'})]}{8 \cdot 3!\, V\omega_j\omega_{j'} \{[\omega_j + \omega_{j'} - (\omega_1 - \omega_2)]^2 + [\gamma_j + \gamma_{j'}]^2 - |R|^2\}} [n_j^0(\mathbf{k}) + \overset{0}{n}_{j'}(\mathbf{k}) + 1]. \tag{31}$$

If the dispersion law for the optical phonons is of the Einstein type, i.e., $\omega_j(\mathbf{k})$ does not depend on **k** and all the other coefficients also depend weakly on **k**, then the summation over **k** reduces to multiplication by N where N is the number of states in the band.

Expression (31) depends on the amplitudes of the fields $E_c$ and $E_d$ and thus takes into account the "saturation effect." For $kT \gg \hbar\omega_j$ Planck's constant cancels out.

In an analogous way the term $M_a$ in (2), (4), and (6) leads to "parametric excitation" $\langle q_j(\mathbf{k}) q_{j'}(-\mathbf{k}) \rangle$ proportional to the first power of the field $E_l(\omega)$ if

$$\omega \approx \omega_j + \omega_{j'}. \tag{32}$$

One finds readily that $\langle q_j(\mathbf{k}) q_{j'}(-\mathbf{k}) \rangle$ is now given by the same equations (27) and (28)—(30), but with the substitution

$$\omega_1 - \omega_2 \to \omega, \tag{33}$$

$$R \to R' = \frac{1}{2} \eta_{jj'} M_b \begin{pmatrix} \mathbf{k} & -\mathbf{k} \\ j' & j \end{pmatrix} E_b(\omega) / \sqrt{\omega_j \omega_{j'}}. \tag{34}$$

Thus

$$\langle n_j(\mathbf{k}) \rangle + \langle n_{j'}(\mathbf{k}) \rangle + 1 = (\langle n_j^0(\mathbf{k}) \rangle + \langle \overset{0}{n}_{j'}(\mathbf{k}) \rangle + 1) \times \frac{[\omega_j + \omega_{j'} - \omega]^2 + [\gamma_j + \gamma_{j'}]^2}{[\omega_j + \omega_{j'} - \omega]^2 + [\gamma_j + \gamma_{j'}]^2 - |R'|^2}, \tag{35}$$

$$A^{jj'} = R'(\langle n_j^0(\mathbf{k}) \rangle + \langle n_{j'}^0(\mathbf{k}) \rangle + 1)(\eta_{jj'})^{-1}. \times \frac{[\omega_j + \omega_{j'} - \omega] + i[\gamma_j + \gamma_{j'}]}{[\omega_j + \omega_{j'} - \omega]^2 + [\gamma_j + \gamma_{j'}]^2 - |R'|^2}. \tag{36}$$

---

[6] In [2] (Sec. 8) it is shown how such equations can be written for the general case.

Expressions (34)—(36) and the relation

$$P_a = \frac{1}{2}\sum_{\mathbf{k}jj'} M_a\begin{pmatrix}\mathbf{k} & -\mathbf{k}\\ j & j'\end{pmatrix}\langle q_j(\mathbf{k})\,q_{j'}(-\mathbf{k})\rangle \qquad (37)$$

determine the "linear" susceptibility with account of the saturation effect

$$\chi_{ab}(\omega) = \sum_{\mathbf{k}} \frac{\hbar M_a\begin{pmatrix}\mathbf{k} & -\mathbf{k}\\ j & j'\end{pmatrix} M_b\begin{pmatrix}\mathbf{k} & -\mathbf{k}\\ j' & j\end{pmatrix}[\omega_j + \omega_{j'} - \omega + i(\gamma_j + \gamma_{j'})]}{8V\omega_j\omega_{j'}[(\omega_j + \omega_{j'} - \omega)^2 + [\gamma_j + \gamma_{j'}]^2 - |R'|^2]} \times [n_j^0(\mathbf{k}) + n_{j'}^0(\mathbf{k}) + 1]. \qquad (38)$$

Analogously one can consider second-order effects connected with $\langle q_j(\mathbf{k})q_{j'}(-\mathbf{k})\rangle$, (35), (36), and the relation (23), as well as with $\langle q_j(\mathbf{k})q_{j'}(-\mathbf{k})\rangle$, (29), (30), and relation (37). Because of lack of space we shall not dwell on these effects.

