

CRYSTAL OPTICS WITH ALLOWANCE FOR SPATIAL DISPERSION; EXCITON THEORY. II \*

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3. CRYSTAL OPTICS WITH ALLOWANCE FOR SPATIAL DISPERSION

CRYSTAL optics with allowance for spatial dispersion deals with the propagation, reflection, and refraction of various normal waves in crystals, using the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$ .

Formally speaking, the scope is broader here than in the case of classical crystal optics, inasmuch as many new problems and questions arise (for example, it becomes necessary to investigate the optical anisotropy of cubic crystals). Actually, however, the situation is different, primarily because of the smallness of the spatial dispersion. Because of the latter, as was already emphasized above, it becomes necessary to consider only problems in which the spatial dispersion leads to qualitatively new effects or, at any rate, does not give rise to only negligible corrections to the formulas of classical crystal optics.

In connection with the foregoing, the following discussion of several crystal-optical problems is fragmentary in character and reduces essentially to a discussion of several phenomena. It is necessary to bear in mind here also the following circumstances. First, the study of the natural optical activity (gyrotropy),

although pertaining to crystal optics with allowance for spatial dispersion, has been carried out long ago and discussed in detail in the corresponding monographs (see, in particular, [22,28,31]). Consequently, with respect to gyrotropic crystals, we shall dwell only on one question of the new waves, a question which as far as we know arose only recently. [5] Second, even if we disregard spatial dispersion (including gyrotropy), the analysis of the propagation of light in absorbing crystals, particularly in the case of low symmetry, is rather cumbersome [22,28]. Furthermore, there are special cases. These include the propagation of light along singular optical axes [28,32,32a], when we can no longer confine ourselves to the consideration of plane waves of the type (1.13). The role of spatial dispersion in the case of absorbing crystals, and in the case of complex  $\mathbf{k}$  in general, was not investigated in any degree of detail.

Third and last, it must be emphasized that only relatively few investigations have been devoted to an account of spatial dispersion in a nongyrotropic medium [or, more accurately, to the account of second-order effects proportional to  $(a/\lambda)^2$ ] as applied to the optics of crystals, even for a transparent or almost transparent medium. In other words, although the question of the effects that are proportional to  $(a/\lambda)^2$  cannot by any means be regarded as being new (see the Introduction), it has for various reasons remained until recently in limbo. It can thus be assumed that not all

\*Part I of the article, containing the introduction and Sections 1 and 2, was published in UFN 76, 643 (1962), Soviet Phys. Uspekhi 5, 323 (1962).

the interesting aspects of crystal optics with account of spatial dispersion have already been noted and discussed. Consequently, the relatively narrow framework within which we discuss crystal optics with account of spatial dispersion is due not only to the smallness of this dispersion, but also to the present status of research in this field.

a) New Wave Near the Absorption Line in a Gyrotropic Crystal. As already indicated, in gyrotropic crystals the spatial dispersion manifests itself in terms of first order of smallness in  $a/\lambda$ . Therefore we can omit in expansion (2.13) the last term in the right half of the equation. Using relations (1.6) and (1.20) and choosing the direction of the wave vector as the  $z$  axis, we obtain the following expressions, which are satisfied by the components of the transverse induction vector  $D'$  (see also [1], Section 82):

$$\begin{aligned} \left(\frac{1}{n^2} - \varepsilon_{xx}^{-1}(\omega)\right) D'_x - \varepsilon_{xy}^{-1}(\omega) D'_y &= i\hat{n}\delta_{123} \frac{\omega}{c} D'_y, \\ -\varepsilon_{yx}^{-1}(\omega) D'_x + \left(\frac{1}{n^2} - \varepsilon_{yy}^{-1}(\omega)\right) D'_y &= -i\hat{n}\delta_{123} \frac{\omega}{c} D'_x. \end{aligned} \quad (3.1)$$

(We can, of course, replace here  $\delta_{123}$  by  $f_{33} = f_{33}s_3^2$  or, if invariant notation is used, by  $f_{ijs_1s_2}$ .) The direction of the  $x$  and  $y$  axes is chosen along the principal axes of the two dimensional tensor  $\varepsilon_{\alpha\beta}^{-1}$ ,  $\alpha = x, y$  and we denote the principal values of this tensor by  $1/n_{01}^2$  and  $1/n_{02}^2$  (we leave out the caret above the  $n$  and assume in most cases, unless otherwise stipulated, that  $n$  is real, i.e., we are dealing with the transparency region). Then Eqs. (3.1) assume the following form:

$$\begin{aligned} \left(\frac{1}{n_{01}^2} - \frac{1}{n^2}\right) D'_x + i\delta_{123} n \frac{\omega}{c} D'_y &= 0, \\ -i\delta_{123} n \frac{\omega}{c} D'_x + \left(\frac{1}{n_{02}^2} - \frac{1}{n^2}\right) D'_y &= 0. \end{aligned} \quad (3.2)$$

The condition that the determinant of this system vanish gives a third-order equation in  $n^2$

$$\left(\frac{1}{n^2} - \frac{1}{n_{01}^2}\right) \left(\frac{1}{n^2} - \frac{1}{n_{02}^2}\right) = \delta_{123}^2 \frac{\omega^2}{c^2} n^2. \quad (3.3)$$

The roots of this equation determine, for a specified direction of  $\mathbf{s}$ , three values of the refractive index  $n_1, n_2,$  and  $n_3$  (we always put  $n = \sqrt{n^2}$ , since the root  $n = -\sqrt{n^2}$  merely denotes the reversal of the sign of  $\mathbf{s}$ ).

In the investigation of Eq. (3.3) we shall distinguish between frequency regions away from and close to resonance. At frequencies sufficiently far away from the resonances, the right half of (3.3) is small. Consequently one of the roots, (for example  $n_3$ ), will be very large,

$$n_3^2 \approx \frac{c^2}{\omega^2 \delta_{123}^2 n_{01}^2 n_{02}^2} \gg 1.$$

Indeed, inasmuch as  $\delta_{123} \sim a \sim 10^{-3} \lambda_0$ , the order of  $n_3$  is  $10^3$ , and the corresponding wavelength in the medium is  $\lambda = \lambda_0/n_3 \sim 10^{-7} - 10^{-8}$  cm. This means that in the optical frequency band waves with refractive indices  $n_3$  for crystals can usually not be considered in the

investigation of the tensor  $\varepsilon_{ij}(\omega, \mathbf{k})$ , and no real significance need be attached to the corresponding solutions. As regards the roots  $n_1$  and  $n_2$ , they can be determined by replacing  $n^2$  in the right half of (3.3) by the product  $n_{01}n_{02}$ . It then follows from (3.2) that in a wave with refractive index  $n_1$  we have

$$D'_y = iqD'_x, \quad (3.4a)$$

while in a wave with refractive index  $n_2$

$$D'_y = -\frac{i}{q} D'_x, \quad (3.4b)$$

where

$$q = \frac{c}{\omega \delta_{123} \sqrt{n_{01} n_{02}}} \left[ \frac{1}{2} \left( \frac{1}{n_{01}^2} - \frac{1}{n_{02}^2} \right) + \sqrt{\frac{1}{4} \left( \frac{1}{n_{01}^2} - \frac{1}{n_{02}^2} \right)^2 + \frac{\omega^2}{c^2} n_{01} n_{02} \delta_{123}^2} \right]. \quad (3.4c)$$

Since, generally speaking,  $n_{01} \neq n_{02}$ , both waves turn out to be polarized along ellipses whose principal axes coincide with  $x$  and  $y$ . These ellipses are thus turned  $90^\circ$  relative to each other, and their rotations are oppositely directed. If the vector  $\mathbf{s}$  is directed along the optical axis, when  $n_{01} = n_{02} = n$  and  $\rho = 1$ , then the ellipses degenerate into circles. Furthermore

$$n_{\pm}^2 = n_0^2 \pm \frac{\omega}{c} \delta_{123} n_0^2, \quad (3.5a)$$

and the angle of rotation of the plane of polarization  $\varphi$  following traversal of a path  $l$  is

$$\varphi = \frac{\pi}{\lambda_0} (n_+ - n_-) l = \frac{\omega^2}{2c^2} n_0^4 \delta_{123} l. \quad (3.5b)$$

We note that in the case under consideration each of the two refractive indices corresponds to its own circular (left- or right-hand) polarization of the wave, since when  $\rho = 1$  we have

$$D'_x = \pm iD'_y.$$

The results pertaining to this case in which only the two roots  $n_1$  and  $n_2$  of Eq. (3.3) need be taken into account, are well known and we touched upon them here only to emphasize the limits of applicability of these results, and also to compare them with the more complicated situation which may occur near resonances. In this case the values of  $n_{01}^2$  and  $n_{02}^2$  (or of only one of them) are large in a certain region of frequencies, and all three roots of (3.3) correspond to relatively long wavelengths, so that all three solutions (as was noted in [5]) can be regarded within the framework of the macroscopic approach. Depending on the frequency, Eq. (3.3) has in the absence of absorption either three real roots, or one real and two complex roots (Fig. 3).<sup>\*</sup> To be specific, we shall assume that  $\delta_{123} > 0$  and that the wave propagates along the optical axis, i.e.,  $n_{01}$

<sup>\*</sup>Fig. 3 is taken from [5], where it was assumed that (for  $\omega = \omega_l$ )

$$\frac{\omega}{c} \delta_{123} = 10^{-8}, \quad n_0^2(\omega) = n_{00}^2 - \frac{2\omega_l^2}{\omega^2 - \omega_l^2} \approx -\frac{2\omega_l^2}{\omega^2 - \omega_l^2}.$$

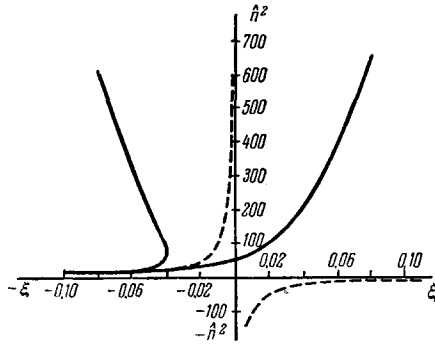


FIG. 3

$n_{02} = n_0$ . In this case the values of  $n^2$  on the upper branch satisfy the inequality  $n^2 > n_0^2$ . Therefore, as follows from (3.2) and (3.3), for the upper branch the following relations are satisfied

$$\frac{D_x}{D_y} = -\frac{i\delta_{123}\frac{\omega}{c}n}{\left(\frac{1}{n_0^2} - \frac{1}{n^2}\right)} = -i.$$

Thus, the upper branch of the solutions  $n^2$  corresponds to the right-hand circular polarization, and the lower branch corresponds to left-hand polarization. If  $\delta_{123} < 0$ , the polarizations of the solutions corresponding to the upper and lower branches must be reversed. As indicated, the dispersion curves shown in Fig. 3 have been obtained in an approximation in which the absorption is disregarded. The quantities  $n_0^2$  (or  $n_{01}^2$  and  $n_{02}^2$ ) and  $\delta_{123}$  in Eq. (3.3) can then be regarded as real, i.e., this equation has real coefficients. Consequently in the frequency region where only one of the solutions is real, the two others are complex-conjugate, and in the case of a half-space they form a standing wave corresponding to a zero Poynting vector (see Section 1c). Absorption can be allowed for by considering  $n_0^2$  and  $\delta_{123}$  complex. As a result the pattern of the dispersion curve changes, particularly in the case when the turning point (see Fig. 3) falls in the region of appreciable absorption. In this connection we note that multiple roots (i.e., a turning point) correspond to values of the frequency  $\omega_m$  satisfying the equation

$$n_0^2(\omega_m) = 2^{2/3}/3 \left( \delta_{123} \frac{\omega_m}{c} \right)^{2/3}.$$

In this case we have a degenerate root

$$n_m^3 = \left( \frac{2}{\delta_{123}} \right)^{3/2},$$

and a smaller root  $n^2 = n_m^2/4$ . Consequently when

$$n_0^2(\omega) \approx \frac{0.2}{|\omega - \omega_j|} \omega_j \text{ and } \omega\delta_{123}/c \sim 10^{-3} \text{ we obtain*}$$

\*The quantity  $\omega\delta_{123}/c$  can be estimated directly from experimental data by using the frequency dependence of the rotation of the plane of polarization and the refractive index of light far from the absorption band under consideration. It follows from Eqs. (7),

$|\omega_m - \omega_j|/\omega_j \sim 4 \times 10^{-3}$ , which corresponds when  $\omega_j \approx 3 \times 10^4 \text{ cm}^{-1}$  to  $|\omega_m - \omega_j| \sim 100 \text{ cm}^{-1}$ . Inasmuch as the widths of the exciton absorption lines in many, say, molecular crystals<sup>[33]</sup> at helium temperatures amount to several times 10 reciprocal centimeters, there are all grounds for assuming that the "three-wave effect" in such crystals should be quite clearly pronounced at low temperatures.

We now stop to discuss the character of the solutions of the field equations when the dispersion equation has multiple roots. The well-known and fairly frequent case of multiple roots corresponds to degeneracy, namely to equality of the refractive indices  $\hat{n}(\omega, \mathbf{s})$  for waves having different polarization (for specified  $\omega$  and  $\mathbf{s}$ ). This takes place for transverse waves in an isotropic medium, and also in some directions for waves in an anisotropic medium. In such cases we can choose two linearly independent solutions of the type  $\mathbf{E}_l = \mathbf{E}_{0,l} \exp[-i\omega(t - (\hat{n}/c)\mathbf{s} \cdot \mathbf{r})]$ , which differ in the vectors  $\mathbf{E}_{0,l}$ , i.e., in the polarization. Other cases occur, however, when the multiple root  $\hat{n}(\omega, \mathbf{s})$  corresponds to only one solution (we refer to a double root). This is the situation in the case when waves propagate along the "singular optical axis" in absorbing crystals of the triclinic and monoclinic systems<sup>[28,32,32a]</sup> (in order for a multiple root to appear, it is important that the principal axes of the tensors  $\epsilon'_{ij}(\omega)$  and  $\epsilon''_{ij}(\omega)$  do not coincide, something that occurs only for triclinic and monoclinic crystals). For singular axes to arise, there is no need for involving spatial dispersion (such axes arise already in classical crystal optics, and in the case of gyrotropic crystals without account of the new waves). In the presence of spatial dispersion the multiple roots appear even if there is no absorption. This is immediately clear from Fig. 3 for a gyrotropic crystal, and say from Figs. 4b and 5b for nongyrotropic crystals. Indeed, as indicated above, the polarization of the wave field is the same for all solutions corresponding to the upper branch of Fig. 3. Consequently, on approaching the "turning point"  $\omega = \omega_m$ ,  $\hat{n} = \hat{n}_m$ , the two solutions

(8), (10), and (11) of [24] that for light propagating along the optical axis we have in this frequency region  $n_0^2(\lambda_0) = 1 + K_1\lambda_0^2/(\lambda_0^2 - \lambda_1^2)$ , and the rotation per unit length of ray path is  $\varphi((\lambda_0)/l) = K_2\lambda_0^2/(\lambda_0^2 - \lambda_1^2)^2$ , where  $\lambda_0$  is the wavelength of light in vacuum,  $\lambda_1^2$  is the wavelength corresponding to resonance, and  $K_2 = 2\pi^2K_1^2\delta_{123}$ . Thus,  $\omega\delta_{123}/c = K_2/\pi\lambda_0K_1^2$ . According to [67] in cinnabar crystals the absorption band at  $\lambda_1 \approx 4930 \text{ \AA}$  corresponds to  $K_1 \approx 0.56$  and  $K_2 = 1.06\pi \times 10^8 \text{ cm}^{-1}$ , from which we get  $(\omega_1/c)\delta_{123} \equiv (2\pi/\lambda_1)\delta_{123} \approx 0.8 \times 10^{-3}$ . For the organic crystal of benzyl the band  $\lambda_1 \approx 2400 \text{ \AA}$  corresponds to  $K_1 \approx 0.4$  and  $K_2 \approx 0.35 \times 10^8 \text{ cm}^{-1}$ . Therefore  $(\omega_1/c)\delta_{123} \approx 10^{-3}$ . According to the same data, in the cubic sodium chlorate crystal the band at  $\lambda_1 \approx 900 \text{ \AA}$  corresponds to  $K_1 = 1.18$  and  $K_2 = 0.06\pi \times 10^8 \text{ cm}^{-1}$ , and consequently  $(\omega_1/c)\delta_{123} \approx 4 \times 10^{-5}$ , while the band at  $\lambda_1 = 1850 \text{ \AA}$  corresponds to  $K_1 = 0.08$  and  $K_2 = -0.07\pi \times 10^9 \text{ cm}^{-1}$ , so that  $(\omega_1/c)\delta_{123} \approx -0.5 \times 10^4$ . We know that for quartz away from the absorption bands (at  $\lambda = 5893 \text{ \AA}$ ) we have  $\varphi/l = 217 \text{ deg/cm}$ ,  $n_0 = 1.54$ , and according to (3.5b)  $(\omega/c)\delta_{123} \approx 1.3 \times 10^{-5}$ .

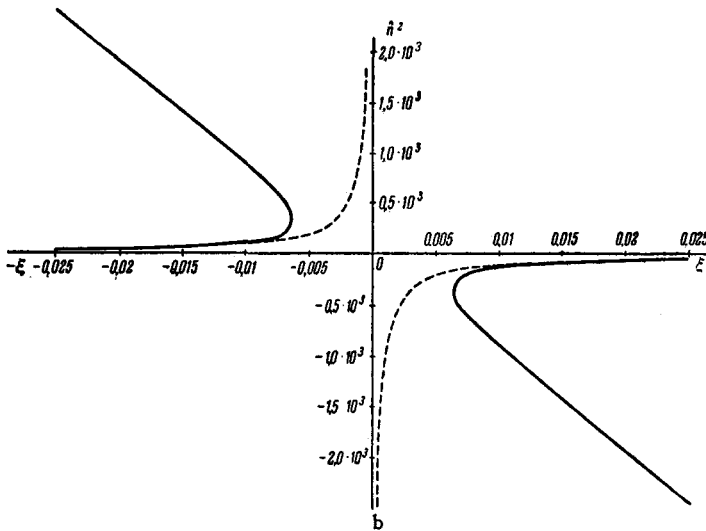
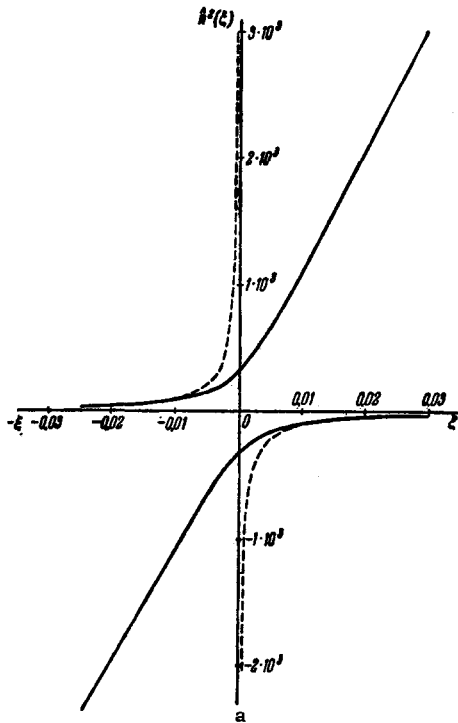


FIG. 4

corresponding to this branch,  $E_1 = E_{0,1} \exp[-i\omega(t - (\hat{n}_1/c) \mathbf{s} \cdot \mathbf{r})]$  and  $E_2 = E_{0,2} \exp[-i\omega(t - (\hat{n}/c) \mathbf{s} \cdot \mathbf{r})]$  tend to a single solution  $E_m^{(1)} = E_{0,m}^{(1)} \exp[-i\omega_m(t - (\hat{n}_m/c) \mathbf{s} \cdot \mathbf{r})]$ .

Under such conditions, as is well known from the theory of linear differential equations with constant coefficients, the second linearly independent solution has the form

$$E_m^{(2)} = E_{0,m}^{(2)}(\mathbf{s}\mathbf{r}) e^{-i\omega_m(t - \frac{\hat{n}_m}{c} \mathbf{s}\mathbf{r})}$$

[we make allowance for the fact that the polarization is the same along the entire considered branch of the function  $\hat{n}(\omega, \mathbf{s})$ ; in the more general case the second

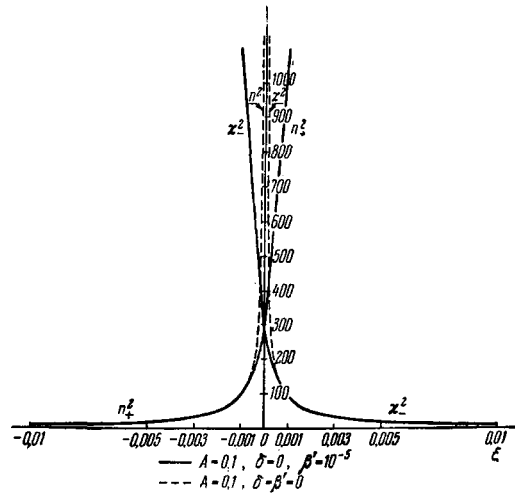


FIG. 5a

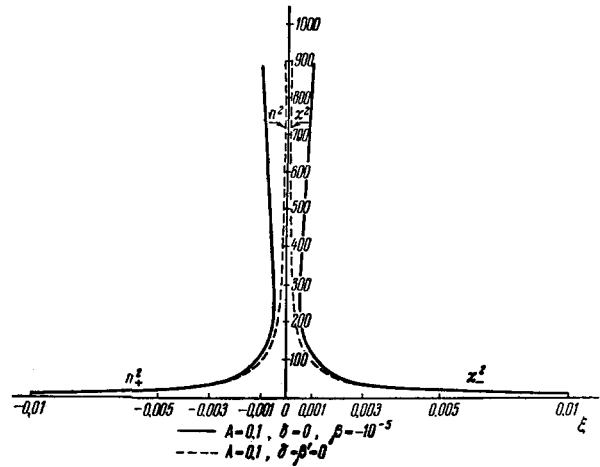


FIG. 5b

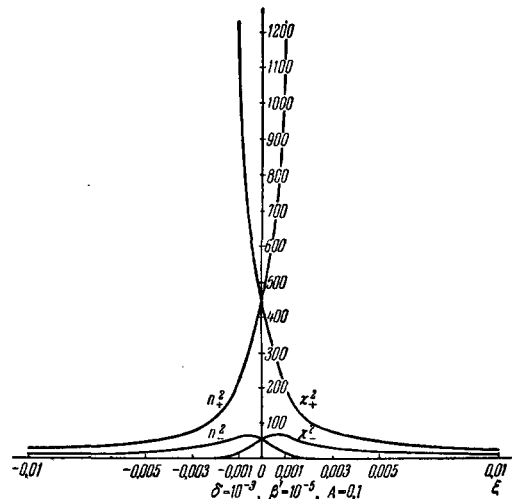


FIG. 5c

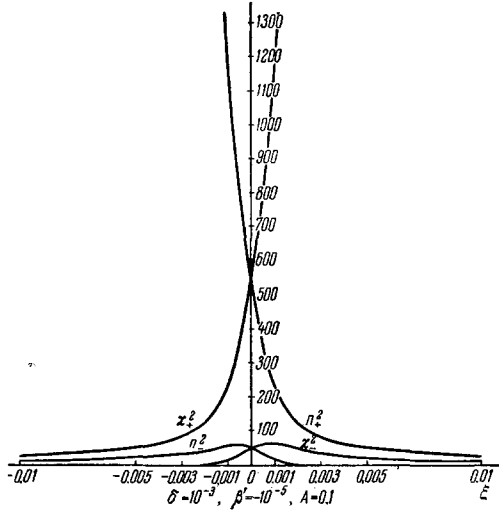


FIG. 5d

solution will be more complicated but also proportional to the coordinates  $x$ ,  $y$ , and  $z$ \*]. The foregoing pertains, of course, also to the singular optical axes (see [32, 32a]). In the latter case, a non-exponential wave can actually propagate in the crystal. For multiple roots corresponding to the "turning points," for example on Fig. 4b, the situation is different, since allowance for absorption eliminates the multiple root  $\hat{n}$  (Fig. 5d). One might think that for more complicated cases in crystal optics with allowance for spatial dispersion (and possibly also in acoustics) one also encounters multiple roots of the dispersion equation which exist in the presence of absorption (we refer to multiple roots with identical polarization and yet different from the roots corresponding to the singular axes, which appear even without account of spatial dispersion). We shall not deal in what follows with the propagation of waves when the dispersion equation has multiple roots. We therefore make only one other remark. It is usually assumed that in a homogeneous medium it is sufficient to consider solutions of the type  $E_0 \exp[-i\omega(t - (\hat{n}/c)\mathbf{s} \cdot \mathbf{r})]$  or  $E_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$ . From this point of view, independently of the question of whether waves can be observed for multiple roots and identical polarization, the very need for considering in such cases, generally speaking, also the solutions of the type

$$\mathbf{E}_m^{(2)} = \mathbf{E}_{0,m}^{(2)}(\mathbf{sr}) e^{-i\omega_m \left( t - \frac{n_m}{c} \mathbf{sr} \right)}$$

\*In the case when the polarization is constant, i.e.,  $E_0$  is independent of  $\omega$  for a given  $\mathbf{s}$ , we arrive at the indicated second solution by considering the following solution near the turning point:

$$\mathbf{E} = \frac{\mathbf{E}_0}{\hat{n}_2 - \hat{n}_1} e^{-i\omega t} \left( e^{i \frac{\omega}{c} \hat{n}_2 \mathbf{sr}} - e^{i \frac{\omega}{c} \hat{n}_1 \mathbf{sr}} \right)$$

In the limit as  $\hat{n}_2 \rightarrow \hat{n}_1$  we obtain from this a solution of the type

$$\frac{d}{d\hat{n}} \mathbf{E}_m^{(1)} = \mathbf{E}_m^{(2)} = \text{const}(\mathbf{sr}) \mathbf{E}_m^{(1)}$$

is quite curious and somewhat unexpected.\*

b) New waves in nongyrotropic crystals [7, 5]. In nongyrotropic crystals, the effects of spatial dispersion are due to the properties of the tensor  $\beta_{ijklm}$ , inasmuch as in such crystals [see (2.13)] we have

$$\epsilon_{ij}^{-1}(\omega, \mathbf{k}) = \epsilon_{ij}^{-1}(\omega) + \beta_{ijklm}(\omega) k_l k_m \quad (3.6)$$

Using this relation, and also (1.57) and (1.58), we obtain

$$\epsilon_{\perp, ij}^{-1}(\omega, \mathbf{k}) = \eta_{il} \epsilon_{lm}^{-1}(\omega) \eta_{mj} + \eta_{ir} \beta_{rslm}(\omega) k_l k_m \eta_{sj}$$

If, as in the preceding section, we align the  $z$  axis with the direction of the wave vector  $\mathbf{s}$ , the expression for  $\epsilon_{\perp, ij}^{-1}$  simplifies:

$$\epsilon_{\perp, ij}^{-1}(\omega, \mathbf{k}) = \eta_{il} \epsilon_{lm}^{-1}(\omega) \eta_{mj} + \eta_{ir} \beta_{rs33}(\omega) \eta_{sj} k^2$$

$$= \epsilon_{ij}^{-1}(\omega) + k^2 \beta_{ij33}(\omega), \quad i, j \neq 3,$$

$$\epsilon_{\perp, i3}^{-1} = \epsilon_{\perp, 3i}^{-1} = 0, \quad i = 1, 2, 3. \quad (3.7)$$

One must not forget here, of course, that in (3.7) the components of the tensors  $\epsilon_{ij}^{-1}(\omega)$  and  $\beta_{ijklm}(\omega)$  depend on the direction of  $\mathbf{s} = \mathbf{k}/k$  by virtue of the choice of the coordinate system.

Inasmuch as the vector  $\mathbf{D}'$  is transverse, we obtain a system of equations similar to the system (3.1):

$$\begin{aligned} & \left( \frac{1}{\hat{n}^2} - \epsilon_{xx}^{-1}(\omega) - \frac{\omega^2}{c^2} \beta_{xx33}(\omega) \hat{n}^2 \right) D'_x \\ & - \left( \epsilon_{xy}^{-1}(\omega) + \frac{\omega^2}{c^2} \beta_{xy33}(\omega) \hat{n}^2 \right) D'_y = 0, \\ & - \left( \epsilon_{yx}^{-1}(\omega) + \frac{\omega^2}{c^2} \beta_{yx33}(\omega) \hat{n}^2 \right) D'_x \\ & + \left( \frac{1}{\hat{n}^2} - \epsilon_{yy}^{-1}(\omega) - \frac{\omega^2}{c^2} \beta_{yy33}(\omega) \hat{n}^2 \right) D'_y = 0. \end{aligned} \quad (3.8)$$

If we choose furthermore the  $x$  and  $y$  axes along the principal axes of the two-dimensional tensor  $\epsilon_{\alpha\beta}^{-1}$ ,  $\alpha, \beta = x, y$ , then the equation for the determination of  $\hat{n}^2$  will assume the form

$$\begin{aligned} & \left( \frac{1}{\hat{n}^2} - \frac{1}{n_{01}^2} \right) \left( \frac{1}{\hat{n}^2} - \frac{1}{n_{01}^2} \right) - \frac{\omega^2}{c^2} n^2 \beta_{xxzz} \left( \frac{1}{\hat{n}^2} - \frac{1}{n_{02}^2} \right) \\ & - \frac{\omega^2}{c^2} n^2 \beta_{yyzz} \left( \frac{1}{\hat{n}^2} - \frac{1}{n_{01}^2} \right) \\ & + \frac{\omega^4}{c^4} \hat{n}^4 (\beta_{xxzz} \beta_{yyzz} - \beta_{xyzz} \beta_{yxzz}) = 0. \end{aligned} \quad (3.9)$$

\*Incidentally, one case of multiple roots for specified polarization is encountered even in the simplest problem of propagation of transverse waves in an isotropic medium. The corresponding wave equation is (here  $E = E_x$  or  $E = E_y$ , for more details see for example [2]):  $d^2 E/dz^2 + \omega^2 \epsilon E/c^2 = 0$ , and if  $n^2 = \epsilon = 0$  then  $E = E_0^{(1)} + E_0^{(2)} z$ . Here, however, the roots coalesce for waves propagating in different directions (with  $n \neq 0$ ) and, in addition, if account of absorption is taken we already have  $\epsilon = \epsilon' + i\epsilon'' = \hat{n}^2 \neq 0$ . We note also that in a magnetoactive plasma in the presence of absorption (but even without account of spatial dispersion) we know of one interesting case of the appearance of multiple roots with identical polarization (see [2], Sections 11 and 28).

