

# Effects of the internal field in the spectra of molecular crystals and the theory of excitons

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It is shown that a very large set of optical properties of molecular crystals (pure crystals, crystals containing impurities, and crystalline solutions) in the region of the lowest singlet electronic (or vibrational) excited states, where the mutual interaction of the molecules does not violate their neutrality, can be treated without bringing in exciton concepts, but by generalizing to anisotropic media the methods of molecular optics that had been developed before Frenkel's ideas on the exciton had appeared. This treatment is based on using the method of the acting field, which goes back to Lorentz, and also on the results of Born and Ewald *et al.*, which permit one to calculate the electric field acting on some particular molecule in the crystal, and in particular, with account taken of the higher multipoles of the polarizability of the molecules. It is shown that this approach permits one to calculate the dielectric constant of the crystal with account taken of spatial dispersion, to treat the polarization and splitting of light-absorption bands in crystals, and polarization of impurity absorption bands, as well as an entire series of other problems that were previously studied in less general form only within the framework of the Frenkel exciton theory. The limits of applicability of the presented approach are also discussed.

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## 1. INTRODUCTION. THE ACTING-FIELD METHOD

As we know, the properties of long-wavelength normal electromagnetic waves in condensed media can most easily be studied within the framework of macroscopic electrodynamics, which is based on using the dielectric-constant tensor  $\epsilon_{ij}(\omega, \mathbf{k})$ . However, to calculate this tensor for any particular medium is already a problem of microtheory. In particular, the methods for calculating the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  for the exciton region of the spectrum in crystals are discussed in the monographs<sup>[1,2]</sup>. These methods are based on using the different types of exciton states of the crystal (Coulomb or mechanical excitons). When one finds a linear response to an external electromagnetic perturbation, these are treated as the states of the zero-order approximation. Of course, the methods mentioned above are rather general. However, this does not imply that a knowledge of the exciton states of the crystal is obligatory in general for calculating the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$ . We shall explain below what we have stated, in treating, for the sake of definiteness, molecular crystals (pure crystals, crystals containing impurities, and crystalline solutions) in the region of the lowest singlet electronic (or vibrational) intramolecular excited states, where their mutual interaction does not violate the neutrality of the molecules. In this case, the intermolecular interaction is purely classical in nature, and it is determined by the van der Waals forces, which only lead to mixing of the molecular configurations.<sup>[2]</sup>

We note that a vast number of studies has been devoted to treating such media. They include both experi-

mental and theoretical studies, and they fundamentally form the content of an entire branch of molecular optics: the optics of molecular crystals and molecular liquids. Even before Frenkel's ideas on the exciton had appeared, an entire series of theoretical methods of describing optical phenomena, both exact and approximate, had been developed within the framework of this branch of optics. Many of them were also confirmed experimentally. However, after excitons had been discovered, these methods began to be used more and more rarely, and many of the results that had been obtained thereby were not sufficiently acknowledged within the framework of exciton theory. This circumstance resulted in suspending the process of their further development and generalization. On the other hand, owing to the underrating of the results of preexcitonic molecular optics, the optical properties of crystals have been discussed only in the language of exciton theory, even in cases in which this could be done considerably more simply by using the earlier, simpler, and no less pictorial physical concepts. Of course, this situation could not be reflected in the development of the theory of optical properties of crystals, and this article is precisely devoted to trying to analyze it. Fundamental attention will be paid herein to calculating the dielectric-constant tensor of crystals that consist of identical or different molecules, and to discussing their optical properties (dispersion and light absorption).

One can use the acting-field method to find the dielectric-constant tensor of this type of system. This method goes back to Lorentz, and it led him to the well-known

formula for the refractive index for light in isotropic media (the Lorentz-Lorenz formula). Let us recall the derivation of this formula.

According to Lorentz, the electric field  $E'$  that acts on an arbitrary molecule in isotropic media, and which causes it to be polarized, is not equal to the mean (macroscopic) field  $E$ , which satisfies the phenomenological Maxwell equations, but is determined by the relationship

$$E' = E + \frac{4\pi}{3} P = \frac{\epsilon + 2}{3} E,$$

Here  $P$  is the polarization per unit volume,  $P = (\epsilon - 1)E/4\pi$ , and  $\epsilon$  is the dielectric constant of the medium. On the other hand, since the polarization per unit volume  $P = N_0 a E'$  (where  $a$  is the polarizability of the molecule, and  $N_0$  is the number of molecules per unit volume), the induction vector  $D$  is determined by the relationship

$$D = E + 4\pi P = \left[ 1 + \frac{4\pi}{3} N_0 a (\epsilon + 2) \right] E = \epsilon E,$$

which directly implies the Lorentz-Lorenz formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} N_0 a.$$

However, even for cubic crystals consisting of isotropic molecules that interact with one another by van der Waals forces, this formula, which expresses the dielectric constant of the medium in terms of the polarizability of an individual molecule, is highly approximate. In particular, it takes no account whatever of spatial dispersion. Moreover, it does not consider the contribution of the higher multipoles of the molecule to the energy of intermolecular interaction, which immediately causes the optical properties of the crystal to differ from those of molecules in rarefied gases.

We shall show below (see Chap. 2 and Appendix 1) how these inaccuracies of the Lorentz-Lorenz formula can be eliminated. Moreover, by using the acting-field method, we shall generalize this formula to the case of anisotropic molecular crystals of complex structure, and we shall discuss an entire series of their optical properties that have previously been treated in less general form only within the framework of the exciton theory.

Here we shall merely show how one can find the dielectric-constant tensor of an anisotropic molecular crystal by using the acting-field method, with account taken of spatial dispersion.

Let the unit cell of the crystal contain  $\sigma$  identical molecules that are differently oriented with respect to the crystallographic axes. As a plane electromagnetic wave of amplitude  $E(\omega, k)$  propagates in the crystal, according to Born and Ewald (see [3], Sec. 30), the electric field  $E^\alpha$  acting on the molecule  $\alpha$  is not equal to the mean field, but is determined by the relationship

$$E_i^\alpha = E_i + \sum_{\beta j} Q_{ij}^{\alpha\beta}(k) p_j^\beta, \quad (1)$$

Here  $p^\alpha$  is the amplitude of the dipole moment induced in the molecules of type  $\alpha$ , and the coefficients  $Q_{ij}^{\alpha\beta}(k)$  (the internal-field coefficients) are determined by the crystal structure alone. If  $a_{ij}^\alpha(\omega)$  is the polarizability of the molecule when in orientation  $\alpha$  (we assume here and everywhere below for simplicity that the molecules have no static dipole moments<sup>1)</sup>), then

$$p_i^\alpha = a_{ij}^\alpha(\omega) E_j. \quad (2)$$

If we substitute (2) into (1), we get the relationship

$$E_i^\alpha = E_i + \sum_{\beta j} Q_{ij}^{\alpha\beta}(k) a_{ij}^\beta(\omega) E_j^\beta, \quad (3)$$

which permits us to express the local fields  $E^\alpha$  in terms of  $E$ :

$$E_i^\alpha(\omega, k) = A_{ij}^\alpha(\omega, k) E_j(\omega, k). \quad (4)$$

A knowledge of the tensor  $A_{ij}^\alpha$  leads directly to an expression for the dielectric-constant tensor of the crystal. In fact, if we take account of the fact that the polarizability per unit volume is

$$P_i = \frac{1}{v} \sum_{\alpha j} a_{ij}^\alpha E_j^\alpha = \frac{1}{v} \sum_{\alpha j} a_{ij}^\alpha A_{jk}^\alpha E_k, \quad (5)$$

where  $v$  is the volume of the unit cell, we get the following for the tensor  $\epsilon_{ij}(\omega, k)$ :

$$\epsilon_{ij}(\omega, k) = \delta_{ij} + \frac{4\pi}{v} \sum_{\alpha j} a_{ij}^\alpha A_{jk}^\alpha. \quad (6)$$

Eq. (6) permits us very simply to treat the problem of how the internal-field correction affects the optical properties of crystals. It seems pertinent to discuss this problem, since there is a great confusion in the existing scientific literature on this topic. Many journal articles and even monographs have taken no account at all of the differing nature of the effect of the internal-field corrections in pure crystals and in crystals containing impurities. There are also studies conducted within the framework of the microscopic exciton theory in which the elementary manifestations of the internal-field effects, etc., were not distinguished in interpreting the results.

Along with the problems mentioned above, we shall discuss below the optical properties of mixed crystalline solutions, we shall account for certain effects of spatial dispersion of the medium in treating the optical properties of an impurity, and we shall also touch upon the theory of resonance interaction of impurity molecules with one another. Here we shall only note that, when we used in Eq. (2) a tensor  $a_{ij}^\alpha$  which does not depend on  $k$  to express the polarizability of an individual molecule, we thus restricted ourselves to accounting only for the dipole polarization of the molecule. This approximation is fully justified when we are dealing with the optical properties of a non-gyrotropic crystal in a region of resonances of the molecule that have large enough oscillator strengths. However, this approximation is in no way fundamental for the entire subsequent presentation.<sup>2)</sup> Since we assume below that the polarizability of the molecule in vacuo is known, we might use the more general expression  $a_{ij}^\alpha(\omega, k)$  for it in Eq. (2). Of course, here we would have to include in the internal-field expression also other terms besides the term given in [3], which corresponds to the internal field of the dipoles in the lattice. These additional terms correspond to the internal field in the lattice of the quadrupoles, octupoles, etc. The electric field created by these multipoles declines with distance more rapidly than the dipole field. Thus the well-known difficulties in summing the series, as were so successfully overcome by Ewald for a lattice of dipoles, no longer arise in distinguishing their internal fields. This fact makes the procedure of distinguishing the internal field for the higher multipoles more or less trivial. In this regard, moreover, we shall spend no further time on it, just as for the dipoles.<sup>3)</sup>

Thus, the abovesaid implies that it is completely unsuitable to use in Eq. (2) the tensor  $a_{ij}^{\alpha}(\omega)$  instead of the tensor  $a_{ij}^{\alpha}(\omega, \mathbf{k})$  in a region of dipole-forbidden transitions. In this regard, while discussing below for the sake of simplicity the optical properties of non-gyrotropic pure and impure crystals, we shall always be considering only the spectral region of dipole-allowed transitions. As we have emphasized, a more general treatment can be conducted in an analogous way (see Appendix 1).

## 2. THE DIELECTRIC CONSTANT OF CUBIC CRYSTALS

As has been shown in the book [3], in cubic crystals with one molecule per unit cell with neglect of spatial dispersion, the tensor  $Q_{ij}^{\alpha\beta}$  is reduced to the scalar  $Q_{ij} = (4\pi/3v)\delta_{ij}$ , where  $v$  is the volume of the unit cell. Since in addition  $a_{ij} = a\delta_{ij}$ , Eq. (3) implies that the tensor  $A_{ij} = A\delta_{ij}$ , where  $A = [1 - (4\pi a/3v)]^{-1}$ . If we substitute this relationship into (6), we find that  $\epsilon_{ij} = \epsilon\delta_{ij}$ , where

$$\epsilon(\omega) = 1 + \frac{4\pi}{v} a \left(1 - \frac{4\pi}{3v} a\right)^{-1}, \quad (7)$$

so that  $A = (\epsilon + 2)/3$ . Eq. (7) directly gives rise to the Lorentz-Lorenz relationship

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3v} a. \quad (7a)$$

Let us consider the dispersion of the quantity  $\epsilon$ , taking into account only one of the resonances of  $a(\omega)$ . In this approximation,

$$a(\omega) = \frac{f_1}{\omega_1^2 - \omega^2}, \quad f_1 = \frac{2p_1^2\omega_1}{h}. \quad (8)$$

Here  $\omega_1$  is the frequency of the  $0 \rightarrow 1$  transition in the isolated molecule, and  $p_1$  is the corresponding dipole moment of the transition. Upon substituting (8) into (7), we find that

$$\epsilon(\omega) = 1 + \frac{(4\pi/v)f_1}{\omega_1^2 - \omega^2 - (8\pi/3v) p_1^2\omega_1}. \quad (9)$$

This relationship implies that accounting for the internal-field correction, i.e., for the fact that  $A \neq 1$ , does not change the oscillator strength of the transition, but only shifts the resonance frequency: the resonance  $\epsilon(\omega)$  proves to be shifted to lower frequencies than that of the transition in the isolated molecule by the amount

$$\Delta\omega = \frac{4\pi}{3vh} p_1^2.$$

One can take account of attenuation by adding to the denominator of (9) the imaginary term  $i\delta(\omega)$ . Since  $\epsilon = (n - i\kappa)^2$ , where  $n$  and  $\kappa$  are the refraction and absorption indices, for small  $\delta \rightarrow 0$  we get the following expression for the integral  $\int_{-\infty}^{+\infty} 2n\kappa d\omega$  (see also, e.g., [1]):

$$\int_{-\infty}^{+\infty} 2n(\omega)\kappa(\omega) d\omega = \frac{2\pi^2 f_1}{\omega_1 v}. \quad (10)$$

The expression for  $\kappa(\omega)$  itself in this case has the form

$$\kappa(\omega) = \frac{(2\pi/v) f_1 \delta(\omega)}{(\omega_1^2 - \omega^2)^2 + \delta^2(\omega)} \frac{1}{n(\omega)}, \quad (10a)$$

where  $\omega_1^2 = \omega_1^2 - (4\pi/3v)f_1$ .