## 6. MICROSCOPIC TREATMENT. CONCLUSION

The theory presented above makes it possible to relate the cross-susceptibilities which determine various effects with one another. All the quantities $M_a(j)$, $M_a(jj')$, $\alpha_{ab}(j)$, etc. can in principle be determined experimentally. Thus, for example, all $\alpha_{ab}(j)$ are determined by a series of Raman experiments, $\alpha_{ab}(jj')$ can be determined from the second-order Raman effect, and $M_a(j)$—from a series of linear resonance experiments on absorption. In general the selection of a given branch j and of the coefficients connected with it can be achieved by a corresponding resonance experiment. Of course, for each given crystal class the number of independent coefficients $M_a(j)$, $M_a(jj')$, etc. can be appreciably smaller than in the general case. After the corresponding coefficients are determined experimentally, one can, using the obtained relations in principle, determine the tensors $\chi_{abc}(\omega_s, \omega_l)$ and $\chi_{abcd}(\omega_s, \omega_l, \omega_r)$ for all values of the frequencies $\omega_s$, $\omega_l$, and $\omega_r$ from zero up to the visible portion of the optical range.

We shall present numerical values obtained from experimental data for certain quantities determining the tensors $\chi_{abc}(\omega_s, \omega_l)$ and $\chi_{abcd}(\omega_s, \omega_l, \omega_r)$. Thus for NaCl[7] $M(j) = 2^{-1/4}\omega(j)(\epsilon_0 - \epsilon_\infty)^{1/2} \approx 4 \times 10^{13}\ \text{sec}^{-1}$. The quantity $\alpha_{ab}(j)$ is given in the following way in terms of the cross section for spontaneous Raman scattering Q:

$$\alpha_{ab}(j) = \left\{\frac{3}{64\pi^5}\frac{Q\lambda^4\omega(j)N}{\hbar}\left[1 - \exp\left(-\frac{\hbar\omega(j)}{kT}\right)\right]\right\}^{1/2}.$$

For nitrobenzene[4] for the 1345-cm$^{-1}$ Raman line $\alpha_{ab}(j) \approx 1.5 \times 10^7$ cgs esu.

The values of $\alpha_{ab}$, $\alpha_{abc}$, $M_a(j)$, etc. can also be found from the microscopic theory. In the microscopic treatment one usually determines the characteristics connected with the local (or acting) field. The macroscopic characteristics $\alpha_{ab}$, $\alpha_{abc}$, etc. can be obtained from the microscopic only after the connection between the macroscopic field and the local field has been established. For nonlinear media this connection can be rather complicated (see, for example,[16]). We note further that not only constants of the type $\alpha_{ab}$ and $\alpha_{abc}$ are renormalized on going over from the local to the macroscopic field, but also the characteristic frequencies $\omega_j$ and the anharmonicity constants $\Phi(jj'j'')$ and $\Phi(jj'j''j''')$. (For the characteristic frequencies this assertion is well illustrated in the book[7], Sec. 9.) In other words, the characteristic frequencies of the free vibrations of the ions and the anharmonicity coefficients differ depending on what is assumed to vanish: $E = 0$ or $E_{loc} = 0$. In fact, the latter condition imposes a limitation on the "free" ion vibrations, since $E_{loc}$ itself depends on the polarization and consequently on the coordinates of the characteristic vibrations $q_j$ for ionic crystals.

The basis of the microscopic treatment is the Hamiltonian of the system of electrons and phonons with account of the electron-phonon interaction

$$H = \sum_{\mathbf{k}j}\hbar\omega_j(\mathbf{k})a_j^+(\mathbf{k})a_j(\mathbf{k}) + \sum_{\mathbf{p}n}\varepsilon_n(\mathbf{p})c_n^+(\mathbf{p})c_n(\mathbf{p}) + \sum_{\mathbf{kp}j}\sum_{n,n'}A_{\mathbf{kp}j}^{nn'}c_n^+(\mathbf{p})c_{n'}(\mathbf{p}-\mathbf{k})\,(a_j^+(-k) + a_j(\mathbf{k})). \qquad (39)$$

In expression (39) $a_j^+(\mathbf{k})$ and $a_j(\mathbf{k})$ are the Bose creation and annihilation operators of the phonon of the j branch of the vibrational lattice spectrum of frequency $\omega_j(\mathbf{k})$ and with a quasimomentum $\hbar\mathbf{k}$; $c_n^+(\mathbf{p})$ and $c_n(\mathbf{p})$ are the Fermi operators of creation and annihilation of an electron with energy $\epsilon_n(\mathbf{p})$ where $\hbar\mathbf{p}$ is the electron quasimomentum, and n is the number of the band; $A_{\mathbf{kp}j}^{nn'}$ is the electron-phonon interaction constant.

