CONTRIBUTION OF THE ANHARMONIC CHARACTER OF CRYSTALLINE LATTICE OSCILLATIONS TO THE NONLINEAR PROPERTIES OF A CRYSTAL

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The nonlinear properties of a crystal due to oscillations of the ion lattice are considered. An expression is obtained for the third-rank cross-susceptibility tensor by means of the three-time temperature Green's function technique. In a certain approximation, the cross-susceptibility tensor $\chi_{abc}(\omega, \omega)$ turns out to be symmetric with respect to the indices a and b.

1. In connection with the development of lasers which can generate electromagnetic waves of high intensity and high monochromaticity, the investigation of the nonlinear properties of crystals becomes necessary. The nonlinear properties of a crystal can in particular be characterized by the expansion of the polarization (the dipole moment per unit volume) in powers of the field (see, for example,[1,2])

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

Here $P_a(t)$ are the components of the polarization vector, $E_b(\omega_l)$ are the Fourier components of the electric field, $\chi_{ab}(\omega_l)$ is the ordinary susceptibility, $\chi_{abc}(\omega_s, \omega_l)$, $\chi_{abcd}(\omega_s, \omega_l, \omega_r)$ are the third and fourth rank cross-susceptibility tensors. In Eq. (1), summation over repeated indices is assumed. One of the most important problems which now arise in solid state physics is the calculation of the values of χ_{abc}, χ_{abcd} etc., which also characterize the nonlinear properties of the medium.

Franken and Ward[3,4] have discussed the role of various mechanisms which can make a contribution to the value of χ_{abc} (and, consequently to the intensity of production of the second harmonic in nonlinear crystals). One of the criteria, on the basis of which an estimate is given in one of these researches[4] of the contribution of some mechanism (electronic or associated with the motion of ions), is the satisfaction of the Kleinman relations.[5] The essence of these relations is that the quantity χ_{abc} is symmetric in the indices a and b for a medium without dispersion or absorption. Experimental data give evidence to the fact that in nonlinear crystals which are used for the transformation of light with frequency doubling the Kleinman relations are satisfied with an accuracy of 5—10%.[6] Inasmuch as the frequencies of the electron transitions are large in comparison with optical frequencies (at which the experiments were carried out), one does not have to take into account dispersion and absorption in the analysis of the role of electronic motions. Thus, the conclusion is drawn in[4] that the principal contribution to χ_{abc} must be made by electronic motion. On the other hand, the characteristic frequencies of oscillation of the lattice are small in comparison with the optical. It then follows that the Kleinman conclusions[5] do not apply, since dispersion is important here. On the basis of this circumstance, Ward and Franken[4] rejected the possibility of an important contribution of ionic motion to the value of χ_{abc}. It must be noted, however, that it has previously been impossible to verify the concept that χ_{abc} will not be symmetrical in the indices a and b when account is taken of the contribution of ionic motions. And actually, as the calculation given below shows, a calculation which takes into account the lattice oscillations, the value of $\chi_{abc}(\omega, \omega)$ which characterizes the transformation of light into its second harmonic is seen to be symmetric in the indices a and b.

We now consider further the contribution to the tensor $\chi_{abc}(\omega_s, \omega_l)$ associated with the oscillations of the crystalline lattice. It is evident that this tensor vanishes in the harmonic approximation, since the medium does not possess non-

linear properties in this case. Thus the entire considered effect is determined by the anharmonic oscillations.