We consider first the simplest case of an isotropic medium [see (2.33)]. In this case, independently of the direction of  $\mathbf{s}$ , we have  $n_{01} = n_{02} = n_0$ ,  $\beta_{xyzz} = 0$ ,  $\beta_{xxzz} = \beta_{yyzz} = \beta$ . Equation (3.9) then breaks up into two identical equations each of the form

$$\frac{1}{\hat{n}^2} - \frac{1}{n_0^2} - \frac{\omega^2}{c^2} \beta n^2 = 0. \quad (3.10)$$

From this we obtain immediately

$$\hat{n}_{1,2}^2 = (n + i\kappa)_{1,2}^2 = \frac{-1}{2\varepsilon_0\beta'} \pm \sqrt{\left(\frac{1}{2\varepsilon_0\beta'}\right)^2 + \frac{1}{\beta'}}, \quad (3.11)$$

where

$$\varepsilon_0(\omega) = n_0^2, \quad \beta' = \frac{\omega^2}{c^2} \beta.$$

Bearing in mind the region of frequencies close to some single absorption line, we obtain the following expression for  $\varepsilon_0$ :

$$\varepsilon_0(\omega) = \varepsilon_{00} + \frac{4\pi e^2 N_{\text{eff}}/m}{\omega_j^2 - \omega^2 - i\omega\nu} \approx \varepsilon_{00} - \frac{A\xi}{\xi^2 + \delta^2} + i \frac{A\delta}{\xi^2 + \delta^2}, \quad (3.12)$$

$$\xi = \frac{(\omega - \omega_j)}{\omega_j}, \quad \delta = \frac{\nu}{2\omega_j}, \quad A = \frac{2\pi e^2 N_{\text{eff}}}{m\omega_j^2}.$$

Here  $e$  and  $m$  are the charge and mass of the electron,  $\nu$  is the "effective" frequency of the collisions that cause the attenuation of the waves in the medium,  $N_{\text{eff}}/N$  is the oscillator strength, with  $N$  the total number of electrons per unit volume and  $N_{\text{eff}}$  the fraction of these electrons which "effectively" determines the optical properties of the medium in the region of the spectrum under consideration.

In the absence of absorption, when  $\delta = 0$ , we get

$$\varepsilon_0(\omega) = n_0^2 = \varepsilon_{00} - \frac{A}{\xi}, \quad (3.13)$$

where  $n_0^2$  is the refractive index neglecting not only absorption but also spatial dispersion. It is clear from (3.11) that if  $\delta = 0$  and

$$\varepsilon_0^2 |\beta'| \ll 1 \quad (3.14)$$

we can put

$$\hat{n}_1^2 \approx \varepsilon_0(1 - \varepsilon_0^2 \beta' + \dots), \quad \hat{n}_2^2 \approx -1/\varepsilon_0 \beta' - \varepsilon_0 + \dots \quad (3.15)$$

When  $\beta' \sim 10^{-6}$ , condition (3.14) assumes the form  $n_0^2 \ll 10^3$  or else it reduces when  $\varepsilon_{00} \sim 1$  and  $A \sim 0.1$  [see (3.13)] to the inequality  $|\xi| = |\omega - \omega_j|/\omega_j \gg 10^{-4}$ . In the optical (visible) region of the spectrum, where  $\omega_j \sim 10^{15} \text{ sec}^{-1} \sim 2 \times 10^4 \text{ cm}^{-1}$ , this means that expressions (3.15) become valid even at a distance  $\Delta\omega = |\omega - \omega_j| \gg 10^{-4} \omega_j \sim 2 \text{ cm}^{-1}$  from the center of the absorption line. If we assume even  $A \sim 1$ , which apparently is not realistic, we arrive at the inequality  $\Delta\omega \gg 20 \text{ cm}^{-1}$ .

In this frequency range, obviously,  $\hat{n}_1^2 \approx n_0^2$ . On the other hand, the root  $\hat{n}_2^2$  is very large and when  $\varepsilon_0 \sim 1$ , as is the case far away from the line,  $|\hat{n}_2^2| \approx 1/|\beta'| \sim 10^6$ . In addition  $\lambda = \lambda_0/n_2 \sim 5 \times 10^{-8} \text{ cm}$  and expression (2.13) is no longer valid. The new root  $\hat{n}_2$  of the dispersion equation has therefore real significance only near the line, in the region where  $\lambda = \lambda_0/n_2 \gg a \sim 3$

$\times 10^{-8} \text{ cm}$ , i.e., so long as  $n_2 \ll \lambda_0/a$ . We shall henceforth assume this condition satisfied.

Account of spatial dispersion near the absorption line introduces even qualitative changes in the  $n^2(\omega)$  curves, as is clear from Figs. 4a and b. Both figures correspond to the case  $A = 1$  and  $\delta = 0$ , but the values chosen for Figs. 4a and 4b are  $\beta' = 10^{-5}$  and  $\beta' = -10^{-5}$ , respectively. The limiting curve (3.13) with  $A = 1$  is shown dashed in both cases (inasmuch as usually  $\varepsilon_{00} \sim 1$ , and we are interested in the region  $|\varepsilon_0| \gg 1$ , we put for the sake of simplicity  $\varepsilon_{00} = 0$  everywhere in Figs. 4a and b). We know that in the absence of absorption and when  $\hat{n}^2$  is real it is obvious that the medium is transparent when  $\hat{n}^2 > 0$  and total reflection of the wave by the medium occurs when  $\hat{n}^2 = -\kappa^2 < 0$ . When  $\beta' = 0$  and  $\beta' > 0$ , one of these cases occurs, since  $\hat{n}^2$  is real. But if  $\beta' < 0$ , then the values of  $\hat{n}^2$  are complex in the region  $|\varepsilon_0| > 1/2\sqrt{|\beta'|}$  [ $\hat{n}^2 = (n + i\kappa)^2$  even in the absence of absorption]. In the case of an exciton absorption line, the sign of  $\beta'$  is determined by the sign of the "effective mass" of the mechanical exciton. In order to verify this, it is sufficient to consider in place of (3.12) the more general expression for  $\varepsilon$ , in which both temporal and spatial dispersion are taken into account:

$$\varepsilon(\omega, \mathbf{k}) = \varepsilon_{00} + \frac{4\pi e^2 N_{\text{eff}}/m}{\omega_j^2(\mathbf{k}) - \omega^2 - i\omega\nu}. \quad (3.16)$$

It is precisely this expression (3.16) which is obtained under simpler assumptions by starting from the microscopic theory (see Sec. 4). By expanding the energy of the "mechanical exciton"  $\hbar\omega_j(\mathbf{k})$  in powers of the wave vector we have in the case of an isotropic and nongyrotropic medium

$$\hbar\omega_j(\mathbf{k}) = \hbar\omega_j(0) + \frac{\hbar^2 k^2}{2m_{\text{exc}}} + \dots, \quad (3.17)$$

where  $m_{\text{exc}}$  is the "effective mass" of the mechanical exciton. Therefore for small  $|\omega - \omega_j(0)|$  we have

$$\frac{1}{\varepsilon(\omega, \mathbf{k})} \approx \frac{1}{\varepsilon_0(\omega)} + \frac{\hbar\omega_j(0)}{4\pi e^2 N_{\text{eff}}/m} \frac{k^2}{m_{\text{exc}}} \quad (3.18)$$

and in accordance with (3.6)

$$\beta = \frac{\hbar\omega_j(0)}{4\pi e^2 N_{\text{eff}}} \frac{m}{m_{\text{exc}}}. \quad (3.19)$$

Thus, the sign of  $\beta$  and  $\beta'$  [see (3.11)] actually coincides in the approximation of (3.16) with the sign of the "effective mass" of the mechanical exciton.

The possibility of observing the new wave near resonance depends to a considerable degree on the extent of absorption. In the absence of absorption the influence of the spatial dispersion is large even in the region where  $4\varepsilon_0^2 |\beta'| \sim 1$ , i.e., when  $|\xi| \sim \xi_k = 2A\sqrt{|\beta'|}$ . Further, if

$$\delta = \frac{\nu}{2\omega_j} \ll \xi_k = 2A\sqrt{|\beta'|}, \quad (3.20)$$

the absorption is small for frequencies with  $|\xi| = |\omega - \omega_j|/\omega_j \gtrsim \xi_k$ , i.e., it changes little the magni-

tude of  $\text{Re } \epsilon_0$ , and at the same time  $|\text{Im } \epsilon_0| \ll |\text{Re } \epsilon_0|$ .

Assume by way of an example that condition (3.20) is satisfied and that we are considering a frequency for which  $4\epsilon_0^2 |\beta'| = 1$ . For  $\xi < 0$  we then have  $n \approx \sqrt{1 + \sqrt{2}} (\beta')^{-1/4}$  and  $\kappa = 1/6 (\delta/\xi_k) \beta^{-1/4}$  which yields  $n \sim 50$  and  $\kappa \sim 5 \times 10^{-4}$  for  $\xi_k \approx 10^{-3}$ ,  $\beta' \approx 10^{-6}$ , and  $\delta \approx 10^{-7}$ . Inasmuch as the intensity of an individual wave attenuates as  $I = I_0 \exp[-2\omega\kappa z/c] = I_0 \exp[-\mu z]$ , this means that the absorption coefficient is  $\mu = (2\omega/c)\kappa \sim 150 \text{ cm}^{-1}$  (for  $\lambda_0 \sim 4000 \text{ \AA}$ ). For the same values of the parameters, but for  $\beta' = -10^{-6}$ , we get  $n = 1/\sqrt{2\epsilon_0} |\beta'| = |\beta'|^{-1/4} \approx 30$ ,  $\kappa \approx (\delta/\xi_k)^{1/2} / 2 |\beta'|^{1/4} \approx 0.15$ , and  $\mu = 2\omega\kappa/c \sim 4 \times 10^4 \text{ cm}^{-1}$ . In this example the intensity decreases by a factor  $e$  over a path equal approximately to  $3 \times 10^{-5} \text{ cm} \sim \lambda_0$ , whereas  $\lambda = \lambda_0/n \sim 10^{-6} \text{ cm}$ . Thus, when  $\delta \sim 10^{-7}$  the attenuation in a wavelength in the medium is not so large even in the second case.

Actually, however, for dipole lines the value of  $\delta$  for crystals is much greater than  $10^{-7}$ . In particular, in all the investigated molecular crystals, where the dipole exciton lines are particularly clearly pronounced<sup>[33]</sup>, the value of  $\delta$  tends as  $T \rightarrow 0$  to a value  $\gtrsim 10^{-3}$ . This causes the inverse inequality

$$\delta \gtrsim \xi_k \equiv 2A \sqrt{|\beta'|} \quad (3.21)$$

to be satisfied in place of (3.20), and all the deductions of the dispersion theory constructed without account of absorption must be reviewed.

Using (3.11) and (3.12), we obtain\*

$$n_{\pm}^2 = \frac{I_1^{\pm}}{2} + \frac{1}{2} \sqrt{(I_1^{\pm})^2 + (I_2^{\pm})^2}, \quad \kappa_{\pm}^2 = -\frac{I_1^{\pm}}{2} + \frac{1}{2} \sqrt{(I_1^{\pm})^2 + (I_2^{\pm})^2}, \quad (3.22)$$

where

$$I_1^{\pm} = \frac{\xi \pm M}{2\beta'A}, \quad I_2^{\pm} = \frac{\delta \pm N}{2\beta'A}, \quad M + iN = \sqrt{(\xi + i\delta)^2 + 4\beta'A^2},$$

$$M = [(\xi^2 - \delta^2 + 4\beta'A^2)^2 + 4\delta^2\xi^2]^{1/4} \cos \varphi,$$

$$N = [(\xi^2 - \delta^2 + 4\beta'A^2)^2 + 4\delta^2\xi^2]^{1/4} \sin \varphi.$$

In relation (3.22) it is necessary to take the arithmetic value of the root, while the angle  $\varphi$  must be determined in accordance with the signs of  $(\xi^2 - \delta^2 + 4\beta'A^2)$  and  $2\delta\xi$ ; here

$$(\xi^2 - \delta^2 + 4\beta'A^2) + 2i\delta\xi = qe^{i\varphi},$$

where

$$q = [(\xi^2 - \delta^2 + 4\beta'A^2)^2 + 4\delta^2\xi^2]^{1/2}.$$

The calculated values of  $n(\omega)$  and  $\kappa(\omega)$  for different values of  $\beta'$ ,  $A$ , and  $\delta$  are clearly illustrated in Fig. 5. It follows from the curves given there that at sufficiently large values of  $\delta$  the anomalous wave corresponds to very large damping. On the other hand, the dependence of the coefficient of absorption of the waves

\*We put here  $\epsilon_0(\omega) \approx -A/(\xi + i\delta)$ , which is true only in the vicinity of a resonance.

on the frequency with account of spatial dispersion does not have a Lorentz form, just as the dependence of  $n^2(\omega)$  no longer follows the Drude-Sellmeier formula. However, at small values of  $\beta'$  and  $\delta \neq 0$ , the functions  $n^2(\omega)$  and  $\kappa(\omega)$  resume their usual form. We note in this connection that whereas  $A$  is, in accord with (3.12), directly proportional to the transition oscillator strength,  $\beta$  is practically independent of the transition oscillator strength [see (3.19)], inasmuch as the "effective mass" of the mechanical exciton is roughly speaking inversely proportional to the transition oscillator strength (we have in mind "mechanical excitons" which can be excited in a dipole transition; see [34]).

According to (3.19), putting for the indicated reason  $N_{\text{eff}} m_{\text{exc}}/m \sim N$ , we have

$$\beta' = \frac{\omega^2}{c^2} \beta = \frac{\hbar\omega_j(0)\omega^2}{\omega_0^2 m c^2},$$

where  $\omega_0 = \sqrt{4\pi e^2 N/m}$  is the "plasma" frequency. In molecular crystals  $N \approx 3 \times 10^{22} - 3 \times 10^{23}$  and  $\omega_0^2 \approx 8 \times 10^{31} - 8 \times 10^{32} \text{ sec}^{-2}$ , so that when  $\omega_j \approx 3 \times 10^{15} \text{ sec}^{-1}$  we have  $\beta' \approx 10^{-6} - 10^{-7}$ . At such small values of  $\beta'$ , absorption assumes a much more important role compared with the case  $\beta' \approx 10^{-5}$  considered above, so that to observe spatial dispersion effects near dipole absorption lines it is necessary to produce very special and favorable conditions. We note that the observation of the effects of spatial dispersion near quadrupole lines is appreciably facilitated by the fact that the width of these lines turns out to be at sufficiently low temperatures several orders of magnitude lower than the width of the dipole absorption lines.

In the analysis of the question of the new waves near quadrupole absorption lines<sup>[41]</sup> we must use within the framework of the phenomenological approach expansions of the type (2.14)–(2.15). We shall return to this question in Sec. 3c.

c) Optical Anisotropy of Cubic Crystals. Quadrupole Absorption Lines. We have already stated in the Introduction that optical anisotropy of cubic crystals\*, which was considered theoretically in [3-5, 40, 41], has been observed experimentally<sup>[6]</sup> ( $\text{Cu}_2\text{O}$  crystal at low temperatures near the quadrupole transition  $\lambda = 6125 \text{ \AA}$ ).

The theory of quadrupole transitions in cubic crystals was recently developed, on the basis of the exciton concept, in articles [36-39], where the question of the influence of stresses and external fields was also considered. Inasmuch as the exciton wave functions are generally speaking unknown, it was possible to cast light in [36-39] on only a few aspects of the phenomenon.

\*We do not consider here the so-called "latent optical anisotropy" of cubic crystals, arising because of the possible presence in the crystal of anisotropic centers connected with local lattice defects (for example, various types of color centers, etc.). If spatial dispersion is neglected and there are no directional external influences, cubic crystals with anisotropic centers (impurities) remain optically isotropic (for more details see [85]).

In particular, the polarization of quadrupole transitions as a function of the direction of light propagation was established, along with the character of the angular dependence of the absorption intensity.

Under the influence of external electric and magnetic fields and mechanical stresses, the crystal symmetry is generally speaking lowered and the degenerate exciton levels may split. The character of this splitting varies with the exciton state and depends on the symmetry of the disturbance. This circumstance may be employed quite effectively to establish the symmetry of quadrupole excited states of a system on the basis of experimental data.

Optical anisotropy in cubic crystals may, of course, manifest itself not only in the region of quadrupole transitions, but also in the region of dipole transitions. The theory of this question was considered phenomenologically in [5] and then, within the framework of exciton theory\*, in [40]. For the same reason as above (the exciton wave functions are unknown) only a few aspects could be explained in this manner in [40] as well as in [5], namely the polarization and the number of independent waves as a function of the direction of light propagation; it was also possible to determine the course of the dispersion near the exciton absorption bands with accuracy to the unknown oscillator strengths, the "effective mass" of the exciton, etc.

We shall show below that an account of the spatial dispersion by expanding the dielectric tensor in powers of the wave vector (see Sec. 2b) makes it possible to obtain in much simpler fashion all the results indicated in [4, 36, 40]. The same method makes it possible to regard the influence of the external perturbations and, in particular, to obtain all the results contained in the articles [36a-39]. In addition, we shall obtain below a series of new results.

Let us consider first the region of frequencies close to the frequency at which the dielectric constant  $\epsilon_0(\omega)$  becomes infinite if spatial dispersion is not taken into account (the dipole line). In this frequency region it is necessary to use an expansion of the type (2.13) to estimate the role of spatial dispersion

$$\epsilon_{ij}^{-1}(\omega, \mathbf{k}) = \delta_{ij}\epsilon_0^{-1}(\omega) + \beta'_{ijlm}(\omega) \hat{n}^2 s_l s_m$$

[the tensor used in (2.13) is  $\beta_{ijlm} = (c^2/\omega^2)\beta'_{ijlm}$ ].

As was already indicated in Section 2b, the tensor  $\beta'_{ijlm}$  becomes simpler if the x, y, z frame is aligned with the four-fold axes. In this case, for the crystal classes  $T_d$ , O, and  $O_h$ , the tensor  $\beta'_{ijlm}$  is determined by the three numbers

\*We note that in the article [40], as well as in all the earlier papers in this direction (see [7, 41]), the effective transverse electromagnetic field is assumed to be equal to the average macroscopic field. Such an assumption can be particularly critical in the investigation of quadrupole transitions. The question of the effective transverse field is discussed in the book [12] (see p. 385), but there is likewise no solution to this problem there. We shall touch upon this question again in Sec. 4.

$$\beta'_1 = \beta'_{xxxx} = \beta'_{yyyy} = \beta'_{zzzz}, \quad \beta'_2 = \beta'_{xxyy} = \beta'_{xzzz} = \beta'_{yyzz}, \\ \beta'_3 = \beta'_{xyxy} = \beta'_{xzzx} = \beta'_{yzyz}.$$

This leads to the following system of equations for the components of the vector  $D'$  [see (1.20)]:

$$\frac{1}{\hat{n}^2} D'_1 = \left( \frac{1}{\epsilon_0} + \beta'_2 \hat{n}^2 \right) D'_1 + \tilde{\beta} \hat{n}^2 s_1^2 D'_1 - \tilde{\beta} \hat{n}^2 s_1 D'_1 s_1^2 \quad (3.23)$$

etc, where account is taken of the condition  $s_1 D'_1 = 0$  and

$$\tilde{\beta} = \beta'_1 - \beta'_2 - 2\beta'_3. \quad (3.23a)$$

It follows from (3.23), naturally, that  $D' \cdot \mathbf{s} = 0$ . Let us consider several particular cases.

a) We assume that the vector  $\mathbf{s}$  is directed along one of the cube edges, for example along the z axis. Then the equation for the components of the vector  $D'$  simplifies to

$$\frac{1}{\hat{n}^2} D'_1 = \left( \frac{1}{\epsilon_0} + \beta'_2 \hat{n}^2 \right) D'_1, \quad \frac{1}{\hat{n}^2} D'_2 = \left( \frac{1}{\epsilon_0} + \beta'_2 \hat{n}^2 \right) D'_2, \quad D'_3 = 0,$$

from which it follows that in the case under consideration  $\hat{n}^2$  is independent of the polarization of the vector  $D'$  and is determined by the equation

$$\frac{1}{\hat{n}^2} = \frac{1}{\epsilon_0} + \beta'_2 \hat{n}^2.$$

An equation of this type was already considered earlier (see Sec. 3b).

b) We now assume that the vector  $\mathbf{s}$  is directed along some principal diagonal of the cube:  $|s_1| = |s_2| = |s_3| = 1/\sqrt{3}$ . We then obtain from (3.23)

$$\frac{1}{\hat{n}^2} D'_i = \left( \frac{1}{\epsilon_0} + \beta'_2 \hat{n}^2 + \tilde{\beta} \frac{\hat{n}^2}{3} \right) D'_i, \quad i = 1, 2, 3.$$

Consequently, in this case  $\hat{n}^2$  is independent of the polarization, and to each polarization there correspond two values of  $\hat{n}^2$ , determined from the equation

$$\frac{1}{\hat{n}^2} = \frac{1}{\epsilon_0} + \left( \beta'_2 + \frac{\tilde{\beta}}{3} \right) \hat{n}^2.$$

The seven considered directions (the 3 four-fold axes and the 4 body diagonals) are thus optical axes of the crystal.

c) Assume now that the vector  $\mathbf{s}$  is directed along the diagonal of the face. For example, let  $s_1 = s_2 = 1/\sqrt{2}$ ,  $s_3 = 0$ . Then the equations for  $D'_i$ ,  $i = 1, 2, 3$ , assume the following form

$$\frac{1}{\hat{n}^2} D'_1 = \left( \frac{1}{\epsilon_0} + \beta'_2 \hat{n}^2 + \frac{1}{2} \tilde{\beta} \hat{n}^2 \right) D'_1, \quad D'_2 = -D'_1,$$

$$\frac{1}{\hat{n}^2} D'_3 = \left( \frac{1}{\epsilon_0} + \beta'_2 \hat{n}^2 \right) D'_3.$$

Thus, in the direction considered, the values of  $\hat{n}^2$  depend essentially on the polarization of the electromagnetic field. If  $D'_3 \neq 0$  and  $D'_1 = D'_2 = 0$ , then

$$\frac{1}{\hat{n}^2} = \frac{1}{\epsilon_0} + \beta'_2 \hat{n}^2.$$

This equation remains unchanged for a wave with  $D'_3 \neq 0$  and, in the more general case, when  $s_3 = 0$ , but  $s_1 \neq s_2$ . On the other hand, if  $D'_3 = 0$ , and  $D'_1 = -D'_2$



$\neq 0$ , then the equation for  $\hat{n}^2$  is

$$\frac{1}{\hat{n}^2} = \frac{1}{\epsilon_0} + \left( \beta'_2 + \frac{1}{2} \tilde{\beta} \right) \hat{n}^2.$$

For each polarization there are two values of the refractive index. We note that when  $D'_3 \neq 0$  the index  $\hat{n}$  for case c) coincides with the index for case a). We note also that the equations obtained for  $\hat{n}^2$  show clearly that the role of the spatial dispersion differs with the direction  $\mathbf{s}$  and with the polarization. Thus, the phenomenological analysis<sup>[5]</sup> is, as in other cases, not only fully adequate for a consideration of the optical isotropy in cubic crystals of classes  $T_d$ ,  $O$ , and  $O_h$ , but also appreciably simpler than the corresponding microscopic theory<sup>[40]</sup> or, more accurately, calculations using exciton wave functions. This, of course, pertains also to crystals of other classes.

In the direct vicinity of a resonance (pole),  $\epsilon_0(\omega)$  must be regarded as complex and, as follows from the foregoing, the absorption coefficient  $\kappa = \text{Im } n$ , like  $n = \text{Re } \hat{n}$ , depends on the direction  $\mathbf{s}$  and the polarization of the light. Thus, in cubic crystals we can have near the poles of the function  $\epsilon_0(\omega)$  not only anisotropy of dispersion, but also of absorption. The poles of  $\epsilon_0(\omega)$  correspond to lines in the absorption spectrum which we shall call dipole absorption lines (since they correspond to nonvanishing matrix elements of the crystal dipole-moment operator, made up of wave functions of the ground and excited states of the crystal; see below for details).

As is clear from the foregoing, account of spatial dispersion near dipole lines in cubic crystals leads to a strong change in the variation of the dispersion curves, and in this respect the spatial dispersion effect is far from small.

We proceed now to consider the anisotropy of dispersion and absorption near the quadrupole absorption lines, in the vicinity of which  $\epsilon_0(\omega)$  varies smoothly, but at least one of the components of the tensor  $\alpha_{ijlm}(\omega)$  has a resonance (pole). To this end we use an expansion of the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  [see (2.12) and (2.33)]:

$$\epsilon_{ij}(\omega, \mathbf{k}) = \delta_{ij} \epsilon_0(\omega) + \alpha_{ijlm}(\omega) \hat{n}^2 s_l s_m. \quad (2.33a)$$

The tensor  $\alpha_{ijlm}$  differs here from the tensor designated by the same letter in (2.12) by a factor  $c^2/\omega^2$ .

Let us assume that the principal absorption of light in the crystal is connected with the quadrupole absorption lines, by virtue of which the tensor  $\epsilon_0(\omega) \delta_{ij}$  will be assumed real and the tensor  $\alpha_{ijlm}(\omega)$  complex:  $\alpha_{ijlm}(\omega) = \alpha'_{ijlm}(\omega) + \alpha''_{ijlm}(\omega)$ .

Inasmuch as in cubic crystals both tensors  $\alpha'_{ijlm}$  and  $\alpha''_{ijlm}$  simplify simultaneously, provided the coordinate axes are chosen along the four-fold axes, the presence of absorption ( $\alpha''_{ijlm} \neq 0$ ) does not complicate the analysis. We use in such a coordinate system the notation  $\alpha_1 = \alpha_{xxxx} = \alpha_{yyyy} = \alpha_{zzzz}$ ,  $\alpha_2 = \alpha_{xxyy} = \alpha_{xxzz} = \alpha_{yyzz}$ ,  $\alpha_3 = \alpha_{xyxy} = \alpha_{xzzx} = \alpha_{yzyz}$ . We

then obtain for the components of the vector  $\mathbf{E}$ , in accordance with (1.16) or (1.20), the following system of equations [see also (2.34) with  $\alpha_2 = \alpha_4$ ]:

$$\hat{n}^2 E_1 = (\epsilon_0 + \alpha_2 \hat{n}^2) E_1 + \tilde{a} \hat{n}^2 s_1^2 E_1 + 2\alpha_3 (\mathbf{E}\mathbf{s}) \hat{n}^2 s_1 + (\mathbf{E}\mathbf{s}) \hat{n}^2 s_1 \quad (3.24)$$

etc, where

$$\tilde{a} = \alpha_1 - \alpha_2 - 2\alpha_3. \quad (3.24a)$$

We consider here, too, several particular cases, when the vector  $\mathbf{s}$  is directed along the symmetry axes of the cube:

a)  $\mathbf{s}$  parallel to the  $z$  axis,  $s_3 = 1$ ,  $s_1 = s_2 = 0$ . In this case the system (3.24) has the following form:

$$\begin{aligned} \hat{n}^2 E_1 &= (\epsilon_0 + \alpha_2 \hat{n}^2) E_1, & \hat{n}^2 E_2 &= (\epsilon_0 + \alpha_2 \hat{n}^2) E_2, \\ & & (\epsilon_0 + \alpha_1 \hat{n}^2) E_3 &= 0. \end{aligned} \quad (3.25)$$

Thus, in this case there is a transverse wave ( $E_3 = 0$ ), for which, independently of the polarization,

$$\hat{n}^2 = (n + i\kappa)^2 = \frac{\epsilon_0}{1 - \alpha'_2 - i\alpha''_2}, \quad (3.26)$$

and a longitudinal wave ( $E_1 = E_2 = 0$ ) with

$$\hat{n}^2 = -\frac{\epsilon_0}{\alpha'_1 + i\alpha''_1}.$$

b) We assume now that the vector  $\mathbf{s}$  is directed along a principal diagonal of the cube:  $s_1 = s_2 = s_3 = 1/\sqrt{3}$ . In this case we have in place of (3.25)

$$\begin{aligned} \hat{n}^2 E_i &= \left( \epsilon_0 + \alpha_2 \hat{n}^2 + \frac{1}{3} \tilde{a} \hat{n}^2 \right) E_i + \frac{1}{3} (1 + 2\alpha_3) \hat{n}^2 (E_1 + E_2 + E_3) \\ & \quad (i = 1, 2, 3). \end{aligned} \quad (3.27)$$

When  $\mathbf{E} = \mathbf{E}\mathbf{s}$  (longitudinal wave)  $\hat{n}^2 = -3\epsilon_0/(\alpha_1 + 2\alpha_2 + 4\alpha_3)$ , whereas for transverse waves  $\mathbf{E} \cdot \mathbf{s} = 0$  independently of the polarization

$$\hat{n}^2 = (n + i\kappa)^2 = \frac{\epsilon_0}{1 - \alpha'_3 - \alpha_2}. \quad (3.28)$$

c) Let the vector  $\mathbf{s}$  be now directed along the diagonal of the face of the cube. For example, let  $s_1 = s_2 = 1/\sqrt{2}$ ,  $s_3 = 0$ . In this case we have on the basis of (3.24)

$$\begin{aligned} \hat{n}^2 E_i &= (\epsilon_0 + \alpha_2 \hat{n}^2) E_i + \frac{\tilde{a}}{2} \hat{n}^2 E_i \\ & \quad + \left( \alpha_3 + \frac{1}{2} \right) (E_1 + E_2) \hat{n}^2 \text{ for } i = 1, 2 \end{aligned}$$

and

$$\hat{n}^2 E_3 = (\epsilon_0 + \alpha_2 \hat{n}^2) E_3. \quad (3.29)$$

It follows from (3.29) that:

1)  $E_3 = 0$ ,  $\mathbf{E} \cdot \mathbf{s} \neq 0$ —longitudinal wave:

$$\hat{n}^2 = -\frac{\epsilon_0}{\tilde{a}/2 + \alpha_2 + 2\alpha_3}.$$

2)  $E_3 = 0$ ,  $\mathbf{E} \cdot \mathbf{s} = 0$ —transverse wave polarized in the plane of the face:

$$\hat{n}^2 = \frac{\epsilon_0}{1 - \alpha_2 - \tilde{a}/2}. \quad (3.30)$$

Table IV. Characters of irreducible representations of the  $O_h$  group

Irreducible representations		Symmetry operations									
		E	$3C_4$	$6C_4$	$6C_2$	$8C_3$	I	$3C_2'$	$6C_2$	$6C_3$	$8C_3$
$A_1$	$x_1x_2 + y_1y_2 + z_1z_2$ (scalar)	1	1	1	1	1	1	1	1	1	1
$A_2$	$x_1x_2 - y_1y_2, 2z_1z_2 -$ $-x_1x_2 - y_1y_2$	1	1	-1	-1	1	1	1	-1	-1	1
$E$		2	2	0	0	-1	2	2	0	0	-1
$F_1$	(pseudovector)	3	-1	1	-1	0	3	-1	1	-1	0
$F_2$	$x_1y_2 + x_2y_1, x_1z_2 +$ $+x_2z_1, y_1z_2 + y_2z_1$	3	-1	-1	1	0	3	-1	-1	1	0
$A_1'$	(pseudoscalar)	1	1	1	1	1	-1	-1	-1	-1	-1
$A_2'$		1	1	-1	-1	1	-1	-1	1	1	-1
$E'$		2	2	0	0	-1	-2	-2	0	0	1
$F_1'$	$x, y, z$ (vector)	3	-1	1	-1	0	-3	1	-1	1	0
$F_2'$		3	-1	-1	1	0	-3	1	1	-1	0

3)  $E_3 \neq 0$ ,  $\mathbf{E} \cdot \mathbf{s} = 0$  —transverse wave polarized perpendicular to the plane of the face:

$$\hat{n}^2 = \frac{\epsilon_0}{1 - a_2} \quad (3.31)$$

We note that in the case when  $s_1 \neq s_2$ ,  $s_3 = 0$ , the equation for  $E_3$ , as in (3.29), separates and relation (3.31) remains in force.