Let us now proceed to the case of a crystal having

some amount of substitutional impurity molecules (the generalization to the case of interstitial impurities is trivial). Evidently, here the internal field depends on the volume distribution of impurities. If we neglect the fluctuations of this distribution and replace the internal field with its mean value, we get<sup>4)</sup>

$$\epsilon(\omega) = 1 + 4\pi N_0 a(\omega) \frac{\epsilon + 2}{3} + 4\pi N_1 [\tilde{a}(\omega) - a(\omega)] \frac{\epsilon + 2}{3}, \quad (11)$$

Here  $N_0 \equiv 1/v$ , and  $N_1$  is the concentration of impurity molecules. If  $\delta\epsilon$  is a small variation in the quantity  $\epsilon$ ,  $\delta\epsilon \sim N_1$ , then we find from (11) that

$$\delta\epsilon = \left(1 - \frac{4\pi N_0 a}{3}\right)^{-1} 4\pi N_1 (\tilde{a} - a) \frac{\epsilon_0 + 2}{3},$$

Here  $\epsilon_0 = \epsilon$  when  $N_1 = 0$ . Hence (see also (7a)),

$$\epsilon(\omega) = \epsilon_0(\omega) + 4\pi N_1 [\tilde{a}(\omega) - a(\omega)] \left(\frac{\epsilon_0 + 2}{3}\right)^2. \quad (12)$$

Bearing in mind (7a), we can also represent this relationship in the form

$$\epsilon(\omega) = \epsilon_0 - \frac{\rho}{3} (\epsilon_0 + 2) (\epsilon_0 - 1) + 4\pi N_1 \tilde{a}(\omega) \left(\frac{\epsilon_0 + 2}{3}\right)^2, \quad (12a)$$

where  $\rho = N_1 v$ .

If we assume that the following relation holds for the impurity molecule instead of (8) (with account taken of attenuation):

$$\tilde{a}(\omega) = \frac{2p_1^2 \tilde{\omega}_1 / h}{\omega_1^2 - \omega^2 + i\delta}$$

and that the frequency  $\tilde{\omega}_1$  lies in a region of transparency of the solvent, we find for frequencies  $\omega \sim \tilde{\omega}_1$  that

$$2n\kappa = 8\pi N_1 \left(\frac{\epsilon_0 + 2}{3}\right)^2 p_1^2 \frac{\tilde{\omega}_1 \delta / h}{[(\omega_1)^2 - \omega^2]^2 + \delta^2}, \quad (10b)$$

Thus the integration in the region of an absorption band  $\omega \sim \tilde{\omega}_1$  gives

$$\int 2n\kappa d\omega = 4\pi^2 N_1 \left(\frac{\epsilon_0(\tilde{\omega}_1) + 2}{3}\right)^2 \frac{p_1^2}{h}. \quad (13)$$

Thus the absorption coefficient of light by an impurity existing in a medium of dielectric constant  $\epsilon_0(\omega)$  and the integral on the left-hand side of Eq. (13) (the Kravets integral) are proportional to the square of the Lorentz factor. The change in the oscillator strength formally implies that, instead of the transition dipole moment  $p_1$ , the impurity acquires under the influence of the light a certain new effective value of this quantity  $(\tilde{p}_1)_{\text{eff}} = p_1[(\epsilon_0 + 2)/3]$ . Since the experimentally measurable quantity in Eq. (13) is its left-hand side, a correct account of the internal-field correction (in this case, an account for the Lorentz factor) permits one to reconstruct the oscillator strength for the isolated molecule from data on the dispersion and absorption by the molecule in solution. Of course, the abovesaid is valid (a fact well known and used) only in cases when no chemical bonds arise between the molecules of the solute and the solvent, no aggregates of impurity molecules are formed, etc.

However, a two-level scheme has been used above for the molecules of the impurity and the solvent. Hence we can naturally discuss the problem of how the existence of many resonances of polarizability of the molecules will affect the conclusions drawn above. The relation (12) derived above does not assume that the mole-

cules of the solvent or the impurity are described by a two-level scheme. Hence this relation remains valid also when we include many resonances. Only the right-hand side of Eq. (13) is altered. Namely, when we include many levels,  $i = 1, 2, \dots$ , it is converted into a sum of contributions from the individual resonances:

$$\sum_i 4\pi^2 N_i \left( \frac{\epsilon_0(\omega_i) + 2}{3} \right)^2 \frac{\tilde{P}_i^2}{h}. \quad (13a)$$

Now let us proceed to the case of a crystal without impurities, and for the sake of simplicity, let us assume that the molecules of the crystal in the isolated state are characterized by the polarizability

$$a(\omega) = a_0 + a_1(\omega), \quad (14)$$

where the function  $a_1(\omega)$  corresponds to Eq. (8), while the quantity  $a_0$  is determined by the contribution to the polarizability from distant resonances. The latter can be considered to be a constant quantity independent of  $\omega$  in the frequency region  $\omega \approx \omega_1$ . If we substitute (14) into (7), we get the following expression for the tensor  $\epsilon(\omega)$  in the case being treated:

$$\epsilon(\omega) = \epsilon_b + \frac{(4\pi/v) f_1 [(\epsilon_b + 2)/3]^2}{\omega_1^2 - \omega^2}, \quad (15)$$

Here

$$\epsilon_b = 1 + \frac{4\pi}{v} a_0 \left( 1 - \frac{4\pi}{3v} a_0 \right)^{-1} \quad (16)$$

is what (see also (7)) the dielectric constant of the crystal would have been if the polarizability of its constituent molecules had lacked the resonance term at the frequency  $\omega_1$  (i.e.,  $a_1(\omega) \equiv 0$ ). Now the value of the resonance frequency  $\omega_1$  that figures in (15) is determined by the relationship

$$\omega_1^2 = \omega_1^2 - \frac{4\pi}{3v} f_1 \left( \frac{\epsilon_b + 2}{3} \right).$$

If we introduce a weak attenuation into (15), then we get the following equation instead of (10):

$$2 \int n(\omega) \kappa(\omega) d\omega = \frac{2\pi^2}{v\omega_1} f_1 \left( \frac{\epsilon_b + 2}{3} \right)^2. \quad (17)$$

We might call the quantity  $\epsilon_b$  the background dielectric constant with respect to the resonance at the frequency  $\omega_1$ . Since generally  $\epsilon_b \neq 1$ , the existence of the background dielectric constant alters the oscillator strength of the transition. This is especially important in a spectral region of low-intensity transitions.

If the molecule has two or more close resonances in the studied frequency region, then in (14) we must also distinguish terms  $a_2(\omega)$ ,  $a_3(\omega)$ , etc., in addition to the terms indicated there. It is also elementary to take them into account, although this leads to somewhat less pictorial formulas for  $\epsilon(\omega)$ .

Equations (15) and (17), which are special cases of the more general relationships derived in the book [2], show how, for the crystal model being discussed, the mixing of molecular configurations due to intermolecular interaction in the crystal affects the oscillator strength of dipole transitions. However, the fact of importance to us here is only that these relationships substantially differ from the analogous relationships (13) and (13a) for impurity molecules in solutions. Whenever we are dealing with impurity molecules in a solution, the dielectric constant of the solvent at the transition frequency of the impurity figures in the

Lorentz factor on the right-hand side of Eq. (13). However, for pure substances (see (17)), the background dielectric constant replaces this quantity in the Lorentz factor, and is not at all equal to the square of the index of refraction of light in the crystal at the transition frequency. However, in the two-level approximation in general,  $\epsilon_b = 1$ ; then Eq. (15) goes over into (9), and (17) into (10).

Finally we note that Eq. (7a) can be used (see [5]) to find resonances of molecular polarizability from data on dispersion and light absorption in the crystal. Since  $\epsilon = (n - i\kappa)^2$ , where  $n$  and  $\kappa$  are the refractive and absorption indices of light in the crystal, Eq. (7a) implies that

$$\text{Im } a(\omega) = \frac{9n\kappa/2\pi N_0}{(n^2 - \kappa^2 + 2)^2 + 4n^2\kappa^2},$$

where  $N_0$  is the number of molecules per unit volume. As was shown in [5] for a number of examples, the maximum of the function  $\text{Im } a(\omega)$ , which is proportional to the molecular absorption coefficient, can be shifted quite substantially with respect to the maxima of  $\kappa(\omega)$ . However, we should note that this way of finding the molecular frequencies can be justified only when we are dealing with the vicinity of rather intense dipole transitions and we can neglect the contribution of higher multipoles (see Appendix 1 for how the higher multipoles are taken into account).

### 3. THE DIELECTRIC CONSTANT OF ANISOTROPIC CRYSTALS

As an example of an anisotropic crystal, let us consider a molecular crystal having  $\sigma \geq 1$  molecules per unit cell. If we are interested in the optical properties of the crystal in the frequency range  $\omega \gtrsim \omega_1$ , where  $\omega_1$  is one of the intrinsic non-degenerate frequencies of dipole vibrations of the isolated molecule, then we can use the following relationship for its polarizability (see Chap. 6 for more general results):

$$a_{ij}(\omega) = \frac{f_1 l_i l_j}{\omega_1^2 - \omega^2}, \quad (18)$$

Here  $f_1$  is a quantity proportional to the oscillator strength of the  $0 \rightarrow 1$  transition, and  $l$  is a unit vector lying along the dipole-moment vector of the same transition. Since the different molecules in the unit cell differ in orientation, evidently their polarizability tensor is

$$a_{ij}^\alpha(\omega) = \frac{f_1 l_i^\alpha l_j^\alpha}{\omega_1^2 - \omega^2} \quad (\alpha = 1, 2, \dots, \sigma). \quad (18a)$$

If we substitute this relation into (3) and find its scalar product on the left with  $l^\alpha$ , we get the following system of  $\sigma$  equations for the quantities  $E^\alpha \cdot l^\alpha$  ( $\alpha = 1, 2, \dots, \sigma$ ):

$$(E^\alpha l^\alpha) - \sum_\beta M_{\alpha\beta}(\omega, \mathbf{k}) (E^\beta l^\beta) = (E l^\alpha), \quad (19)$$

where

$$M_{\alpha\beta}(\omega, \mathbf{k}) = \frac{f_1}{\omega_1^2 - \omega^2} \sum_{ij} Q_{ij}^{\alpha\beta}(\mathbf{k}) l_i^\alpha l_j^\beta. \quad (20)$$

For a crystal with one molecule per unit cell, we find directly from (19) that

$$(E^1 l^1) = [1 - M_{11}(\omega, \mathbf{k})]^{-1} (E l^1),$$

so that the polarization per unit volume is

$$P_i = \frac{1}{v} a_{ij}^{(1)}(\omega) E_j^{(1)} = \frac{f_1 l_i^{(1)} l_j^{(1)}}{v(\omega_1^2 - \omega^2)} \frac{E_j}{1 - M_{11}(\omega, \mathbf{k})}.$$

By using this relationship as well as (20), we get the following expression for the dielectric-constant tensor  $\epsilon_{ij}^0(\omega, \mathbf{k})$ :

$$\epsilon_{ij}^0(\omega, \mathbf{k}) = \delta_{ij} + \frac{(4\pi f_1/v) l_i l_j}{\omega_1^2 - \omega^2 - f_1 \sum_{i_1 j_1} Q_{i_1 j_1}(\mathbf{k}) l_{i_1} l_{j_1}} \quad (21)$$