2. The expression for the third-rank cross-susceptibility tensor χ_{abc} of a quantum mechanical system has the following form:[2]

$$\chi_{abc}(\omega_s, \omega_l) = {}^1/_2[\varkappa_{abc}(\omega_s, \omega_l) + \varkappa_{acb}(\omega_l, \omega_s)], \quad (2)$$

$$\varkappa_{abc}(\omega_s, \omega_l) = \frac{(i\hbar)^{-2}}{V}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \exp\{i\omega_s(t-t_1)$$

$$+ i\omega_l(t-t_2)\}\langle[[\hat{x}_a(t), \hat{x}_b(t_1)], x_c(t_2)]\rangle. \quad (3)$$

Here $\hat{x}_a(t)$ is the operator of the dipole moment of the lattice in the Heisenberg representation, and V is the volume of the crystal. Making use of the fact that averaging in (3) takes place with the help of the density matrix $\hat{\rho}(-\infty)$, which corresponds to the stationary state of the crystal, we transform the quantity κ_{abc} to the form

$$\varkappa_{abc}(\omega_s, \omega_l) = (2\pi)^{-2}\int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2$$

$$\times \exp\{i(\omega_s + \omega_l)\tau_1 + i\omega_l\tau_2\} K_{abc}(\tau_1, \tau_2)$$

$$\equiv K_{abc}(\omega_s + \omega_l, \omega_l), \quad (4)$$

where $K_{abc}(\omega_s + \omega_l, \omega_l)$ denotes the Fourier component of the function $K_{abc}(\tau_1\tau_2)$;

$$K_{abc}(\tau_1, \tau_2) = -(4\pi^2/V\hbar^2)\theta(\tau_1)\theta(\tau_2)\langle[[x_a(\tau_1), x_b(0)],$$

$$x_c(-\tau_2)]\rangle,$$

$$\theta(\tau) = \begin{cases} 1 & \text{for } \tau > 0, \\ 0 & \text{for } \tau < 0. \end{cases} \quad (5)$$

Thus the problem reduces to the calculation of the Fourier components of the three-time temperature retarded Green's function.

The operators of the dipole moment of the lattice are written in the following form:[7,8]

$$\hat{x}_a(\tau_1) = \sum_j M_a^j(\hbar N/2\omega(0, j))^{1/2}[\hat{a}_{0j}^+(\tau_1) + \hat{a}_{0j}(\tau_1)],$$

$$\hat{x}_b(0) = \sum_i M_b^i(\hbar N/2\omega(0, i))^{1/2}[\hat{a}_{0i}^+(0) + \hat{a}_{0i}(0)],$$

$$\hat{x}_c(-\tau_2)$$

$$= \sum_z M_c^z(\hbar N/2\omega(0, z))^{1/2}[\hat{a}_{0z}^+(-\tau_2) + a_{0z}(-\tau_2)]. \quad (6)$$

Here $\hat{a}_{kj}^+$ and $\hat{a}_{kj}$ are the Heisenberg creation and annihilation operators for a phonon of the j-th branch of the oscillation spectrum of a lattice of frequency $\omega(k, j)$ and quasimomentum $\hbar k$; N is the number of cells in the crystal, M_a^j is the projection on the a axis of the vector $\mathbf{M}^j$:

$$\mathbf{M}^j = \sum_p \frac{\varepsilon_p \mathbf{e}(p|0j)}{\sqrt{m_p}} \quad (7)$$

where ϵ_p and m_p are the charge and the mass of the ion at the lattice site with number p. Summation is carried out in the unit cell, and $\mathbf{e}(p|0j)$ is the eigenvector of the displacement of the ion with number p corresponding to a phonon of the j-th branch and quasimomentum $\hbar k = 0$.

Summation in (6) takes place over the optical branches of the lattice oscillations, since the values of M^j for the acoustic oscillations vanish.[9] This corresponds to the well known physical fact that the fundamental contribution to infrared absorption is made by the optical branches of the lattice oscillations, since there arises a variable dipole moment for such oscillations.

We also note that the operators a^+ and a of phonons with $k = 0$ enter into Eq. (6). This is connected with the fact that we do not take into account the effects of spatial dispersion. It is not difficult to understand that these effects are unimportant in the optical range of electromagnetic waves (see also the book of Born and Huang[7]).