So far we have not made specific the character of those excited states in the crystal, the presence of which leads to a resonant behavior of the functions  $\epsilon_0(\omega)$  or  $\alpha_{ijlm}(\omega)$ . Inasmuch as we are interested here primarily in exciton states, let us stop, before we proceed to a further exposition of the theory of optical anisotropy of cubic crystals, to discuss the classification of these states.\*

It is well known that stationary states in a crystal, and particularly exciton states (see, for example, [42-44]), can be classified in terms of the irreducible representations of the crystal space group. Each space group contains a subgroup of parallel translations, including all the possible parallel translations of the lattice into itself. The complete space group is obtained from this subgroup by adding to it H elements ("rotation" elements), which contain rotations or reflections, with H equal to the number of elements of the group of the corresponding crystal class. Any space group element can be regarded as a product of one of the elements of the translational subgroup by one of the "rotation" elements. If the space group

\*Transitions whose probability is proportional to  $k^2$  can, of course, also be classified without resorting to the notion of excitons and their wave functions. Actually, these transitions correspond to radiation of a scalar source [in this case only longitudinal waves can be obtained; see (3.35)-(3.35a) below], and to radiation from a quadrupole and a magnetic dipole. In other words as in the case of dipole radiation, there is no special need to resort here to quantum language. The latter, however, will be done with an aim towards application to exciton lines.

does not contain essential screw axes and glide planes, the aggregate of "rotational" elements forms a point group, namely the group of the corresponding crystal class [42]. Inasmuch as we are considering in the present article weak spatial dispersion, which corresponds to the method of expanding in powers of the wave vector, the tensors  $\epsilon_{0ij}(\omega)$ ,  $\alpha_{ijlm}(\omega)$  etc, contained in an expansion of the type (2.19), are determined by the properties of the exciton states as  $\mathbf{k} \rightarrow 0$ . The wave functions of exciton states with  $\mathbf{k} = 0$  are invariant under the elements of the translation subgroup [see expression (3) in the Introduction]. Therefore the corresponding exciton states can be classified in accordance with the irreducible representations of the point group of the crystal class\*, which characterizes the symmetry of the directions in the crystal. This is precisely the classification of the exciton states which we shall use below.

Let us consider in greater detail crystals of the type of  $\text{Cu}_2\text{O}$ , which belong to the most symmetrical class  $O_h$  of the cubic system. The characters of the irreducible representations of the group  $O_h$  are indicated in Table IV (using the notation of [45]). The second column of this table shows how the corresponding wave functions are transformed under the symmetry operations from  $O_h$ . Thus, for example, it follows from Table IV that three wave functions corresponding to the triply degenerate (when  $\mathbf{k} = 0$ ) exciton term and having the symmetry of the irreducible representation  $F_2$ , are transformed like symmetrized products of unlike components of two polar vectors  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$ .

As in the case of the lowest electron terms of polyatomic molecules (see [45], Sec. 98), it is customary

\*The latter is connected with the fact that the point group of the crystal class is isomorphic to the factor group relative to the translation subgroup. More details on this subject can be found, for example, in [44].

to use for crystals an empirical rule, according to which the wave function of the ground state of the crystal has complete symmetry with respect to the crystal symmetry transformations. In the case under consideration, for example, this means that the ground state has the symmetry of the irreducible representation  $A_1$ , which will be assumed. Then, taking account of the fact that the dipole moment operator transforms like a polar vector, the matrix element of the dipole moment operator will differ from zero only on going from the ground state into such exciton states, whose wave functions are transformed when  $\mathbf{k} = 0$  in accordance with the irreducible representation  $F_2'$  (see Table IV). Nonvanishing matrix elements of the dipole moment operator correspond to nonvanishing transition oscillator strengths, meaning that at the transition frequency the dielectric constant  $\epsilon_0(\omega)$  becomes infinite if absorption and spatial dispersion are not taken into account. Thus, the results obtained in Item 3b by using for the tensor  $\epsilon_{ij}^{-1}$  an expansion of the type (2.13) make it possible to take into account the spatial dispersion connected with the contribution of those exciton bands, whose wave functions are transformed when  $\mathbf{k} = 0$  in accordance with the irreducible representation  $F_1'$ . As regards those exciton bands, whose wave functions are transformed when  $\mathbf{k} = 0$  in accordance with irreducible representations other than  $F_1'$ , these bands manifest themselves only if spatial dispersion is taken into account. Thus, for example, as is the case for atoms and molecules (see, for example, [42]), the contribution to quadrupole absorption and emission of light is obtained only from those exciton bands, whose wave functions transform when  $\mathbf{k} = 0$  as products of the components of two polar vectors. The aggregate of these products in the  $O_h$  group generates the reducible representation  $V^2$ , which breaks up into a sum of irreducible representations\* (Table IV and [42]):

$$V^2 = A_1 + E + F_1 + F_2. \quad (3.32)$$

Here the scalar product of the two polar vectors  $I = x_1x_2 + y_1y_2 + z_1z_2$  reduces in accordance with the representation  $A_1$ , the two independent linear combinations  $II = x_1x_2 - z_1z_2$  and  $III = 2y_1y_2 - x_1x_2 - z_1z_2$  transform in accordance with the doubly degenerate representation  $E$ , the three components of the vector product of two polar vectors  $IV = y_1y_2 - y_2z_1$ ,  $V = z_1z_2 - z_2x_1$ , and  $VI = x_1y_2 - x_2y_1$  transform in accordance with the triply degenerate representation  $F_1$ , while the three symmetrical linear combinations  $VII = y_1z_2 + y_2z_1$ ,  $VIII = z_1x_2 + x_1z_2$ , and  $IX = x_1y_2 + y_1x_2$  trans-

\*The representations  $A_2$ ,  $A_2'$ ,  $E'$ , and  $F_2'$  (see Table IV) correspond to higher multipoles, which are apparently of no interest. We note also that we classify here as quadrupole absorption all the absorption whose probability is proportional to  $k^2$ . Therefore, in addition to the true quadrupole absorption (the representations  $E$  and  $F_2$ ), this includes also the magnetic-dipole (representation  $F_1$ ) and scalar (representation  $A_1$ ) absorptions.

form in accordance with the triply degenerate representation  $F_2$ .

Each of these quadrupole exciton states can, generally speaking, make a contribution to the quadrupole absorption of light by the crystal. However, near a given resonance one can usually confine oneself to an examination of one transition, i.e., one excited exciton state. Here, as will be shown in Sec. 4, for the transition from the ground state zero to the excited states of the  $L$ -th band (for  $\mathbf{k} = 0$ ) we have

$$\alpha_{ijlm}(\omega) \sim \frac{1}{2} \sum_{\alpha} \{ \langle 0, L_q | \hat{T}_{il} | 0 \rangle \langle 0 | \hat{T}_{jm} | 0, L_q \rangle + \langle 0, L_q | \hat{T}_{im} | 0 \rangle \langle 0 | \hat{T}_{jl} | 0, L_q \rangle \}. \quad (3.33a)$$

Here the operator

$$T_{ij} = \sum_{\alpha=1}^N (p_i^{\alpha} r_j^{\alpha} + r_j^{\alpha} p_i^{\alpha}), \quad (3.33b)$$

$\rho$  is the number of degenerate excited states (for  $\mathbf{k} = 0$ ) in the  $L$ -th band, and  $\mathbf{r}^{\alpha}$  and  $\mathbf{p}^{\alpha}$  are the coordinate and momentum of the  $\alpha$ -th electron in the crystal. The fact that the  $T_{ij}$  transform like products of the components of two polar vectors causes indeed the tensor  $\alpha_{ijlm}(\omega)$  to be determined by the contribution of the exciton states, whose wave functions are transformed in accordance with one of the irreducible representations  $A_1$ ,  $E$ ,  $F_1$ , or  $F_2$ .

In the case of a degenerate exciton term we shall choose the wave functions such that they transform, apart from a coefficient, as the corresponding linear combinations of the products of the components of a polar vector. Thus, for example, in the case of a doubly degenerate term the wave functions  $\Psi_E^{II}$  and  $\Psi_E^{III}$  will be chosen such that in cubic-symmetry transformations they transform\* as  $\sqrt{3} II = \sqrt{3} (x_1x_2 - z_1z_2)$  and  $III = 2y_1y_2 - x_1x_2 - z_1z_2$ . It is clear that the scalar product  $\int \Psi_E^{II} \Psi_E^{III} d\mathbf{r}$  of such functions  $\Psi_E^{II}$  and  $\Psi_E^{III}$  vanishes. (When  $\mathbf{k} = 0$  all the functions can be regarded as real, a fact which has been taken into account above when writing out the scalar product; when the coordinate system is rotated through an angle  $\pi/2$  about the  $y$  axis, the function  $\Psi_E^{II}$  reverses sign, and the function  $\Psi_E^{III}$  remains unchanged; thus the invariant quantity—the scalar product—should reverse sign under such a coordinate transformation and consequently vanish.) We can prove analogously the mutual orthogonality of the functions  $\Psi_{F_1}^{IV}$ ,  $\Psi_{F_1}^{V}$ ,  $\Psi_{F_1}^{VI}$ , etc. We shall henceforth use the following identities:

$$\left. \begin{aligned} x_1x_2 &= \frac{1}{2} II - \frac{1}{6} III + \frac{1}{3} I, & y_1y_2 &= \frac{1}{3} III + \frac{1}{3} I, \\ z_1z_2 &= -\frac{1}{2} II - \frac{1}{6} III + \frac{1}{3} I, & \left. \begin{aligned} x_1y_2 \\ y_1x_2 \end{aligned} \right\} &= \frac{1}{2} IX \pm \frac{1}{2} VI, \\ \left. \begin{aligned} y_1z_2 \\ z_1y_2 \end{aligned} \right\} &= \frac{1}{2} VII \pm \frac{1}{2} IV, & \left. \begin{aligned} z_1x_2 \\ x_1z_2 \end{aligned} \right\} &= \frac{1}{2} VIII \pm \frac{1}{2} V. \end{aligned} \right\} \quad (3.34)$$

\*The factor  $\sqrt{3}$  follows from the normalization requirement for the basis functions.

Let us stop to discuss some particular cases.

1) We assume that when  $\mathbf{k} = 0$  the exciton state  $L$  transforms in accordance with the nondegenerate representation  $A_1$ , by which the ground state of the system is likewise transformed. Then, taking (3.34) into account, we obtain

$$\langle 0, L | \sum_{\alpha=1}^N r_i^\alpha p_i^\alpha | 0 \rangle = \frac{\delta_{il}}{3} \langle 0, L | \sum_{\alpha=1}^N r^\alpha p^\alpha | 0 \rangle. \quad (3.35)$$

From this we obtain immediately with the aid of (3.33) [see also (2.31) and (2.32)]

$$\alpha_1 = \alpha \neq 0, \alpha_2 = 0, \alpha_3 = \frac{\alpha}{2}, \tilde{\alpha} \equiv \alpha_1 - \alpha_2 - 2\alpha_3 = 0. \quad (3.35a)$$

Since in this case we have in accord with (3.24)

$$(\hat{n}^2 - \varepsilon_0) E = (1 + \alpha) \hat{n}^2 (E \mathbf{s}),$$

it is clear that the considered excited state manifests itself only for longitudinal waves (independently of the direction  $\mathbf{s}$ , we have for this wave  $\hat{n}^2 = -\varepsilon_0/\alpha$ , whereas for transverse waves  $\hat{n}^2 = \varepsilon_0$ ).

2) We now consider the case of the doubly degenerate term  $E$ . Then

$$\int \Psi_E^{II} (2\hat{T}_{22} - \hat{T}_{11} - \hat{T}_{33}) \Psi_0 \, dr = \int \Psi_E^{III} (\hat{T}_{11} - \hat{T}_{33}) \Psi_0 \, dr = 0.$$

Therefore in accordance with (3.34) we have

$$\langle \Psi_E | \hat{T}_{ij} | \Psi_0 \rangle = \delta_{ij} M_{jj}, \quad (3.36a)$$

where  $M_{jj}$  is the diagonal element and not the trace, and

$$\left. \begin{aligned} M_{11}(II) &\equiv \langle \Psi_E^{II} | \hat{T}_{11} | \Psi_0 \rangle = \frac{1}{2} \langle \Psi_E^{II} | \hat{T}_{11} - \hat{T}_{33} | \Psi_0 \rangle \equiv \frac{1}{2} M_1, \\ M_{22}(II) &= 0, \quad M_{33}(II) = -\frac{1}{2} M_1, \\ M_{11}(III) &\equiv \langle \Psi_E^{III} | \hat{T}_{11} | \Psi_0 \rangle = -\frac{1}{6} \langle \Psi_E^{III} | 2\hat{T}_{22} - \hat{T}_{11} - \hat{T}_{33} | \Psi_0 \rangle \\ &\equiv -\frac{1}{6} M_2, \quad M_{22}(III) = \frac{1}{3} M_2, \quad M_{33}(III) = -\frac{1}{6} M_2. \end{aligned} \right\} \quad (3.36b)$$

Here we used also the relation

$$\int \Psi_E^{II, III} (\hat{T}_{11} + \hat{T}_{22} + \hat{T}_{33}) \Psi_0 \, dr = 0,$$

which holds true by virtue of the fact that the functions  $\Psi_E$  and the operator  $(\hat{T}_{11} + \hat{T}_{22} + \hat{T}_{33})$  transform in accordance with different irreducible representations of the  $O_h$  group.

It is easy to verify that

$$M_2 = \sqrt{3} M_1. \quad (3.37)$$

Indeed, by carrying out under the integral sign

$$M_1 = \langle \Psi_E^{II} | \hat{T}_{11} - \hat{T}_{33} | \Psi_0 \rangle$$

the operation  $g$  (rotation through  $\pi/2$  about the  $z$  axis), taking into account the invariance of the integral, and also the relation

$$g\Psi_0 = \Psi_0,$$

$$g(\hat{T}_{11} - \hat{T}_{33}) = (\hat{T}_{22} - \hat{T}_{33})$$

$$\equiv \frac{1}{2} (\hat{T}_{11} - \hat{T}_{33}) + \frac{1}{2} (2\hat{T}_{22} - \hat{T}_{11} - \hat{T}_{33}),$$

$$g\Psi_E^{II} = \frac{1}{2} \Psi_E^{II} + \frac{\sqrt{3}}{2} \Psi_E^{III},$$

we find that

$$M_1 = \frac{1}{4} (M_1 + \sqrt{3} M_2), \text{ i.e. } M_2 = \sqrt{3} M_1.$$

Using now (3.33) and also (3.36) and (3.37), we get

$$\alpha_1 = \alpha \neq 0, \alpha_2 = 0, \alpha_3 = -\frac{1}{4} \alpha,$$

$$\tilde{\alpha} \equiv \alpha_1 - \alpha_2 - 2\alpha_3 = \frac{3}{2} \alpha, \quad (3.38)$$

For this case, the system (3.24) still remains cumbersome:

$$\frac{\hat{n}^2 - \varepsilon_0}{\hat{n}^2} E_1 = \frac{3\alpha}{2} E_1 s_1^2 + \left(1 - \frac{\alpha}{2}\right) (E \mathbf{s})_1 \text{ etc.} \quad (3.38a)$$

Consequently, the expression for  $\hat{n}^2$  for arbitrary  $\mathbf{s}$  will be derived below by perturbation methods. We now note one consequence of (3.26), (3.28), (3.30), and (3.31). Namely, the presence in the crystal of a quadrupole exciton state of the type considered here manifests itself neither in the dispersion nor in the absorption if the light propagates along the edges of the cube, and to the contrary, does manifest itself for any polarization, when the light is propagated along the principal diagonals of the cube. In the case, however, when the vector  $\mathbf{s}$  is directed along the diagonal of the face of the cube, the exciton state of type  $E$  manifests itself only when the electric vector lies in the plane of the face.\*

3) Let us discuss the case of the triply degenerate term  $F_1$ , whose wave functions transform as the components of a pseudovector. In this case, in accord with the chosen basis, and also by virtue of (3.34), we have

$$\langle \Psi_{F_1} | \hat{T}_{ij} | \Psi_0 \rangle = (1 - \delta_{ij}) M_{ij}, \quad (3.39)$$

where, of course, no summation is carried out over  $i$  and  $j$ , and

$$\left. \begin{aligned} M_{23}(IV) &\equiv \langle \Psi_{F_1}^{IV} | \hat{T}_{23} | \Psi_0 \rangle = \frac{1}{2} \langle \Psi_{F_1}^{IV} | \hat{T}_{23} - \hat{T}_{32} | \Psi_0 \rangle \\ &= -M_{32}(IV), \\ M_{12}(IV) &= M_{21}(IV) = M_{13}(IV) = M_{31}(IV) = 0, \quad M_{13}(V) \\ &\equiv \langle \Psi_{F_1}^V | \hat{T}_{13} | \Psi_0 \rangle = -\frac{1}{2} \langle \Psi_{F_1}^V | \hat{T}_{31} - \hat{T}_{13} | \Psi_0 \rangle = -M_{31}(V), \\ M_{12}(VI) &= M_{21}(VI) = M_{23}(VI) = M_{32}(VI) = 0, \\ M_{12}(VI) &\equiv \langle \Psi_{F_1}^{VI} | \hat{T}_{12} | \Psi_0 \rangle = \frac{1}{2} \langle \Psi_{F_1}^{VI} | \hat{T}_{12} - \hat{T}_{21} | \Psi_0 \rangle \\ &= -M_{21}(VI), \quad M_{23}(VI) = M_{32}(VI) = M_{13}(VI) \\ &= M_{31}(VI) = 0. \end{aligned} \right\} \quad (3.40)$$

\*These deductions, as applied to absorption, coincide with those made in [3<sup>e</sup>]. The question of the anisotropy of the dispersion, i.e., of the dependence of  $n$  on  $\mathbf{s}$ , was not considered in [3<sup>e</sup>].

In addition, it is easy to verify that

$$M_{23}(\text{IV}) = M_{31}(\text{V}) = M_{12}(\text{VI}) \equiv M(F_1). \quad (3.41)$$

Using now (3.33), and also (3.39), (3.40), and (3.41), we find that

$$\alpha_1 = 0, \quad \alpha_2 = \alpha \neq 0, \quad \alpha_3 = -\frac{\alpha}{2}, \quad \tilde{\alpha} = \alpha_1 - \alpha_2 - 2\alpha_3 = 0. \quad (3.41a)$$

Since we have here, in accord with (3.24),

$$(\hat{n}^2 - \varepsilon_0) E_i = \alpha \hat{n}^2 E_i + \hat{n}^2 (\mathbf{E}\mathbf{s}) s_i (1 - \alpha), \quad i = 1, 2, 3,$$

we reached the conclusion that the absorption and dispersion are completely isotropic. For transverse waves we have

$$\hat{n}^2 = \frac{\varepsilon_0}{1 - \alpha' - i\alpha''}. \quad (3.42)$$

4) Let us consider, finally, the situation that arises when the exciton term for  $\mathbf{k} = 0$  is triply degenerate and corresponds to the representation  $F_2$  (see Table IV).

In this case, in analogy with (3.39),

$$\langle \Psi_{F_2} | \hat{T}_{ij} | \Psi_0 \rangle = (1 - \delta_{ij}) M_{ij}, \quad (3.43)$$

where as a result of (3.34) we get

$$\begin{aligned} M_{23}(\text{VII}) &\equiv \langle \Psi_{F_2}^{\text{VII}} | \hat{T}_{23} | \Psi_0 \rangle = \frac{1}{2} \langle \Psi_{F_2}^{\text{VII}} | \hat{T}_{23} + \hat{T}_{32} | \Psi_0 \rangle \\ &= M_{32}(\text{VII}), \\ M_{12}(\text{VII}) &= M_{21}(\text{VII}) = M_{13}(\text{VII}) = M_{31}(\text{VII}) = 0, \\ M_{31}(\text{VIII}) &\equiv \langle \Psi_{F_2}^{\text{VIII}} | \hat{T}_{31} | \Psi_0 \rangle = \frac{1}{2} \langle \Psi_{F_2}^{\text{VIII}} | \hat{T}_{31} + \hat{T}_{13} | \Psi_0 \rangle \\ &= M_{13}(\text{VIII}), \\ M_{12}(\text{VIII}) &= M_{21}(\text{VIII}) = M_{23}(\text{VIII}) = M_{32}(\text{VIII}) = 0, \\ M_{12}(\text{IX}) &\equiv \langle \Psi_{F_2}^{\text{IX}} | \hat{T}_{12} | \Psi_0 \rangle = \frac{1}{2} \langle \Psi_{F_2}^{\text{IX}} | \hat{T}_{12} + \hat{T}_{21} | \Psi_0 \rangle \\ &= M_{21}(\text{IX}), \quad M_{23}(\text{IX}) = M_{32}(\text{IX}) \\ &= M_{13}(\text{IX}) = M_{31}(\text{IX}) = 0. \end{aligned} \quad (3.44)$$

In addition, as in the case of (3.41), the following relation is satisfied

$$M_{23}(\text{VII}) = M_{31}(\text{VIII}) = M_{12}(\text{IX}) \equiv M(F_2). \quad (3.45)$$

Hence, and also on the basis of (3.33), we find that

$$\alpha_1 = 0, \quad \alpha_2 = \alpha \neq 0, \quad \alpha_3 = \frac{\alpha}{2}, \quad \tilde{\alpha} = \alpha_1 - \alpha_2 - 2\alpha_3 = -2\alpha. \quad (3.46)$$

Therefore, as follows from (3.26), (3.28), (3.30), and (3.31), the quadrupole transition under consideration leads to a noticeable anisotropy in the dispersion and absorption of light. If the vector  $\mathbf{s}$  is directed along an edge of the cube, then, independently of the polarization,

$$\hat{n}^2 = \frac{\varepsilon_0}{1 - \alpha' - i\alpha''}. \quad (3.47)$$

For the vector  $\mathbf{s}$ , which is directed along the principal diagonal of the cube, independently of the polarization,

we get

$$\hat{n}^2 = \frac{\varepsilon_0}{1 - (\alpha' + i\alpha'')/3}. \quad (3.48)$$

On the other hand, if the vector  $\mathbf{s}$  is directed along the diagonal of the face of the cube, then for the wave polarized in the plane of the face we have

$$\hat{n}^2 = \varepsilon_0, \quad (3.49)$$

and for the wave polarized perpendicular to the plane of the face

$$\hat{n}^2 = \frac{\varepsilon_0}{1 - \alpha' - i\alpha''}. \quad (3.50)$$

In the general case of arbitrary  $\mathbf{s}$ , one has to use the system (3.24) to determine  $\hat{n}^2$ . In the case of (3.46) considered here, this system assumes the form

$$\frac{\hat{n}^2 - \varepsilon_0}{\hat{n}^2} E_{\mathbf{f}} = \alpha E_{1,-} - 2\alpha E_1 s_1^2 + (1 + \alpha) (\mathbf{E}\mathbf{s}) s_1 \text{ etc.} \quad (3.51)$$

Exact calculation of  $\hat{n}^2$  by means of (3.51), with account of the terms  $(\alpha')^2$ ,  $(\alpha'')^2$ , etc, is quite cumbersome and generally speaking would correspond to an exaggeration in accuracy, for in our approximation (for non-longitudinal waves) it is meaningful to determine only the corrections for  $\hat{n}^2$  which are linear in  $\alpha$ . For this purpose it is sufficient to use perturbation theory. Indeed, let us introduce the notation

$$L_{ij}^{(0)} = \alpha \delta_{ij} + (1 + \alpha) s_i s_j, \quad L_{ij}^{(1)} = -2\alpha s_i^2 \delta_{ij}$$

and rewrite the system (3.51) in the form

$$(L^{(0)} + L^{(1)}) \mathbf{E} = \varrho \mathbf{E}, \quad \varrho = \frac{\hat{n}^2 - \varepsilon_0}{\hat{n}^2}.$$

In the zeroth approximation  $(L^{(0)} - \rho) \mathbf{E} = 0$  and complete isotropy occurs, the waves can be either strictly transverse (in which case  $\rho_0^{\perp} = \alpha$ ) or strictly longitudinal ( $\rho_0^{\parallel} = 1 + 2\alpha$ ).

The first-approximation correction is

$$\varrho_1 = \frac{1}{|\mathbf{E}_0|^2} (\mathbf{E}_0, L^{(1)} \mathbf{E}_0) = -2\alpha (s_1^2 e_1^2 + s_2^2 e_2^2 + s_3^2 e_3^2),$$

where the wave polarization vector is  $\mathbf{e} = \mathbf{E}/|\mathbf{E}|$ .

Thus, for transverse waves we have, accurate to small quantities of first order of smallness in  $\alpha$ ,

$$\frac{\hat{n}^2 - \varepsilon_0}{\hat{n}^2} = \alpha - 2\alpha s_i^2 e_i^2,$$

or

$$\hat{n}_{\perp}^2 = \varepsilon_0 - \alpha \varepsilon_0 (1 - 2s_i^2 e_i^2). \quad (3.52)$$

For longitudinal waves ( $\mathbf{e} = \pm \mathbf{s}$ )

$$\frac{\hat{n}^2 - \varepsilon_0}{\hat{n}^2} = 1 + 2\alpha - 2\alpha (s_1^4 + s_2^4 + s_3^4),$$

or

$$\hat{n}_{\parallel}^2 = \frac{\varepsilon_0}{2\alpha (1 - s_1^4 - s_2^4 - s_3^4)}.$$

It is sometimes convenient to consider the optical properties of a medium in spherical coordinates (Fig. 6)

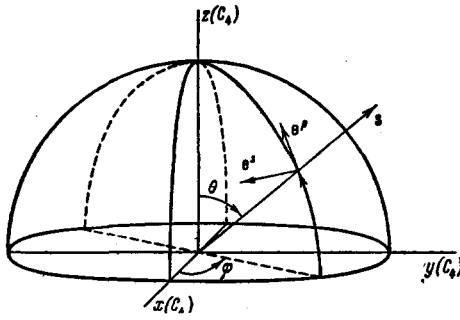


FIG. 6

for two mutually perpendicular polarization directions  $e^p$  and  $e^s$ , where  $e^p$  corresponds to polarization in the meridional plane containing the  $z$  axis and the light propagation direction.\*

The components of the vectors  $e^p$  and  $e^s$  are determined by the relations

$$\begin{aligned} e_1^s &= \sin \varphi, \quad e_2^s = -\cos \varphi, \quad e_3^s = 0, \\ e_1^p &= -\cos \theta \cos \varphi, \quad e_2^p = -\cos \theta \sin \varphi, \quad e_3^p = \sin \theta. \end{aligned} \quad (3.53)$$

At the same time, the components of the vectors  $s = \mathbf{s}/k$  are obviously

$$s_1 = \sin \theta \cos \varphi, \quad s_2 = \sin \theta \sin \varphi, \quad s_3 = \cos \theta.$$

Substituting (3.53) in (3.52) for the  $s$ - and  $p$ -polarizations, we obtain

$$\begin{aligned} \hat{n}_s^2 &= \epsilon_0 - \alpha \epsilon_0 (1 - \sin^2 \theta \sin^2 2\varphi), \\ \hat{n}_p^2 &= \epsilon_0 - \frac{\alpha \epsilon_0}{4} (\sin^2 2\theta \sin^2 2\varphi + \cos^2 2\theta). \end{aligned} \quad (3.54)$$

Recognizing now that  $\hat{n} = n + i\kappa$ , we obtain in first order of  $\alpha$  (we recall that these formulas pertain to the level which transforms in accord with representation  $F_2$ ):

$$\left. \begin{aligned} n_s^2 &= \epsilon_0 - \alpha' \epsilon_0 (1 - \sin^2 \theta \sin^2 2\varphi), \\ \kappa_s &= -\frac{1}{2} \alpha'' \sqrt{\epsilon_0} (1 - \sin^2 \theta \sin^2 2\varphi), \\ n_p^2 &= \epsilon_0 - \frac{\alpha' \epsilon_0}{4} (\sin^2 2\theta \sin^2 2\varphi + \cos^2 2\theta), \\ \kappa_p &= -\frac{\alpha'' \sqrt{\epsilon_0}}{8} (\sin^2 2\theta \sin^2 2\varphi + \cos^2 2\theta). \end{aligned} \right\} \quad (3.55)$$

We can obtain quite analogously, accurate to the first power of  $\alpha$ , expressions for the complex refractive index  $\hat{n}$  in the previously considered case of a doubly degenerate exciton term ( $E$  representation). Using (3.38a), we find that for quasi-transverse waves (i.e., for waves that are transverse when  $\alpha = 0$ ) we get

$$\hat{n}^2 = \epsilon_0 + \frac{3\alpha\epsilon_0}{2} (s_1^2 e_1^2 + s_2^2 e_2^2 + s_3^2 e_3^2), \quad (3.56)$$

or

$$\begin{aligned} \hat{n}_s^2 &= \epsilon_0 + \frac{3\alpha\epsilon_0}{4} \sin^2 \theta \sin^2 2\varphi, \\ \hat{n}_p^2 &= \epsilon_0 + \frac{3\alpha\epsilon_0}{16} \sin^2 2\theta (3 + \cos^2 2\varphi). \end{aligned} \quad (3.57)$$

\*The superscript  $s$  corresponding to the polarization  $e^s$  has no relation here and below to the vector  $s = \mathbf{k}/k$ .