The resonance of this expression occurs at  $\omega = \Omega_1(\mathbf{k})$ , where

$$\Omega_1^2(\mathbf{k}) = \omega_1^2 - f_1 \sum_{i_1 j_1} Q_{i_1 j_1}(\mathbf{k}) l_{i_1} l_{j_1} \quad (22)$$

The tensor (21) corresponds to a uniaxial crystal. If one of the coordinate axes, e.g., the x axis, lies along  $\mathbf{l}$ , the tensor (21) is reduced to diagonal form with the following non-zero components:

$$\epsilon_x = \epsilon_3 = 1 \text{ and } \epsilon_y = \epsilon_z = 1 + \frac{4\pi f_1/v}{\omega_1^2 - \omega^2} (1 - M_{11})^{-1}.$$

Now let us proceed to treating crystals having two molecules per unit cell. The optical properties of this type of molecular crystals have currently been studied in especial detail, and this is precisely the group that includes the crystals of anthracene, naphthalene, and many others of the aromatic series, with which the overwhelming majority of the most competent experimental studies have been concerned. Crystals of the anthracene type possess symmetry operations that transform molecules with  $\alpha = 1$  into molecules with  $\alpha = 2$ . Hence, when  $\mathbf{k} = 0$ , or when vectors  $\mathbf{k} \neq 0$  lie parallel or perpendicular to the monoclinic axis, the relationships hold that  $M_{11}(\omega, \mathbf{k}) = M_{22}(\omega, \mathbf{k})$ , and  $M_{12}(\omega, \mathbf{k}) = M_{21}(\omega, \mathbf{k})$ . It is less cumbersome to solve the system of equations (19) for such values of  $\mathbf{k}$ . We can easily convince ourselves that in this case

$$\langle \mathbf{E}^{(\alpha)} | \mathbf{I}^{(\alpha)} \rangle = \frac{1}{2} \left[ \frac{L_j^{(\alpha)}}{1 - M_{11}(\omega, \mathbf{k}) - M_{12}(\omega, \mathbf{k})} - \frac{(-1)^\alpha L_j^{(\alpha)}}{1 - M_{11}(\omega, \mathbf{k}) + M_{12}(\omega, \mathbf{k})} \right] E_j \quad (\alpha = 1, 2), \quad (23)$$

where

$$L^{(1)} = I^{(1)} + I^{(2)}, \quad L^{(2)} = I^{(1)} - I^{(2)}. \quad (23a)$$

If we substitute these relationships into the expression for the polarization  $\mathbf{P}$  (see (5)), we also find an expression for the dielectric-constant tensor<sup>5)</sup>:

$$\epsilon_{ij}(\omega, \mathbf{k}) = \delta_{ij} + \frac{2\pi}{v} f_1 \left[ \frac{L_i^{(1)} L_j^{(1)}}{\Omega_1^2(\mathbf{k}) - \omega^2} + \frac{L_i^{(2)} L_j^{(2)}}{\Omega_2^2(\mathbf{k}) - \omega^2} \right], \quad (24)$$

where

$$\begin{aligned} \Omega_1^2(\mathbf{k}) &= \omega_1^2 - f_1 \sum_{ij} Q_{ij}^{(1)}(\mathbf{k}) l_i^{(1)} l_j^{(1)} - f_1 \sum_{ij} Q_{ij}^{(2)}(\mathbf{k}) l_i^{(2)} l_j^{(2)}, \\ \Omega_2^2(\mathbf{k}) &= \omega_1^2 - f_1 \sum_{ij} Q_{ij}^{(1)}(\mathbf{k}) l_i^{(2)} l_j^{(2)} + f_1 \sum_{ij} Q_{ij}^{(2)}(\mathbf{k}) l_i^{(1)} l_j^{(1)}. \end{aligned} \quad (25)$$

Since the quantities  $Q_{ij}^{\alpha\beta}(\mathbf{k})$  are analytic functions of  $\mathbf{k}$ , this same property holds also for the frequencies  $\Omega(\mathbf{k})$  (see also (22)). Of course, the abovesaid is not remarkable. As has been emphasized in<sup>11)</sup>, the resonances of the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  occur at the so-called mechanical-exciton frequencies, which are analytic functions of  $\mathbf{k}$ , regardless of the model. The vectors  $L^{(1)}$  and  $L^{(2)}$  are orthogonal. Hence, if e.g., the x and y coordinate axes lie along the directions of  $L^{(1)}$  and  $L^{(2)}$ , the tensor  $\epsilon_{ij}$  proves to be reduced to diagonal form with the following non-zero components:

$$\left. \begin{aligned} \epsilon_{xx}(\omega, \mathbf{k}) &= 1 + \frac{2\pi}{v} \frac{F_1}{\Omega_1^2(\mathbf{k}) - \omega^2}, \\ \epsilon_{yy}(\omega, \mathbf{k}) &= 1 + \frac{2\pi}{v} \frac{F_2}{\Omega_2^2(\mathbf{k}) - \omega^2}, \\ \epsilon_{zz}(\omega, \mathbf{k}) &= 1, \quad F_1 = f_1 |L^{(1)}|^2, \quad F_2 = f_1 |L^{(2)}|^2. \end{aligned} \right\} \quad (26)$$

These relationships imply that absorption of light propagating along the z axis with a direction of electric vector  $\mathbf{E} \parallel L^{(1)}$  must occur at the frequency  $\Omega_1(\mathbf{k})$ . However, if the direction of the electric vector  $\mathbf{E} \parallel L^{(2)}$ , light absorption occurs at  $\omega = \Omega_2(\mathbf{k})$ . Thus, although we have assumed the vibration in the isolated molecule at the frequency  $\omega_1$  to be non-degenerate, the absorption spectrum of a crystal containing two molecules per unit cell should exhibit two differently polarized light absorption lines.<sup>9)</sup> This phenomenon (Davydov splitting) has now been studied in many objects. Interestingly, although Davydov discovered it upon generalizing Frenkel's exciton theory to the case of crystals having several molecules, the theory of excitons of small radius was not necessary for understanding it, nor for explaining the well-known experiments of Obreimov and Prikhot'ko and their associates. As was shown above, it sufficed merely to generalize the Lorentz-Lorenz formula to the case of anisotropic crystals in order to do this. This cannot be said about exciton spectra in semiconductors. As we know, it has required the creation of the theory of excitons of large radius to explain them. Of course, the abovesaid in no way diminishes the significance of the development of the theory of excitons of small radius, as stimulated by the studies of Frenkel', Peierls, Davydov, etc. As we know, only within the framework of this theory can one to some extent discuss such a phenomenon as transport of electronic excitation energy in crystals, or optical properties of crystals at high excitation levels, or nonlinear optical effects, or fine details of the structure of light absorption and luminescence spectra in crystals, and many other matters.

Let us now continue to discuss the optical properties of crystals in the region of impurity light absorption. Above, in Chap. 2, we considered only cubic crystals. However, here we shall study anisotropic crystals by using the equations derived above relating the acting field to the mean field. In speaking of the optics of impurity centers in crystals, we should bear in mind the fact that, although this branch of solid state physics already has a rich history, interest in it is still not slackening. And this arises not only from the fact that many crystals containing impurities are used as materials for inventing optical devices, but also from the discovery of an optical analog of the Mössbauer effect (the Shpol'skiĭ effect), from capture of excitons by impurities, and from many other interesting optical phenomena. To analyze them would exceed the limits of this methodological remark. Yet, returning to its main theme, let us now discuss the problem of how the dielectric properties of the matrix affect the optical properties of an impurity in an anisotropic medium.

#### 4. THE DIELECTRIC CONSTANT OF MIXED CRYSTALLINE SOLUTIONS AND THE POLARIZATION OF IMPURITY ABSORPTION BANDS

Let us begin again with a very simple model of a crystal in which the polarizability of the molecules of the main substance in vacuo is determined by Eq. (18a). However, for the sake of simplicity, we shall consider the impurity to be a substitutional impurity for which the polarizability tensor  $\tilde{a}_{ij}^{\alpha}(\omega)$  differs from (18a) only in the value of the resonance frequency and the oscillator strength, so that

$$\tilde{a}_{ij}^{\alpha}(\omega) = \frac{\tilde{f}_1^{(\alpha)} l_i^{(\alpha)} l_j^{(\alpha)}}{(\omega_1)^2 - \omega^2}. \quad (27)$$

If we assume that the impurity is uniformly distributed, the acting field on the average can be approximately represented as follows (the mean-polarizability approximation):

$$E_i^\alpha = E_i + \sum_{\beta} Q_{ij}^{\alpha\beta}(\mathbf{k}) \bar{p}_j^\beta, \quad (28)$$

Here  $\bar{p}^\beta$  is the mean polarization of the site  $\beta$ :

$$\bar{p}^\beta = (1-c) a_{ij}^\beta E_j^\beta + c \bar{a}_{ij}^\beta E_j^\beta, \quad (29)$$

and  $c$  is the ratio of the number of impurity molecules to the total number of molecules in the crystal. Now, upon using (28), (29), (18), and (27), we get an equation for the quantities  $E^\alpha \cdot l^\alpha$ , with  $\alpha = 1, 2, \dots, \sigma$ , analogous to Eq. (19). We can easily convince ourselves that this equation has the form

$$(E^\alpha l^\alpha) - \sum_{\beta} \bar{M}_{\alpha\beta}(\omega, \mathbf{k}) (E^\beta l^\beta) = (l^\alpha E), \quad (30)$$

where

$$\bar{M}_{\alpha\beta}(\omega, \mathbf{k}) = \sum_{ij} Q_{ij}^{\alpha\beta}(\mathbf{k}) l_i^\alpha l_j^\beta \left[ \frac{(1-c) f_i}{\omega_i^2 - \omega^2} + \frac{c \tilde{f}_i}{\omega_i^2 - \omega^2} \right]. \quad (30a)$$

For crystals having one molecule per unit cell, the polarization per unit volume is

$$P_i = \frac{1}{v} [(1-c) a_{ij}^\beta(\omega) E_j^\beta + c \bar{a}_{ij}^\beta(\omega) E_j^\beta],$$

so that we get the following expression for the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$ :

$$\epsilon_{ij}(\omega, \mathbf{k}) = \delta_{ij} + \frac{4\pi}{v} \left[ \frac{(1-c) f_i}{\omega_i^2 - \omega^2} + \frac{c \tilde{f}_i}{(\omega_i^2 - \omega^2)} \right] [1 - \bar{M}_{ii}(\omega, \mathbf{k})]^{-1} l_i l_j. \quad (31)$$

When  $c \rightarrow 0$ , (31) goes over into (21). Here, however, we are interested in it for  $c \ll 1$ . Then it suffices to retain only the term linear in  $c$ , along with  $\epsilon_{ij}^0$ , in the power-series expansion of Eq. (31) in  $c$ . We can easily convince ourselves that here

$$\epsilon_{ij}(\omega, \mathbf{k}) = \epsilon_{ij}^0(\omega, \mathbf{k}) + 4\pi N_i [\tilde{a}_{ij}(\omega) - a_{ij}(\omega)] [1 + \xi(\epsilon_i^0 - 1)]^{\alpha}, \quad (32)$$

where  $\epsilon_{ij}^0(\omega, \mathbf{k})$  is the dielectric-constant tensor of the pure crystal as defined by Eq. (21), the coefficient is

$$\sum_{ij} v Q_{ij}(\mathbf{k}) l_i l_j, \text{ and } N_i = \frac{c}{v}.$$

Thus, Eq. (32) is analogous to the previously derived relationship (12a) for cubic crystals, and is a generalization of it to the case of an anisotropic crystal of the studied type.

Before we proceed to study a crystal having two molecules per unit cell, we note that the so-called mean-polarizability approximation, which permits one to treat an ideal crystal whose molecules have the mean polarizability of (29), in lieu of a disordered system of crystal plus impurity, is actually very old. In former times (see, e.g., [6], Sec. 6), the term for this approximation, as applied to systems composed of molecules in van der Waals interaction, was the "additive-refraction approximation." However, we emphasize that, although Eq. (31) is only a certain very convenient extrapolation, its accuracy increases with declining  $c$ , so that the linear term in  $c$  in (32) already proves to be exactly determined.