After substitution of (6) in (5), the function $K_{abc}(\tau_1, \tau_2)$ takes the form

$$K_{abc}(\tau_1, \tau_2) = -\frac{(2\pi)^2 N^{3/2}}{V\hbar^{1/2}2\sqrt{2}} \sum_i \frac{M_a^j M_b^i M_c^z}{\sqrt{\omega(z)\omega(j)\omega(i)}} \sum_{l=1}^{8} G^{(l)}, \quad (8)$$

where $\omega(z) \equiv \omega(0, z)$, etc., and the functions $G^{(l)}$ have the form

$$G^{(1)} = \theta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{0j}^+(\tau_1), \hat{a}_{0i}^+(0)], \hat{a}_{0z}^+(-\tau_2)]\rangle,$$

$$G^{(2)} = \theta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{0j}^+(\tau_1), \hat{a}_{0i}(0)], \hat{a}_{0z}^+(-\tau_2)]\rangle,$$

$$G^{(3)} = \theta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{0j}(\tau_1), \hat{a}_{0i}^+(0)], \hat{a}_{0z}^+(-\tau_2)]\rangle,$$

$$G^{(4)} = \theta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{0j}(\tau_1), \hat{a}_{0i}(0)], \hat{a}_{0z}^+(-\tau_2)]\rangle,$$

$$G^{(5)} = \theta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{0j}^+(\tau_1), \hat{a}_{0i}^+(0)], \hat{a}_{0z}(-\tau_2)]\rangle,$$

$$G^{(6)} = \theta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{0j}^+(\tau_1), \hat{a}_{0i}(0)], \hat{a}_{0z}(-\tau_2)]\rangle,$$

$$G^{(7)} = \theta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{0j}(\tau_1), \hat{a}_{0i}^+(0)], \hat{a}_{0z}(-\tau_2)]\rangle,$$

$$G^{(8)} = \theta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{0j}(\tau_1), \hat{a}_{0i}(0)], \hat{a}_{0z}(-\tau_2)]\rangle. \quad (9)$$

To find these quantities, we shall make use of a Hamiltonian describing the lattice oscillations with account of anharmonism of third order (see, for example,[10]):

$$H = \sum_{kj}\hbar\omega(kj)\hat{a}_{kj}^+\hat{a}_{kj} + {}^1/_2\sum_{k_1j_1;\,k_2j_2;\,k_3j_3} V'_{k_1j_1\,k_2j_2\,k_3j_3}$$

$$\times\{{}^1/_3\hat{a}_{k_1j_1}\hat{a}_{k_2j_2}\hat{a}_{k_3j_3} + {}^1/_3\hat{a}_{-k_1j_1}^+\hat{a}_{-k_2j_2}^+\hat{a}_{-k_3j_3}^+$$

$$+ \hat{a}_{-k_1j_1}^+\hat{a}_{-k_2j_2}^+\hat{a}_{k_3j_3} + \hat{a}_{-k_1j_1}^+\hat{a}_{k_2j_2}\hat{a}_{k_3j_3}\}. \quad (10)$$

Here

$$V'_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2 \mathbf{k}_3 j_3} = V_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2 \mathbf{k}_3 j_3} \Delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3),$$

$$\Delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) = \begin{cases} 1, & \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 2\pi\mathbf{K}, \\ 0, & \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 \neq 2\pi\mathbf{K}, \end{cases}$$

where $2\pi\mathbf{K}$ is any of the vectors of the reciprocal lattice, and the coefficients of anharmonism $V'_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2 \mathbf{k}_3 j_3}$ are symmetric in any pair of indices [7,10] and posses the following property:

$$V_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2 \mathbf{k}_3 j_3} = V^*_{-\mathbf{k}_1 j_1, -\mathbf{k}_2 j_2, -\mathbf{k}_3 j_3}. \quad (11)$$