Because we are considering ionic crystals, we shall consider the interaction of an electron with longitudinal optical (polarization) phonons which is stronger than the interaction with other types of phonons. The expression for the electron-phonon interaction constant with longitudinal optical phonons is of the following form:

$$A_{\mathbf{kp}j}^{nn'} = i\left(\frac{\delta_{nn'}}{k} + \Omega^{nn'}(\mathbf{p})\right)\left[\frac{2\pi\hbar\omega_j(\mathbf{k})e^2}{V}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)\right]^{1/2}. \qquad (40)$$

In Eq. (40) $\Omega^{nn'}(\mathbf{p})$ is the matrix element of the operator Ω characterizing the interband transitions (the definition and properties of this operator are given in the review[17]). We note that in order of magnitude $\Omega^{nn'}(\mathbf{p}) \sim a$ where a is the lattice constant.

It should be noted that the above interaction constant describes in addition to the Froelich interaction also the interaction of electrons in various bands (the term with $\Omega^{nn'}$) with a phonon; an analogous expression for the electron-phonon interaction constant with acoustic phonons has been obtained in the work of Semenenko.[18] We note that unlike $A^{nn}_{\mathbf{kp}j}$ the constant $A^{nn'}_{\mathbf{kp}j}$ contains no singularity for $\mathbf{k} \to 0$.

Starting from the Hamiltonian (39), one can determine all the quantities $\alpha_{ab}$, $\alpha_{ab}(j)$, etc. by the method of many-time Green functions in analogy with what was done in[19,20]. Because of the lack of space we shall not present this derivation and the obtained expressions here. We merely note that for $\omega_s$, $\omega_l$, and $\omega_r \ll \omega_e$ (where $\omega_e$ is the characteristic eigenfrequency of the electrons) these quantities do not depend on the frequency and we shall present estimates of them. Further we shall (in the estimates) express all tensors in terms of the estimated values of the tensors $\alpha_{ab}$, $\alpha_{abc}$, and $\alpha_{abcd}$ connected with allowance for pure electron motion. Estimates of these tensors are of the form (see, for example,[21])

$$\alpha_{ab} \approx \frac{N}{V}\frac{e^2a^2}{\hbar\omega_e} \sim \frac{e^2}{a\hbar\omega_e} \sim 1, \qquad (41)$$

since $\hbar\omega_e \sim e^2/a$;

$$\alpha_{abc} \approx \frac{N}{V}\frac{e^3a^3}{\hbar^2\omega_e^2} \sim \frac{a^2}{e} = \frac{1}{E_{at}}, \qquad (42)$$

where $E_{at} = ea^{-2}$ is the "atomic" field, and in order of magnitude it is $10^6$—$10^7$ egs esu,

$$\alpha_{abcd} \approx \frac{N}{V}\frac{e^4a^4}{\hbar^3\omega_e^3} \sim \frac{a^4}{e^2} = \frac{1}{E_{at}^2}. \qquad (43)$$

We shall now write estimates for all the tensors entering in our considerations:

$$M(j) \sim \omega_0, \quad M(jj') \sim \alpha_{abc}\omega_0^2, \quad M(jj'j'') \sim \alpha_{abcd}\omega_0^3,$$
$$\alpha_{ab}(j) \sim \omega_0\alpha_{abc}, \quad \alpha_{ab}(jj') \sim \omega_0^2\alpha_{abcd}, \quad \alpha_{abc}(j) \sim \omega_0\alpha_{abcd},$$
$$\Phi(jj'j'') \sim \omega_0^3\alpha_{abc}, \quad \Phi(jj'j''j''') \sim \omega_0^4\alpha_{abcd},$$

where $\omega_0$ is the characteristic frequency of the ion motion.

In these estimates we neglect in essence the difference between the local and macroscopic characteristics. This corresponds to the approximate value of the statistical dielectric permittivity $\epsilon_0 \sim 1$. In such an estimate we immediately find that at low frequencies $\omega_s$, $\omega_l$, $\omega_r \ll \omega_0$ the tensors $X_{abc}$, $Y_{abc} \approx \alpha_{abc}$, while $X_{abcd}$, $Y_{abcd}$, $Z_{abcd}$, ... $\sim \alpha_{abcd}$. However, from experiment it is known that the ion motions make, generally speaking, a greater contribution both to the linear and nonlinear properties of ionic crystals. Thus, for example, the dielectric constant of potassium dihydrogen phosphate (KDP) $\epsilon_0 \sim 20$, whereas $\epsilon_\infty = n^2 \sim 2$[22] (the latter quantity is connected with the electron contribution only). The measurements carried out by one of the authors[13] on second-harmonic generation in the ultrahigh frequency range ($\omega \ll \omega_0$) on a KDP crystal yield a value of $X_{abc}(\omega, \omega) \sim 10^{-5}$ cgs esu instead of $6 \times 10^{-9}$ cgs esu[23] in the optical region.