Now let us proceed to crystals of the anthracene type with two molecules per unit cell. Since the system of equations (30) differs from that of (19) only in the substitution  $M_{\alpha\beta}(\omega, \mathbf{k}) \rightarrow \bar{M}_{\alpha\beta}(\omega, \mathbf{k})$ , we can use (23) to write directly the values of the quantities  $E^\alpha \cdot l^\alpha$ , which satisfy the system of equations (30):

$$(E^\alpha l^\alpha) = \frac{1}{2} \left[ \frac{L_j^{(1)}}{1 - \bar{M}_{11} - \bar{M}_{12}} - \frac{(-1)^\alpha L_j^{(2)}}{1 - \bar{M}_{11} + \bar{M}_{12}} \right] E_j \quad (\alpha = 1, 2). \quad (33)$$

Moreover, since the dielectric-constant tensor of the studied system is determined by the relationship

$$\epsilon_{ij}(\omega, \mathbf{k}) E_j = E_i + \frac{4\pi}{v} (1-c) \sum_{\alpha} a_{ij}^\alpha E_j^\alpha + \frac{4\pi}{v} c \sum_{\alpha} \bar{a}_{ij}^\alpha E_j^\alpha, \quad (34)$$

we finally find by substituting (33) into (34) that

$$\epsilon_{ij}(\omega, \mathbf{k}) = \delta_{ij} + \frac{2\pi}{v} \left[ \frac{(1-c) f_i}{\omega_i^2 - \omega^2} + \frac{c \tilde{f}_i}{\omega_i^2 - \omega^2} \right] \times \left( \frac{L_i^{(1)} L_j^{(1)}}{1 - \bar{M}_{11}(\omega, \mathbf{k}) - \bar{M}_{12}(\omega, \mathbf{k})} + \frac{L_i^{(2)} L_j^{(2)}}{1 - \bar{M}_{11}(\omega, \mathbf{k}) + \bar{M}_{12}(\omega, \mathbf{k})} \right). \quad (35)$$

If we take (30a) into account, Eq. (35) completely defines the relation of the dielectric-constant tensor to the impurity concentration  $c$  in the studied approximation (the "additive-refraction approximation" or "mean-polarizability approximation"). Chapter 5 will take up the optical properties of mixed crystals at large concentrations  $c$ . Here, however, as we did earlier with crystals having one molecule per unit cell, we shall treat the case of small values of  $c$ , where we can omit the terms of order  $c^2$ ,  $c^3$ , etc. in expanding the tensor of (35) in powers of  $c$ . In this case, as (35) implies (henceforth we shall assume for simplicity that  $\tilde{f}_1 = f_1$ , as is justified for an isotopic mixture),

$$\epsilon_{ij}(\omega, \mathbf{k}) = \epsilon_{ij}^0(\omega, \mathbf{k}) + \frac{2\pi}{v} c f_i \left( \frac{1}{\omega_i^2 - \omega^2} - \frac{1}{\omega_i^2 - \omega^2} \right) \times \left[ \frac{L_i^{(1)} L_j^{(1)}}{(1 - \bar{M}_{11} - \bar{M}_{12})^2} + \frac{L_i^{(2)} L_j^{(2)}}{(1 - \bar{M}_{11} + \bar{M}_{12})^2} \right]. \quad (36)$$

Upon taking account of (20), we can easily convince ourselves that the term of the order of  $c/(\omega_i^2 - \omega^2)$  that figures in (36) identically vanishes as  $\omega \rightarrow \omega_1$  (an analogous situation happens also for the previously discussed cubic crystals and anisotropic crystals containing one molecule per unit cell; see (12a) and (32), respectively). Thus, in the frequency region of impurity absorption, i.e., absorption whose intensity is proportional to the concentration of the impurity, the only resonating term in (36) has the form

$$\delta \epsilon_{ij}(\omega, \mathbf{k}) = \frac{2\pi}{v} c \frac{f_i}{\omega_i^2 - \omega^2} \left[ \frac{L_i^{(1)} L_j^{(1)}}{(1 - \bar{M}_{11} - \bar{M}_{12})^2} + \frac{L_i^{(2)} L_j^{(2)}}{(1 - \bar{M}_{11} + \bar{M}_{12})^2} \right]. \quad (37)$$

However, if we recall what we have said in Chap. 2 about the role of the local-field correction in impurity spectra, we could write Eq. (37) directly without resorting to expansion of Eq. (35) in a power series in  $c$ . Actually, the transition dipole moment is  $p^\alpha = p l^\alpha$  in an isolated molecule of an isotopic impurity having the orientation  $\alpha$ . The effective value corresponding to this dipole moment must be determined by the condition

$$-p^\alpha E^\alpha = -p_{\text{eff}}^\alpha E. \quad (38)$$

Now, if we use Eq. (23), we find that

$$p_{\text{eff}}^\alpha = \frac{p}{2} \left( \frac{L^{(1)}}{1 - \bar{M}_{11} - \bar{M}_{12}} - \frac{(-1)^\alpha L^{(2)}}{1 - \bar{M}_{11} + \bar{M}_{12}} \right). \quad (39)$$

Since, on the other hand, by definition,

$$\delta \epsilon_{ij}(\omega, \mathbf{k}) = \frac{4\pi}{v} c \frac{f_i}{v^2} \sum_{\alpha} \frac{(p_{\text{eff}}^\alpha)_i (p_{\text{eff}}^\alpha)_j}{\omega_i^2 - \omega^2}, \quad (40)$$

a substitution of (39) into (40) immediately gives Eq. (37).

Equation (37) permits us to analyze the relation of the intensity of impurity absorption to the polarization of the incident light. Rashba has discussed this problem (see [7] and also [2]) within the framework of the theory of excitons of small radius, and precisely for im-

purities of the type being studied. For the crystal model under discussion, the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  proves to be reduced to diagonal form when the coordinate axes, e.g., the  $x$  and  $y$  axes, lie in the directions of the vectors  $\mathbf{L}^{(1)}$  and  $\mathbf{L}^{(2)}$ . In this case,

$$\left. \begin{aligned} \epsilon_{11}(\omega, \mathbf{k}) &= \epsilon_{xx}^0(\omega, \mathbf{k}) + \frac{2\pi}{v} c \frac{f_1}{\omega_1^2 - \omega^2 + i\delta} \frac{|\mathbf{L}^{(1)}|^2}{(1 - M_{11} - M_{12})^2}, \\ \epsilon_{22}(\omega, \mathbf{k}) &= \epsilon_{yy}^0(\omega, \mathbf{k}) + \frac{2\pi c}{v} \frac{f_1}{\omega_1^2 - \omega^2 + i\delta} \frac{|\mathbf{L}^{(2)}|^2}{(1 - M_{11} + M_{12})^2}, \\ \epsilon_{33}(\omega, \mathbf{k}) &= 1, \end{aligned} \right\} \quad (41)$$

where we have also taken account of a possible weak attenuation. For example, let us assume that the light is polarized along the  $x$  axis. If we assume that the matrix is transparent at the frequency  $\omega \approx \tilde{\omega}_1$ , we find the following expression for the absorption coefficient  $\kappa_I$  of the impurity:

$$\kappa_I(\omega) = \frac{\pi c}{2v\omega_1} \frac{1}{n_1^2(\omega)} \frac{f_1 |\mathbf{L}^{(1)}|^2 \delta(\omega - \tilde{\omega}_1)}{(1 - M_{11} - M_{12})^2}, \quad (42)$$

Here  $n_1^0(\omega) = \sqrt{\epsilon_{xx}^0(\omega, \mathbf{k})}$  is the refractive index of the matrix for light polarized along the  $x$  axis (see (26)). Analogously, for light polarized along the  $y$  axis,

$$\kappa_{II}(\omega) = \frac{\pi c}{2v\omega_1} \frac{1}{n_2^2(\omega)} \frac{f_1 |\mathbf{L}^{(2)}|^2 \delta(\omega - \tilde{\omega}_1)}{(1 - M_{11} + M_{12})^2}, \quad (43)$$

where  $n_2^0(\omega) = \sqrt{\epsilon_{yy}^0(\omega, \mathbf{k})}$  (see (26)). The ratio of the integral absorption intensities  $\bar{\kappa}$  corresponding to these values of  $\kappa_I$  and  $\kappa_{II}$ , as defined by  $\int \kappa(\omega) d\omega$ , will evidently be

$$\frac{\bar{\kappa}_I(\tilde{\omega}_1)}{\bar{\kappa}_{II}(\tilde{\omega}_1)} = \frac{n_2^2(\tilde{\omega}_1)}{n_1^2(\tilde{\omega}_1)} \frac{|\mathbf{L}^{(1)}|^2 (1 - M_{11} + M_{12})^2}{|\mathbf{L}^{(2)}|^2 (1 - M_{11} - M_{12})^2}. \quad (44)$$

In order to give a more graphic character to this relationship, let us return anew to the dielectric-constant tensor of the pure crystal in (26). Bearing the relationships (20) and (25) in mind, we can rewrite (44) as follows:

$$\frac{\bar{\kappa}_I(\tilde{\omega}_1)}{\bar{\kappa}_{II}(\tilde{\omega}_1)} = \frac{n_2^2(\tilde{\omega}_1) F_1 [\tilde{\omega}_1^2 - \Omega_2^2(\mathbf{k})]^2}{n_1^2(\tilde{\omega}_1) F_2 [\tilde{\omega}_1^2 - \Omega_1^2(\mathbf{k})]^2}. \quad (45)$$

If the frequency  $\tilde{\omega}_1$  is close to the intrinsic absorption frequencies, so that the difference  $|\tilde{\omega}_1 - \Omega_{1,2}|$  is rather small, we can also write (45) in the form

$$\frac{\bar{\kappa}_I}{\bar{\kappa}_{II}} = \frac{n_2^2(\tilde{\omega}_1) F_1 (\tilde{\omega}_1 - \Omega_2(\mathbf{k}))^2}{n_1^2(\tilde{\omega}_1) F_2 (\tilde{\omega}_1 - \Omega_1(\mathbf{k}))^2}. \quad (46)$$

This relationship implies that the quantity  $\bar{\kappa}_I$  can become anomalously large with respect to  $\bar{\kappa}_{II}$  as the frequency  $\tilde{\omega}_1$ , e.g., approaches the frequency  $\Omega_1$ . Thus, absorption at the impurity frequency becomes sharply polarized, even though sharp polarization of the impurity absorption may be absent far from the frequencies  $\Omega_1$  and  $\Omega_2$ . Indeed, Rashba derived Eq. (46) for  $\mathbf{k} = 0$ .<sup>[7]</sup> We shall discuss somewhat later the significance of accounting for spatial dispersion in Eq. (46). Here, however, we wish only to say some words on the nature of the effect expressed by Eq. (46). As (39) implies, this effect arises completely from accounting for the internal-field correction, which directly increases as the frequency  $\tilde{\omega}_1$  approaches the resonances of the dielectric-constant tensor of the pure crystal. Of course, this mechanism of the effect of the matrix also occurs in crystal of any structure, and also for interstitial impurities. However, the structure and effect of the internal field can differ in different cases. For example, for cubic crystals, as we see from (12a), and also for crystals having one molecule per unit cell, given the same dependence on the frequency  $\tilde{\omega}_1$ , the quantity  $\bar{\kappa}$  proves to be proportional to the square of

the transition oscillator strength in the matrix, rather than to the first power, as in (42).