We now proceed to find the values of $G^{(l)}$. We first compute $G^{(1)}(\tau_1, \tau_2)$. For this purpose, we carry out differentiation of $G^{(1)}(\tau_1, \tau_2)$ with respect to τ_1:

$$i\partial G^{(1)}/\partial\tau_1 = i\delta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{0j}^+(0), \hat{a}_{0i}^+(0)], \hat{a}_{0z}^+(-\tau_2)]\rangle$$
$$+ (1/\hbar)\theta(\tau_1)\theta(\tau_2)$$
$$\times \langle[[[\hat{a}_{0j}^+(\tau_1), H], \hat{a}_{0i}^+(0)], \hat{a}_{0z}^+(-\tau_2)]\rangle. \quad (12)$$

Here use is made of the well known relation between $\theta(t)$ and $\delta(t)$: $d\theta/dt = \delta(t)$ and the equation of motion $i\hbar d\hat{A}/dt = [\hat{A}, \hat{H}]$. From the commutation relations between the creation and annihilation operators, it follows that the first term on the right hand side of (10) vanishes. Furthermore, we shall carry out all calculations with accuracy up to terms of first order in the coefficients of anharmonism $V_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2 \mathbf{k}_3 j_3}$. The equation for $G^{(1)}$ takes the form (with account of the commutation relations)

$$i\frac{\partial G^{(1)}}{\partial\tau_1} = -\omega(j)G^{(1)} - \frac{1}{2\hbar}\sum_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2} V'_{0j\mathbf{k}_1 j_1 \mathbf{k}_2 j_2} F^{(1)}_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2}, \quad (13)$$

where

$$F^{(1)}_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2} = \theta(\tau_1)\theta(\tau_2)\langle[[\hat{a}_{\mathbf{k}_1 j_1}(\tau_1)\hat{a}_{\mathbf{k}_2 j_2}(\tau_1), \hat{a}_{0i}^+(0)], \hat{a}_{0z}^+(-\tau_2)]\rangle,$$

and it is not difficult to obtain the equation

$$i\partial F^{(1)}/\partial\tau_1 = -\delta(\tau_1)[-i\theta(\tau_2)\langle[\hat{a}_{0z}(\tau_2)\hat{a}_{0z}^+(0)]\rangle]$$
$$\times \delta_{\mathbf{k}_1 0}\delta_{\mathbf{k}_2 0}(\delta_{j_1 z}\delta_{j_2 i} + \delta_{j_2 z}\delta_{j_1 i}) + (\omega_{\mathbf{k}_1 j_1} + \omega_{\mathbf{k}_2 j_2})F^{(1)}. \quad (14)$$

for the function $F^{(1)}$ in the given approximation. Making use of the fact that the relation in the square bracket on the right hand side of Eq. (14) is a single phonon free retarded Green's function (see, for example, [11]), the Fourier transform of which has the form

$$G_z(\omega) = \frac{1}{2\pi}\frac{1}{\omega - \omega(z)}, \quad (15)$$

we find the Fourier transform of the function $F^{(1)}$ without difficulty, and then, after substitution in (13), we also find the Fourier transform of the function $G^{(1)}$:

$$G^{(1)}(\omega_1, \omega_2) = \frac{1}{\hbar(2\pi)^2}\frac{V_{0j0z0i}}{(\omega_1 + \omega(j))(\omega_2 - \omega(z))(\omega_1 - \omega(z) - \omega(i))} \quad (16)$$

We note immediately that the value of V_{0j0z0i} differs from zero only for crystals which do not possess a center of inversion; for crystals with an inversion center, λ_{abc} is equal to zero in the general case.