Hence

$$\left. \begin{aligned} n_s^2 &= \epsilon_0 + \frac{3\alpha' \epsilon_0}{4} \sin^2 \theta \sin^2 2\varphi, \\ \kappa_s &= \frac{3\alpha'' \sqrt{\epsilon_0}}{8} \sin^2 \theta \sin^2 2\varphi, \\ n_p^2 &= \epsilon_0 + \frac{3\alpha' \epsilon_0}{16} \sin^2 2\theta (3 + \cos^2 2\varphi), \\ \kappa_p &= \frac{3\alpha'' \sqrt{\epsilon_0}}{32} \sin^2 2\theta (3 + \cos^2 2\varphi). \end{aligned} \right\} \quad (3.58)$$

d) Influence of mechanical stresses and external electric and magnetic fields. The need for a theoretical study of the influence of external action on the form of the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  and on the exciton states in crystals becomes particularly clear, if one recognizes that a large number of experimental papers are devoted to this subject [37, 46-48, 50-52]. As applied to cubic crystals, the subject of the investigation is the artificial anisotropy of the optical properties of the crystal near the exciton absorption lines, as a function of the character of the deformation, the direction of the magnetic or electric field, etc. As applied to crystals of the  $\text{Cu}_2\text{O}$  type, many of the aforementioned problems were considered in [38b-39] within the framework of exciton theory.

From the point of view of the phenomenological crystal optics with spatial dispersion developed here, the influence of the external action can be considered in the account of the dependence of the tensors contained in (2.12) and (2.13) on the external fields and stresses.

In the presence of external actions, the symmetry of the crystal is generally speaking lowered, and as a result the limitations imposed on the components of the tensors  $\epsilon_{ij}(\omega, \mathbf{E}^{(0)}, \mathbf{H}^{(0)}, \sigma_{ij}^{(0)})$ ,  $\gamma_{ijl}(\omega, \mathbf{E}^{(0)}, \mathbf{H}^{(0)}, \sigma_{lm}^{(0)})$ ,  $\alpha_{ijlm}(\omega, \mathbf{E}^{(0)}, \mathbf{H}^{(0)}, \sigma_{nr}^{(0)})$ , etc are different from those prevailing when

$$\mathbf{E}^{(0)} = \mathbf{H}^{(0)} = \sigma_{ij}^{(0)} = 0$$

[ $\mathbf{E}^{(0)}$  and  $\mathbf{H}^{(0)}$  are the intensities of the external electric and magnetic fields,  $\sigma_{ij}^{(0)}$  is the stress tensor; the medium is assumed nonmagnetic, by virtue of which we do not distinguish between  $\mathbf{H}^{(0)}$  and  $\mathbf{B}^{(0)}$ ].

An account of this fact enables us to determine, similar to what was done in Sec. c), the polarization of the normal electromagnetic waves, and also the anisotropy of the dispersion and absorption in the region of the exciton absorption lines. We are unable to consider this problem in detail for crystals of different classes, for lack of space. We therefore confine ourselves only to a few pertinent problems.

Let us consider, for example, the influence of a constant electric field on the exciton lines in the  $\text{Cu}_2\text{O}$  crystal. We also assume, for the sake of simplicity, that the electric field is directed along the four-fold symmetry axis. If the  $z$  axis is directed along the field, then the operator for the perturbation of the crystal by the field has in the first order in the field the form  $H' = -\mathbf{E}^{(0)} \mathbf{P}_z$ , where  $\mathbf{P}$  is the crystal dipole moment operator. From the form of the operator  $H'$

**Table V.** Characters of irreducible representations of the  $C_{4V}$  group

Irreducible representations		Symmetry operation				
		E	$C_4^2$	$2C_4$	$2IC_4^2$	$2IC_4$
$A_1$	$z, x_1x_2, x_1x_2 + y_1y_2$	1	1	1	1	1
$A_2$	$x_1y_2 - x_2y_1$	1	1	1	-1	-1
$B_1$	$x_1x_2 - y_1y_2$	1	1	-1	1	-1
$B_2$	$x_1y_2 + x_2y_1$	1	1	-1	-1	1
$E$	$x, y$	2	-2	0	0	0

it follows immediately that in the presence of a field the crystal symmetry is reduced and characterized by the  $C_{4V}$  group, for which the characters of the irreducible representations are indicated in Table V. Comparing the characters of the  $C_{4V}$  group with the characters of the  $O_h$  group (Table IV), it is easy to establish in the usual manner that under the influence of the electric field there should arise not a single dipole absorption line but a doublet (the representation  $F'_1$ , which is irreducible in the  $O_h$  group, breaks up in the  $C_{4V}$  group, so that  $F'_1 = A_1 + E$ ).

In accordance with Table V, one of the components of the doublet should be polarized along the field and the other perpendicular to the field, so that the crystal becomes anisotropic (uniaxial) even if the spatial dispersion is neglected, and in this case the nonzero components of the  $\epsilon_{ij}$  tensor are  $\epsilon_{11} = \epsilon_{22}$ , and  $\epsilon_{33}$ .

The quadrupole exciton states also undergo interesting transformations.\* In particular, the nondegenerate exciton state which has the symmetry of representation  $A_1$  of group  $O_h$ , has in the presence of an electric field along the  $z$  axis the symmetry of representation  $A_1$  of group  $C_{4V}$ ; as a result the transitions to this state from the ground state of symmetry  $A_1$  become allowed in the dipole approximation (see Table V).† Independently of the spatial dispersion, the intensity of lines of this kind should increase with increasing electric field. It is clear that in the vicinity of these exciton lines, when the crystal behaves like a uniaxial crystal, we have

$$\epsilon_{ij}(\omega, \mathbf{E}^{(0)}) = \epsilon_{11}(\omega, \mathbf{E}^{(0)})\delta_{ij} + \Delta\epsilon_{33}(\omega, \mathbf{E}^{(0)})\delta_{i3}\delta_{j3}.$$

The equations for the components of the electric field in the light wave assume in accord with (3.24) the form

$$\hat{n}E_i = \epsilon_{11}E_i + \Delta\epsilon_{33}\delta_{i3}E_3 + \hat{n}^2(\mathbf{E}\mathbf{s})s_i.$$

It follows therefore directly that in any direction  $\mathbf{s}$  two types of waves can propagate. For one of these waves the electric vector  $\mathbf{E}$  is perpendicular to the plane passing through the  $z$  axis and the vector  $\mathbf{s}$ , with  $n^2$

\*Many problems connected with the influence of a constant electric field on the quadrupole exciton lines in  $\text{Cu}_2\text{O}$  were considered in [36b].

†The possibility of "flare-up" of exciton lines in  $\text{Cu}_2\text{O}$  in the presence of an electric field was first pointed out in [49].

$= n_S^2 = \epsilon_{11}$  and  $\kappa = \kappa_S = 0$ . For the second wave

$$\hat{n}^2 = \hat{n}_p^2 = \epsilon_{11} \frac{\epsilon_{33} + \Delta\epsilon_{33}/\epsilon_{11}}{1 + \Delta\epsilon_{33} \cos^2 \theta / \epsilon_{11}},$$

where  $\theta$  is the angle between the vector  $\mathbf{s}$  and the  $z$  axis. For weak fields  $\Delta\epsilon_{33}/\epsilon_{11} \ll 1$  and

$$\hat{n}_p^2 = \epsilon_{11} + \Delta\epsilon_{33} \sin^2 \theta.$$

Consequently, introducing the notation  $\Delta\epsilon_{33} = \Delta\epsilon'_{33} + i\Delta\epsilon''_{33}$ :

$$n_p^2 = \epsilon_{11} + \Delta\epsilon'_{33} \sin^2 \theta,$$

$$\kappa_p = \frac{\Delta\epsilon''_{33}}{2\sqrt{\epsilon_{11}}} \sin^2 \theta,$$

where account is taken of the fact that  $\kappa_p^2 \ll n_p^2$ . In these formulas there is no factor  $k^2$ , from which it is also clear that one is dealing with dipole transitions.

An analogous situation ("flare-up") occurs also for quadrupole lines, whose wave functions in the absence of a field have the symmetry of representations  $E$ ,  $F_1$ , and  $F_2$ . Inasmuch as these terms split under the influence of the electric field

$$E \rightarrow A_1 + B_1, \quad F_1 \rightarrow E + A_2, \quad F_2 \rightarrow E + B_2,$$

and at the same time the transitions to the exciton states, having the symmetry of the representations  $A_1$  and  $E$ , according to Table V, are allowed in the dipole approximation.

As regards the transitions to the exciton states with the symmetry of representations  $B_1$ ,  $B_2$ , and  $A_2$  of group  $C_{4V}$ , these transitions remain quadrupole, and for an analysis of the corresponding anisotropy of the refractive index  $\hat{n}$  it is sufficient to make use of the method developed in the preceding section. In the group  $C_{4V}$  the quantities transformed in accord with the representations  $A_2$  are of the type  $x_1y_2 - x_2y_1$ , in accord with  $B_1$ —of the type  $x_1x_2 - y_1y_2$ , and in accord with  $B_2$ —of the type  $x_1y_2 + y_1x_2$ . Therefore, as can be readily verified, in the vicinity of the exciton line  $A_2$  the only nonvanishing components of the tensor  $\alpha_{ijlm}$  are the components  $\alpha_{1122} = \alpha_{2211} = \alpha$ ,  $\alpha_{1212} = \alpha_{2112} = \alpha_{2121} = \alpha_{1221} = -\alpha/2$ , and in the vicinity of the exciton line  $B_1$  we have  $\alpha_{1111} = \alpha_{2222} = \alpha$ ;  $\alpha_{1212} = \alpha_{2121} = \alpha_{1221} = \alpha_{2112} = -\alpha/2$ , while in the vicinity of the  $B_2$  line—the components  $\alpha_{1122} = \alpha_{2211} = \alpha$ ,  $\alpha_{1212} = \alpha_{2112} = \alpha_{2121} = \alpha_{1221} = \alpha/2$ . The knowledge of these nonvanishing components of the tensor  $\alpha_{ijlm}$  makes it possible to make a complete analysis of the anisotropy of the optical properties of the crystal in the vicinity of lines of the type  $A_2$ ,  $B_1$ , and  $B_2$ . Inasmuch as the corresponding calculations are analogous to those in Sec. 2, we give here only the results obtained by the perturbation theory method.

For transverse waves the following holds true (see Fig. 6):

$$\hat{n}^2 = \epsilon_0 + \epsilon_0\alpha(A_2) [\mathbf{e}\mathbf{s}]_3^2$$

for the type  $A_2$  transition,

$$\hat{n}^2 = \varepsilon_0 + \varepsilon_0 \alpha (B_1) (\varepsilon_1 s_1 - \varepsilon_2 s_2)^2 -$$

for the type  $B_1$  transition, and

$$\hat{n}^2 = \varepsilon_0 + \varepsilon_0 \alpha (B_2) (\varepsilon_1 s_2 + \varepsilon_2 s_1)^2 -$$

for the type  $B_2$  transition.

From this it follows, in particular, that  
for the type  $A_2$  transition:

$$n_s^2 = \varepsilon_0 + \varepsilon_0 \alpha' (A_2) \sin^2 \theta, \quad \kappa_s = \frac{1}{2} \sqrt{\varepsilon_0 \alpha''} (A_2) \sin^2 \theta, \\ n_p^2 = \varepsilon_0, \quad \kappa_p = 0;$$

for the type  $B_1$  transition:

$$n_s^2 = \varepsilon_0 + \varepsilon_0 \alpha' (B_1) \sin^2 \theta \sin^2 2\varphi, \\ \kappa_s = \frac{1}{2} \sqrt{\varepsilon_0 \alpha''} (B_1) \sin^2 \theta \sin^2 2\varphi, \\ n_p = \varepsilon_0 + \frac{1}{4} \varepsilon_0 \alpha'' (B_1) \sin^2 2\theta \sin^2 2\varphi, \\ \kappa_p = \frac{1}{8} \sqrt{\varepsilon_0 \alpha''} (B_1) \sin^2 2\theta \sin^2 2\varphi;$$

for the type  $B_2$  transition:

$$n_s^2 = \varepsilon_0 + \varepsilon_0 \alpha' (B_2) \sin^2 \theta \cos^2 2\varphi, \\ \kappa_s = \frac{1}{2} \sqrt{\varepsilon_0 \alpha''} (B_2) \sin^2 \theta \cos^2 2\varphi, \\ n_p^2 = \varepsilon_0 + \varepsilon_0 \frac{\alpha' (B_2)}{4} \sin^2 2\theta \sin^2 2\varphi, \\ \kappa_p = \frac{1}{8} \sqrt{\varepsilon_0 \alpha''} (B_2) \sin^2 2\theta \sin^2 2\varphi.$$

In the foregoing expressions  $\alpha = \alpha' + i\alpha''$ , and the argument of  $\alpha$  (for example  $\alpha(A_2)$ ) indicates the state corresponding to the value of  $\alpha$ . The choice of the angles and polarization directions is clear from Fig. 6.

We can investigate quite analogously the effects produced by a constant magnetic field or by mechanical stresses, and to determine the resulting new symmetry group of the crystal it is necessary to use the following general principle: a crystal under the influence of an external action will have only those symmetry elements, which are common to the Hamiltonian of the crystal in the absence of the action and the part of the Hamiltonian dependent on the action (of the magnetic field, stresses, etc.).

So far we have not considered the question of the explicit dependence of the magnitude of the effects on the magnitude of the applied external actions. In the case when the external actions are sufficiently weak, the explicit dependence on the intensity of the external action can be established by expanding the tensors in (2.11)–(2.15) in powers of  $\mathbf{E}^{(0)}$ ,  $\mathbf{H}^{(0)}$ , and  $\sigma_{ij}^{(0)}$ , in full accord with what is done in ordinary crystal optics (see, for example, [26]). Inasmuch as the account of spatial dispersion introduces in this case singularities, we shall discuss some of them, confining ourselves to the influence of an external electric or magnetic field, or of the two simultaneously.

In the presence of weak external electric and magnetic fields we use in lieu of (2.11) the expansion

$$\varepsilon_{ij}(\omega, \mathbf{k}, \mathbf{E}^{(0)}, \mathbf{H}^{(0)}) = \varepsilon_{0ij}(\omega) + i\gamma_{ijl}(\omega) k_l + \alpha_{ijklm}(\omega) k_l k_m \\ + A_{ijl}(\omega) E_l^{(0)} + A'_{ijl}(\omega) H_l^{(0)} + A_{ijlm}^{(1)}(\omega) H_l^{(0)} k_m \\ + A_{ijlm}^{(2)}(\omega) H_l^{(0)} E_m^{(0)} + A_{ijlm}^{(3)}(\omega) E_l^{(0)} k_m + A_{ijlm}^{(4)}(\omega) H_l^{(0)} H_m^{(0)} \\ + A_{ijlm}^{(5)}(\omega) E_l^{(0)} E_m^{(0)} + A_{ijlmn}(\omega) E_l^{(0)} H_m^{(0)} k_n + \dots \quad (3.59)$$

Inasmuch as here  $\mathbf{H}^{(0)}$  is an axial vector while  $\mathbf{k}$  and  $\mathbf{E}^{(0)}$  are polar, the quantities  $A_{ijl}$ ,  $A_{ijlm}^{(3)}$ ,  $A_{ijlm}^{(4)}$ , and  $A_{ijlm}^{(5)}$  are ordinary tensors, while  $A'_{ijl}$ ,  $A_{ijlm}^{(1)}$ ,  $A_{ijlm}^{(2)}$  and  $A_{ijlmn}$  are pseudotensors.

The principle of the symmetry of the kinetic coefficients requires [see (1.10)] that the tensor (3.59) satisfy the relation (as was already pointed out, we do not distinguish here between  $\mathbf{B}^{(0)}$  and  $\mathbf{H}^{(0)}$ , assuming the medium to be nonmagnetic)

$$\varepsilon_{ij}(\omega, \mathbf{k}, \mathbf{E}^{(0)}, \mathbf{H}^{(0)}) = \varepsilon_{ji}(\omega, -\mathbf{k}, \mathbf{E}^{(0)}, -\mathbf{H}^{(0)}). \quad (3.59a)$$

From this it follows directly that

$$\left. \begin{aligned} \gamma_{ijl} = -\gamma_{jil}, \quad A'_{ijl} = -A'_{jil}, \quad A_{ijlm}^{(2)} = -A_{jilm}^{(2)}, \quad A_{ijlm}^{(3)} = -A_{jilm}^{(3)}, \\ A_{ijlm}^{(4)} = A_{jilm}^{(4)}, \quad A_{ijlm}^{(5)} = A_{jilm}^{(5)}, \\ A_{ijlmn} = A_{jilmn}. \end{aligned} \right\} \quad (3.60)$$

The condition that there be no absorption calls for the dielectric tensor to be Hermitian,  $\varepsilon_{ij} = \varepsilon_{ji}^*$ . In this case, the tensors that are antisymmetrical in  $ij$ , contained in (3.35), are pure imaginary. We note also that the pseudotensor  $A'_{ijl}$  [and also  $B'_{ijl}$  in (3.61)] produce magneto-optical effects in crystals (see [1]) with

$$A'_{ijl} = \varepsilon_{ijm} A_{ml}, \quad B'_{ijl} = \varepsilon_{ijm} B_{ml}, \quad (3.60a)$$

Here  $A_{ml}$  and  $B_{ml}$  are second-rank tensors, which generally speaking are asymmetrical.

The symmetry of the crystal greatly reduces the number of independent components of the tensors contained in (3.59). The components of these tensors should be invariant under a change in reference frame corresponding to any of the crystal symmetry operations. It follows, in particular, that in crystals with an inversion center the third-rank tensors are  $\gamma_{ijl} = A_{ijl} = 0$ . Analogously, we reach the conclusion that in such crystals the fourth-rank pseudotensors  $A_{ijlm}^{(1)}$  and  $A_{ijlm}^{(2)}$  vanish, inasmuch as these quantities reverse sign upon inversion. A relation analogous to (3.59) can also be written for the inverse dielectric tensor  $\varepsilon_{ij}^{-1}(\omega, \mathbf{k}, \mathbf{E}^{(0)}, \mathbf{H}^{(0)})$ :

$$\varepsilon_{ij}^{-1}(\omega, \mathbf{k}, \mathbf{E}^{(0)}, \mathbf{H}^{(0)}) = \varepsilon_{0ij}^{-1}(\omega) + i\delta_{ijl}(\omega) + \beta_{ijlm} k_l k_m \\ + B_{ijl}(\omega) E_l^{(0)} + B'_{ijl}(\omega) H_l^{(0)} + B_{ijlm}^{(1)}(\omega) H_l^{(0)} k_m \\ + B_{ijlm}^{(2)}(\omega) H_l^{(0)} E_m^{(0)} + B_{ijlm}^{(3)}(\omega) E_l^{(0)} k_m + B_{ijlm}^{(4)}(\omega) H_l^{(0)} H_m^{(0)} \\ + B_{ijlm}^{(5)}(\omega) E_l^{(0)} E_m^{(0)} + B_{ijlmn}(\omega) E_l^{(0)} H_m^{(0)} k_n + \dots$$

Here, of course, all the considerations advanced above regarding the limitations connected with the principle of symmetry of kinetic coefficients and crystal symmetry remain in force. At the same time, the following very important remark must be made. Expansions



of the type (3.59) or (3.61) are valid only if the coefficients  $A_{ij\dots}(\omega)$  and  $B_{ij\dots}(\omega)$  are sufficiently small. Otherwise, we can no longer confine ourselves to terms with the lowest powers of the field  $\mathbf{E}^{(0)}$ . This is precisely the situation that arises, for example, for cubic crystals in the vicinity of a degenerate level, for which a linear Stark effect takes place.\* It is assumed below, naturally, that the expansions employed are valid.

Under the conditions when the tensors  $\epsilon_{ij}(\omega, \mathbf{k}, \mathbf{E}^{(0)})$  or  $\epsilon_{ij}^{-1}(\omega, \mathbf{k}, \mathbf{E}^{(0)})$  cannot be simply expanded in powers of the corresponding variable, we can in all the cases known to us represent these tensors as ratios of polynomials [in the case of expansion in  $\mathbf{k}$ , see, for example (2.14)]. For the example given above it is obviously necessary to make use of the relation

$$\epsilon(\omega, \mathbf{E}^{(0)}) = \frac{(\omega^2 - \omega_{j0}^2)^2 - 2a(\omega^2 - \omega_{j0}^2) - \mu^2 |\mathbf{E}^{(0)}|^2}{(\omega^2 - \omega_{j0}^2)^2 - \mu^2 |\mathbf{E}^{(0)}|^2} \quad (3.61)$$

As was already indicated in Sec. 1b, knowledge of the dielectric tensor and its inverse enables us to determine the dispersion of the natural frequencies of the Coulomb problem, the "fictitious" longitudinal waves, and the "polarization waves," which correspond to poles of  $n^2(\omega)$  if spatial dispersion is disregarded, and which consequently determine the line positions in the absorption spectrum. If spatial dispersion is taken into account, the determination of the absorption line positions is generally speaking more complicated, but for the case of weak dipole and also quadrupole absorption lines, when the "mixing" of the transverse photon and exciton states of the Coulomb problem can be neglected, the line position in the absorption spectrum is determined by the value of the natural frequency of the Coulomb problem, taken for a wave vector value equal to the light wave vector in vacuum  $Q = 2\pi s/\lambda_0$  (for more details see [63]).<sup>†</sup> In the presence of the external actions considered here, the dependence of the frequencies of the "fictitious" longitudinal waves and "polarization wave" frequencies on the wave vector is determined, in accord with (1.35) and (1.36), from the equations

$$\epsilon_{ij}(\omega, \mathbf{k}, \mathbf{E}^{(0)}, \mathbf{H}^{(0)}) s_i s_j = 0, \quad \mathbf{D}' \neq 0 \quad (3.62a)$$

and

\*In order to explain this, let us consider a medium for which  $\epsilon = 1 - 2a/(\omega^2 - \omega_{j0}^2)$  when  $\mathbf{E}^{(0)} = 0$ , and

$$\omega_j = \omega_{j0} \pm \frac{\mu}{2\omega_{j0}} E(0)$$

in the presence of the field. Then in first approximation

$$\epsilon(\mathbf{E}^{(0)}) = 1 - \frac{a}{\omega^2 - \omega_{j0}^2 + \mu |\mathbf{E}^{(0)}|} - \frac{a}{\omega^2 - \omega_{j0}^2 - \mu |\mathbf{E}^{(0)}|}.$$

Hence

$$\epsilon^{-1}(\omega, \mathbf{E}^{(0)}) \approx 1 + \frac{2a}{\omega^2 - \omega_{j0}^2 - 2a} + \frac{2a\mu^2 |\mathbf{E}^{(0)}|^2}{(\omega^2 - \omega_{j0}^2 - 2a)^2 (\omega^2 - \omega_{j0}^2)}.$$

Obviously, the term with  $|\mathbf{E}^{(0)}|^2$  increases without limit in this expansion as  $\omega \rightarrow \omega_{j0}$ .

<sup>†</sup>For the sake of simplicity we disregard here the influence of other resonances.

$$|\epsilon_{ij}^{-1}(\omega, \mathbf{k}, \mathbf{E}^{(0)}, \mathbf{H}^{(0)})| = 0, \quad (\mathbf{k}\mathbf{D}') = 0, \quad \mathbf{D}' \neq 0 \quad (3.62b)$$

respectively.

If only an external magnetic field is present ( $\mathbf{H}^{(0)} \neq 0$ ,  $\mathbf{E}^{(0)} = 0$ ), then we have in crystals with an inversion center  $A_{ijlm}^{(1)} = B_{ijlm}^{(1)} = 0$ , and the spatial dispersion, as follows from (3.59) and (3.61), manifests itself only in the second order in  $\mathbf{k}$ , while in crystals without an inversion center the expansions (3.59) and (3.61) contain also terms that are linear in  $\mathbf{k}$ . This circumstance leads to the "magnetic field reversal effect": in this case, generally speaking,  $\epsilon_{ij}(\omega, \mathbf{k}, \mathbf{H}^{(0)}) \neq \epsilon_{ij}(\omega, \mathbf{k}, -\mathbf{H}^{(0)})$ , so that the frequencies of the Coulomb problem, and consequently also the position of the absorption lines in the spectrum, change upon reversal of the magnetic field.

For the analysis that follows it is convenient to represent the tensors  $A_{ijlm}^{(1)}$  and also  $B_{ijlm}^{(1)}$  in the form of sums:

$$A_{ijlm}^{(1)} = A_{ijlm}^{(1)c} + A_{ijlm}^{(1)a}, \quad (3.63a)$$

$$B_{ijlm}^{(1)} = B_{ijlm}^{(1)e} + B_{ijlm}^{(1)a}, \quad (3.63b)$$

where

$$A_{ijml}^{(1)c} = A_{ijml}^{(1)e}, \quad A_{ijlm}^{(1)a} = -A_{ijml}^{(1)a} \text{ etc.}$$

With respect to their symmetry properties under rotations and permutation of the indices, the pseudotensors  $A_{ijlm}^{(1)c}$  and  $B_{ijlm}^{(1)c}$  are perfectly analogous to the tensor  $\alpha_{ijlm}$  (see Section 2b, Table III, for noncentrosymmetric classes). As regards the pseudotensors  $A_{ijlm}^{(1)a}$  and  $B_{ijlm}^{(1)a}$ , they can be represented in the form

$$A_{ijlm}^{(1)a} = e_{ilm} C_{nij}, \quad (3.64a)$$

$$B_{ijlm}^{(1)a} = e_{ilm} D_{nij}. \quad (3.64b)$$

Inasmuch as the completely antisymmetrical unit matrix  $e_{ilm}$  is a pseudotensor,  $C_{nij}$  and  $D_{nij}$  are ordinary third-rank tensors, with  $C_{nij} = C_{nji}$  and  $D_{nij} = D_{nji}$ . Consequently, the symmetry properties of the tensors  $C_{nij}$  and  $D_{nij}$  fully coincide with those of the tensor which determines the piezoelectric effect (see [26], Chapter VII). In view of the fact that [26] indicates the nonvanishing components of this tensor for different crystal classes, we shall not dwell on this in detail here. Using (3.63) and (3.64) we find that

$$A_{ijlm}^{(1)} H_l^{(0)} k_m = C_{nij} [\mathbf{H}^{(0)} \mathbf{k}]_n + A_{ijlm}^{(1)c} H_l^{(0)} k_m, \quad (3.65a)$$

$$B_{ijlm}^{(1)} H_l^{(0)} k_m = D_{nij} [\mathbf{H}^{(0)} \mathbf{k}]_n + B_{ijlm}^{(1)c} H_l^{(0)} k_m. \quad (3.65b)$$

Let us consider first the influence of an external magnetic field on the dispersion of the frequencies of the "fictitious" longitudinal waves. To this end, substituting in (3.62a) the expression (3.59) with  $\mathbf{E}^{(0)} = 0$ , we conclude that the sought frequencies satisfy the equation

$$s_i \epsilon_{oij}(\omega) s_j + s_i s_j \alpha_{ijlm} k_l k_m + (C [\mathbf{H}^{(0)} \mathbf{k}]) + s_i s_j A_{ijlm}^{(1)c} H_l^{(0)} k_m + s_i s_j A_{ijlm}^{(1)a} H_l^{(0)} H_m^{(0)} = 0, \quad (3.66)$$

where the components of the vector  $\mathbf{C}$  are

$$C_n = C_{n_{ij} s_i s_j}, \quad n = 1, 2, 3. \quad (3.66a)$$

Confining ourselves to the vicinity of one of the resonances, we set

$$\varepsilon_{0ij}(\omega) = \varepsilon_{0ij}^0 + \frac{g_{ij}}{\omega^2 - \omega_L^2(0)}, \quad (3.67)$$

where  $\hbar\omega_L(0)$  is the exciton energy in the  $L$ -th band for  $\mathbf{k} = 0$ . Substituting now (3.67) in (3.66) and confining ourselves to terms linear in  $\mathbf{H}^{(0)}$ , we find that the sought frequency of the "fictitious" longitudinal wave is determined by the relation

$$\omega(\mathbf{k}, \mathbf{H}^{(0)}) = \omega_L(0) - \frac{1}{2\omega_L(0)} \frac{\varepsilon_{0ij}^0 s_i s_j}{\varepsilon_{0ij}^0 s_i s_j} \{g_{ij} s_i s_j - (\mathbf{C}[\mathbf{H}^{(0)} \mathbf{k}]) - a_{ijlm} s_i s_j k_l k_m - A_{ijlm}^{(1)c} s_i s_j H_l^{(0)} k_m\}, \quad (3.68)*$$

and thus  $\omega(\mathbf{k}, \mathbf{H}^{(0)}) \neq \omega(\mathbf{k}, -\mathbf{H}^{(0)})$ .