Now let us continue to discuss Eq. (46). Let the frequency  $\tilde{\omega}_1$  lie in the region of an intense dipole transition in the matrix, such that this transition is precisely the one that determines the dispersion of the refractive indices  $n_{1,2}^0(\omega)$  in this frequency range. Then, when  $\tilde{\omega}_1 < \Omega_1(0)$ ,  $\Omega_2(0)$ , and the differences  $|\Omega_{1,2} - \omega_1|$  are small, but yet great enough that we can neglect the spatial dispersion of the medium, we have

$$n_1^0(\omega) \sim \sqrt{\frac{F_1}{\omega - \Omega_1(0)}}, \quad n_2^0(\omega) \sim \sqrt{\frac{F_2}{\omega - \Omega_2(0)}}.$$

Under these conditions Eq. (46) acquires the form

$$\frac{\bar{\kappa}_I}{\bar{\kappa}_{II}} = \sqrt{\frac{F_1}{F_2}} \left( \frac{\tilde{\omega}_1 - \Omega_2(0)}{\tilde{\omega}_1 - \Omega_1(0)} \right)^{3/2}. \quad (47)$$

However, if it becomes important to account for spatial dispersion, then, since for small  $\mathbf{k}$ ,

$$\begin{aligned} \Omega_1(\mathbf{k}) &= \Omega_1(0) + \mu_1 (n_1^0)^2(\omega), \\ \Omega_2(\mathbf{k}) &= \Omega_2(0) + \mu_2 (n_2^0)^2(\omega), \end{aligned} \quad (48)$$

we can write Eq. (46) as follows:

$$\frac{\bar{\kappa}_I}{\bar{\kappa}_{II}} = \frac{F_1}{F_2} \left\{ \frac{\sqrt{n_2^0(\tilde{\omega}_1)} [\tilde{\omega}_1 - \Omega_2(0) - \mu_2 (n_2^0)^2(\tilde{\omega}_1)]}{\sqrt{n_1^0(\tilde{\omega}_1)} [\tilde{\omega}_1 - \Omega_1(0) - \mu_1 (n_1^0)^2(\tilde{\omega}_1)]} \right\}^2. \quad (49)$$

Here the  $n_{1,2}^0$  satisfy the equations

$$\begin{aligned} n_1^0(\tilde{\omega}_1) &= \epsilon_{xx}^0(\tilde{\omega}_1, \mathbf{k}) = 1 + \frac{2\pi}{v} \frac{F_1}{\Omega_1^2(0) + \mu_1 n_1^2 - \tilde{\omega}_1^2}, \\ n_2^0(\tilde{\omega}_1) &= \epsilon_{yy}^0(\tilde{\omega}_1, \mathbf{k}) = 1 + \frac{2\pi}{v} \frac{F_2}{\Omega_2^2(0) + \mu_2 n_2^2 - \tilde{\omega}_1^2}. \end{aligned} \quad (50)$$

As we know (see, e.g.,<sup>[11]</sup>), the nature of the  $n_1(\omega)$  and  $n_2(\omega)$  relationships is determined by the signs of the coefficients  $\mu_1$  and  $\mu_2$ , respectively. Hence, in principle, we could use an experimental study of the ratio in Eq. (49) to reveal spatial-dispersion effects of the crystal matrix. However, this is hindered by the decay of the excited states of both the impurity and of the matrix. If the levels of these states are wide enough, then it becomes practically impossible to "sneak up" on the frequency  $\Omega_1(0)$  and to distinguish the impurity absorption from the matrix absorption. Nevertheless, for comparing the relationships derived above with the analogous ones derived within the framework of the microtheory (the exciton theory), we shall consider the broadening of the terms impurity and crystal. This is because the immediate vicinity of the frequency  $\Omega_1(0)$  is precisely where not only the above-mentioned effects of spatial dispersion are manifested, but also the differences from the results of the microtheory. Let us examine these results in greater detail. It is implied in<sup>[7]</sup> that the integral absorption intensities  $\bar{\kappa}_I$  are proportional to the quantities  $F_{\mu}/(\tilde{\omega}_1 - \Omega_{\mu})^2$  that figure in (42) and (43), but also to the very same coefficient  $|u(0)|^2$ , which is defined by the relationship (see also Appendix 2):

$$|u(0)|^2 = \frac{\tilde{\omega}_1 - \omega_1}{N_0} \sum_{\mathbf{k}, \mu=1, 2} \frac{|u_{\mu}(\mathbf{k})|^2}{[\omega_{ic} - \Omega_{\mu}(\mathbf{k})]^2}, \quad (51)$$

Here the coefficients  $u_{\mu}(\mathbf{k})$  satisfy the normalization condition

$$\sum_{\mu} |u_{\mu}(\mathbf{k})|^2 = 1 \quad (52)$$

and  $\omega_{ic}$  is the frequency of an impurity center. As  $\tilde{\omega}_1 \rightarrow \Omega_1(0)$ , the latter already begins to differ appreciably from  $\tilde{\omega}_1$ . However, for frequencies  $\tilde{\omega}_1$  sufficiently

remote from  $\Omega_1(0)$ , the frequency  $\omega_{1c} \approx \tilde{\omega}_1$ , and apart from small terms of the order of  $\delta = |[\Omega_1(0) - \Omega_2(0)]/(\tilde{\omega}_1 - \Omega_1)|$ , the value of  $|u(0)|^2$  proves to be unity. Hence, the results obtained above and those of the microtheory prove to coincide in this frequency range, not only for the ratio  $\bar{\kappa}_I/\bar{\kappa}_{II}$ , but for the quantities  $\bar{\kappa}_I$  and  $\bar{\kappa}_{II}$  themselves. However, as  $\tilde{\omega}_1$  approaches  $\Omega_1(0)$ , the quantity  $|u(0)|^2$  decreases. For example, when  $\mu_1 > 0$ , then  $|u(0)|^2 \sim \sqrt{\Omega_1(0) - \tilde{\omega}_1}$  (see [7]). Under these conditions, as was shown in [7], the excited state of the local center already encompasses not only the impurity molecule, but also a certain number of solvent molecules nearest to the impurity. However, under these conditions  $|u(0)|^2$  determines the probability that the impurity molecule itself should be in the excited state, and its decline as  $\tilde{\omega}_1 \rightarrow \Omega_1(0)$ , which is due to the "spreading" of the local excited state, thus has a quite clear physical meaning.

It is precisely in terms of this "spreading" that all of the studies known to us on impurity absorption have interpreted the sharp polarization of impurity lines as  $\tilde{\omega}_1 \rightarrow \Omega_1(0)$ . However, as is implied by the above, actually the main effect that leads to sharp polarization is the long-known effect of the internal-field correction, and here the quantity  $|u(0)|^2$  doesn't enter into the ratio  $\bar{\kappa}_I/\bar{\kappa}_{II}$  at all, but it leads in the expressions for  $\bar{\kappa}_I$  and  $\bar{\kappa}_{II}$  only to the appearance of additional, relatively weak root-law dependences on the frequency.<sup>7)</sup>

Curiously, the relative weakness of the "spreading" effect is actually implied by the experimental data. Thus, a variation in  $\bar{\kappa}_I$  by almost two orders of magnitude was observed in [8] for deuterated naphthalene in naphthalene, while under these same conditions, as estimated by the authors [8] themselves, even the minimum value of  $|u(0)|^2$  proved to be about 0.5 (according to [8], the minimum value of  $|u(0)|^2$  for deuterated benzene was even 0.8). Of course, the fact is not remarkable that the internal-field corrections remain invariant in the "spreading" of the excited state of a local center. It stems from the fact that the internal-field correction is practically independent of the radius of the cited state whenever this radius is small in comparison with the wavelength of the light (see also [18] for how to account for the internal-field corrections in ionic crystals).

## 5. OPTICAL PROPERTIES OF MIXED CRYSTALLINE SOLUTIONS

We shall discuss in this chapter some features of the spectrum of electromagnetic waves in mixed crystalline solutions by using expressions for the dielectric-constant tensor of the solution found in the mean-polarizability approximation. As we know, effects of concentration broadening of absorption spectra prove to be lost in this approximation. At the same time, as was shown in [9], where they actually studied the corrections to the mean-polarizability approximation, this approximation proves to be more or less suitable for studying the relatively coarse features of a spectrum, such as, e.g., the relation of the position of the center of an absorption band to the composition of the solution, and certain others.

However, the mean-polarizability approximation may even have a very high accuracy in describing dispersion and optical anisotropy of crystalline solutions outside an absorption band. This accuracy of description stems from the fact that the concentration broadening in crystals of this type (with only van der Waals forces acting

between the molecules) does not affect the integral oscillator strength of a transition. Moreover, for a large number of isotropic mixtures, both liquid and crystalline, the mean-polarizability approximation or the long-known and equivalent additive-refraction approximation, at least in a region of transparency, is even the basis of the analysis developed by Obreimov of the composition of many-component systems (for the details, see [10] and also the book [6], Sec. 6).

Evidently, the reason for the high accuracy of the additive-refraction approximation is that the error introduced into the refractive indices far from absorption bands proves to be a small quantity of the order of  $\delta/|\omega - \Omega| \ll 1$  (where  $\delta$  is the width of the resonance,  $\Omega$  is the resonance frequency, and  $\omega$  is the frequency in the region of transparency), in spite of the fact that this approximation proves to give the band structures incorrectly. Even when  $\delta \approx 10^3 \text{ cm}^{-1}$  and  $|\omega - \Omega| = 10^4 \text{ cm}^{-1}$ , this error is of the order of  $10^{-2}$ .<sup>8)</sup> We know of no mention in the literature of the equivalence, at least as applied to molecular crystals, of the mean-polarizability approximation and the additive-refraction approximation. Apparently this fact has not been noted, so that many of the results and approaches obtained before the appearance of the first studies on the theory of excitons of small radius have proved to be utterly forgotten. However, when even more recently the need arose of analyzing the properties of mixed crystalline solutions, the process began of repeated "discovery", in particular, of approaches developed long ago, but alas forgotten.

Let us illustrate the mean-polarizability method with the example of the spectrum of a binary mixture of isotopic molecules in a cubic crystal. For this case Eq. (11) implies that

$$\epsilon(\omega) = 1 + \frac{4\pi N_0 \bar{a}}{1 - (4\pi/3) N_0 \bar{a}}, \quad (53)$$

$$\bar{a} = (1 - c) a + c \bar{a}$$

( $c$  is the relative concentration of the impurity). Thus the resonances of  $\epsilon(\omega)$  correspond to frequencies that depend on  $c$ , and which satisfy the equation

$$\frac{1}{A} = \frac{1-c}{\omega_1^2 - \omega^2} + \frac{c}{\omega_2^2 - \omega^2}, \quad (54)$$

where  $A = (4\pi/3) N_0 f_1$ .

In deriving this relationship, we have used the fact that the polarizabilities of the different isotopic molecules have the form (8), and they differ from one another only in the values of the resonance frequencies. Eq. (54) permits us to trace in the studied approximation the shift of the absorption lines of the mixture as a function of its composition. However, we can trace the dependence on the composition of the mixture for the frequencies of the longitudinal lines from the equation  $\epsilon(\omega) = 0$ . We find by using (53) that these frequencies satisfy the equation

$$-\frac{1}{2A} = \frac{1-c}{\omega_1^2 - \omega^2} + \frac{c}{\omega_2^2 - \omega^2}. \quad (55)$$

Analogously, we can find the dependence on the composition of the mixture, e.g., of the frequencies of the surface waves (from the condition  $\epsilon(\omega) = -1$ ; the accuracy of definition of these frequencies is increased by the remoteness from resonance), as well as many other characteristics of the mixture that are determined by its dielectric constant. Anisotropic crystalline solutions



can also be treated in just as elementary a fashion. The dielectric tensor in the additive-refraction approximation has been derived above for such solutions consisting of two types of isotopic molecules in a lattice with two molecules per unit cell (see Eq. (35)). This expression implies that in the polarization  $L^{(1)}$  the resonances of the tensor  $\epsilon_{ij}$  correspond to frequencies  $\omega$  that satisfy the equation

$$1 - \tilde{M}_{11}(\omega, \mathbf{k}) - \tilde{M}_{12}(\omega, \mathbf{k}) = 0, \quad (55a)$$

In the polarization  $L^{(2)}$ , they satisfy the equation

$$1 - \tilde{M}_{11}(\omega, \mathbf{k}) + \tilde{M}_{12}(\omega, \mathbf{k}) = 0. \quad (56)$$

By using (30a), we can represent Eqs. (55) and (56) in the form

$$\frac{1}{A_{11} - A_{12}(-1)^\rho} = \frac{1-c}{\omega_1^2 - \omega^2} + \frac{c}{\omega_2^2 - \omega^2} \quad (\rho = 1, 2), \quad (57)$$

where

$$A_{11} = f_1 \sum_{ij} Q_{ij}^{\alpha\beta} l_i^\alpha l_j^\beta, \quad A_{12} = f_1 \sum_{ij} Q_{ij}^{\alpha\beta} l_i^\alpha l_j^\beta.$$