Calculation of the other functions of $G^{(l)}$ is carried out in the same manner. After some simple but somewhat tedious calculation of the remaining $G^{(l)}$, by summing them we finally obtain for the Fourier transform of the function $K_{abc}(\tau_1, \tau_2)$:

$$K_{abc}(\omega_1, \omega_2) = \frac{2\sqrt{2}N^{3/2}}{\hbar^{3/2}V} \times \sum_{ijz} \frac{V_{0j0z0i} M_a^j M_b^i M_c^z (\omega(i)\omega(j)\omega(z))^{1/2}[\omega_1(2\omega_2 + \omega_1) + \omega^2(z) - \omega^2(i)]}{(\omega_1^2 - \omega^2(j))(\omega_2^2 - \omega^2(z))[(\omega - \omega(z))^2 - \omega^2(i)][(\omega_1 + \omega(z))^2 - \omega^2(i)]} \quad (17)$$

Furthermore, making use of the relations (4) and (17), we obtain an expression for $\kappa_{abc}(\omega_s, \omega_l)$:

$$\kappa_{abc}(\omega_s, \omega_l) = \frac{2\sqrt{2}N^{3/2}}{\hbar^{3/2}V}\sum_{ijz} V_{0j0i0z} M_a^j M_b^i M_c^z (\omega(i)\omega(z)\omega(j))^{1/2}$$
$$\times \frac{(\omega_s + \omega_l)(\omega_s + 3\omega_l) + \omega^2(z) - \omega^2(i)}{[(\omega_s + \omega_l)^2 - \omega^2(j)][\omega_l^2 - \omega^2(z)][(\omega_s + \omega_l)^2 - (\omega(z) + \omega(i))^2]}$$
$$\times [(\omega_s + \omega_l)^2 - (\omega(z) - \omega(i))^2]^{-1}. \quad (18)$$

We can also find the desired value of $\chi_{abc}(\omega_s, \omega_l)$ from the relation (2). It is not difficult to establist the fact that this tensor satisfies the relation [2,12]

$$\chi_{abc}(\omega_r, \omega_l) = \chi_{cba}(\omega_r, \omega_s) = \chi_{bac}(\omega_s, \omega_l), \quad (19)$$

which holds if the frequencies ω_s and ω_l satisfy the condition

$$\omega_r + \omega_l + \omega_s = 0 \quad (20)$$

and there is no absorption in the system.

We note that the Kleinman relations mentioned above follow from (19), (20), as $\omega_r, \omega_s, \omega_l \to 0$. (Approach to zero of these frequencies essentially means a neglect of dispersion—the condition under which the Kleinman relations are satisfied.)

From what follows we shall now be interested in a case of practical importance, in which

$$\omega_s^2, \omega_l^2 \gg \omega^2(i). \quad (21)$$

In this case, we get the following expression for

the third rank cross susceptibility tensor:

$$\chi_{abc}(\omega_s, \omega_l) = \frac{2\sqrt{2}N^{3/2}}{\hbar^{3/2}V}\sum_{ijz}[\omega(z)\omega(i)\omega(j)]^{1/2}$$

$$\times V_{0i\,0j\,0z} M_a{}^j M_b{}^i M_c{}^z [(\omega_s+\omega_l)^2\omega_s{}^2\omega_l{}^2]^{-1}. \quad (22)$$

For a tensor characterizing the splitting, it follows from (22) that

$$\chi_{abc}(\omega, \omega) = \frac{N^{3/2}}{\sqrt{2}\hbar^{3/2}V\omega^6}\sum_{ijz}[\omega(z)\omega(i)\omega(j)]^{1/2}$$

$$\times\ V_{0i\,0j\,0z} M_a{}^j M_b{}^i M_c{}^z. \quad (23)$$

It is a consequence of the latter expression that the value of $\chi_{abc}(\omega, \omega)$ is symmetric in the indices a and b (since the quantity V is symmetric in any pair of indices). This symmetry is formally identical with the Kleinman condition. But it must be emphasized that the symmetry in the indices a and b in our case holds when dispersion is important and, consequently, one of the conditions for the applicability of the Kleinman relations is not satisfied.