Let us consider in greater detail the influence of the reversal of the magnetic field on the frequencies of the "fictitious" longitudinal waves in crystals of the CdS type (space group  $C_{6v}^4$ ). The characters of the group  $C_{6v}$  are listed in Table VI (in the notation of [45]).

It follows from this table that the states of the mechanical excitons at  $\mathbf{k} = 0$ , which can be excited by light in the dipole approximation, have the symmetry of representations  $A_1$  and  $E_2$  of group  $C_{6v}$ . If the wave functions of the exciton in the  $L$ -th band transform at  $\mathbf{k} = 0$  in accordance with representation  $A_1$ , then  $g_{ij} = g_{A_1} \delta_{i3} \delta_{j3}$ , and if they transform in accord with  $E_2$ , then  $g_{ij} = g_{E_2} (\delta_{i1} \delta_{j1} + \delta_{i2} \delta_{j2})$ .

For crystals belonging to class  $C_{6v}$ , the nonvanishing components of the tensor  $C_{nij}$  are

$$C_{333}, C_{223} = C_{332} = C_{113} = C_{131}, C_{311} = C_{322}. \quad (3.69)$$

Using further Table III, we find the nonvanishing components of the pseudotensor  $A_{ijlm}^{(1)c}$  in crystals of the  $C_{6v}$  class:†

$$\begin{aligned} A_{1223}^{(1)c} &= A_{1112}^{(1)c} = -A_{2213}^{(1)c} = -A_{1211}^{(1)c}, \\ A_{2313}^{(1)c} &= -A_{1233}^{(1)c}. \end{aligned} \quad (3.70)$$

It follows from (3.66a) and (3.69) that

$$C_1 = 2C_{113} s_1 s_3, \quad C_2 = 2C_{223} s_2 s_3, \quad C_3 = C_{311} (s_1^2 + s_2^2) + C_{333} s_3^2. \quad (3.71)$$

Thus, the vector  $\mathbf{C}$ , being, like the gyration vector, a

$$*(\mathbf{C}[\mathbf{H}^{(0)} \mathbf{k}]) = \mathbf{C} \cdot [\mathbf{H}^{(0)} \times \mathbf{k}].$$

†We assume in (3.70) that the  $x$  and  $y$  axes lie in mutually perpendicular planes of symmetry  $\sigma_v$  and  $\sigma'_v$ . In order to establish the nonvanishing of the component of the pseudotensor  $A_{ijlm}^{(1)c}$ , we can proceed as follows. We first use the limitations imposed on the pseudotensor  $A_{ijlm}^{(1)c}$  by the presence of a sixfold axis. These limitations cause the nonvanishing components of  $A_{ijlm}^{(1)c}$  in class  $C_{6v}$  to correspond to those non-vanishing components of the tensor  $\alpha_{ijlm}$  in the crystal class  $C_6$ , which reverse sign upon reflection in the symmetry planes  $\sigma_v$  and  $\sigma'_v$  of the group  $C_{6v}$ . The latter is connected with the fact that the components of the pseudotensor  $A_{ijlm}^{(1)c}$  remain unchanged in this case.

Table VI. Characters of irreducible representations of the  $C_{6v}$  group

Symmetry operations / Irreducible representations	$E$	$C_2$	$2C_3$	$2C_6$	$3\sigma_v$	$3\sigma'_v$
$A_1; z$	1	1	1	1	1	1
$A_2$	1	1	1	1	-1	-1
$B_2$	1	-1	-1	-1	1	-1
$B_1$	1	-1	-1	-1	-1	1
$E_2$	2	2	-1	-1	0	0
$E_1; x, y$	2	-2	1	1	1	0

function of the direction of the vector  $\mathbf{s}$ , is generally speaking not directed along the optical axis. The latter occurs when the wave vector  $\mathbf{k}$  is either perpendicular to the optical axis or parallel to it.

To interpret the magnetic field reversal effect, it is proposed in [52] that in the expression for the exciton energy there enters an additional term  $(\hbar/cm_{\text{exc}}) \times (\mathbf{d} \cdot [\mathbf{H}^{(0)} \times \mathbf{k}])$ , corresponding to the interaction between the dipole moment of the exciton and the electric field  $(\hbar/cm_{\text{exc}}) [\mathbf{k} \times \mathbf{H}^{(0)}]$ , which in the opinion of the authors of [52] (see also [50, 51]) occurs in the presence of an external magnetic field in the coordinate frame connected with the moving exciton. It follows from (3.68) that in the expression for the exciton energy  $\hbar\omega(\mathbf{k}, \mathbf{H}^{(0)})$  a term of the type  $\mathbf{C} \cdot [\mathbf{H}^{(0)} \times \mathbf{k}]$  does indeed arise but the vector  $\mathbf{C}(\mathbf{s})$  is not fixed along the optical axis even in a uniaxial crystal. It also follows from (3.68) that the effect of the reversal of the magnetic field vanishes when  $\mathbf{H}^{(0)} \parallel \mathbf{k}$ , for in this case  $\mathbf{H}^{(0)} \times \mathbf{k} = 0$  and  $A_{ijlm}^{(1)c} s_i s_j s_l s_m = 0$  [see (3.70)].

The same takes place if the vector  $\mathbf{k}$  is directed along the  $x$  axis, and the magnetic field along the optical axis, for in this case  $A_{ijlm}^{(1)c} s_i s_j s_l s_m = 0$  and  $\mathbf{C} \cdot [\mathbf{H}^{(0)} \times \mathbf{k}] = 0$ .

We recall that the frequencies of the "fictitious" longitudinal waves determine the positions of the absorption lines of light propagating only in such directions, for which the light waves are not transverse. For crystals of the CdS type this occurs if the wave vector  $\mathbf{k}$  is directed neither along the optical axis nor perpendicular to it. Otherwise the position of the absorption lines is determined by the polarization wave frequencies. We therefore consider the influence of the external magnetic field on the frequency dispersion of the polarization waves, confining ourselves to one particular case of type CdS crystals and assuming that the vectors  $\mathbf{H}^{(0)}$  and  $\mathbf{k}$  as well as the optical axis form a mutually orthogonal triplet. Let, for example, in accordance with this choice,  $k_2 = k_3 = 0$  and  $H_1^{(0)} = H_3^{(0)} = 0$ . As already indicated in Sec. 2, the gyrotropy of crystals belonging to class  $C_{6v}$  leads to second-order effects in powers of  $(a/\lambda)$ . We are interested here in whether the expression for the po-

larization-wave frequencies contains terms of the order of  $H^{(0)}$  and  $kH^{(0)}$ . Therefore, in investigating the dipole lines we confine ourselves to the following expression for the tensor  $\epsilon_{ij}^{-1}$ :

$$\epsilon_{ij}^{-1}(\omega, \mathbf{k}, H^{(0)}) = \epsilon_{0ij}^{-1} + B'_{ijl}H^{(0)} + B'_{ijlm}H^{(0)}k_m. \quad (3.72)$$

In crystals of class  $C_{6v}$ , the tensor  $B_{mjl}$  in (3.60a) is diagonal, with  $B_{11} = B_{22} \neq B_{33}$ . Therefore, and also by virtue of relations (3.65b),

$$\epsilon_{ij}^{-1}(\omega, \mathbf{k}, H^{(0)}) = \epsilon_{0ij}^{-1} + e_{ij2}B_{22}H^{(0)} + D_{3ij}H^{(0)}k + 2B_{ij12}^{(1)\epsilon}H^{(0)}k. \quad (3.73)$$

Inasmuch as, in analogy with (3.69) and (3.70),  $D_{3ij} \neq 0$ , only if  $i = j = 1$ , or if  $i = j = 2$ , or if  $i = j = 3$ , while  $B_{ij12}^{(1)\epsilon} \neq 0$  only if  $i = j = 1$  or  $i = j = 2$ , and furthermore  $\epsilon_{0ij}^{-1} = \delta_{ij}\epsilon_{0ij}^{-1}$ , Eqs. (3.62b) for the transverse components of the vector  $D'$  ( $D'_2$  and  $D'_3$ ) have the following form [see also (1.37)]:

$$\left. \begin{aligned} (\epsilon_{022}^{-1} + D_{322}H^{(0)}k + 2B_{2212}^{(1)\epsilon}H^{(0)}k)D'_2 &= 0, \\ (\epsilon_{033}^{-1} + D_{333}H^{(0)}k)D'_3 &= 0. \end{aligned} \right\} \quad (3.74)$$

It follows from (3.74) that the position of the line polarized perpendicular to the optical axis is determined in this case by the equation

$$\epsilon_{022}^{-1}(\omega) + D_{322}H^{(0)}k + 2B_{2212}^{(1)\epsilon}H^{(0)}k = 0, \quad (3.74a)$$

whereas the position of the line polarized along the optical axis is determined by the equation

$$\epsilon_{033}^{-1}(\omega) + D_{333}H^{(0)}k = 0. \quad (3.74b)$$

Thus, the reversal effect can occur both for lines that are polarized perpendicular to the optical axis (representation  $E_1$ ) and for lines polarized along the optical axis (representation  $A_1$ ) (see Table VI).

Let us now assume that external electrical and magnetic fields are present simultaneously. Let us consider, as before, a crystal of the type CdS and assume that the magnetic field is directed along the  $y$  axis, the vector  $\mathbf{k}$  along the  $x$  axis, and the external electric field along the optical axis. In this case in lieu of (3.73) we have on the basis of (3.61), accurate to terms linear in  $H^{(0)}$ ,

$$\begin{aligned} \epsilon_{ij}^{-1}(\omega, \mathbf{k}, E^{(0)}, H^{(0)}) &= \epsilon_{0ij}^{-1} + e_{ij2}B_{22}H^{(0)} + (D_{3ij} + 2B_{ij12}^{(1)\epsilon})H^{(0)}k \\ &+ B_{ij3}E^{(0)} + 2B_{ij23}^{(2)}H^{(0)}E^{(0)} + B_{ij21}^{(3)}E^{(0)}k + B_{ij33}^{(5)}(E^{(0)})^2 \\ &+ B_{ij123}kH^{(0)}E^{(0)}. \end{aligned} \quad (3.75)$$

We note that the tensor  $B_{ijl}$  is analogous in its symmetry properties to the tensor  $C_{lij}$ , the tensor  $B_{ijlm}^{(2)}$  is analogous to the pseudotensor  $A_{ijlm}^{(1)}$ , while the tensors  $B_{ijlm}^{(3)}$  and  $B_{ijlm}^{(5)}$  are analogous to the tensor  $\alpha_{ijlm}$ . Using (3.69), (3.70), Table III, and also [26] we arrive at the conclusion that

$$\begin{aligned} B_{233} &= B_{323} = 0, \quad B_{223} \neq 0, \quad B_{333} \neq 0, \\ B_{222}^{(2)} &= B_{322}^{(2)} = B_{232}^{(2)} = 0, \quad B_{221}^{(3)} = B_{321}^{(3)} = B_{212}^{(3)} = 0, \\ B_{233}^{(5)} &= B_{323}^{(5)} = 0, \quad B_{223}^{(5)} \neq 0, \quad B_{333}^{(5)} \neq 0. \end{aligned}$$

As regards the fifth-rank pseudotensor  $B_{ijlmn}$ , it

is necessary to take account here of the fact that when an external electric field is applied along the hexagonal axis, the symmetry of the CdS crystal does not change, so that the nonzero components of the pseudotensor  $B_{ijlmn}$  correspond to nonzero components of the fourth-rank pseudotensor  $B_{ijlm}^{(1)}$ . On the basis of the remarks made, we reach the conclusion that in the case under consideration the Eqs. (3.62b) have the following form:

$$\left. \begin{aligned} \epsilon_{022}^{-1}(\omega) + (D_{322} + 2B_{2212}^{(1)\epsilon})H^{(0)}k + B_{223}E^{(0)} + \\ + B_{2233}^{(6)}(E^{(0)})^2 + B_{22123}kH^{(0)}E^{(0)} = 0, \\ D'_1 = D'_3 = 0, \quad D'_2 \neq 0; \end{aligned} \right\} \quad (3.76a)$$

$$\left. \begin{aligned} \epsilon_{033}^{-1}(\omega) + D_{333}H^{(0)}k + B_{333}E^{(0)} + B_{3333}^{(5)}(E^{(0)})^2 + B_{33123}kH^{(0)}E^{(0)} = 0, \\ D'_1 = D'_2 = 0, \quad D'_3 \neq 0. \end{aligned} \right\} \quad (3.76b)$$

Let us examine in greater detail the vicinity of the dipole line, polarized along the optical axis. In this case, according to (3.67), for  $\omega \approx \omega_L(0)$ , we have

$$\epsilon_{033}^{-1} \approx \frac{\omega^2 - \omega_L^2(0)}{\epsilon}.$$

Therefore, as follows from (3.76), the position of the absorption line is determined by the following relation:

$$\begin{aligned} \omega(\mathbf{k}, H^{(0)}, E^{(0)}) &= \omega_L(0) - \frac{\epsilon}{2\omega_L(0)} \{ D_{333}H^{(0)}k + B_{333}E^{(0)} \\ &+ B_{3333}^{(5)}(E^{(0)})^2 + B_{33123}kH^{(0)}E^{(0)} \}. \end{aligned} \quad (3.77)$$

It follows from (3.77) that for fixed values of  $\mathbf{k}$ ,  $H^{(0)}$ , and  $E^{(0)}/E^{(0)}$ , but with variation of  $E^{(0)}$ , the frequency of the absorption line is displaced along a parabola, whose position changes, in particular, upon reversal of the direction of the magnetic field. An effect of this type is indeed observed in CdS crystals [50, 51]. According to [50, 51], the effect of the absorption frequency shift is interpreted in the following manner. In the presence of a magnetic field, in a coordinate system connected with a moving exciton, an additional electric field arises, the intensity of which is  $(\hbar/cm_{\text{exc}}) \times [\mathbf{k} \times \mathbf{H}^{(0)}]$ . Therefore, the external field acting in the exciton on the electron and hole is equal to  $E^{(0)} + (\hbar/cm_{\text{exc}}) [\mathbf{k} \times \mathbf{H}^{(0)}]$ , which leads (in media where the quadratic Stark effect occurs) with a change of  $E^{(0)}$  to a shift in the exciton energy along a parabola similar to (3.77).

Were such an interpretation of the effect correct, then the determination from the experimental data of that value of  $E^{(0)}$  which corresponds to the minimum displacement of the term would enable us to determine the "effective mass" of the Coulomb exciton,  $m_{\text{exc}}$ , from the known  $H^{(0)}$  and  $\mathbf{k}$ . Actually, as follows from (3.77), it is possible to determine in this manner not the "effective mass" of the exciton, but merely the relation between the coefficients contained in (3.77), and in particular the ratio  $B_{33123}/B_{3333}^{(5)}$ , which although it does have the dimensionality of the ratio  $\hbar/m_{\text{exc}}c$ , does not, generally speaking, reduce to the latter. We note also that the aforementioned parabola should shift upon reversal of the magnetic field not only because

(3.77) contains a term proportional to  $B_{33123}$ , but also because of the presence of the term  $D_{333}H^{(0)}k$ , which leads to a reversal even when  $E^{(0)} = 0$ . In this connection it must be borne in mind that no reversal of the magnetic field was observed in CdS at  $E^{(0)} = 0$  in [51], in contrast with [52]. Consequently, further research in this field is highly desirable. In conclusion, we note that to investigate the fine effects connected with external influences on absorption spectra, it is possible to use not only crystals but also, for example, gyrotropic amorphous media, provided the absorption spectra of these substances display at low temperatures sufficiently narrow lines, similar to those observed in [84] for molecules in frozen solutions.

e) The problem of boundary conditions. We have considered above only the propagation of waves in an unbounded medium. Yet in crystal optics one deals always, strictly speaking, with a bounded medium, so that the question of boundary conditions arises. If we use the general relation (1.3), it is sufficient to take into account the ordinary electrodynamic conditions. On the other hand, the introduction of the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  corresponds to relation (1.4), which is rigorously valid only in an unbounded medium [the presence of a boundary leads to the dependence of the kernel of  $\hat{\epsilon}_{ij}$  in (1.3) on more than just the difference  $\mathbf{r} - \mathbf{r}'$ ]. At the same time, it is clear from physical considerations that the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  can actually be employed for a bounded medium, provided the characteristic dimensions of the latter are  $R \gg a \sim 3 \times 10^{-8}$  cm. Such a conclusion is valid, but at the same time there may arise the need for supplementary boundary conditions (SBC). Indeed, this usually occurs when using expansions of the type (2.12) and (2.13), which are patently connected with an increase in the order of the field equations and with the appearance of new waves (in particular, we have in mind longitudinal waves).

The character of the SBC is determined by the physical properties of the medium and of its surface, and consequently is not universal. For example, in the case of a relation of the type (3.13) and specular reflection of the electrons from a semi-infinite plasma, the SBC have the form  $E_n = 0$ , where  $E_n$  is the normal component of the field  $\mathbf{E}$  on the internal surface of the plasma (we have in mind the problem of a wave with field  $\mathbf{E}$  lying in the plane of incidence, impinging from vacuum on the plasma boundary [81]). In crystals the form of the SBC differs with the spectral region under consideration. Thus, in article [7] the SBC for the vicinity of the absorption line corresponding to the excitation of dipole excitons in nongyrotropic crystals was found to be  $\mathbf{P} = 0$ , where  $\mathbf{P}$  is the part of the polarization due to the contribution of the considered exciton band. In [82] the method of [7] was used to derive the SBC in a gyrotropic crystal with the space group  $D_2^4$ . The case considered was that of propagation of light along the optical axis of a crystal with

boundary planes perpendicular to the optical axis. It turned out that the SBC depend essentially on which molecules within the unit cell terminate the crystal, and reduces to the vanishing of only one of the transverse components of the polarization vector [for example,  $P_x(0) = 0$ , etc]. This makes the directions  $x$  and  $y$  no longer optically equivalent. So sharp a dependence of the SBC on the structure of the surface layer should either not influence the measured physical quantities, or contradicts the main assumptions on which the use of the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  is based when finite crystals are considered.

We note also the article [83], in which a conceptually correct method was proposed for considering electromagnetic waves in finite crystals with account of spatial dispersion. In addition, the question of the SBC in the vicinity of dipole and quadrupole exciton absorption bands is considered in [83]. It is shown there that the SBC assumed in [7] are, generally speaking, incorrect.

Let us consider the problem of the SBC from a point of view that is somewhat different from that in [7, 82, 83]. We note first of all that when account is taken of spatial dispersion with accuracy to terms of order  $k^2$ , away from the surface of the crystal, the polarization

$$\frac{D' - E}{4\pi} = \mathbf{P}'(\mathbf{r}, t) \equiv \mathbf{P}(\mathbf{r}) e^{i\omega t}$$

in the vicinity of one selected dipole exciton absorption band satisfies the following system of equations (see [24, 86])

$$-\omega^2 P'_i(\mathbf{r}) + \beta_{ij} P'_j(\mathbf{r}) + \gamma_{ijl} \frac{\partial P'_j(\mathbf{r})}{\partial x_l} + \alpha_{ijlm} \frac{\partial^2 P'_j(\mathbf{r})}{\partial x_l \partial x_m} = \lambda_{ij} E_j(\mathbf{r}), \quad (3.78)$$

where the tensors  $\beta_{ij}$ ,  $\gamma_{ijl}$ ,  $\alpha_{ijlm}$ , and  $\lambda_{ij}$  do not depend in first approximation on  $\omega$  and are determined by the crystal symmetries. In nongyrotropic crystals,  $\gamma_{ijl} = 0$ , whereas in gyrotropic crystals in first approximation we can put  $\alpha_{ijlm} = 0$ . In the system (3.78) the electric field intensity  $\mathbf{E}(\mathbf{r})$  appears as an external force, in which connection  $\mathbf{E}(\mathbf{r})$  should be contained in the boundary conditions for the polarization  $\mathbf{P}'(\mathbf{r})$  (these boundary conditions are, strictly speaking, indeed the SBC). The general form of the boundary conditions which the polarization  $\mathbf{P}'(\mathbf{r})$  should satisfy in the presence of  $\mathbf{E}(\mathbf{r}) \neq 0$  is obviously the following (the subscript zero corresponds to the surface of the crystal):

$$(-\omega^2 \delta_{ij} + \beta'_{ij}) P'_j(0) + \gamma'_{ijl} \left( \frac{\partial P'_j}{\partial x_l} \right)_0 = \lambda_{ij} E_j(0), \quad (3.79)$$

and it is very important that the tensor  $\beta'_{ij} \neq \beta_{ij}$ ,  $\lambda'_{ij} \neq \lambda_{ij}$ , and  $\gamma'_{ijl} \neq \gamma_{ijl}$ .\* Inasmuch as the SBC serve

\*Thus, in media with an inversion center, where  $\gamma_{ijl} = 0$ , the tensor  $\gamma'_{ijl} \neq 0$ . This is connected with the fact that in the presence of a boundary surface even a nongyrotropic crystal is not invariant against inversion. The problem of boundary conditions and the meaning of Eq. (3.68) can be understood qualitatively by using a one-dimensional chain of coupled oscillators as an example.

only to establish the relations between the wave amplitudes, the contribution of the terms containing derivatives  $\partial P'_j / \partial x_l$  can be neglected in (3.79) (long waves). Therefore the SBC can be rewritten in the form

$$P'_i(0) + \Gamma_{ij} E_j(0) = 0, \quad (3.80)$$

where the tensor  $\Gamma_{ij}$  is practically independent of the frequency in the spectral region under consideration, by virtue of the fact that  $\beta'_{ij} \neq \beta_{ij}$ . For specific crystals we can determine the tensor  $\Gamma_{ij}$  only from the microscopic theory. The symmetry properties of this tensor are determined by the symmetry of the finite crystal. Thus, for example, in the case of a uniaxial crystal, bounded by a plane perpendicular to the optical axis (the  $z$  axis), the only nonvanishing components are  $\Gamma_{xx} = \Gamma_{yy}$  and  $\Gamma_{zz}$ . In the case when the plane bounding the crystal is parallel to the optical axis,  $\Gamma_{xx} \neq \Gamma_{yy} \neq \Gamma_{zz}$ . Relation (3.80) goes over into that obtained in [7] if we put  $\Gamma_{ij} = 0$ , which generally speaking is not correct. In the case of gyrotropic media, the use of (3.80) does not lead to redundant conditions only if the transition  $\alpha_{ijlm} \rightarrow 0$  is made in the final expressions for the amplitudes.

We note that all the SBC assumed in [5,7] are of the type (3.80). We have considered above dipole transitions, as manifest in the fact that the tensor  $\lambda_{ij}$  in (3.78) was independent of  $\mathbf{k}$ . For quadrupole transitions  $\lambda_{ij} = \mu_{ijlm} k_l k_m$  and the resultant SBC are the conditions (3.80) with  $\Gamma_{ij}$  replaced by a certain tensor  $\Gamma_{ij}(\omega, \mathbf{k}) = \Omega_{ijlm} k_l k_m$ , so that when terms of order  $k^2$  are neglected we have in lieu of (3.80) the conditions

$$P'_i = 0, \quad i = 1, 2, 3.$$

The tensor  $\Gamma_{ij}(\omega, \mathbf{k})$  is equivalent within the framework of the phenomenological theory to the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  in the sense that both these tensors are specified and only their general properties and the expressions obtained when they are used in the field equations need to be analyzed. On the other hand, the calculation of  $\Gamma_{ij}(\omega, \mathbf{k})$ , like the calculation of  $\epsilon_{ij}(\omega, \mathbf{k})$ , is a problem in the microscopic theory.

We note that in the absence of new waves, the refinement of the boundary condition may also be of interest. Thus, account of the terms of order  $a/\lambda$  in the microscopic calculation of the reflection of light from a cubic lattice is equivalent to introducing a certain transition layer on the surface of the crystal (and the appearance of the transition layer leads in turn to deviations from the Fresnel formulas). [83a]

In conclusion we wish to emphasize the following. The specific form of the SBC governs only the ratios of the amplitudes of the different waves. The latter feature is essential (many specific results obtained on the basis of certain particular SBC can be found in [7, 82, 83]), but is nevertheless of secondary importance within rather wide limits—from the point of view of an investigation of crystals, the principal role is played by a determination of the dispersion curves  $n_l(\omega, \mathbf{s})$

themselves, and not of the reflection or transmission coefficients. In this connection we note also that the dependence  $n_l(\omega, \mathbf{s})$ , i.e., the function  $\omega_l(\mathbf{k})$ , can be determined not only from crystal optics. For example, the function  $\omega_l(\mathbf{k})$  can be found by studying the combination (Raman) scattering of x-rays [80]. In this case the character of the boundary conditions for the excitons generally does not play any role at all.

Finally, we note that when solving the problem of reflection and refraction of light on a boundary, as well as more general electrodynamic problems, it is sometimes advantageous to use the reciprocity theorem (see, for example, [1], Sec. 69, and [2], Sec. 29). In the presence of an external magnetic field this theorem is not valid in its usual form, but there is a generalized reciprocity theorem [2]. When spatial dispersion is taken into account, both the ordinary and the generalized reciprocity theorems remain fully in force [2].

f) Experimental investigations of effects of spatial dispersion in crystal optics. Let us dwell on the results of the experimental investigations of spatial dispersion, first in gyrotropic, and then in nongyrotropic crystals.

Gyrotropic crystals. The problem of the nature of the gyrotropy of crystals is far from new, for it was already pointed out in [65, 66] that one is dealing in this case with the effect of spatial dispersion of order  $a/\lambda$ . Nonetheless, experimental investigations of the optical properties of gyrotropic crystals are quite scanty. In particular, the data are most skimpy on the frequency dependence of the angle of rotation of the plane of polarization in crystals near individual absorption bands. The only results in this respect are those of [67], where several crystals with the symmetry of quartz were investigated (quartz, cinnabar, benzyl). It was shown there that in the vicinity of the investigated individual bands (with the light propagating along the optical axis), the rotation of the plane of polarization per unit length of light beam path in the crystal (the specific rotation) has the following dependence on the frequency of the light\*

$$Q(\omega) = \frac{K_{11}\omega^2}{(\omega^2 - \omega_0^2)^2}, \quad (3.81)$$

When the light propagates at an angle to the optical axis, the circularly polarized waves are replaced by elliptically polarized ones with different signs of rotation and with different orientations of the axes of the ellipse. In this case when the waves pass through the crystal, a phase difference is produced in them, which is determined not only by the gyration effect, but also by the ordinary birefringence, which naturally complicates somewhat the investigation of the rotation dispersion. It is shown in [67] that in quartz with light

\*The theory of the rotating ability of crystals in the visible region of the spectrum and in the ultraviolet is developed in [24, 68, 69]. This theory permits, in particular, an interpretation of the results of [67].

propagating perpendicular to the optical axis the rotation dispersion also obeys a relation of the type (3.81), but with a different coefficient  $K_{\perp} \neq K_{\parallel}$ .

Particular interest is attached to investigations of the effect of gyrotropy at low temperatures, the only time when manifestation of the fine effects of spatial dispersion, connected in particular with the structure of the exciton bands, etc. can be expected. We know of only one investigation of this type<sup>[70]</sup>, in which circular dichroism was investigated at helium and hydrogen temperatures near individual absorption lines in a sodium uranyl acetate crystal.

For molecules in solution, the magnitude of the circular dichroism is usually small, of order  $a/\lambda$ , where  $a$  is the dimension of the molecule and  $\lambda$  is the wavelength of light, so that  $a/\lambda \approx 10^{-2}$ – $10^{-3}$ . In sodium uranyl acetate, however, the circular dichroism, i.e., the ratio of the difference of the coefficients of absorption of light circularly polarized in the right-hand and left-hand directions, to their sum turned out to be close to unity for individual lines, corresponding to strong absorption of only one of the circularly polarized waves. Inasmuch as sodium uranyl acetate consists of nongyrotropic molecules, the observed phenomenon is only characteristic of the crystalline state and is the consequence of the difference between the structure of the exciton bands, corresponding to the right-hand and left-hand circular polarizations of the dipole-moment vector (see<sup>[63,71]</sup>). Research in this direction is of undoubted interest.

There are still no experimental investigations of the effects connected with new waves in gyrotropic crystals (see Sec. 3a). In this connection it should be noted that such research at low temperatures would be of great interest, since the presence of three waves in a crystal, having the same frequency and different refractive indices, absorption coefficients, and polarization, can lead to the manifestation of a unique oscillatory dependence of the specific rotation on the thickness of the crystal. It would be natural here to investigate first of all gyrotropic cubic crystals or the propagation of waves along the optical axis in crystals of lower symmetry (in these cases normal waves are circularly polarized).