Equation (57) implies that each of the polarizations  $\rho = 1, 2$  in the light-absorption spectrum must correspond to a doublet of lines. If we denote the solutions of Eq. (57) for each of the polarizations  $\rho$  by  $\Omega_{\rho\lambda}^2$ ,  $\lambda = 1, 2$ , then after expansion into elementary fractions, we can also represent the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  as follows:

$$\epsilon_{ij}(\omega, \mathbf{k}) = \delta_{ij} + \sum_{\rho, \lambda} \frac{\Pi_{\rho\lambda}}{\Omega_{\rho\lambda}^2 - \omega^2} L_i^{(\rho)} L_j^{(\rho)}, \quad (58)$$

where

$$\Pi_{\rho\lambda} = \frac{2\pi}{v} \frac{f_1}{[A_{11} - (-1)^\rho A_{12}]^2} \left[ \frac{1-c}{(\omega_1^2 - \Omega_{\rho\lambda}^2)^2} + \frac{c}{(\omega_2^2 - \Omega_{\rho\lambda}^2)^2} \right]^{-1} \quad (\rho = 1, 2, \lambda = 1, 2). \quad (59)$$

In the studied approximation, the solutions of Eq. (57) and also of Eqs. (58) and (59) fully determine as functions of  $c$  not only the intensities and positions of the light-absorption bands in the crystal, but also the dispersion of the refractive index. The relationships derived above can be generalized in an elementary way also to the case of many-component isotopic solutions. Here Eqs. (30) and (58) retain their forms, but instead of (30a) and (57) and (59), respectively, we have the more general relationships

$$\tilde{M}_{\alpha\beta}(\omega, \mathbf{k}) = \sum_{\mathbf{k}} \frac{f_{\mathbf{k}} c_{\mathbf{k}}}{(\omega_{\mathbf{k}}^2 - \omega^2)} \sum_{ij} Q_{ij}^{\alpha\beta}(\mathbf{k}) l_i^\alpha l_j^\beta, \quad (60)$$

where the  $c_{\mathbf{k}}$  are the relative concentrations, with  $\mathbf{k} = 1, 2, \dots, s$ , such that  $\sum_{\mathbf{k}} c_{\mathbf{k}} = 1$ ,

$$\frac{1}{A_{11} - (-1)^\rho A_{12}} = \sum_{\mathbf{k}} \frac{c_{\mathbf{k}}}{\omega_{\mathbf{k}}^2 - \omega^2}, \quad (57a)$$

$$\Pi_{\rho\lambda} = \frac{2\pi}{v} \frac{f_1}{[A_{11} - (-1)^\rho A_{12}]^2} \left[ \sum_{\mathbf{k}} \frac{c_{\mathbf{k}}}{(\omega_{\mathbf{k}}^2 - \Omega_{\rho\lambda}^2)^2} \right]^{-1}, \quad (59a)$$

where the  $\Omega_{\rho\lambda}^2$  ( $\lambda = 1, 2, \dots, s$ ) are the roots of Eq. (57a) for fixed  $\rho = 1, 2$ .

We emphasize that the results obtained here for the line positions and the absorption intensities of such solutions agree with the results of [11], which were obtained by using the theory of excitons of small radius with an approximation identical with the mean-polarizability approximation (the additive-refraction approximation; the tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  was not found at all in this study).

Within the framework of the acting-field method pre-

sented here, one can treat quite analogously not only isotopic mixtures, but also molecular mixtures made of quite different molecules. Here we must bear in mind the fact that the resonance frequencies  $\omega_{\mathbf{k}}$  for the individual molecules in the solution in this more general case become functions of the composition. This is in contrast to isotopic molecules, for which we can consider all the static multipoles to be independent of the isotopic composition to a high degree of accuracy. The reason for the appearance of this dependence is elementary, being the shift in the resonance frequency of the individual molecule that was mentioned in Chap. 1. As was stated, this shift is due to the change upon excitation in the energy of interaction of the static multipoles of the molecules with the environment. This environment differs for different compositions of the mixture, and this leads to the stated dependence. Let us take it into account, for which we shall introduce the following notation:  $\omega_{\mathbf{k}}^0$  is the resonance of the molecule in vacuo, and  $D_{\mathbf{k}l}$  is the shift of this resonance in the presence of an environment consisting only of molecules of type  $l$ . Evidently, in the mean-polarizability approximation for the mixture,

$$\omega_{\mathbf{k}}^{\pm} \equiv \omega_{\mathbf{k}}^{\pm}(c_1, c_2, \dots) = \omega_{\mathbf{k}}^0 + \sum_l D_{\mathbf{k}l} c_l. \quad (61)$$

## 6. POLARIZABILITY OF THE MEDIUM AND THE ENERGY OF RESONANCE INTERACTION OF IMPURITY MOLECULES WITH ONE ANOTHER

An entire series of problems exists in the optics of crystals containing impurities for whose solution we must know the matrix element of the operator for the interaction energy of the impurity molecules with one another. The latter corresponds to transport of energy of intramolecular (electronic or vibrational) excitation from one impurity molecule to another. As the most important examples of this type, we shall point out the problem of finding the structure of an impurity exciton band, and also that of calculating the probability of radiationless energy transport between rather remote impurity molecules.

Here we shall restrict ourselves to the situation in which the fundamental role is played by the energy of dipole-dipole interaction, as happens in the Forster-Dexter-Galanin mechanism. In vacuo the operator for this energy is

$$\hat{V}_{AB}^0 = \frac{\hat{P}_A \hat{P}_B r^2 - 3(\hat{P}_A r)(\hat{P}_B r)}{r^5}, \quad (62)$$

Here  $\hat{P}_A$  and  $\hat{P}_B$  are the dipole-moment operators of the impurity molecules A and B, and  $r$  is the vector between the centers of these molecules. If in the initial state the molecule A was in the excited state  $f$ , and molecule B in the ground state, and vice versa in the final state, with molecule A in the ground state and molecule B in the  $f$ -th excited state (for the sake of simplicity, we assume the molecules to be identical), then the matrix element of the operator  $\hat{V}_{AB}^0$  corresponding to this transition will evidently have the form

$$V_{AB}^{f,0} = \frac{r^2 P_A^0 P_B^0 - 3(P_A^0 r)(P_B^0 r)}{r^5}. \quad (63)$$

If the impurity molecules are in a polarizing medium, then the appropriate correctives must be applied to the interaction-energy operator and its matrix element. At first glance, it might seem that in order to

do this, e.g., in an isotropic medium for  $c/\omega_{of} \gg r \gg d$ , where  $d$  is the lattice parameter of the crystal, it would suffice simply to divide the matrix element (63) by  $\epsilon(\omega_{of})$ , where  $\epsilon(\omega_{of})$  is the dielectric constant of the solvent at the frequency  $\omega_{of}$ . However, such a conclusion would be not quite right, even though it corresponds to the well-known result derived within the framework of the phenomenological Maxwell equations. If we introduce a point dipole  $\mu_A(\omega_{of})$  at some point  $A$  into these equations as a source, the electric field created by this dipole proves to be of the order of  $\mu_A/\epsilon r^3$ . Thus we get an interaction energy of the order of

$$u \sim \frac{\mu_A \mu_B}{\epsilon(\omega_{of}) r^2}. \quad (64)$$

However, we must take account of the fact that all of the quantities entering into the phenomenological Maxwell equations must also be treated as phenomenological quantities, which can greatly differ from their corresponding microscopic values. For example, this fact is, of course, well known for the dielectric constant  $\epsilon(\omega)$ . In the given case, it is expressed in the difference between the polarizability of the individual molecules and the polarizability of the crystal. It turns out (see [12]) that this type of effect occurs also with the transition dipole, or matrix element of the dipole moment of the molecule, and it consists in the fact that the phenomenological or effective value of this dipole in the medium differs substantially from the corresponding value in vacuo. In particular, the following relationship holds for an isotropic medium instead of (63):

$$(V_{AB}^{j_0, 0j})_{eff} = \frac{1}{\epsilon} \left( \frac{\epsilon + 2}{3} \right)^2 V_{AB}^{j_0, 0j}, \quad (65)$$

where  $\epsilon$  is the dielectric constant of the medium at the transition frequency.

Derivation of the latter using the microtheory is given in [12], where also certain corrections of a microscopic nature have been taken into account (the shift in the impurity term and a certain delocalization of the excitation). However, if the transition frequency  $\omega_{of}$  is far enough from the resonances of  $\epsilon(\omega)$ , as we shall assume henceforth for simplicity, these corrections are not significant, and we shall not consider them. However, we note here that, inasmuch as the factors in (65) that are new in comparison with (63) are macroscopic in nature, we can easily understand how they arise on the basis of very elementary and rather general arguments.

In fact, the effect of polarization of the medium at the energy of dipole-dipole interaction is due to exchange of virtual electromagnetic-field quanta in the medium, which specifically obeys the phenomenological Maxwell equations. Hence we need to know the interaction energy of the impurities with precisely this field. Turning to Eq. (38), we conclude that the dipole moment that figures in this energy is not its vacuum value, but some effective value that is found by taking account of the internal-field correction. In an isotropic medium, this is  $\mu_A = [(\epsilon + 2)/3] P_A^{0j}$ . Upon taking account of (64), this precisely gives (65). Of course, what we have said holds for non-conducting media as applied to local centers of any nature. However, the method presented in Chap. 3 of accounting for the internal-field corrections permits one to treat in a very elementary way the effect of polarization of the solvent on the energy of resonance exchange in molecular media of any symmetry.

In connection with the broad scope of experimental studies on energy transfer, let us define the general form of the energy of dipole-dipole resonance radiationless interaction in anisotropic molecular crystals (for some more special results for crystals containing one molecule per unit cell, see [12, 13]). In order to do this, we shall have to generalize somewhat the results presented in Chap. 3. Let us assume that  $a_\nu(\omega)$ , where  $\nu = 1, 2, 3$ , are the principal values of the polarizability tensor of the individual molecule, and that the  $l^\nu$  are the directions of its principal axes. Then, evidently, we can represent this tensor in the form

$$a_{ij}^\alpha(\omega) = \sum_\nu a_\nu(\omega) l_i^{\alpha\nu} l_j^{\alpha\nu}. \quad (66)$$

If we consider just one of the excited states in the molecule, Eq. (66) goes over into (18a). However, in a region of transparency, many excited states make comparable contributions to the polarizability of the molecule, so that the approximation (18a) becomes insufficient. Of course, an analogous situation happens also in crystalline solutions. In this case, we must use the following relationship in the mean-polarizability approximation (the additive-refraction approximation), e.g., for isotropic mixtures, instead of (66):

$$a_{ij}^\alpha(\omega) = \sum_\nu \bar{a}_\nu(\omega) l_i^{\alpha\nu} l_j^{\alpha\nu}, \quad (66a)$$

$$\bar{a}_\nu(\omega) = \sum_\rho c_\rho a_\nu^\rho(\omega),$$

Here  $c_\rho$  is the relative concentration of isotope  $\rho$ , and  $a_\nu^\rho(\omega)$ , with  $\nu = 1, 2, 3$ , are the corresponding principal values of the polarizability tensor of the molecule. Now using Eqs. (1), (2), and (66), we find that the projections of the internal field  $E^\alpha$  on the directions  $l^{\alpha\nu}$ , i.e., the quantities  $E^\alpha \cdot l^{\alpha\nu}$ , satisfy a system of equations ( $\alpha = 1, 2, \dots, \sigma$ ,  $\nu = 1, 2, 3$ ):

$$(E^\alpha l^{\alpha\nu}) = (E l^{\alpha\nu}) + \sum_{\beta\nu'} M_{\alpha\beta}^{\nu\nu'}(\omega, \mathbf{k}) (E^\beta l^{\beta\nu'}), \quad (67)$$

where

$$M_{\alpha\beta}^{\nu\nu'}(\omega, \mathbf{k}) = a^{\nu'}(\omega) \sum_{ij} Q_{ij}^{\alpha\beta}(\mathbf{k}) l_i^{\alpha\nu} l_j^{\beta\nu'}. \quad (68)$$

Since for fixed  $\alpha$  the unit vectors  $l^{\alpha\nu}$  form a triple of mutually orthogonal vectors, solution of the inhomogeneous system of equations of (67) permits us to find the form of the tensor  $A_{ij}^{\alpha\beta}(\omega, \mathbf{k})$  in Eq. (4). Hence, if  $p_A^{0j, \alpha}$  is the vacuum value of the matrix element of the dipole moment of the substitutional impurity at the site  $\alpha$ , then we get the following for its effective value:

$$\mu_{A_i}^{0j, \alpha} = (p_A^{0j, \alpha})_j A_{ji}^\alpha(\omega, \mathbf{k}),$$

Thus, if we neglect spatial dispersion, the sought dipole-dipole interaction energy takes on the form

$$V_{AB}(r) = - (p_A^{0j, \alpha})_{ji} A_{ji}^\alpha(\omega^{0j}) A_{jj'}^{\alpha'}(\omega^{0j'}) (p_B^{0j', \alpha'})_{j'j} \frac{\partial^2}{\partial x_1 \partial x_j} \frac{1}{\sqrt{\epsilon_{\alpha\beta}^{-1} \alpha^x \beta^x}} (\det \epsilon_{\alpha\beta})^{1/2}, \quad (68a)$$

where  $\epsilon_{\alpha\beta}(\omega^{of})$  is the dielectric-constant tensor of the solvent at the frequency  $\omega^{of}$ .