3. We shall discuss briefly the expressions that have been obtained and carry out numerical estimates. As was pointed out above (see Sec. I), the symmetry of the tensor χ_{abc} in the indices a and b is verified by experiment. In our case, this symmetry holds upon satisfaction of the condition (21). Thus, for a KDP (KH_2PO_4) crystal, for which we shall carry out estimates in what follows, at frequencies of the ruby laser and for frequencies of the lattice $\nu \sim 2800\ cm^{-1}$ symmetry in a and b will be satisfied with an accuracy of the order of 10% (the characteristic frequencies of the infrared absorption of the lattice in the KDP crystal are given, for example, in [13]). Thus, in this aspect the mechanism of nonlinearity under consideration does not contradict the experimental data.

We now undertake an estimate of the quantity $\chi_{abc}(\omega, \omega)$ according to Eq. (23) for KDP. The quantity $\chi_{abc}(\omega, \omega)$ can be written in the following fashion:

$$\chi_{abc}(\omega, \omega) = \frac{\varepsilon^3 N}{4\omega^6 m^{3/2}V}\sum_{ijz}\Phi\begin{pmatrix}0&0&0\\ i&j&z\end{pmatrix} e_a(k|0i)e_b(k|0j)e_c(k|0z). \quad (24)$$

In Eq. (24) i, j, z take on values from 1 to 3(n − 1), where n is the number of ions per unit cell. To obtain Eq. (24), the following formulas were used:[7-9]

$$V_{0i\,0j\,0z} = \Phi\begin{pmatrix}0&0&0\\ i&j&z\end{pmatrix} 2^{-3/2}\hbar^{3/2}N^{-1/2}[\omega(i)\omega(j)\omega(z)]^{-1/2}, \quad (25)$$

$$\Phi\begin{pmatrix}0&0&0\\ i&j&z\end{pmatrix} = \sum_{l'l''}\sum_{kk'k''}\sum_{\alpha\beta\gamma}\Phi_{\alpha\beta\gamma}\begin{pmatrix}0&l'&l''\\ k&k'&k''\end{pmatrix}[m_k m_{k'} m_{k''}]^{-1/2}$$

$$\times\ e_\alpha(k|0i)e_\beta(k'|0j)e_\gamma(k''|0z), \quad (26)$$

$$\Phi_{\alpha\beta\gamma}\begin{pmatrix}l&l'&l''\\ k&k&k''\end{pmatrix} = \left(\partial^3\Phi \Big/ \partial u_\alpha\begin{pmatrix}l\\k\end{pmatrix}\partial u_\beta\begin{pmatrix}l'\\k'\end{pmatrix}\partial u_\gamma\begin{pmatrix}l''\\k''\end{pmatrix}\right)_0. \quad (27)$$

We note that in the calculation of $\chi_{abc}(\omega, \omega)$ [Eq. (24)], we take into account the contribution only of the lightest ion (for KDP—the hydrogen ion); the mass of this ion is denoted by m with the number k. This is associated with the fact that the contribution of the lightest ion predominates by reason of the fact that the masses enter into the denominator in the coefficients M_a^j, M_b^i, M_c^z (Eq. (7)). Corresponding to this, we also set $m_k = m_{k'} = m_{k''} = m$ in Eq. (26).

We carry out a numerical estimate of the value of $\chi_{abc}(\omega, \omega)$. Here we shall consider only the interaction energy of the opposite nearest neighboring ions, which depends on the modulus of the distance between the ions, that is, we assume:[7]

$$\Phi(r) = -A/r + B\exp(-r/\rho),$$

$$A = \varepsilon^2\alpha', \quad B = M\lambda. \quad (28)$$

Here M is the number of nearest neighbors, α' is Madelung's constant, ρ and λ are constants in the expression for the potential overlap between the neighboring opposite ions.