**Nongyrotropic crystals.** Experimental investigations of optical effects connected with spatial dispersion of the dielectric tensor were carried out with the inorganic crystals  $\text{Cu}_2\text{O}$ <sup>[37,46-48]</sup> and  $\text{CdS}$ <sup>[50-52]</sup>, and also with organic crystals (anthracene, stilbene, and others)<sup>[72-74]</sup>. We have already mentioned (see the Introduction and Secs. 3c and d) the investigations of optical anisotropy in the cubic crystal  $\text{Cu}_2\text{O}$  in the vicinity of the quadrupole absorption line, and also investigations of the external influences on the optical properties of  $\text{Cu}_2\text{O}$  and  $\text{CdS}$ .

A method for proving experimentally the existence of additional (new or anomalous) light waves was proposed in<sup>[74]</sup>. The method reduces to a measurement

of the intensity of the monochromatic light passing through a plane parallel plate of the crystal, as a function of the thickness of the plate. The indication of the existence of two waves in a crystal would be their interference on leaving the crystal; this interference should lead to oscillations in the intensity as a function of the thickness. It is assumed here that the oscillations connected with the reflection and triple passage of one of the waves are either insignificant or can be suitably accounted for.

The experimental data obtained in<sup>[74]</sup> show that the absorption of light in anthracene plates in the region of the intrinsic absorption band with maximum at  $\omega_j = 25,200 \text{ cm}^{-1}$  at  $T = 20^\circ\text{K}$  actually oscillates as the thickness is varied. With this, an oscillatory dependence on the distance is obtained for  $\ln I/I_0$  ( $I$  is the intensity of the transmitted light and  $I_0$  that of the incident light) in the thickness region  $0.05$ – $0.3 \mu$  with a distance (difference in plate thickness) between abscissas of the maxima amounting to  $\Delta d \approx 0.06 \mu$ . The oscillations were most clearly pronounced at a light frequency  $\omega = 25,108 \text{ cm}^{-1}$ . The authors of<sup>[74]</sup> propose that the presence of the oscillations is evidence of the presence of two identically polarized waves with a difference of 6.9 in the refractive indices.

It must be noted, however, that such an interpretation of the oscillations contradicts the calculations given in Sec. 3c for the absorption and dispersion curves. Indeed, according to the data of<sup>[72]</sup> and also<sup>[33]</sup>, in anthracene this transition corresponds to a value  $A \approx 0.1$  [see (3.12)]; such a value of  $A$  at  $\xi = (\omega - \omega_j)/\omega_j \approx 4 \times 10^{-3}$  yields  $n^2 = -A/\xi = 25$ , in accordance with<sup>[72]</sup>, which gives for  $\delta = 10^{-3}$ ,  $\xi = -4 \times 10^{-3}$  (Fig. 5d) for the anomalous wave  $n_+ \approx 35$  and  $\kappa_+ \approx 9$ . Consequently, the anomalous wave practically cannot "reach" the second surface even when  $d \approx 0.1 \mu$ , inasmuch as the factor  $\exp(-2\pi\kappa d/\lambda_0) \approx 10^{-6} \ll 1$  when  $\lambda_0 = 0.4 \mu$ . The estimates made correspond to  $|\beta'| = 10^{-5}$ . Actually, however, the quantity  $|\beta'|$  is apparently (see Sec. 3b) much smaller than this value, so that the role of the absorption increases even further.

The source of the oscillations observed in<sup>[74]</sup> is not clear. It is possible that they may be due to the interference of a ray that has passed through the plate once and one that has passed through the plate three times. Another possibility is apparently an effect, not controlled in<sup>[74]</sup>, due to the interference of rays reflected from the front and rear sides of the film. If it is assumed that the singly and triply transmitted rays interfere and absorption is neglected, then anthracene should have a refractive index  $n = \lambda_0/2\Delta d \approx 3.45$  (see<sup>[74,75]</sup> and below). This contradicts the value  $n \geq 5$ , obtained in<sup>[72]</sup>, but this discrepancy is still not convincing, since the relation  $n = \lambda_0/2\Delta d$  is incorrect in the presence of noticeable absorption.

Analogous experiments were made in<sup>[76]</sup> with a cuprous oxide crystal (see in this connection also the

theoretical paper [77]). The difference between these experiments and those reported in [74] lies in that the oscillations were observed in the cuprous oxide in the region of the quadrupole exciton absorption for the quadrupole line  $\lambda_0 = 6125 \text{ \AA}$  at  $T = 77^\circ\text{K}$ ; this line is attributed to the "yellow" exciton series of  $\text{Cu}_2\text{O}$ , and is ascribed a value  $n = 1$ . The measurements were carried out at  $T = 93^\circ\text{K}$ , and the distance between the abscissas of the oscillation maxima was approximately 0.2 mm, which is three orders of magnitude larger than the period of oscillations which would occur in the case of interference of multiply reflected waves ( $\Delta d = \lambda_0/2n \approx 10^{-4} \text{ mm}$ ). On the other hand, if we assume that the observed oscillations are due in this case to the manifestation of the anomalous wave, we must assume that the distance between maxima\*  $\Delta d = \lambda_0/2(n_1 - n_2)$ , where  $n_1$  and  $n_2$  are the refractive indices of the ordinary and anomalous waves. Therefore, when  $\Delta d \approx 2 \times 10^{-2} \text{ cm}$  and  $\lambda_0 \approx 6 \times 10^{-5} \text{ cm}$ , we obtain  $n_1 - n_2 \approx 10^{-3}$ .

In the vicinity of an isolated quadrupole resonance, in accord with (2.14), without account of absorption, the refractive index satisfies the equation

$$\hat{n}^2 = \epsilon_0(\omega) + \frac{\nu_1 \hat{n}^2}{\xi - \mu_1 \hat{n}^2}, \quad (3.82)$$

where

$$\nu_1 = \nu \frac{\omega^2}{c^2}, \quad \mu_1 = \mu \frac{\omega^2}{c^2}, \quad \xi = \frac{\omega - \omega_j}{\omega_j},$$

with

$$\nu_1 \sim \mu_1 \sim (a/\lambda_0)^2 \sim 10^{-6}.$$

It follows from (3.82) that

$$\hat{n}_{1,2}^2 = \frac{1}{2} \left( \frac{\xi}{\mu_1} + \epsilon_0 - \frac{\nu_1}{\mu_1} \right) \pm \frac{1}{2} \sqrt{\left( \frac{\xi}{\mu_1} + \epsilon_0 - \frac{\nu_1}{\mu_1} \right)^2 - 4\epsilon_0 \frac{\xi}{\mu_1}}.$$

When  $\xi = 0$  we have  $\hat{n}_1^2 = 0$  and  $\hat{n}_2^2 = \epsilon_0 - \nu_1/\mu_1$ . Therefore, if  $\epsilon_0$  is approximately equal to the ratio  $\nu_1/\mu_1$ , the difference  $\hat{n}_1 - \hat{n}_2$  can be very small. Inasmuch as both  $\epsilon_0$  and  $\nu_1/\mu_1$  can, generally speaking, assume independently different values for different quadrupole lines, and also in different crystals, the small value  $n_1 - n_2 \approx 10^{-3}$  obtained in  $\text{Cu}_2\text{O}$  is probably not characteristic. In this sense a study of analogous effects in the vicinity of other quadrupole lines is of great interest. In expression (3.82),  $\nu_1$  is in fact a certain combination of components of a fourth-rank tensor [see (2.24)–(2.15) and (2.33a)]. It is obvious therefore that  $\nu_1 \neq 0$  only for waves that experience quad-

rupole absorption. Thus, for example, for a wave propagating along the diagonal of a face, a new wave in the vicinity of the exciton transition, corresponding to the representation  $F_2$ , can appear only if the vector  $\mathbf{E}$  is perpendicular to the plane of the face of the cube [see (3.49) and (3.50); this indeed occurs in  $\text{Cu}_2\text{O}$  [76]].

We note that in gyrotropic crystals in the region of quadrupole absorption, when the wave vector of the light is directed along the optical axis, we have generally speaking

$$\begin{aligned} \epsilon_{ij}(\omega, \mathbf{k}) = & \epsilon_{0ij}(\omega) + \alpha_{ijklm}(\omega) k_l k_m [\omega^2 - \omega_i^2(0) \\ & - g_l k_l + g_{nn} k_n k_n]^{-1} \\ & + \alpha_{ijklm}(\omega) k_l k_m [\omega^2 - \omega_i^2(0) + g_l k_l + g_{nn} k_n k_n]^{-1}. \end{aligned}$$

It follows therefore that an equation of the type (3.82) can have in a definite frequency region not two but three solutions. Therefore a study of the dispersion of waves in the region of quadrupole absorption lines in gyrotropic crystals may also turn out to be quite promising.

In conclusion we note that an attempt to observe oscillations in the intensity of the transmitted light was undertaken also in [78]. However, no phenomena that could not be explained on the basis of ordinary crystal optics were observed.

In order to disclose the role of spatial dispersion under certain conditions we can use the dispersion relations. Thus, for an optically isotropic medium in the absence of spatial dispersion and of an external magnetic field, the dispersion relations (1.12) have the form

$$\epsilon'_0(\omega) - 1 = \frac{2}{\pi} \int_0^\infty \frac{\omega' \epsilon''(\omega') d\omega'}{\omega'^2 - \omega^2}, \quad \epsilon''_0(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{\epsilon'_0(\omega') - 1}{\omega'^2 - \omega^2} d\omega'. \quad (1.12a)$$

On the other hand, under the conditions discussed here we have

$$\epsilon_0 = \epsilon'_0 + i\epsilon''_0 = (n + i\kappa)^2.$$

Therefore, substituting in (1.12a) the experimentally obtained values of  $\epsilon'_0 = n^2 - \kappa^2$  and  $\epsilon''_0 = 2n\kappa$ , we can verify whether these relations between  $\epsilon'_0$ ,  $\epsilon''_0$ , and  $n$  and  $\kappa$  are correct or not [in the presence of spatial dispersion the formulas  $\epsilon'_0(\omega) = n^2 - \kappa^2$  and  $\epsilon''_0(\omega) = 2n\kappa$  are of course no longer valid; see, for example, formula (1.29) for transverse waves in an isotropic medium]. An attempt to disclose the role of spatial dispersion by this method was undertaken in [73]. For several crystals at low temperatures, it was observed that relations of type (1.12a), which do not take spatial dispersion into account, are violated, and that these violations gradually disappeared with increasing temperature. It is obvious that these investigations should be continued.

We note also the possibility of observing anomalous waves by exciting them with charged particles [5, 79], and also the possibility indicated in [80] of investigating the law of dispersion of light waves (excitons) in

\*Obviously, we are referring here to the addition of two oscillations  $A \cos(\omega t - \omega n_1 d/c)$  and  $B \cos(\omega t - \omega n_2 d/c)$ . The time average of the square of the amplitude of the resultant oscillation is

$$I = \frac{A^2 + B^2}{2} + AB \cos \frac{2\pi}{\lambda_0} (n_1 - n_2) d;$$

When the thickness of the plate  $d$  changes by an amount  $\Delta d$ , the value of  $I$  changes such that  $\Delta d = \lambda_0/2(n_1 - n_2)$  for the neighboring minima or maxima. This result changes little provided only that the absorption is sufficiently weak.

crystals by studying the angular dependence of x-rays inelastically scattered by a crystal, and accompanying the excitation of excitons. With this, we refer here primarily to excitons connected with the predominant excitation of electrons. As regards excitons with which the lattice vibrations are essentially connected, these can be investigated also by using neutron scattering and a few other methods.

#### 4. CALCULATION OF THE TENSOR $\epsilon_{ij}(\omega, \mathbf{k})$ BY QUANTUM MECHANICAL METHODS

##### a) Quantum mechanical expression for $\epsilon_{ij}(\omega, \mathbf{k})$ .

Calculation of the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  for a crystal or for any of its models is a problem in microscopic theory. For ionic crystals, such a theory was developed in the infrared portion of the spectrum long ago (it is described in detail in [12], see also [17]). Along with it, several important methodological factors were clarified, with a bearing on crystals of arbitrary nature. In particular, with ionic crystals as an example, the question was considered of the dependence of the frequencies of the normal oscillations (waves) on the direction of the wave vector  $\mathbf{k}$  as  $\mathbf{k} \rightarrow 0$ . It was shown, for example, that when full account is taken of the Coulomb interaction, but retardation is neglected, the frequencies of the normal oscillations can be non-analytic functions of  $\mathbf{k}$  (as  $\mathbf{k} \rightarrow 0$ ). In this connection it must be noted that within the scope of a general investigation of such problems, the consideration of the Heitler-London model of the crystal [53, 54] introduces nothing new. It is sufficient to state that in the calculation of the energy of the excitons in such a model, sums of dipole-dipole, dipole-quadrupole, and other terms arise (see, for example, [43]), the dependence of which on  $\mathbf{k}$  was already considered before (see [12], Sec. 30, and also [55, 56]). We leave alone the fact that many factors are utterly unnecessary in the microscopic analysis, since the corresponding deductions follow directly from the field equations and from the existence of the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$ . By way of an example we can point to relation (1.35) and (1.39), from which the dependence of the frequency of the "fictitious" longitudinal waves  $\omega_{||}$  on the direction of  $\mathbf{k}$  as  $\mathbf{k} \rightarrow 0$  is obvious. We have already essentially dwelt on all these factors in the introduction to this article.

Let us therefore proceed directly to a derivation, by quantum mechanical means, of a general expression for  $\epsilon_{ij}(\omega, \mathbf{k})$ . The corresponding procedure is well known and consists of finding the density of the current induced by an external classical electromagnetic field. It is convenient in this case to choose a gauge for the potentials, in which the scalar potential of the perturbing field is equal to zero, and thus

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \delta \mathbf{A}}{\partial t},$$

where  $\delta \mathbf{A}$  is the vector potential of the field, induced

in the medium by the external sources. The vector potential of the total field  $\mathbf{E} + \mathbf{E}_\mu$  will be denoted by  $\mathbf{A}_\mu + \delta \mathbf{A}$  ( $\mathbf{E}_\mu$  is the microscopic field existing in the medium even when  $\mathbf{E} = 0$ ). We denote further by  $\Psi_{n0}(\mathbf{r}, t)$  the wave functions of the medium in the absence of or disregarding the field  $\mathbf{E}$ , and by  $\Psi_n = \Psi_{n0} + \delta \Psi_n$  the corresponding functions in the presence of a field  $\mathbf{E}$ . The operator of the interaction between the charges in the external field is, in the linear approximation,

$$U = - \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}c} \{ \hat{\mathbf{P}}^{\alpha} \delta \mathbf{A}(\mathbf{r}_{\alpha}, t) + \delta \mathbf{A}(\mathbf{r}_{\alpha}, t) \hat{\mathbf{P}}^{\alpha} \},$$

where  $\mathbf{r}_{\alpha}$  is the radius vector of the  $\alpha$ -th particle with charge  $e_{\alpha}$  and mass  $m_{\alpha}$ , while  $\sum_{\alpha}$  denotes summation over all particles of the crystal and

$$\hat{\mathbf{P}}^{\alpha} = -i\hbar \frac{\partial}{\partial \mathbf{r}_{\alpha}} - \frac{e_{\alpha}}{c} \mathbf{A}_{\mu}(\mathbf{r}_{\alpha}, t).$$

Putting [see (1.40)]

$$\delta \mathbf{A} = -\frac{ic}{2\omega} [E_0 e^{i(\mathbf{k}\mathbf{r} - \omega t)} - E_0^* e^{-i(\mathbf{k}\mathbf{r} - \omega t)}],$$

we find that

$$U = \hat{F} e^{-i\omega t} + \hat{G} e^{i\omega t},$$

where

$$\hat{F}(\mathbf{k}) = \hat{G}^*(\mathbf{k}) = -\frac{ic}{2\omega} \hat{\mathbf{M}}(\mathbf{k}) \mathbf{E}_0,$$

$$\hat{\mathbf{M}}(\mathbf{k}) \equiv - \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}c} \{ \hat{\mathbf{P}}^{\alpha} e^{i\mathbf{k}\mathbf{r}_{\alpha}} + e^{i\mathbf{k}\mathbf{r}_{\alpha}} \hat{\mathbf{P}}^{\alpha} \}. \quad (4.1)$$

Therefore, using perturbation theory, we obtain in first approximation (see [45])

$$\Psi_n = \Psi_{n0} - \sum_{m \neq n} \left\{ \frac{F_{mn} e^{-i\omega t}}{\hbar(\omega_{mn} - \omega)} + \frac{F_{nm}^* e^{i\omega t}}{\hbar(\omega_{mn} + \omega)} \right\} \Psi_{m0} = \Psi_{n0} + \delta \Psi_n,$$

where

$$F_{mn} = \int \Psi_{m0}^* \hat{F} \Psi_{n0} d\tau, \quad \hbar\omega_{mn} \equiv W_m - W_n \equiv \hbar(\omega_m - \omega_n),$$

( $W_m$  — eigenvalue of the energy corresponding to the function  $\Psi_{m0}$ ). The mean value of the current density in the state  $\Psi_n$  is

$$\mathbf{j}^{(n)}(\mathbf{r}, t) = \langle \Psi_n^* | \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}} \left\{ \left[ -i\hbar \frac{\partial}{\partial \mathbf{r}_{\alpha}} - \frac{e_{\alpha}}{c} \mathbf{A}(\mathbf{r}_{\alpha}, t) \right] \delta(\mathbf{r} - \mathbf{r}_{\alpha}) + \delta(\mathbf{r} - \mathbf{r}_{\alpha}) \left[ -i\hbar \frac{\partial}{\partial \mathbf{r}_{\alpha}} - \frac{e_{\alpha}}{c} \mathbf{A}(\mathbf{r}_{\alpha}, t) \right] \right\} | \Psi_n \rangle,$$

where

$$\langle \Psi_n^* | \hat{O} | \Psi_n \rangle = \int \Psi_n^* \hat{O} \Psi_n d\tau, \quad d\tau = d\mathbf{r}_1 \dots d\mathbf{r}_N.$$

In the linear approximation the mean value of the density of the current  $\delta \mathbf{j}^{(n)}$  induced by the field  $\mathbf{E}$  has the form

$$\begin{aligned} \delta \mathbf{j}^{(n)} = & \langle \delta \Psi_n^* | \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}} \{ \hat{\mathbf{P}}^{\alpha} \delta(\mathbf{r} - \mathbf{r}_{\alpha}) + \delta(\mathbf{r} - \mathbf{r}_{\alpha}) \hat{\mathbf{P}}^{\alpha} \} | \Psi_{n0} \rangle \\ & + \langle \Psi_{n0}^* | \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}} \{ \hat{\mathbf{P}}^{\alpha} \delta(\mathbf{r} - \mathbf{r}_{\alpha}) + \delta(\mathbf{r} - \mathbf{r}_{\alpha}) \hat{\mathbf{P}}^{\alpha} \} | \delta \Psi_n \rangle \\ & - \langle \Psi_{n0}^* | \sum_{\alpha} \frac{e_{\alpha}^2}{m_{\alpha}c} \delta(\mathbf{r} - \mathbf{r}_{\alpha}) \delta \mathbf{A}(\mathbf{r}_{\alpha}, t) | \Psi_{n0} \rangle. \end{aligned} \quad (4.2)$$



Before we proceed to the Fourier components of the current density, let us indicate the selection rules for  $F_{mn}$ .

Inasmuch as the wave functions  $\Psi_{m0}$  have the symmetry of the irreducible representations of the crystal space group, action on the wave function  $\Psi_{m0}$  by the operator  $\hat{T}_a$  of the translation of all the electron coordinates by a whole-number lattice vector  $\mathbf{a}$  leads to the following result:

$$\hat{T}_a \Psi_{m0} = e^{-i\mathbf{q}_m \cdot \mathbf{a}} \Psi_{m0},$$

where the vector  $\mathbf{q}_m$  determines the corresponding irreducible representation of the translation subgroup (see, for example, [42]).

According to (4.1)

$$\hat{T}_a \hat{M}(\mathbf{k}) = e^{i\mathbf{k} \cdot \mathbf{a}} \hat{M}(\mathbf{k}), \quad (4.3)$$

by virtue of which we reach the conclusion that the matrix elements  $M_{mn}(\mathbf{k})$ , and consequently  $F_{mn}(\mathbf{k})$  differ from zero only if  $\mathbf{q}_m = \mathbf{q}_n - \mathbf{k} + 2\pi\mathbf{b}$ ; the matrix elements  $M_{nm}(\mathbf{k})$  and  $F_{nm}(\mathbf{k})$  differ from zero if  $\mathbf{q}_m = \mathbf{q}_n + \mathbf{k} + 2\pi\mathbf{b}$ , where  $\mathbf{b}$  is an arbitrary whole-number reciprocal lattice vector. Taking the foregoing into account and using the expression

$$\delta(\mathbf{r} - \mathbf{r}_\alpha) = \frac{1}{V} \sum_{\mathbf{k}'} e^{i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}_\alpha)},$$

where  $V$  is the volume of the crystal, we obtain from (4.2)

$$j_i^{(n)}(\mathbf{k}, \omega) = \sum_{\mathbf{b}} \sigma_{ij}^{(n), \mathbf{b}}(\omega, \mathbf{k}) E_j(\mathbf{k} + 2\pi\mathbf{b}, \omega). \quad (4.4)$$

In the derivation of (4.4) the essential factor, of course, are the foregoing selection rules for the matrix elements of the operator  $\hat{M}(\mathbf{k}')$ , by virtue of which, for example,

$$\langle \Psi_{n0}^* | \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}} \{ \hat{\mathbf{p}}^{\alpha} e^{-i\mathbf{k}' \cdot \mathbf{r}_{\alpha}} + e^{-i\mathbf{k}' \cdot \mathbf{r}_{\alpha}} \hat{\mathbf{p}}^{\alpha} \} | \delta \Psi_n \rangle \neq 0,$$

provided only

$$\mathbf{k}' = \pm \mathbf{k} + 2\pi\mathbf{b}.$$

As a result we find that the tensor\* is

$$\begin{aligned} \sigma_{ij}^{(n), \mathbf{b}}(\omega, \mathbf{k}) = & \frac{i\delta_{ij}}{V\omega} \sum_{\alpha} \frac{e_{\alpha}^2}{m_{\alpha}} \delta_{\mathbf{k}-\mathbf{k}'} + \frac{i}{V\hbar\omega} \sum_{m \neq n} \frac{e_{\alpha}^2}{4m_{\alpha}m_{\beta}} \\ & \times \left\{ \frac{(P_i^{\alpha} e^{-i\tilde{\mathbf{k}} \cdot \mathbf{r}_{\alpha}} + e^{-i\tilde{\mathbf{k}} \cdot \mathbf{r}_{\alpha}} P_i^{\alpha})_{nm}}{\omega - \omega_m + \omega_n} (P_j^{\beta} e^{i\mathbf{k} \cdot \mathbf{r}_{\beta}} + e^{i\mathbf{k} \cdot \mathbf{r}_{\beta}} P_j^{\beta})_{mn} \right. \\ & \left. - \frac{(P_i^{\alpha} e^{-i\tilde{\mathbf{k}} \cdot \mathbf{r}_{\alpha}} + e^{-i\tilde{\mathbf{k}} \cdot \mathbf{r}_{\alpha}} P_i^{\alpha})_{mn} (P_j^{\beta} e^{i\mathbf{k} \cdot \mathbf{r}_{\beta}} + e^{i\mathbf{k} \cdot \mathbf{r}_{\beta}} P_j^{\beta})_{nm}}{\omega + \omega_m - \omega_n} \right\}, \quad (4.4a) \end{aligned}$$

where  $\tilde{\mathbf{k}} = \mathbf{k} + 2\pi\mathbf{b}$ ,  $\delta_{\mathbf{q}} = 1$ ,  $\mathbf{q} = 0$ ;  $\delta_{\mathbf{q}} = 0$ ,  $\mathbf{q} \neq 0$ . Knowing the conductivity tensor, we can also determine the dielectric tensor, using the relation

\*From this relation it follows directly that the components of the tensor  $\sigma_{ij}^{(n), \mathbf{b}}$  decrease with increasing  $|\mathbf{b}|$  like Fourier components of a smooth function.

$$\epsilon_{ij}^{(n)}(\omega, \mathbf{k}) = \delta_{ij} + i \frac{4\pi}{\omega} \sigma_{ij}^{(n)}(\omega, \mathbf{k}). \quad (4.4b)$$

Thus, relation (4.4) is equivalent to a relation of the type (2.4). By definition, the tensor  $\epsilon_{ij}$  relates the vector  $\mathbf{D}'$  with the macroscopic electric field  $\mathbf{E}$ , which is contained in Maxwell's equations (1.1). Therefore, in using expressions (4.4) and (4.4b), we should take  $\mathbf{E}$  to mean the macroscopic field. In this case, consequently, in the calculation of the frequencies and of the wave functions of the mechanical excitons, it is necessary to take into account also that part of the interaction, which is related with the difference between the field  $\mathbf{E}$  and the so-called effective field  $\mathbf{E}_g$  (in the simplest case of point-like dipoles, located at the points of a cubic lattice we have, as is well known,  $\mathbf{E}_g = \mathbf{E} + 4\pi\mathbf{P}/3$ ). On the other hand, if we take  $\mathbf{E}$  in expressions (4.1) and (4.4) to mean the effective field  $\mathbf{E}_g$ , we obtain a relation between  $\mathbf{D}'$  and  $\mathbf{E}_g$ . The frequencies and wave functions of the mechanical excitons must then be calculated in a manner different from that in the preceding case (that is, without account of the polarization correction of the type  $4\pi\mathbf{P}/3$ ). It must be emphasized that by calculating the characteristics of the mechanical excitons with account of the polarization correction, we take into consideration by the same token, to some extent, also a certain portion of the long-wave field.\* This circumstance, however, does not lead to a non-analytic dependence of the mechanical-exciton frequencies on  $\mathbf{k}$ .

Above the frequencies of the mechanical excitons,  $\omega_m$  are assumed to be real and it is assumed that the denominators in (4.4a) do not vanish. In other words, no absorption was considered here (see Sec. 4c). By virtue of the statements made in Sec. 2a, we shall take into consideration in (4.4) only the term with  $\mathbf{b} = 0$ . In addition, inasmuch as we are not interested here in the infrared region of the spectrum, we disregard the contribution to the tensor  $\sigma_{ij}$  by the direct interaction between the ions and the field of the electromagnetic wave [this means that in expression (4.4a) the mass  $m_{\alpha}$  is assumed to be infinite for ions]. Under these assumptions, the tensor  $\epsilon_{ij}^{(n)}(\omega, \mathbf{k})$  for the ground state ( $n = 0$ ) of a non-conducting crystal assumes the form

$$\begin{aligned} \epsilon_{ij}(\omega, \mathbf{k}) = & \delta_{ij} \left( 1 - \frac{4\pi e^2 N_0}{m\omega^2} \right) - \frac{4\pi c^2}{\hbar\omega^2 V} \\ & \times \sum \left\{ \frac{M_{0m}^i(-\mathbf{k}) M_{m0}^j(\mathbf{k})}{\omega - \omega_m} - \frac{M_{m0}^i(-\mathbf{k}) M_{0m}^j(\mathbf{k})}{\omega + \omega_m} \right\}, \quad (4.5) \end{aligned}$$

where  $N_0$  is the total concentration of the electrons. We note that the second order pole at  $\omega = 0$  in the expression for  $\epsilon_{ij}(\omega, \mathbf{k})$  is only illusory, since by using the sum rule it can be eliminated (see [59]). Since the region of small  $\omega$  is of no interest to us here, we shall not eliminate the pole at  $\omega = 0$ .

\*In this sense the difference between the real and mechanical exciton consists precisely of an account or failure to account for the microscopic field  $\mathbf{E}$  in the equations of motion (see also [12], Sec. 30).

In the ground state of a dielectric, the quasimomentum is zero, since the wave function of this state is invariant under all crystal symmetry operations. On the other hand, we note that we are interested here in the contribution made to the dielectric tensor of the crystal by the presence of exciton states only. These states, as is well known, (see, for example, [57,58]) are characterized by a single continuous quantum number—the quasimomentum  $\mathbf{q}$ , and also, generally speaking, by a set of discrete quantum numbers  $s$ . Therefore

$$\Psi_{m0}(r_1, r_2, \dots) \equiv \Psi_{qs}(r_1, r_2, \dots),$$

with [see also (3)]

$$\hat{T}_a \Psi_{qs} = e^{-i\mathbf{q}a} \Psi_{qs}. \quad (4.6)$$

If the vector  $\mathbf{q}$  is chosen within the fundamental reciprocal lattice cell, then at small  $|\mathbf{k}|$  we can readily verify that

$$\begin{aligned} M_{m0}^i(\mathbf{k}) &\equiv M_{qs;0}^i(\mathbf{k}) = M_{-ks;0}^i(\mathbf{k}) \delta_{\mathbf{q}+\mathbf{k}}, \\ M_{0m}^i(\mathbf{k}) &\equiv M_{0;qs}^i(\mathbf{k}) = M_{0;ks}^i(\mathbf{k}) \delta_{\mathbf{k}-\mathbf{q}}. \end{aligned} \quad (4.7)$$

Using (4.7) we find on the basis of (4.5) that

$$\begin{aligned} \epsilon_{ij}(\omega, \mathbf{k}) &= \delta_{ij} \left( 1 - \frac{4\pi e^2 N_0}{m\omega^2} \right) - \frac{4\pi c^2}{V\hbar\omega^2} \\ &\times \sum_s \left\{ \frac{M_{0;-ks}^i(-\mathbf{k}) M_{-ks;0}^j(\mathbf{k})}{\omega - \omega_s(-\mathbf{k})} - \frac{M_{ks;0}^i(-\mathbf{k}) M_{0;ks}^j(\mathbf{k})}{\omega + \omega_s(\mathbf{k})} \right\}. \end{aligned} \quad (4.8)$$

In the vicinity of the isolated  $s$ -th absorption line, the change in the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  with the frequency  $\omega$  is determined essentially by one of the resonant terms in the dispersion formula (4.8). In this case we have approximately

$$\begin{aligned} \epsilon_{ij}(\omega, \mathbf{k}) &= \epsilon_{ij}^{(0)}(\omega) - \frac{4\pi c^2}{V\hbar\omega^2} \\ &\times \left\{ \frac{M_{0;-ks}^i(-\mathbf{k}) M_{-ks;0}^j(\mathbf{k})}{\omega - \omega_s(-\mathbf{k})} - \frac{M_{ks;0}^i(-\mathbf{k}) M_{0;ks}^j(\mathbf{k})}{\omega + \omega_s(\mathbf{k})} \right\}, \end{aligned} \quad (4.8a)$$

where  $\epsilon_{ij}^{(0)}(\omega)$  is a smooth function of  $\omega$  in the frequency interval under consideration. For those exciton states  $(\mathbf{q}, s)$ , the wave functions of which transform when  $\mathbf{q} = 0$  like the components of a polar vector, the matrix elements  $M_{qs;0}^i(0)$ ,  $i = 1, 2, 3$  (at least some of them) differ from zero. It is clear that only these exciton states (we previously called them dipole exciton states) contribute to the dielectric tensor without account of spatial dispersion. Inasmuch as in this case

$$M_{0s;0}^i(0) = i \frac{\omega_s(0)}{c} \sqrt{N} D_{s0;0}^i,$$

where  $D_{s0;0}^i$  is the matrix element of the dipole moment operator of the unit cell of the crystal and  $N$  is the number of unit cells in the fundamental volume of the crystal, we have

$$\epsilon_{ij}(\omega, 0) = \left( 1 - \frac{4\pi e^2 N_0}{m\omega^2} \right) \delta_{ij} - \frac{8\pi}{\Omega\hbar\omega^2} \sum_s \frac{D_{0;0s}^i(0) D_{0s;0}^j(0)}{\omega^2 - \omega_s^2(0)} \omega_s^3(0), \quad (4.8b)$$

where  $\Omega$  is the volume of the unit cell of the crystal.