Accounting for spatial dispersion results (see [2, 12]) in appearance in  $V_{AB}(r)$  of additional terms that decline more quickly with increasing  $r$ . However, these terms are important only for frequencies  $\omega^{of}$  that are close enough to the intrinsic absorption frequencies of the medium. For an isotropic medium, naturally, (68) goes over into (65). However, in the special case of a crystal having one anisotropic molecule per cell,

and moreover in the approximation of (18a), Eq. (68) goes over into the expression derived by Konobeyev and Kamenogradskii (see <sup>[13]</sup>), who used, as in <sup>[12]</sup>, the apparatus of the theory of excitons of small radius.

Finally, we note that solution of the system of equations of (67), both for pure crystals and for isotopic crystalline solutions (here  $M_{\alpha\beta}^{\nu\nu'} \rightarrow \bar{M}_{\alpha\beta}^{\nu\nu'}$ , and  $a^{\nu}(\omega) \rightarrow \bar{a}^{\nu}(\omega)$ ), permits us to generalize all of the results presented above to the case including many resonances in the molecule (i.e., we account for the mixing of molecular configurations effected by the intermolecular interaction).

## 7. CONCLUDING REMARKS

In the earlier chapters of this article, we have treated a number of problems of the crystal optics of molecular crystals within the framework of the acting-field method that had previously been treated only by using the exciton theory.

On the other hand, we have also derived above some new relationships that can prove useful in analyzing certain optical effects in crystals of this type. Such a treatment seems pertinent, since one can more clearly delineate thereby the set of physical phenomena in crystals (concerning these, see below) for which we truly need the concepts of the exciton theory to understand them. Here, by no means all of the potentialities of the acting-field method have been used. In particular, it would be of great interest to treat the gyrotropy of molecular crystals, both pure crystals and those containing impurities, and in particular, to treat the gyrotropy of crystalline solutions as a function of their composition. In view of the ideas presented in Chap. 5, we have every justification for hoping that using the mean-polarizability approximation for solutions in a region of transparency of the crystal will permit one to calculate the rotatory power of a crystalline solution from a knowledge of the properties of the individual molecules with an accuracy no poorer than for the refractive indices of light in non-gyrotropic disordered media. It is of no lesser interest also to study the effect of static electric fields (the Kerr effect) and magnetic fields (the Faraday effect) on the optical properties of molecular crystals. We mention these effects, not only because they have been studied extremely poorly in molecular crystals, but mainly in line with the fact that treating them within the framework of the acting-field method would also probably be very simple and convenient.

We recall that the acting-field method is based on Eq. (1), in which the internal-field tensor  $Q_{ij}^{\alpha\beta}(\mathbf{k})$  is assumed to be known. Hence, the simplicity and graphic quality of this method is evidently due to the possibility of effectively using the previously derived results of Born, Ewald, and many other authors (see <sup>[3,4]</sup>).

However, there is a vast set of optical phenomena in crystals which in principle cannot be treated within the framework of this approach. Some of them have been mentioned in Chap. 3. Moreover, we might point out light-absorption processes in which the energy of one photon in one event gives rise directly in the crystal to several of its elementary excitations. In general, such processes manifest the entire region of allowed values of energies of quasiparticles. One can find the latter, when dealing with elementary excitations, only within the framework of the exciton theory. An example of the

limited applicability of the approach used in this article is light absorption to states of the biphonon type, i.e., excited states of the crystal in which two elementary excitations, e.g., two optical phonons, are bound together and migrate through the crystal as a unit (Van Kranendonk <sup>[14]</sup> first studied this type of states in molecular crystals; for their properties and manifestations in Raman spectra, see <sup>[15]</sup>). Whenever the radius of this state is shorter than or of the order of the lattice constant, both excitations "sit" at the same lattice site. Here (the case of limiting strong anharmonicity: the anharmonicity constant  $A \gg \Gamma$ , where  $\Gamma$  is the width of the phonon band), we can neglect the effect of delocalization, and consider the transition, which corresponds to creation in a molecule of two intramolecular vibrations, to be accounted for in the molecular-polarization tensor  $a_{ij}(\omega, \mathbf{k})$ . Conversely, if  $A$  is less than or of the order of  $\Gamma$ , the approach used in this article becomes quite inapplicable, since one cannot take account within its framework of effects of delocalization of an excited state of the molecule of the type that was discussed in Chap. 4 for impurity molecules.

And finally, above we have not treated at all effects of broadening of light-absorption lines in crystals arising from interaction of intramolecular excitations with lattice vibrations. Treatment of this problem also exceeds the limits of applicability of the used model, and it can be most effectively carried out only by using the existing methods of exciton theory (see, e.g., <sup>[1,2,16]</sup>).

The problem of the role of the local field in molecular crystals has been touched upon repeatedly in discussing particular problems of crystal optics, and on particular, at the sessions of the All-Union Seminar on Excitons. In this regard, I wish to thank my colleagues, whose discussions have aroused me to consider this set of problems more systematically. I consider it my pleasant duty to thank also V. L. Ginzburg, Yu. E. Lozovik, and V. I. Yudson for remarks and advice that were taken into account in the final editing of the text of this article.

## APPENDICES

### 1. ON TAKING ACCOUNT OF THE HIGHER MULTIPOLES IN THE ACTING-FIELD METHOD

In order to explain how one can take account of the higher multipoles within the framework of the acting-field method, let us consider, along with the dipole polarization, also the quadrupole  $q_{ij}$  and octupole  $q_{ijl}$  polarizations of the molecule. In this approximation, the operator for the energy of interaction of the molecule with an external monochromatic electric field  $\mathbf{E}(\mathbf{r}, t)$  is  $\hat{V}$ , where

$$\hat{V} = \sum_i \hat{p}_i E_i + \sum_{ij} \hat{q}_{ij} E_{ij} + \sum_{ijl} \hat{q}_{ijl} E_{ijl}, \quad (1.1)$$

Here the  $\hat{p}_i$ ,  $\hat{q}_{ij}$ , and  $\hat{q}_{ijl}$  are the operators for the dipole, quadrupole, and octupole moments of the molecule, and  $E_{ij} = \partial E_i / \partial x_j$  and  $E_{ijl} = \partial^2 E_i / \partial x_j \partial x_l$ .

By using Eq. (1.1) and the results of time-dependent perturbation theory (see <sup>[17]</sup>, Sec. 40), we can find the values of the studied multipoles that are induced by the external field. However, as was stated above (see Chap. 1), the so-called acting field performs as the perturbing field for the molecules in a crystal. Hence, we can represent the corresponding multipole values for the  $\alpha$ th molecule in the unit cell as follows:

$$p_i^\alpha = \sum_j a_{ij}^\alpha E_j^\alpha + \sum_{jl} b_{ij,lm}^\alpha E_{lm}^\alpha + \sum_{jlm} c_{ijl,mnp}^\alpha E_{mnp}^\alpha, \quad (1.2a)$$

$$q_{ij}^\alpha = \sum_l b_{ij,l}^\alpha E_l^\alpha + \sum_{lm} b_{ij,lm}^\alpha E_{lm}^\alpha + \sum_{lmn} b_{ij,l,mn}^\alpha E_{lmn}^\alpha, \quad (1.2b)$$

$$q_{ijl}^\alpha = \sum_m c_{ijl,m}^\alpha E_m^\alpha + \sum_{mn} c_{ijl,mn}^\alpha E_{mn}^\alpha + \sum_{mnp} c_{ijl,mnp}^\alpha E_{mnp}^\alpha. \quad (1.2c)$$

The tensors  $a^\alpha$ ,  $b^\alpha$ , and  $c^\alpha$  that figure in (1.2a)-(1.2c), and which depend on  $\omega$ , have the form of sums of resonance terms, each of which corresponds to a transition from the ground state to one of the excited states of the molecule. If for the sake of simplicity we bear in mind only any one of the resonances corresponding to a transition from the ground state to a non-degenerate excited state of the molecule having the excitation energy  $\hbar\omega_1$ , the tensors  $a^\alpha$ ,  $b^\alpha$ , and  $c^\alpha$  can be factored. This substantially simplifies the treatment. In this approximation, which corresponds to neglecting the mixing of molecular configurations, e.g., the tensor  $b_{ij,lmn}^\alpha$  has the form

$$b_{ij,lmn}^\alpha(\omega) = \frac{2\omega_1}{\omega_1^2 - \omega^2} (q_{ij}^\alpha)^{01} (q_{lmn}^\alpha)^{10}$$

etc., so that we can write the relationships (1.2a)-(1.2c) as follows:

$$\left. \begin{aligned} p_i^\alpha &= \frac{2\omega_1}{\omega_1^2 - \omega^2} (p_i^\alpha)^{01} V_\alpha^{10}, \\ q_{ij}^\alpha &= \frac{2\omega_1}{\omega_1^2 - \omega^2} (q_{ij}^\alpha)^{01} V_\alpha^{10}, \\ q_{ijl}^\alpha &= \frac{2\omega_1}{\omega_1^2 - \omega^2} (q_{ijl}^\alpha)^{01} V_\alpha^{10}, \end{aligned} \right\} \quad (1.3a)$$

where

$$V_\alpha^{10} = \sum_i (p_i^\alpha)^{10} E_i^\alpha + \sum_{ij} (q_{ij}^\alpha)^{10} E_{ij}^\alpha + \sum_{ijl} (q_{ijl}^\alpha)^{10} E_{ijl}^\alpha. \quad (1.3b)$$

Equations (1.3a) are a generalization of Eq. (2) of the main text. When one takes account of the higher multipoles within the framework of the method used here, they imply that one must distinguish the internal-field corrections in the expression, not only for the amplitude of the acting field, but also for the amplitudes of its derivatives. Bearing this in mind, as well as the results of [3,5], we represent the values of the acting field and its derivatives as follows:

$$E_i^\alpha = E_i + \sum_{\beta j} Q_{ij}^{\alpha\beta} p_j^\beta + \sum_{\beta j l} \tilde{Q}_{ijl}^{\alpha\beta} p_{jl}^\beta + \sum_{\beta j l m} \tilde{\tilde{Q}}_{ijlm}^{\alpha\beta} p_{lm}^\beta, \quad (1.4a)$$

$$E_{ij}^\alpha = E_{ij} + \sum_{\beta l} \tilde{Q}_{ijl}^{\alpha\beta} p_l^\beta + \sum_{\beta l m} \tilde{\tilde{Q}}_{ijlm}^{\alpha\beta} p_{lm}^\beta + \sum_{\beta l m n} \tilde{\tilde{\tilde{Q}}}_{ijlmn}^{\alpha\beta} p_{lmn}^\beta, \quad (1.4b)$$

$$E_{ijl}^\alpha = E_{ijl} + \sum_{\beta m} \tilde{\tilde{Q}}_{ijlm}^{\alpha\beta} p_m^\beta + \sum_{\beta mn} \tilde{\tilde{\tilde{Q}}}_{ijlmn}^{\alpha\beta} p_{mn}^\beta + \sum_{\beta mnp} \tilde{\tilde{\tilde{\tilde{Q}}}}_{ijlmnp}^{\alpha\beta} p_{mnp}^\beta. \quad (1.4c)$$

The internal-field coefficients  $Q^{\alpha\beta}$ ,  $\tilde{Q}^{\alpha\beta}$ , and  $\tilde{\tilde{Q}}^{\alpha\beta}$  are determined only by the crystal structure, and one can get their explicit expressions, which are not written down here, from [3,5]. Evidently, Eqs. (1.4a)-(1.4c) generalize Eq. (1) of the main text, and they are reduced to the latter when  $q_{ij}^\alpha = q_{ijl}^\alpha = 0$ .