Using the relations of orthonormality of the eigen vectors [7], we assume that

$$e_\alpha(k|0i) \sim (3n)^{-1/2}. \quad (29)$$

In such an estimate, it is not taken into consideration that the different characteristic sites can have different signs; this can reduce the value of χ_{abc}. As a result, we get the following expression:

$$\chi_{abc}(\omega, \omega) \sim (N\varepsilon^3\Phi'''(r_0)/Vm^3\omega^6)(n-1)^3n^{-3}. \quad (30)$$

In Eq. (30), r_0 is the equilibrium distance between the nearest neighboring ions under consideration.

Assuming that for ionic crystals [7] $\lambda \sim 10^{-9}$ erg, $r_0/\rho \sim 10$, $a' \sim 1$, taking $r_0 \sim 10^{-8}$ cm for KDP for $m \approx 1.6\times10^{-24}$ g at a frequency $\omega = 1.78\times10^{15}\ sec^{-1}$ (neodymium laser), we obtain $\chi_{abc}(\omega, \omega) \sim 10^{-10}$ cgs esu.

The experimentally measured value of the component of the cross susceptibility tensor has the following value:[14]

$$|\chi_{zxy}(\omega, \omega)| = (3\pm1)\cdot10^{-9}\ \text{CGSE}.$$

An estimate of the value of χ_{abc} in the infra-

red region is of interest. As is seen from Eqs. (18) and (24), χ_{abc} possesses a large frequency dispersion as one goes from the optical range to the range of the eigenfrequencies of the lattice (the infrared region). Upon further decrease in frequency, the value of χ_{abc} begins to depend weakly on the frequency and to approach its static value. The sharpest increase in χ_{abc} should of course be observed in the presence of resonance between the frequencies of the external field ω_s and $\omega_s + \omega_l$ and the characteristic frequencies of the lattice. Thus, under resonance conditions, Eq. (30) takes the form

$$\chi_{abc}(\omega, \omega) \sim 3\cdot 10^{-2} \frac{N\varepsilon^3 \Phi'''(r_0)}{Vm^3\omega^4(\Delta\omega)^2}\left(\frac{p}{n}\right)^2 \frac{n-1}{n}, \quad (31)$$

with $\omega - \omega_0$ replaced by $\Delta\omega$—the line width of the characteristic oscillation of the lattice. In Eq. (31), p is the number of frequencies of the lattice in resonance with the radiation field of frequency ω. In the region of frequencies ω_s and $\omega_s + \omega_l$ smaller than the characteristic frequencies of the lattice, the estimated expression for χ_{abc} has the form

$$\chi_{abc}(\omega, \omega) \sim \frac{N\varepsilon^3 \Phi'''(r_0)}{Vm^3} \sum_{ijz} \frac{e_a^2(k|0i)\, e_b^2(k|0j)\, e_c^2(k|0z)}{\omega^2(i)\,\omega^2(j)\,\omega^2(z)}. \quad (32)$$

For numerical estimates, we consider the same KDP crystal with the eigenfrequencies of the order of $\nu \sim 2800$ cm^{-1} ($\lambda \sim 3.6\mu$). Upon a change in the wavelength of the external field from $\lambda = 1.06\mu$ (neodymium laser) to $\lambda \approx 3.6\mu$ the value of $\chi_{abc}(\omega, \omega)$ increases to 10^{-7} cgs units. In this case the line width of the lattice is taken to be $\Delta\omega \sim 10^{+12}$ sec^{-1}.

In conclusion, we note that there is undoubted interest in the behavior of the nonlinear characteristics of the crystals close to the point of phase transitions of the second kind. We propose in subsequent research to consider this problem in more detail. Here, it shall only be noted that in connection with the fact that the expressions (2) and (18) [with account of (25) for the cross susceptibility tensor] have no singularities upon approach to zero of one of the eigenfrequencies of the crystal, it is difficult to expect singularities in the temperature behavior of χ_{abc} close to points of phase transitions of the second kind (where, of course, one of the eigenfrequencies of the lattice vanishes[15]).

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