Accordingly, in place of (4.8a) we have in this case

$$\epsilon_{ij}(\omega, 0) \cong \epsilon_{ij}^{(0)}(\omega) - \frac{8\pi}{\Omega\hbar} \frac{D_{0;0s}^i(0) D_{0s;0}^j(0)}{\omega^2 - \omega_s^2(0)} \omega_s^3(0). \quad (4.8c)$$

Among the other exciton states, it is convenient to separate the quadrupole exciton states, the wave functions of which transform when  $\mathbf{q} = 0$  like the products of the components of two polar vectors. Similar to what was done in [34], it can be shown that for such states, in the first approximation in  $\mathbf{k}$ , we get

$$M_{ks;0}^i(\mathbf{k}) = -i \frac{e}{2mc} \sum_{l=1}^3 \langle 0, s | (P_l^\alpha r_l^\alpha + r_l^\alpha P_l^\alpha) | 0 \rangle k_l. \quad (4.9)$$

The difference between (4.9) and the analogous equation in [34] is that (4.9) was derived for the wave functions of "mechanical" and not "Coulomb" excitons, the wave functions of which, generally speaking, are non-analytically dependent on the quasimomentum, something not taken into consideration in [34]. Taking the notation (3.33b) into account, we find that\*

$$\begin{aligned} M_{0;-ks}^i(-\mathbf{k}) M_{-ks;0}^j(\mathbf{k}) &= -\frac{e^2}{4m^2 c^2} \sum_{i,m=1}^3 \langle 0 | \hat{T}_{ii} | 0s \rangle \langle 0s | \hat{T}_{jm} | 0 \rangle k_i k_m \\ &\equiv -\frac{e^2}{8m^2 c^2} \sum_{i,m=1}^3 \{ \langle 0 | \hat{T}_{ii} | 0s \rangle \langle 0s | \hat{T}_{jm} | 0 \rangle \\ &+ \langle 0 | \hat{T}_{im} | 0s \rangle \langle 0s | \hat{T}_{ji} | 0 \rangle \} k_i k_m. \end{aligned}$$

If the frequency is  $\omega \approx \omega_s(0)$ , the main contribution to the sum (4.8) is made by the  $s$ -th term, which is proportional to  $[\omega - \omega_s^{(0)}]^{-1}$ . Since the exciton term  $\hbar\omega_s(0)$  may be degenerate ( $s = s_1, s_2, \dots$ ), we arrive at the relation (3.43), which we have already used before.

In connection with the foregoing calculation of  $\epsilon_{ij}(\omega, \mathbf{k})$ , we make one remark which, incidentally, pertains to the very introduction of this quantity, and could therefore be made even in Sec. 1. The tensor  $\epsilon_{ij}(\omega, \mathbf{k})$ , by definition, establishes the connection between the harmonic fields  $\mathbf{D}$  and  $\mathbf{E}$ :

$$\begin{aligned} D_i(\mathbf{r}, t) &= D_i(\mathbf{k}, \omega) e^{i(\mathbf{k}\mathbf{r} - \omega t)} = \epsilon_{ij}(\omega, \mathbf{k}) E_j(\mathbf{r}, t) \\ &= \epsilon_{ij}(\omega, \mathbf{k}) E_j(\mathbf{k}, \omega) e^{i(\mathbf{k}\mathbf{r} - \omega t)}. \end{aligned} \quad (4.10)$$

But if we consider waves in a medium, then by virtue of the field equation  $\omega = \omega(\mathbf{k})$ , and thus  $\omega$  and  $\mathbf{k}$  cannot be regarded as independent variables. On the other hand, if  $\omega$  and  $\mathbf{k}$  are related, then the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  depends only on  $\omega$  and it is not clear what constitutes the spatial dispersion. The answer frequently given to this question is as follows. Equations (1.17) and (1.18)

\*We note that in Chapt. 5 of [10] the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  was incorrectly expanded in a series in powers of  $\mathbf{k}$ , for no account was taken of the dependence of the wave functions of the excited states of the crystal on the quasimomentum.

are obtained only by starting from equations (1.1) or (1.14) for the free field, equations which are valid if there are no extraneous current and charge densities  $\mathbf{j}_0$  and  $\rho_0$ . On the other hand, in the presence of extraneous current and charge, the field  $\mathbf{E}(\mathbf{r}, t)$  is defined by the quantities  $\mathbf{j}_0(\mathbf{r}, t)$  and  $\rho_0(\mathbf{r}, t)$ . In particular,  $\mathbf{j}_0$  and  $\rho_0$  can be chosen such that the field has the form

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{k}, \omega) e^{i(\mathbf{k}\mathbf{r} - \omega t)}$$

with some values of  $\omega$  and  $\mathbf{k}$  which are not related at all (by way of a simple example we point to the obvious possibility of producing a static electric field with arbitrary  $\mathbf{k}$  by means of a system of external charges). The tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  then defines  $\mathbf{D}'(\mathbf{k}, \omega)$  in terms of  $\mathbf{E}(\mathbf{k}, \omega)$  and is a function of the independent variables  $\omega$  and  $\mathbf{k}$ .

b) Mechanical excitons and the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  in molecular crystals and in the case of the classical oscillator model. To calculate the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  it is obviously necessary to know the wave functions  $\Psi_{\mathbf{m}0}$  and the eigenvalues of the energy  $W_{\mathbf{m}}$  for mechanical excitons. With this, in accordance with the statements made in the Introduction and in Sec. 4a, the excited states, called mechanical excitons, correspond to a solution of the problem without account of the action of the macroscopic (long-wave) field.

Let us develop here a theory for mechanical excitons in the case of molecular crystals in the fixed-molecule approximation.

We note that the Heitler-London approximation can be used for this purpose only when the interaction between molecules is sufficiently weak. Actually, we encounter a whole series of molecular crystals, where the oscillator strengths are large, and the interaction between the molecules cannot be regarded as weak in many spectral regions (although this interaction does not lead to violation of the neutrality of individual molecules, it does cause an intense mixing of the electron configurations). The corresponding theory, without use of the Heitler-London approximation, was developed in [62]. For the sake of simplicity, however, we use here the Heitler-London method, since the results obtained below can be made more exact in a manner similar to that used in [62].

Let us assume that the elementary crystal cell contains  $\sigma$  molecules. The Hamiltonian of the complete Coulomb problem is

$$\hat{H} = \sum_{n\alpha} \hat{H}_{n\alpha} + \frac{1}{2} \sum_{n\alpha \neq m\beta} V_{n\alpha, m\beta}, \quad (4.11)$$

where  $\mathbf{n}$  and  $\mathbf{m}$  are whole-number sites of the crystal lattice;  $\alpha, \beta = 1, 2, \dots, \sigma$ ;  $\hat{H}_{n\alpha}$  is the Hamiltonian of the molecule  $(\mathbf{n}, \alpha)$ , and  $\hat{V}_{n\alpha, m\beta}$  is the operator of the Coulomb interaction between the molecules  $n\alpha$  and  $m\beta$ . In the construction of the wave functions of the ground and excited states of the crystal, we shall disregard the intermolecular electron exchange, since

in the region of the lower excited states this exchange does not play any appreciable role. We introduce functions  $\varphi_{n\alpha}^{\dagger}$  which are normalized and antisymmetrized over all the coordinates

$$\hat{H}_{n\alpha} \varphi_{n\alpha}^{\dagger} = E_0^f \varphi_{n\alpha}^{\dagger} \quad (4.12)$$

(here  $f = 0$  corresponds to one state of the molecule: in the case when the molecular term is degenerate, the index  $f$  should be regarded as compound:  $f \rightarrow (f, r)$ ,  $r = 1, 2, \dots, t$ , where  $t$  is the multiplicity of the degeneracy).

In the Heitler-London approximation the wave function of the ground state of the crystal is

$$\Phi_0 = \prod_{n\alpha} \varphi_{n\alpha}^0, \quad (4.13)$$

while for the excited state we have

$$\Phi^f = \sum_{n\alpha, r} a_{n\alpha}^{fr} \chi_{n\alpha}^{fr}, \quad (4.14)$$

where

$$\chi_{n\alpha}^{fr} = \varphi_{n\alpha}^{fr} \prod_{m\beta \neq n\alpha} \varphi_{m\beta}^0. \quad (4.15)$$

The energy of the ground state is  $E_0 = \langle \Phi_0, \hat{H} \Phi_0 \rangle$ . Minimizing  $H = \langle \Phi^f, \hat{H} \Phi^f \rangle$  over the set  $\{a_{n\alpha}^{fr}\}$  subject to the additional condition

$$\sum_{n\alpha, r} |a_{n\alpha}^{fr}|^2 = 1,$$

we find that the quantities  $a_{n\alpha}^{fr}$  satisfy the system of equations

$$\sum_{m\beta \neq n\alpha} M_{m\beta, n\alpha}^{f, fr'} a_{m\beta}^{fr'} - \epsilon^f a_{n\alpha}^{fr} = 0, \quad \epsilon^f = E - E_0 - \Delta_f, \quad (4.16)$$

where  $\Delta_f \equiv E_f^0 - E_0^0$  is the excitation energy of the isolated molecule

$$M_{m\beta, n\alpha}^{f, fr'} = \int \varphi_{n\alpha}^{*fr} \varphi_{m\beta}^0 \hat{V}_{n\alpha, m\beta} \varphi_{n\alpha}^0 \varphi_{m\beta}^{fr'} d\tau. \quad (4.17)$$

From considerations of translational symmetry it is clear that

$$a_{n\alpha}^{fr} = \frac{1}{\sqrt{N}} a_{\alpha}^{fr}(\mathbf{k}) e^{-i\mathbf{k}\mathbf{r}_{n\alpha}}, \quad (4.18)$$

where  $N$  is the total number of cells in the fundamental volume. Consequently we obtain in place of (4.16)

$$\sum_{\beta \neq \alpha} \Gamma_{\beta\alpha}^{f, fr'}(\mathbf{k}) a_{\beta}^{fr'}(\mathbf{k}) - \epsilon^f a_{\alpha}^{fr}(\mathbf{k}) = 0, \quad (4.19)$$

where the prime on the summation sign denotes that the term  $\mathbf{n} = \mathbf{m}$ ,  $\alpha = \beta$  has been left out

$$\Gamma_{\beta\alpha}^{f, fr'}(\mathbf{k}) = \sum_{m} M_{m\beta, n\alpha}^{f, fr'} e^{-i\mathbf{k}(\mathbf{r}_{m\beta} - \mathbf{r}_{n\alpha})}. \quad (4.20)$$

It follows from (4.19) that the values of the excitation energy are in the complete Coulomb problem the eigenvalues of the Hermitian matrix  $\Gamma_{ij}(\mathbf{k})$ , while the numbers

$$a_{\alpha}^r(\mathbf{k}), \quad \alpha = 1, 2, \dots, \sigma, \\ r = 1, 2, 3, \dots, t$$

are the corresponding components of the eigenvectors.

To change over to the mechanical exciton problem, let us separate from the interaction matrix  $\hat{\Gamma}(\mathbf{k})$  the interaction due to the long-wave macroscopic field (we are essentially interested only in the region of small values of  $|\mathbf{k}|$ ; it is precisely for these values of the wave vector that the Ewald procedure employed leads to the separation of the long-wave field).

To this end, we represent the interaction operator between molecules  $(n\alpha)$  and  $(m\beta)$  in the form of the sum

$$\hat{V}_{n\alpha, m\beta} = \hat{V}_{n\alpha, m\beta}^I + V_{n\alpha, m\beta}^{II}, \quad (4.21)$$

where the index I denotes the operator of dipole-dipole interaction between molecules, while II denotes the sum of the interaction operators of higher multipolarity. Analogously, by virtue of (4.17) and (4.20) we have

$$M_{m\beta, n\alpha}^{Irr'} = M_{m\beta, n\alpha}^{Irr'} + M_{m\beta, n\alpha}^{IIrr'}, \quad (4.22)$$

$$\Gamma_{\beta\alpha}^{Irr'}(\mathbf{k}) = \Gamma_{\beta\alpha}^{Irr'}(\mathbf{k}) + \Gamma_{\beta\alpha}^{IIrr'}(\mathbf{k}). \quad (4.23)$$

The dipole-dipole interaction operator is

$$\hat{V}_{n\alpha, m\beta}^I = \frac{1}{|\mathbf{r}_{n\alpha} - \mathbf{r}_{m\beta}|^3} \times \left\{ \hat{\mathbf{P}}_{n\alpha} \hat{\mathbf{P}}_{m\beta} - \frac{1}{|\mathbf{r}_{n\alpha} - \mathbf{r}_{m\beta}|^2} (\hat{\mathbf{P}}_{n\alpha}, \mathbf{r}_{n\alpha} - \mathbf{r}_{m\beta}) (\mathbf{P}_{m\beta}, \mathbf{r}_{n\alpha} - \mathbf{r}_{m\beta}) \right\}, \quad (4.24)$$

where  $\hat{\mathbf{P}}_{n\alpha}$  is the dipole-moment operator of the  $(n\alpha)$  molecule. Therefore, using also (4.17), we find that

$$\Gamma_{\beta, \alpha}^{Irr'}(\mathbf{k}) = -\mathbf{P}_{\alpha}^{0/r} \mathbf{E}_{n\alpha, m\beta}^{r'/0}(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}_{n\alpha}}, \quad (4.25)$$

where

$$\mathbf{P}_{\alpha}^{0/r} = \int_{\varphi_{n\alpha}}^{\tau} \hat{\mathbf{P}}_{n\alpha} \varphi_{n\alpha}^0 d\tau, \quad (4.26)$$

$$\mathbf{E}_{n\alpha, \beta}^{r'/0}(\mathbf{k}) = -\sum_m \frac{e^{-i\mathbf{k}(\mathbf{r}_{m\beta} - \mathbf{r}_{n\alpha})}}{|\mathbf{r}_{n\alpha} - \mathbf{r}_{m\beta}|^3} \times \left\{ \mathbf{P}_{\beta}^{r'/0} - \frac{\mathbf{r}_{n\alpha} - \mathbf{r}_{m\beta}}{|\mathbf{r}_{n\alpha} - \mathbf{r}_{m\beta}|^2} (\mathbf{P}_{\beta}^{r'/0}, \mathbf{r}_{n\alpha} - \mathbf{r}_{m\beta}) \right\}. \quad (4.27)$$

From the form of (4.27) it is clear that  $\mathbf{E}_{n\alpha, \beta}^{f0}(\mathbf{k})$  is the electric field at the point  $\mathbf{r} = \mathbf{r}_{n\alpha}$ , produced by the dipoles situated in the lattice sites of the type  $\beta$ , with the magnitude of the dipoles varying from site to site as

$$\mathbf{P}(m\beta) = \mathbf{P}_{\beta}^{r'/0} e^{-i\mathbf{k}\mathbf{r}_{m\beta}}. \quad (4.28)$$

Inasmuch as the operation of separation of the macroscopic part of the field from the total field (4.27) is described in detail in [12], Sec. 30, we give here only the final result:

$$[E_{n\alpha, \beta}^{r'/0}(\mathbf{k})]_j = E_j^{r'/f} e^{-i\mathbf{k}\mathbf{r}_{n\alpha}} + e^{-i\mathbf{k}\mathbf{r}_{n\alpha}} \sum_{j'} Q_{jj'} \left( \frac{\mathbf{k}}{\alpha \beta} \right) P_{\beta j'}^{r'/0}, \quad (4.29)$$

where  $E_j^{r'/f}$  is the amplitude of the macroscopic part of the field  $e^{-i\mathbf{k}\mathbf{r}}$ :

$$E_j^{r'/f} = -\frac{4\pi}{\Omega} \frac{k_j}{|\mathbf{k}|} \left( \frac{\mathbf{k}}{|\mathbf{k}|} \sum_{\alpha} P_{\alpha}^{r'/0} \right). \quad (4.30)$$

The coefficients  $Q_{jj'} \left( \frac{\mathbf{k}}{\alpha \beta} \right)$  for a specified value of the wave vector  $\mathbf{k}$  are determined only by the structure of the cell [their form is determined by formula (3.31) in the book [12]]. What is essential is that the coefficients  $Q_{jj'} \left( \frac{\mathbf{k}}{\alpha \beta} \right)$  are when  $\mathbf{k} = 0$  analytic functions of the wave vector, so that the entire non-analyticity of the sum (4.27) is concentrated in (4.30). The coefficients  $Q_{jj'} \left( \frac{\mathbf{k}}{\alpha \beta} \right)$  satisfy the following relations:

$$Q_{jj'} \left( \frac{\mathbf{k}}{\alpha \beta} \right) = Q_{j'i} \left( \frac{\mathbf{k}}{\alpha \beta} \right), \quad (4.31)$$

$$Q_{jj'} \left( \frac{-\mathbf{k}}{\alpha \beta} \right) = Q_{j'i}^* \left( \frac{\mathbf{k}}{\alpha \beta} \right), \quad (4.32)$$

$$Q_{jj'} \left( \frac{\mathbf{k}}{\alpha \beta} \right) = Q_{j'i}^* \left( \frac{\mathbf{k}}{\beta \alpha} \right). \quad (4.33)$$

Omitting in (4.29) the first term in the right half of the equation, we see that part of the interaction matrix  $\Gamma_{\beta\alpha}^I(\mathbf{k})$  has in the mechanical exciton problem the following form

$$\tilde{\Gamma}_{\beta\alpha}^{Irr'}(\mathbf{k}) = -\sum_{j'} Q_{jj'} \left( \frac{\mathbf{k}}{\alpha \beta} \right) P_{\alpha j'}^{0/r} P_{\beta j'}^{r'/0}. \quad (4.34)$$

Thus, the complete interaction matrix in the mechanical exciton problem, unlike the interaction matrix in the problem where the Coulomb interaction is fully accounted for, is an analytic function of the wave vector, with

$$\tilde{\Gamma}_{\alpha\beta}(\mathbf{k}) = \tilde{\Gamma}_{\alpha\beta}^I(\mathbf{k}) + \Gamma_{\alpha\beta}^{II}(\mathbf{k}). \quad (4.35)$$

It is clear that in the problem of the mechanical exciton the relation (4.18) also holds true, but the amplitudes  $\mathbf{a}_{\alpha}^{rf}(\mathbf{k})$  satisfy, unlike (4.19), the system of equations

$$\sum_{\beta \neq \alpha} \tilde{\Gamma}_{\beta\alpha}^{r'f}(\mathbf{k}) \tilde{a}_{\beta}^{r'/f}(\mathbf{k}) - \tilde{\epsilon}^f \tilde{a}_{\alpha}^{r'/f}(\mathbf{k}) = 0. \quad (4.36)$$

For each  $\mathbf{k}$  the operator  $\tilde{\Gamma}^f(\mathbf{k})$  has  $\sigma t$  eigenvalues  $\tilde{\epsilon}_{\mu}^f$ ,  $\mu = 1, 2, \dots, \sigma t$ . The corresponding orthonormalized eigenvectors will be denoted by  $\{\tilde{\mathbf{a}}_{\mu}^f\}$ . It is

clear that in the approximation considered here the discrete quantum number is  $s \equiv (f, \mu)$ . In crystals containing one molecule per unit cell, the  $f$ -th non-degenerate molecular term corresponds to only one exciton band. In this case

$$\tilde{\mathbf{e}}^f = \tilde{\Gamma}_{11}^f(\mathbf{k}), \quad \tilde{a}_1^f = 1. \quad (4.37)$$

In more complicated crystals, containing for example two molecules per unit cell, the values of  $\tilde{\epsilon}_{\mu}^f$ ,  $\mu = 1, 2$ , are determined as roots of the equation (the molecular term is assumed nondegenerate)

$$(\tilde{\Gamma}_{11}^f(\mathbf{k}) - \tilde{\epsilon}^f)(\tilde{\Gamma}_{22}^f(\mathbf{k}) - \tilde{\epsilon}^f) - \tilde{\Gamma}_{12}^f \tilde{\Gamma}_{21}^f = 0. \quad (4.38)$$

Using the relations (4.25), (4.29), and (4.30), and also taking into account the analyticity of the coefficients

$Q_{jj'} \left( \begin{smallmatrix} \mathbf{k} \\ \alpha \beta \end{smallmatrix} \right)$  as  $\mathbf{k} \rightarrow 0$ , we can readily verify that  $\tilde{\Gamma}_{11}^f(0) = \tilde{\Gamma}_{22}^f(0)$ , whereas  $\Gamma_{11}^f(\mathbf{k})|_{\mathbf{k} \rightarrow 0} \neq \Gamma_{22}^f(\mathbf{k})|_{\mathbf{k} \rightarrow 0}$ .

It is precisely by virtue of this that the molecular term  $f$  corresponds when  $\mathbf{k} = 0$  to the two mechanical exciton states, for which

$$\begin{aligned} \tilde{\epsilon}'_1(0) &= \tilde{\Gamma}'_{11}(0) + \tilde{\Gamma}'_{12}(0), & \tilde{a}'_1(0) &= -\tilde{a}'_2(0) = \frac{1}{\sqrt{2}}, \\ \tilde{\epsilon}'_2(0) &= \tilde{\Gamma}'_{22}(0) - \tilde{\Gamma}'_{12}(0), & \tilde{a}'_2(0) &= \tilde{a}'_1(0) = \frac{1}{\sqrt{2}}. \end{aligned} \quad (4.39)$$

Knowledge of the wave functions of the mechanical excitons makes it possible to represent all the quantities in the expression for the dielectric tensor directly in terms of the characteristics of the individual molecules. Using (4.13) and (4.14), and also (4.2), we can readily show that

$$\begin{aligned} \frac{1}{\sqrt{V}} M_{0; -\mathbf{k}s}^i(\mathbf{k}) &= \frac{1}{\sqrt{\Omega}} \sum_{\alpha} a_{\alpha}^{\prime\mu}(-\mathbf{k}) \\ &\times \int \varphi_{n\alpha}^* \sum_{\nu \in n\alpha} (P_{\nu}^y e^{i\mathbf{k} \cdot \mathbf{r}_{\nu}} + e^{i\mathbf{k} \cdot \mathbf{r}_{\nu}} P_{\nu}^y) \varphi_{n\alpha}^0 d\tau, \\ \frac{1}{\sqrt{V}} M_{0; -\mathbf{k}s}^i(-\mathbf{k}) &= \frac{1}{\sqrt{\Omega}} \sum_{\alpha} a_{\alpha}^{\prime\mu}(-\mathbf{k}) \\ &\times \int \varphi_{n\alpha}^0 \sum_{\nu \in n\alpha} (P_{\nu}^y e^{-i\mathbf{k} \cdot \mathbf{r}_{\nu}} + e^{-i\mathbf{k} \cdot \mathbf{r}_{\nu}} P_{\nu}^y) \varphi_{n\alpha}^{\prime} d\tau, \end{aligned} \quad (4.40)$$

where  $\nu$  is the number of the electron belonging to the molecule  $n\alpha$  and  $\mathbf{r}_{\nu}$  is the radius vector of this electron relative to the lattice site  $\mathbf{r}_{n\alpha}$ . As regards the frequencies  $\omega_s(\mathbf{k})$  contained in (4.8), these frequencies, in accord with (4.16), are determined in the Heitler-London approximation by the relation

$$\omega_s(\mathbf{k}) \equiv \omega_{\mu}^s(\mathbf{k}) = \frac{1}{h} [E_0 + \Delta_f + \tilde{\epsilon}_{\mu}^{\prime}(\mathbf{k})]. \quad (4.41)$$

The molecular crystal model considered above includes as a limiting case the classical model of a crystal with point dipoles at its sites.

In order to verify the correctness of the foregoing remark, we must recognize that the crystal has along with the lattice constant  $a$  also a whole set of parameters  $a_i$ , equal to the effective dimensions of the atoms and molecules in different states. The values of  $a_i$  determine the matrix elements for different multipole (dipole, quadrupole, etc) transitions. In place of the parameters  $a$  and  $a_i$  we can therefore use  $a$  and the values of certain effective multipole moments (more accurately, their matrix elements), assuming these multipoles to be point like and located at the lattice sites. In the vicinity of the intense dipole lines we can confine ourselves only to the dipole moments, so that we arrive at a model of a crystal consisting of point-like dipoles. With this, the only interaction present is the dipole-dipole interaction, so that  $\Gamma^{\text{II}}(\mathbf{k}) = 0$  and by virtue of (4.35)

$$\tilde{\Gamma}_{\alpha\beta}^f(\mathbf{k}) = \tilde{\Gamma}_{\alpha\beta}^f(\mathbf{k}).$$

Along with this, (4.40) is replaced by the following relations

$$\begin{aligned} \frac{1}{\sqrt{V}} M_{0; -\mathbf{k}s}^j(-\mathbf{k}) &= \frac{1}{\sqrt{V}} M_{-\mathbf{k}s; 0}^j(\mathbf{k}) \\ &= \frac{i}{\sqrt{\Omega}} \sum_{\alpha r} a_{\alpha}^{\prime\mu}(-\mathbf{k}) \omega_{\mu}^{\prime}(-\mathbf{k}) P_{\alpha j}^{\prime r}, \end{aligned}$$

where  $P_{\alpha j}^{\text{rf}}$  is the  $j$ -th component of the  $r$ -th dipole moment, located at a type- $\alpha$  site. We assume, for example, that the Bravais lattice of the crystal is cubic and that there is one isotropic molecule per unit cell. In such a molecule, the excited states to which transitions are allowed in the dipole approximation are triply degenerate. We choose the corresponding three wave functions such that the vectors  $\mathbf{P}^{\text{rf}}$ ,  $r = 1, 2, 3$ , are directed along the cube axes. In this case, obviously,

$$\frac{1}{\sqrt{V}} M_{s-\mathbf{k}; 0}^j(\mathbf{k}) = -\frac{1}{\sqrt{V}} M_{0; s-\mathbf{k}}^j(-\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \omega_{\mu}^{\prime}(\mathbf{k}) a^{j\prime\mu}(\mathbf{k}) P_j^{\text{rf}}.$$

But then

$$\begin{aligned} \frac{1}{V} M_{s-\mathbf{k}; 0}^i(\mathbf{k}) M_{0; s-\mathbf{k}}^j(-\mathbf{k}) &= \frac{1}{\Omega} [\omega_{\mu}^{\prime}(-\mathbf{k})]^2 a^{i\prime\mu}(-\mathbf{k}) a^{j\prime\mu}(-\mathbf{k}) P_i^{\text{rf}} P_j^{\text{rf}} \\ &= \frac{1}{\Omega} [\omega_{\mu}^{\prime}(-\mathbf{k})]^2 a^{i\prime\mu}(-\mathbf{k}) a^{j\prime\mu}(-\mathbf{k}) P_j^{\text{rf}}. \end{aligned}$$

If we neglect the anisotropy of the effective mass of mechanical excitons, then accurate to terms  $\sim k^2$

$$\omega_1^{\prime}(\mathbf{k}) = \omega_2^{\prime}(\mathbf{k}) = \omega_3^{\prime}(\mathbf{k}) = \omega_f(\mathbf{k}).$$

In this approximation, for the model under consideration, the dielectric tensor

$$\begin{aligned} \epsilon_{ij}(\omega, \mathbf{k}) &= \delta_{ij} \epsilon(\omega, \mathbf{k}) \\ &= \left\{ 1 - \frac{4\pi e^2 N_0}{m\omega^2} - \frac{8\pi}{e^2 h \Omega \omega^2} \sum_j \frac{P_j^2 \omega_j^2(\mathbf{k})}{\omega^2 - \omega_j^2(\mathbf{k})} \right\} \delta_{ij} \end{aligned}$$

reduces to a scalar.\* A similar expression for the dielectric tensor, but with  $\omega_f = \text{const}$ , follows also from [15], where an analogous model was used but spatial dispersion was disregarded. In our model the refractive index for the transverse waves is obviously  $n = [\epsilon(\omega, \omega n/c)]^{1/2}$ . The normal waves in any direction are either longitudinal or transverse. The frequencies of the transverse waves, disregarding retardation, that is, the frequencies of the "polarization waves" (see Introduction and Sec. 1), correspond to the poles of  $\epsilon(\omega, \mathbf{k})$ , whereas at the frequencies of the longitudinal waves  $\epsilon(\omega, \mathbf{k})$  vanishes.