Let us now present estimates of the temperature effects of Sec. 5. The tensor describing the second-order Raman effect at frequencies $\omega_j \pm \omega_{j'}$ is of the order $\omega_0/\omega_e$ compared with the tensor describing the first-order Raman effect of the vibrations $\omega_j$. An analogous absorption described by the tensor (38) at a frequency $\omega_j \pm \omega_{j'}$ is smaller by a factor $\omega_0/\omega_e$ than the resonance absorption at a frequency $\omega_j$. Saturation is determined by the ratios $R/\gamma_j$ and $R'/\gamma_j$ respectively. These quantities are of the order of magnitude

$$\frac{R}{\gamma_j} \sim \alpha_{abcd}E^2\frac{\omega_0}{\gamma_j} \sim \left(\frac{E}{E_{at}}\right)^2\frac{\omega_0}{\gamma_j}, \qquad (44)$$

$$\frac{R'}{\gamma_j} \sim \alpha_{abc}E\frac{\omega_0}{\gamma_j} \sim \left(\frac{E}{E_{at}}\right)\frac{\omega_0}{\gamma_j}. \qquad (45)$$

For example, for $\gamma_j \sim 10^{-2}\,\omega_0$ saturation of absorption at frequencies $\omega_j \pm \omega_{j'}$ will take place in fields of the order of $E \sim 10^{-2}E_{at} \sim 10^{-6}$ V/cm. In the latter estimates we have assumed that $n_j^0 \sim 1$.

---

[1] V. M. Faĭn and É. G. Yashchin, JETP 46, 695 (1964), Soviet Phys. JETP **19**, 474 (1964).

[2] V. M. Faĭn and Ya. I. Khanin, Kvantovaya radiofizika (Quantum Radiophysics), Soviet Radio, 1965, pp. 160 and 268.

[3] S. A. Akhmanov and R. V. Khokhlov, Problemy nelineĭnoĭ optiki (Problems of Nonlinear Optics), AN SSSR, 1964.

[4] N. Bloembergen, Nonlinear Optics, W. A. Benjamin, 1965.

[5] G. F. Efremov, JETP **51**, 156 (1966), Soviet Phys. JETP **24**, 132 (1967).

[6] G. Placzek, Rayleigh and Raman Scattering, Russ. transl., 1935, p. 64. [Engl. transl. U. of Cal., Livermore, 1959].

[7] M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Russ. transl. IIL, 1958, pp. 233 and 424. [Oxford, 1954].

[8] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Gostekhizdat, 1957, p. 77.

[9] R. G. Miller, Phys. Rev. **131**, 95 (1963).

[10] V. N. Kashcheev and M. A. Krivoglaz, FTT **3**, 1528 (1961), Soviet Phys. Solid State **3**, 1107 (1961).

[11] R. F. Wallis and A. A. Maradudin, Phys. Rev. **125**, 1277 (1962).

[12] R. G. Miller, D. A. Kleinman, and A. Savage, Phys. Rev. Letters **11**, 146 (1963).

[13] E. P. Volkova and E. G. Yashchin, Trans. Second All-union Symposium on Nonlinear Optics, Siberian Div. AN SSSR, 1967.

[14] V. N. Genkin, A. F. Dite, and V. M. Faĭn, Trans. All-union Symposium on Nonlinear Optics, Siberian Div. AN SSSR, 1967.

[15] V. L. Ginzburg, UFN **77**, 621 (1962), Soviet Phys. Uspekhi **5**, 649 (1963); P. Anderson, Fizika diélektrikov (The Physics of Dielectrics), AN SSSR, 1960, p. 290.

[16] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

[17] I. M. Lifshitz and M. I. Kaganov, UFN **69**, 419 (1959), Soviet Phys. Uspekhi

[18] A. I. Semenenko, FTT **7**, 1216 (1965), Soviet Phys. Solid State **7**, 975 (1965).

[19] G. M. Genkin and V. M. Faĭn, JETP **49**, 1118 (1965), Soviet Phys. JETP **22**, 779 (1965).

[20] G. M. Genkin, V. M. Faĭn, and E. G. Yashchin, FTT **8**, 3310 (1966), Soviet Phys. Solid State **8**, 2646 (1967).

[21] V. M. Faĭn, Izv. AN BSSR, ser. fiz.-mat. nauk, No. 4, 1965.

[22] F. Jona and D. Shirane, Ferroelectric Crystals, Russ. transl., Mir, 1965, p. 96.

[23] A. Askin, G. D. Boyd, and J. M. Dziedzic, Phys. Rev. Letters **11**, 14 (1963).

Translated by Z. Barnea
114