As was already indicated in Sec. 1c, to calculate the refractive indices of light one can also use the

\*In the derivation of this formula it must be taken into account that

$$\sum_{\mu} a^{i\prime\mu}(\mathbf{k}) a^{j\prime\mu}(\mathbf{k}) = \delta_{ij}.$$

tensor\*  $\epsilon_{\perp,ij}(\omega, \mathbf{k})$ , with the aid of which the transverse induction vector  $\mathbf{D}'$  is expressed in terms of the transverse part of the electric field intensity  $E_{\perp}$ .<sup>†</sup> The tensor  $\epsilon_{\perp,ij}(\omega, \mathbf{k})$  can be obtained on the basis of (1.66) and the expression for the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$ . However, it is simpler to find an expression for this tensor by using as the system of unperturbed functions the functions of the complete Coulomb problem (without account of retardation), and by using for the perturbation the transverse part of the electric field. In this case, in complete analogy with the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$ , the tensor  $\epsilon_{\perp,ij}(\omega, \mathbf{k})$  is obtained directly as an expansion in terms of the poles. It must be borne in mind here that both in the derivation presented here for  $\epsilon_{ij}(\omega, \mathbf{k})$ , and in the derivation of the expression for  $\epsilon_{\perp,ij}$  (see [25]) a certain transverse part of the effective field is disregarded (see [12], Sec. 44). As already indicated in Sec. 4a, the difference between the effective and the macroscopic field should be taken into consideration in the mechanical exciton problem. The Ewald method, which we have used earlier, enables us to separate only the longitudinal part of this field. As to the transverse part of the effective field, it is connected with the retarded interaction in a bounded region. So long as the time necessary to cover this distance with the velocity of light  $c$  is small compared with the period of the oscillations under consideration, the transverse part of the internal field can be neglected in nonmagnetic crystals. For distances on the order of  $10^{-8}$ – $10^{-7}$  cm, the required time is approximately  $10^{-17}$  sec, whereas the oscillation period in the visible part of the spectrum is of the order of  $10^{-15}$  sec. Thus, it is not clear a priori whether the contribution of the transverse part of the internal field can be neglected in a theory that takes into account spatial dispersion the magnitude of which is also connected with the small parameter  $a/\lambda \approx 10^{-3}$ . This entire problem is not fully understood and apparently needs special analysis. We note, however, that in the micro-

scopic theory<sup>[59]</sup> these difficulties do not arise. Within the framework of this theory the dispersion of the electromagnetic waves in crystals can be developed with any degree of accuracy.

In conclusion we present the general formula for the refractive index of light in a crystal<sup>[59]</sup>, which could be obtained by substituting in (1.66) an expression for  $\epsilon_{ij}(\omega, \mathbf{k})$  and then representing the tensor  $\epsilon_{\perp,ij}(\omega, \mathbf{k})$  in the form of an expansion in terms of the poles. Accurate to small quantities proportional to  $(a/\lambda)^2$ , we have in crystals with an inversion center

$$n_{1,2}^2(\omega, \mathbf{s}) = 1 - \frac{1}{2} \sum_s \frac{\omega_0^2 F_s(s) \sin^2 \varphi(s, \mathbf{s})}{\omega^2 - \Omega_s^2(\mathbf{k})} \pm \frac{1}{2} \left\{ \left[ \sum_s \frac{\omega_0^2 F_s(s) (\cos^2 \varphi_1(s, \mathbf{k}) - \cos^2 \varphi_2(s, \mathbf{k}))}{\omega^2 - \Omega_s^2(\mathbf{k})} \right]^2 + 4 \left[ \sum_s \frac{\omega_0^2 F_s(s) \cos \varphi_1(s, \mathbf{k}) \cos \varphi_2(s, \mathbf{k})}{\omega^2 - \Omega_s^2(\mathbf{k})} \right]^2 \right\}^{1/2}, \quad (4.42)$$

where  $\omega_0^2$  is the square of the plasma frequency,  $\Omega_s(\mathbf{k}) = E_s(\mathbf{k})/\hbar$ , and  $E_s(\mathbf{k})$  is the energy of the Coulomb exciton\* in the  $s$ -th band with complete account of the Coulomb interaction,  $\varphi(s, \mathbf{s})$  is the angle between the vector  $\mathbf{s}$  and the dipole moment vector  $\mathbf{D}_{0;0s}$  of the transition from the ground state (0) into the state with the exciton (0,  $s$ ); furthermore  $\varphi_i(s, \mathbf{k})$  with  $i = 1, 2$  is the angle between the vector  $\mathbf{D}_{0;0s}$  and the two unit vectors perpendicular to  $\mathbf{k}$ . In (4.42) spatial dispersion is taken into account only in the resonant denominators, which is sufficient in the analysis of spatial-dispersion effects in the vicinity of the dipole exciton absorption bands. Formula (4.42) enables us to analyze the dependence of  $n^2$  on the direction of light propagation in the crystal and can be used to determine the direction of the transition vector  $\mathbf{D}_{0;0s}$  in an experimental study of the function  $n^2(\omega, \mathbf{s})$ . Thus, for example, in the vicinity of an isolated exciton transition we have

$$n_1^2(\omega, \mathbf{s}) = \epsilon^{(0)} - \frac{\omega_0^2 F(s)}{\omega^2 - \Omega^2(\mathbf{k})} \sin^2 \varphi(s),$$

$$n_2^2(\omega, \mathbf{s}) = \epsilon^{(0)}. \quad (4.42a)$$

The equations (4.42a) can, of course, be established directly on the basis of (1.33) and (4.8a, c) provided we neglect the nondiagonal elements of the tensor  $\epsilon_{ij}^{(0)}(\omega)$  and assume that  $\epsilon_{ij}^{(0)}(\omega) = \epsilon^{(0)}(\omega) \delta_{ij}$ . Indeed, in this case the approximate expression for the dielectric tensor has the symmetry of this tensor in a uniaxial crystal, with

$$\epsilon_{\perp} = \epsilon^{(0)}, \quad \epsilon_z = \epsilon^{(0)} - \frac{8\pi |\mathbf{D}_{0;0s}|^2}{\Omega \hbar (\omega^2 - \omega_0^2(0))} \omega_s(0).$$

Hence, bearing in mind (1.31), we find directly that for

\*A Coulomb exciton is one corresponding to the exact solution of the Coulomb problem. In accordance with the terminology previously employed, Coulomb excitons are longitudinal and "fictitious" longitudinal waves, and also "polarization waves."

\*It follows from (1.58) that the determinant of the matrix  $\eta_{ij}$  vanishes, and consequently [see (1.57)] the determinant of the matrix  $\epsilon_{\perp,ij}^{-1}$  also vanishes. It is easy to see, for example, that in a coordinate system where the  $z$  axis is directed along the vector  $\mathbf{k}$ , all the components of the tensor  $\epsilon_{\perp,ij}^{-1}$  for which at least one of the indices,  $i$  or  $j$ , corresponds to the  $z$  axis, vanish. This tensor can therefore be regarded as a tensor in two-dimensional space, that is, as  $\epsilon_{\perp,\alpha\beta}^{-1}$ ,  $\alpha, \beta = x, y$ . The tensor  $\epsilon_{\perp,\alpha\beta}$ , introduced in (1.61), is the inverse of the tensor  $\epsilon_{\perp,\alpha\beta}^{-1}$  in the same two-dimensional space:  $\epsilon_{\perp,\alpha\beta} \epsilon_{\perp\alpha'}^{-1} = \delta_{\alpha\alpha'}$ , so that the indices  $i$  and  $j$  in (1.61) can assume only the values  $x$  and  $y$  (this was unfortunately not emphasized in Part I). It is clear that in three-dimensional space the tensor  $\epsilon_{\perp,ij}$  has a structure similar to that possessed by the tensor  $\epsilon_{\perp,ij}^{-1}$ , and is not the reciprocal of the tensor  $\epsilon_{\perp,ij}^{-1}$  simply because the latter does not exist at all, since  $\|\epsilon_{\perp,ij}^{-1}\| = 0$ .

†It is precisely for this reason that the tensor  $\epsilon_{\perp,ij}$  is not suitable for an analysis of the energy losses of a charge moving in a medium, since the electric field of the charge acting on the crystal does not satisfy the condition  $\text{div } \mathbf{D}' = 0$ .

a wave polarized perpendicular to the vector  $D_{0;0s}$  we have  $n^2 = n_1^2 = \epsilon^{(0)}$ , whereas for a wave polarized in the plane formed by the vectors  $\mathbf{s}$  and  $D_{0;0s}^{(0)}$

$$n^2 = n_s^2 = \epsilon^{(0)} - \frac{8\pi |D_{0;0s}|^2 \omega_s(0) \sin^2 \varphi(s)}{\Omega \hbar (\omega^2 - \omega_s^2(0))}.$$

Analogously, we can obtain from (4.42) expressions for  $n^2(\omega, \mathbf{s})$  in such spectral regions where not one but several exciton transitions appear. It should be borne in mind here that the dependence of the frequencies  $\Omega_S(\mathbf{q})$  on  $\mathbf{q}$  for small  $|\mathbf{q}|$  can be readily established provided the tensor  $\epsilon_{ij}(\omega, \mathbf{q})$  is known. In the simplest case, when it is sufficient to consider one of the mechanical exciton bands which are not degenerate when  $\mathbf{q} = 0$  in the investigated spectral region, we find by using (1.39) and (4.8a, c) that\*

$$\Omega^2(\mathbf{k}) = \omega_s^2(\mathbf{k}) + f_s(\mathbf{k}) \cos^2 \varphi, \quad (4.43)$$

where  $\varphi$  is the angle between the vectors  $D_{0;0s}(\mathbf{k})$  and  $\mathbf{s}$ , while  $f_s(\mathbf{k}) = (8\pi/\Delta h) |D|^2 \omega_s(\mathbf{k})$ . If not one but several mechanical exciton bands must be taken into consideration in the expression for  $\epsilon_{ij}$ , the angular dependence of  $\Omega(s)$  becomes more complicated.

In some cases it is interesting to know not only the angular dependence of  $\Omega(\mathbf{k})$  when  $\mathbf{k} = 0$ , but also the form of the Coulomb exciton band for small  $|\mathbf{k}|$ . In the case of dipole exciton bands it is necessary to use the expansion

$$\epsilon_{ij}^{\dagger}(\omega, \mathbf{q}) = \epsilon_{ij}^{\dagger}(\omega, 0) + \beta_{ijlm} q_l q_m, \quad (4.44)$$

and then determine the frequencies  $\Omega_{\mu}(\mathbf{q})$  from equation (1.60), which is obtained by equating to zero the determinant of the tensor  $\hat{\eta} \hat{\epsilon}^{-1}(\omega, \mathbf{k}) \hat{\eta}^{\dagger}$ .

c) Absorption mechanism and calculations. The damping of electromagnetic waves in crystals is connected primarily with the possibility of irreversible transfer of energy from the waves under consideration to other degrees of freedom. In non-metals, the absorption of electromagnetic waves in the visible portion of the spectrum and in the ultraviolet is due essentially to the conversion of the electron excitation energy into vibration energy of the crystal lattice nuclei (see, for example, [43]). The possibility of this process causes the states of the photon in the medium (the real exciton) to become quasistationary, and the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  to become non-Hermitian even for real  $\omega$  and  $\mathbf{k}$ . The dielectric tensor in the presence of absorption has been calculated for several particular crystal models, with and without account of spatial dispersion, in several papers (see, for example, [87]). The procedure for determining this tensor is quite analogous to that developed in Sec. 4a, and the main difference arises only

\*One must not forget that as  $\mathbf{k} \rightarrow 0$  the values of  $\omega_s(\mathbf{k})$  and  $f_s(\mathbf{k})$  are independent of the direction  $\mathbf{s}$ .

†We note that this procedure of determining the dependence  $\Omega(\mathbf{s})$ , and also the form of the exciton band at small values of the wave vector, holds true regardless of whether the exciton is of the Frenkel type or of the Mott type.

in connection with the fact that when the lattice vibrations are taken into account the state of the crystal is characterized not only by the state of the electrons, but also by the state of the nuclear motion.

The need to take into account not only electron motion but also the motion of the crystal nuclei, generally speaking, complicates appreciably the problem of finding the stationary states of the unperturbed problem (that is, the problem in which retardation and the macroscopic electric field are disregarded). By far not all aspects of the theory of absorption of light in crystals have been studied in sufficient detail, and the theory needs to be discussed. However, in the present article we are unable to do so. We therefore present only a few remarks and assume that the stationary states of the unperturbed problem are known, at least approximately.\* Under this assumption, the calculation of the current induced by the external electromagnetic field enables us to obtain an expression for the dielectric tensor, similar to (4.5). The corresponding expression must also be averaged over the possible initial states of the unperturbed system, that is, in practice over the initial phonon distribution function (for a particular model of a molecular crystal see the detailed discussion in [87]).

The picture is particularly simple in the case of weak coupling between the excitons and the photons, when in the initial (zeroth) approximation the transverse electromagnetic field can be regarded to be the same as in vacuum. This means that the normal waves of the unperturbed problem are photons in vacuum, with a dispersion law†  $\omega = k_0 c = 2\pi c/\lambda_0$ , Coulomb excitons, and phonons.‡ Under the influence of the perturbing electromagnetic field of the photon, and also owing to the coupling between the Coulomb excitons and the phonons, transitions occur between the states of the unperturbed problem, as a result of which the energy, say of the photon, can be transformed into lattice vibration energy, etc.

An analysis of the expressions for the probability of photon absorption or else for the anti-Hermitian part of the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  shows that in the region of the exciton absorption the damping of the light waves (photons) is connected principally with processes corresponding to the transformation of the photon with

\*A discussion of the problems related with this can be found in [60, 43, 13].

†In order to take into account the influence of other resonances, we must write here and below  $\lambda_0/n_{00}$  in lieu of  $\lambda_0$ , where the refractive index  $n_{00}$  is determined in the considered region of frequencies by the contribution of the resonances other than the one considered. In cubic crystals  $n_{00} = \sqrt{\epsilon_{00}}$  [see (3.12)].

‡Phonons, like Coulomb excitons, are among the solutions of the Coulomb problem. We designate as phonons those quasiparticles, the consideration of which is essentially connected with an account of the motion of the nuclei (atoms). The arbitrariness in the division of the excitations into phonons and Coulomb excitons is of no importance whatever to what follows.

energy  $\hbar\omega = \hbar 2\pi c/\lambda_0$  into a Coulomb exciton with energy  $E_S(\mathbf{k})$  and one or several phonons.

When we can confine ourselves in the weak exciton-phonon interaction operator to terms that are linear in the displacements of the nuclei from the equilibrium positions, the basic processes are those in which only one phonon with energy  $\hbar\Omega_1(\mathbf{q})$  and momentum  $\mathbf{q}$  participates:

$$\hbar \frac{2\pi c}{\lambda_0} \equiv \hbar\omega(\mathbf{k}_0) = E_S(\mathbf{k}) \pm \hbar\Omega_1(\mathbf{q}), \quad (4.45)$$

where  $\lambda_0$  is the wavelength of the monochromatic light incident on the crystal from the outside, and accurate to a whole-number reciprocal-lattice vector

$$\mathbf{k}_0 = \mathbf{k} \pm \mathbf{q}. \quad (4.46)$$

The plus and minus signs in (4.45) and (4.46) correspond to the emission or absorption of a phonon.

Relation (4.45) determines directly that region of frequencies  $\omega = 2\pi c/\lambda_0$ , which corresponds in our approximation to the exciton absorption line, but this relation enables us to study the shape of the exciton absorption band only approximately. Indeed, let us assume for the sake of simplicity that the crystal is at the temperature of absolute zero, so that the photon decay can occur only with emission of a phonon [the plus sign in (4.45)]. We assume, in addition, that in the exciton band under consideration the minimum energy corresponds to a quasimomentum  $\mathbf{k} = 0$ . In this case, as can be readily seen, relation (4.45) can be satisfied only for frequencies  $\omega \geq E_S(0)/\hbar$ . This means that the frequency  $E_S(0)/\hbar$  is in this approximation the long-wave edge of the exciton absorption band. But such a conclusion, as applied to not very weak dipole absorption lines, turns out to be incorrect, inasmuch as in the vicinity of these lines the real exciton differs appreciably both from the photon and from the Coulomb exciton. The same shortcoming, namely the incorrect determination of the course of the absorption near the long-wave edge, is inherent in the calculations in which one first determines the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  using for  $\omega_m$  [see (4.5)] the frequencies of the mechanical or Coulomb excitons (see, in particular, [87, 25]).

It is quite clear how to approach more correctly the question of the absorption of light waves in crystals.

We first neglect the interaction with the phonons and consider in this approximation the real excitons (photons in the medium). This means that we are considering normal electromagnetic waves in a crystal, neglecting absorption\* but with full allowance for all the remaining electromagnetic interaction. The frequency of the real exciton  $\omega_j(\mathbf{k})$  is in this case real. Of course, in the case when light with frequency  $\omega$  is incident on the crystal, the real exciton produced and

propagating in the crystal has the same frequency, that is,

$$\omega_j(\mathbf{k}) = \omega(\mathbf{k}_0) = \frac{2\pi c}{\lambda_0}.$$

In the account of the interaction between a real exciton and phonons, the exciton is split into another real exciton and phonons, that is, an apparent combination scattering of real excitons occurs [14, 87a]. If only one phonon is emitted, then

$$\hbar\omega = \hbar\omega_j(\mathbf{k}) = \hbar\omega_j(\mathbf{k}') + \hbar\Omega_1(\mathbf{q}), \quad \hbar\mathbf{k} = \hbar\mathbf{k}' + \hbar\mathbf{q}. \quad (4.47)$$

The dispersion law of the real excitons—the dependence  $\omega_j(\mathbf{k})$ —is much different for exciton bands corresponding to large oscillator strengths from the dispersion law for Coulomb or mechanical excitons (see, for example, Figs. 1 and 2). This circumstance leads, in particular, to a situation wherein relation (4.47) can also be satisfied in the region  $\omega < E_S(0)/\hbar$ , as a result of which long-wave absorption appears in the frequency region  $\omega < E_S(0)/\hbar$ . For large oscillator strengths (in those cases when the point  $\mathbf{k} = 0$  corresponds to a minimum of the exciton band), this long-wave absorption completely determines the shape of the long-wave fall-off of the exciton absorption band [63, 64].

Thus, we can find in this manner the absorption coefficient  $\kappa$  in the case of sufficiently weak absorption of normal waves (real excitons) in crystals.

Calculations of  $\epsilon_{ij}(\omega, \mathbf{k})$  in the analogous approximation, that is, with a more accurate account of the interaction between the real excitons and the phonons, particularly in the region of frequencies smaller than the limiting frequency of the mechanical or Coulomb excitons, have not been carried out, as far as we know. The calculation of  $\epsilon_{ij}(\omega, \mathbf{k})$  in this and in the higher approximations can be made by using the temperature Green's functions [88, 89].

## CONCLUDING REMARKS

In the study of excitons by optical means, the prevailing practice so far was to measure only the absorption and forego the analysis of the absorption line shape. This procedure is natural so long as one deals merely with the determination of more or less sharp excited levels in crystals, the clarification of the corresponding series laws, etc. The situation here (particularly if the crystal can be assumed to be optically isotropic) is analogous to a certain degree to that prevailing in the determination of atomic levels of gases. It is quite obvious, however, that in a detailed investigation of the energy spectrum of crystals in the region of optical frequencies, a more general formulation of the problem is necessary. On the one hand, the absorption line shape must be analyzed; on the other hand, in addition to absorption, it is possible and necessary to study the dispersion, that is, to measure the refractive index. One cannot be restricted here to an

\*The absorption is thus, for the sake of simplicity, assumed to be solely connected with the energy transfer to the phonons.



optically isotropic medium, all the more since even cubic crystals are optically anisotropic when spatial dispersion is taken into account. In other words, a study of the excitons is inseparably connected both with classical crystal optics and with crystal optics in which spatial dispersion is included. Some work has already been done in this direction, both experimental and theoretical, but much is still left to do. In particular, attention should be paid to the question of new waves in gyrotropic and non-gyrotropic crystals, to the dispersion and absorption near the quadrupole absorption lines in crystals, to the influence of external electrical and magnetic fields on the optical properties, and also to the influence of stresses and strains.

For a correct analysis of the experimental data and to extract from them definite information on crystal properties, it is necessary to take into account and to use the formulas and results of crystal optics. As far as we know, these results had not yet been expounded with sufficient detail or from a unified point of view with account of spatial dispersion. This is precisely the purpose of the present article, which contains rather extensive material. At the same time, it cannot be stated that all the problems of interest have already been investigated within the framework of crystal optics with account of spatial dispersion. Suffice it to say that even in classical crystal optics, which has been developing for many decades, new aspects are still being encountered and some cases have not been sufficiently studied (we mention, for example, singular optical axes). The number of crystal optics problems which could be solved with account of spatial dispersion is very large. However, the solution of many such problems will be far from justified from the point of view of real requirements, which are determined by the experimental capabilities and the value of the particular information to the theory of crystals. Therefore, it seems to us that further development of the theory (we refer now to calculations analogous to those of Sec. 3) must be primarily closely linked with an analysis of the experimental data and the experimental capabilities. Incidentally, even without a direct connection with experiment one can hardly consider an investigation of the influence of weak spatial dispersion on the propagation of electromagnetic waves in crystals of different classes, near the optical axes, for crystal plates, etc superfluous.

An important point, which we have already emphasized in the article and mention here once more, is that the neglect or differentiation of the macroscopic (phenomenological) crystal optics, which uses the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$ , and the microscopic theory, is utterly unfounded. At first glance it may seem that the microscopic calculations [for example, the calculation of  $\epsilon_{ij}(\omega, \mathbf{k})$  or of  $\hat{n}(\omega, \mathbf{s})$  for some particular model] immediately yield more than the macroscopic theory (in this case, crystal optics). And indeed, the results of a correct calculation for a given reasonable model

will not only not contradict the macroscopic theory and will not fail to contain all its consequences as applied to this model, but will make it possible to specify several relationships, such as the frequency dependence of  $\epsilon_{ij}(\omega, \mathbf{k})$ . It remains still unclear, however, what depends on the given model and what should be obtained for any model (that is, what is entirely independent of the model). It is quite obvious that the use of a model or an approximation, and a comparison of the results of the corresponding calculations with experiment is valuable only if one talks of consequences or aspects that are specific for the given model, and are not common and independent of the choice of the model. Thus, the use of macroscopic theory generally speaking is not only advantageous but even necessary for a determination whether a certain model or approximation is of value. In addition, under such a formulation of the problem we get rid of the need of carrying out microscopic calculations for quantities which are essentially derivatives of more fundamental quantities [for example, it is advantageous to calculate  $\epsilon_{ij}(\omega, \mathbf{k})$  and not  $\hat{n}(\omega, \mathbf{s})$ ]. The foregoing, of course, is not specific to the macroscopic and microscopic theory of optical crystal properties, but has a general (and well known) character. But, as was already indicated above, in the theory of excitons for various reasons no harmonious combination of the microscopic and macroscopic approaches has yet been reached. The purpose of the present article will be attained to a considerable degree if this important and simple aspect is duly recognized. As a result of the extensive use of crystal optics with account of spatial dispersion and of a correct combination of crystal optics with microscopic exciton theory, further development of research in the field of optical and certain other properties of crystals will become much easier and will proceed at a much faster rate.

Note added in proof: Following the first part of the present article (cited below as I), a paper was published in UFN by S. I. Pekar<sup>[90]</sup>, devoted to the same group of problems. A comparison of that paper with ours may give rise to some misunderstanding on the part of the reader, in connection with the different estimate and different interpretation of several aspects. We therefore find it necessary to point out that in the articles of the authors<sup>[5, 8, 24]</sup> (a bibliography is given in I), many critical remarks regarding the articles by Pekar<sup>[7, 14, 25]</sup> were already made both explicitly and implicitly. Inasmuch as we did not encounter in the literature any objections to these remarks, we find it unnecessary to repeat the criticism and indicate specifically the sources of the incorrect or inaccurate statements. The gist of the matter has been discussed in our article with sufficient detail, and therefore we hope that the readers will themselves be able to estimate the character of the different works (including Pekar's and ours), particularly if they take the trouble to read Pekar's articles<sup>[7, 25]</sup>, and not only the review articles<sup>[14, 90]</sup>, in which opinions and results obtained both by us and by other authors are to a certain extent included.

Here we are able only to make the following specific remarks concerning the article<sup>[90]</sup>.

1. Pekar's statement that in a magnetoactive plasma with account of spatial dispersion no new waves occur is in error. In the absence of spatial dispersion the equation for  $\hat{n}^2$  in an anisotropic medium (in particular, in a magnetoactive plasma) is quadratic and has two roots  $\hat{n}_1^2$  and  $\hat{n}_2^2$ , corresponding to the ordinary and extraordinary waves. If we disregard the direction along the magnetic field or the transition to an isotropic plasma in the absence of the field, when the longitudinal (plasma) wave occurs, no third wave exists at all. On the other hand, in the presence of spatial dispersion the equation for  $\hat{n}^2$  becomes one of the third degree and a new wave appears due to the new finite root  $\hat{n}_3^2$  (for more details see, for example<sup>[2]</sup>, Sec. 12). Incidentally, the longitudinal wave in an isotropic medium is also a new wave, for if no spatial dispersion is taken into account we have not a root but a single discrete oscillation. In general it should be noted that the appearance of new waves — new roots of the dispersion equation — is an obvious and well-known consequence of the inclusion of spatial dispersion.

2. In an article by one of the authors<sup>[5]</sup>, as in Pekar's first paper<sup>[7]</sup>, only dipole lines were considered. In this case account of spatial dispersion in crystal optics is included in its entirety by expanding the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  or  $\epsilon_{ij}^{-1}(\omega, \mathbf{k})$  in powers of  $k_i$ , retaining only the first essential terms of the series. However, if we consider quadrupole or higher multiple transitions, it may become necessary to represent  $\epsilon_{ij}$  or  $\epsilon_{ij}^{-1}$  as a ratio of two polynomials in  $k_i$ . This was mentioned in [8] and in greater detail in I. It is important that from our point of view the functions  $\epsilon_{ij}(\omega, \mathbf{k})$  and  $\epsilon_{ij}^{-1}(\omega, \mathbf{k})$  can be regarded in crystal optics as having no essential singularities or branch points. Yet in the articles by Pekar<sup>[7, 25]</sup> and others the "mechanical excitons" chosen were exact solutions of the Coulomb problem ("Coulomb excitons") which in some cases (for "fictitious" longitudinal waves) have singularities at  $\mathbf{k} = 0$ . An impression remains therefore that the functions  $\epsilon_{ij}$  and  $\epsilon_{ij}^{-1}$  can also have essential singularities at  $\mathbf{k} = 0$ .

The foregoing will permit the reader to judge the extent to which the remark made at the end of the paper<sup>[90]</sup>, concerning the "contradiction" between the deductions of [5] and the data of [76] concerning the new wave near the quadrupole absorption line is unfounded. The questions of absorption or of the new wave near the quadrupole line are discussed in Secs. 3c and 3f of the present article.

3. In Sec. 3f of the present article we pointed out that absorption near the dipole line in anthracene, investigated in [74], should lead to attenuation of the new wave by at least a factor of  $10^6$ , even in a film with thickness  $d = 0.1 \mu$ . We therefore cannot see how the oscillations observed in [74] can be related with the occurrence of a new wave, unless a radical change takes place in the parameters (we know of no grounds for this). In the article<sup>[90]</sup>, however, this important item was circumvented by complete silence in the discussion of the experiments of [74].

Recently S. I. Pekar published still another review article<sup>[91]</sup> devoted to the same problems. We cannot dwell on it here. One of us hopes to demonstrate in an article in "Fizika tverdogo tela" (Solid State Physics) the incorrectness of many statements made ... in [91].

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Corrections to Part 1 of the Review [UFN 76, 643 (1962), Soviet Phys. Uspekhi 5, 323 (1962)].

In Table II (p. 341) in the column "principal axes of the tensor" it is shown which axes are fixed from symmetry considerations. This, of course, does not always pertain to the principal axes of the second-rank tensor  $\epsilon_{ij}(\omega)$ . For example, for cubic crystals this tensor has the form  $\epsilon_{ij} = \epsilon\delta_{ij}$  in any coordinate frame. We hope that this does not lead to misunderstandings, inasmuch as everything is essentially explained in the text of the article.

On p. 327 (second line below Fig. 1) it should read  $\epsilon_y(\omega_{\parallel})$  in lieu of  $\epsilon_y(\omega)$ .

On p. 332 [fourth line following Eq. (1.22a)]: printed (1.23), should be (1.22a).

On p. 333 [first line following Eq. (1.32)]: printed "indices  $\epsilon'_{\perp}$  and . . ." should be (quantities  $\epsilon'_{\perp}$  and . . .").

On p. 334. The fifth, sixth, and seventh lines following Table I are superfluous.

On p. 335. Eq. (1.49). Printed  $\frac{\partial B^2}{\partial t 4\pi}$ , should read  $\frac{\partial B^2}{\partial t 8\pi}$ .

On p. 342 (last line of left column). Printed  $\begin{pmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_2 & 0 \\ 0 & 0 & \epsilon_3 \end{pmatrix}$ , should read  $\begin{pmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_1 & 0 \\ 0 & 0 & \epsilon_3 \end{pmatrix} = \begin{pmatrix} \epsilon_{\perp} & 0 & 0 \\ 0 & \epsilon_{\perp} & 0 \\ 0 & 0 & \epsilon_{\parallel} \end{pmatrix}$ .

On p. 337. In place of  $\epsilon_{ij}$  formula (1.66) should contain everywhere  $\epsilon_{ij}$ .

Translated by Z. Barnea and J. G. Adashko