Now if we multiply Eq. (1.4a) by  $(p_i^\alpha)^{10}$ , Eq. (1.4b) by  $(q_{ij}^\alpha)^{10}$ , and Eq. (1.4c) by  $(q_{ijl}^\alpha)^{10}$ , and sum over the subscripts  $i, j$ , and  $l$ , we can easily convince ourselves by using (1.3a) and (1.3b) that the quantities  $V_\alpha^{10}$  ( $\alpha = 1, 2, \dots, \sigma$ ) satisfy the following system of  $\sigma$  equations:

$$V_\alpha^{10} = K_\alpha + \sum_{\beta} M_{\alpha\beta}^{\text{eff}}(\mathbf{k}) V_\beta^{10}, \quad (1.5)$$

where

$$M_{\alpha\beta}^{\text{eff}}(\mathbf{k}) = \frac{2\omega_1}{\omega_1^2 - \omega^2} \left\{ \sum_{ij} Q_{ij}^{\alpha\beta}(\mathbf{k}) (p_i^\alpha)^{01} (p_j^\beta)^{10} + \sum_{ijl} [Q_{ijl}^{\alpha\beta}(\mathbf{k}) (p_i^\alpha)^{01} (q_{jl}^\beta)^{10} + \tilde{Q}_{ijl}^{\alpha\beta}(\mathbf{k}) (q_{ij}^\alpha)^{01} (p_l^\beta)^{10}] + \sum_{ijlm} [Q_{ijlm}^{\alpha\beta}(\mathbf{k}) (p_i^\alpha)^{01} (q_{jm}^\beta)^{10} + \tilde{Q}_{ijlm}^{\alpha\beta}(\mathbf{k}) (q_{ij}^\alpha)^{01} (q_{lm}^\beta)^{10}] \right\}$$

$$+ \tilde{\tilde{Q}}_{ijlm}^{\alpha\beta}(\mathbf{k}) (q_{ij}^\alpha)^{01} (p_m^\beta)^{10}] + \sum_{ijlmn} [Q_{ijlmn}^{\alpha\beta}(\mathbf{k}) (q_{ij}^\alpha)^{01} (q_{lmn}^\beta)^{10} + \tilde{Q}_{ijlmn}^{\alpha\beta}(\mathbf{k}) (q_{ij}^\alpha)^{01} (q_{mn}^\beta)^{10}] + \sum_{ijlmnp} \tilde{\tilde{\tilde{Q}}}_{ijlmnp}^{\alpha\beta}(\mathbf{k}) (q_{ij}^\alpha)^{01} (q_{mnp}^\beta)^{10} \}. \quad (1.6)$$

$$K_\alpha = \sum_i (p_i^\alpha)^{10} E_i + \sum_{ij} (q_{ij}^\alpha)^{10} E_{ij} + \sum_{ijl} (q_{ijl}^\alpha)^{10} E_{ijl}. \quad (1.7)$$

As compared with the tensor  $M_{\alpha\beta}$  (see Eq. (20) of the main text), we have also taken account in the tensor  $M_{\alpha\beta}^{\text{eff}}$  of dipole-quadrupole, dipole-octupole, quadrupole-

octupole, and other interactions, in addition to the dipole-dipole interaction. However, if we are dealing with crystals of the type of anthracene or naphthalene that consist of molecules having an inversion center, then matrix elements  $(q_{ij}^\alpha)^{01}$  of the quadrupole-moment operator vanish for the dipole-allowed  $0 \rightarrow 1$  transitions. Then only the dipole-dipole, dipole-octupole, and octupole-octupole interactions contribute to (1.6). Moreover, we can omit in (1.7) for these transitions the second and third terms, since for macrofields  $E_i(\mathbf{r}) = E_i e^{i\mathbf{k} \cdot \mathbf{r}}$  their derivatives with respect to the coordinates are small (it is important to account for these terms only in analyzing gyrotropy effects, in which we must take account also in (1.1) of the interaction of the molecule with the magnetic field, and also in a frequency region of dipole-forbidden transitions). Bearing this in mind, we conclude that the system of equations (1.5) proves to be completely analogous to the system of equations (19) of the main text. The only difference consists in the fact that the intermolecular interaction has been taken into more exact account in the matrix of (1.6). This circumstance has the result that accounting for the higher multipoles for a region of dipole-allowed transitions only shifts somewhat the resonances of the dielectric-constant tensor. Yet the rest of the results cited in the main text of the article remain unchanged here.

It becomes quite necessary to account for the higher multipoles in a region of dipole-forbidden transitions, as well as in studying gyrotropy. Discussion of the features that arise here exceeds the limits of this article, and it must be carried out separately.

## 2. CALCULATION OF THE FIELD ACTING ON AN IMPURITY MOLECULE WHEN THE COULOMB GAUGE OF POTENTIALS IS USED

In microscopic calculations based on exciton theory of the optical properties of crystals arising from the presence of impurity molecules, one usually uses the Coulomb gauge of the vector potential. In this gauge, one first calculates the local states of the crystal (ground and excited states) with full account of Coulombic interaction. Then one determines the matrix elements of the transitions for the found states (dipole, quadrupole, etc.). It is essential in this method of calculation that one must consider as the perturbing field in the light wave only the transverse component of the electric-field intensity, for which the local corrections are infinitesimally small (see [3]). The expressions derived here for the oscillator strengths of the transitions in the local centers prove to be expressed in terms of solution of the Coulomb problem for the crystal, and in particular, in terms of the energy and wave functions of Coulomb excitons. Since one can express the dielectric-constant tensor of the crystal most simply in terms of the characteristics of mechanical,

rather than Coulomb excitons (see <sup>[1]</sup>), the fact cited above somewhat complicates discussion of the problem of the nature of the effect of the macroscopic properties of the matrix (its dielectric constant) on the optical properties of the impurity molecules. However, within the framework of the acting-field method used in this article, this problem can be solved very simply, and it leads to very graphic results (see Chaps. 2-4). However, evidently, to use any particular gauge should not affect the final results. As applied to the problem under discussion, we shall illustrate what we have said by the example of an impurity molecule incorporated in a cubic crystal consisting of isotropic molecules with one molecule per cell. It is precisely by using the Coulomb gauge that we shall first find the transition dipole moment at the local center. Then we shall express it in terms of the dielectric constant of the crystal. We also shall compare the expression derived thus with the results based on using the model of Onsager (see <sup>[18]</sup>), and shall point out the discrepancies that arise here.

Thus we shall assume that an impurity molecule is located at the point  $\mathbf{p}$ , which lies within the unit cell of the crystal. In contrast to the molecules of the main substance, we shall use a two-level system for the impurity molecules (0 for the ground state, and  $f$  for the excited state). We can write the Hamiltonian of this system (see <sup>[2]</sup>) as expressed in terms of the Bose operators  $B_{si}^+$  and  $B_{si}$  for creation and annihilation of the  $i$ th excited state of the molecule  $s$ , as follows:

$$\mathcal{H}_0 = \mathcal{H}_0 + \mathcal{H}_1, \quad (2.1)$$

$$\mathcal{H}_0 = E^{(0)} + \sum_{ni} \Delta_i B_{ni}^+ B_{ni} + \sum_{n \neq m} V_{nm} (0ij0) B_{ni}^+ B_{mj} + \frac{1}{2} \sum_{n \neq m} V_{nm} (00ij) (B_{ni} B_{mj} + B_{ni}^+ B_{mj}^+), \quad (2.2)$$

$$\mathcal{H}_1 = \Delta_f B_{pf}^+ B_{pf} + \sum_{mj} V_{pm} (0fj0) (B_{pi}^+ B_{mj} + B_{mi}^+ B_{pf}) + V_{pm} (00fj) (B_{pi}^+ B_{mj}^+ + B_{pi} B_{mj}). \quad (2.3)$$

In the expressions (2.2),  $E^{(0)}$  is the energy of the crystal in the ground state,  $\Delta_f$  and  $\Delta_i$  are the energies of excitation of isolated molecules of the impurity and of the main substance, and the  $V_{nm}$  are the matrix elements of the operator for the energy of interaction of the molecules  $n$  and  $m$ . In particular, the matrix element  $V_{nm}(0ij0)$  corresponds to a process in which the state  $B_{mj}^+ |0\rangle$  goes over into the state  $B_{ni}^+ |0\rangle$ ;  $V_{nm}(00ij)$  corresponds to a process in which the state  $|0\rangle$  goes over into the state  $B_{ni}^+ B_{mj}^+ |0\rangle$ , etc. One can show (see <sup>[2]</sup>) that the matrix elements  $V_{nm}(0ij0)$  and  $V_{nm}(00ij)$  differ only when one accounts for the exchange corrections. However, for molecular crystals in a region of singlet excited states, these corrections are infinitesimally small, and hence we shall not consider them here.

In order to determine the energies and wave functions of the excited states of the studied system, let us transform to the new Bose operators  $B_{\nu}^+$  and  $B_{\nu}$ :

$$B_{ni} = \sum_{\nu} [B_{\nu} u_{\nu}(ni) + B_{\nu}^* v_{\nu}^*(ni)], \quad (2.4)$$

where the coefficients  $u$  and  $v$  satisfy the normalization condition

$$\sum_{ni} [|u_{\nu}(ni)|^2 - |v_{\nu}(ni)|^2] = 1 \quad (2.5)$$

and are determined by the following system of equations (see also <sup>[2]</sup>):

$$(E - \Delta_i) u(ni) = -(E + \Delta_i) v(ni) = \sum_{mj} V_{nm} (0ij0) \tilde{u}(mj) + V_{np} (0fi0) \tilde{u}(pf), \quad (2.6)$$

$$(E - \Delta_f) u(pf) = -(E + \Delta_f) v(pf) = \sum_{mj} V_{nm} (0fj0) \tilde{u}(mj), \quad (2.7)$$

where  $\tilde{u} = u + v$ .

Equations (2.6) and (2.7) imply that

$$\tilde{u}(mj) = \frac{2\Delta_j}{E + \Delta_j} u(mj), \quad \tilde{u}(pf) = \frac{2\Delta_f}{E + \Delta_f} u(pf), \quad (2.8)$$

Thus, we can represent the system of equations for the quantities  $a(mj) \equiv \tilde{u}(mj)/\sqrt{\Delta_j}$  in the following form:

$$(E^2 - \Delta_i^2) a(ni) - \sum_{mj} \tilde{V}_{nm} (0ij0) a(mj) = \tilde{V}_{np} (0if0) a(pf), \quad (2.9a)$$

$$(E^2 - \Delta_f^2) a(pf) - \sum_{mj} \tilde{V}_{pm} (0fj0) a(mj) = 0. \quad (2.9b)$$

where

$$\tilde{V}_{nm} (0ij0) = 2 \sqrt{\Delta_i \Delta_j} V_{nm} (0ij0).$$

In an ideal crystal the coefficients  $a(ni)$  satisfy the system of equations (2.9a) if therein we set  $\tilde{V}_{np} = 0$ . Then, owing to translational symmetry, the quantities  $a(ni) \equiv a^{(0)}(ni)$  that correspond to the exciton  $\mu\mathbf{k}$  are determined by the relationship

$$a_{\mu\mathbf{k}}^{(0)}(ni) = \frac{1}{\sqrt{N}} e^{i\mathbf{k}n} a_{\mu\mathbf{k}}^0(i), \quad (2.10)$$

Here  $\mu$  is the number of the exciton band, and  $\mathbf{k}$  is its wave vector. Hence, considering the normalization condition (2.5), we can represent the Green's function of the ideal crystal in the form

$$G_{ni, mj}(E) = \frac{1}{N} \sum_{\mathbf{k}\mu} \frac{a_{\mu\mathbf{k}}^{(0)}(i) a_{\mu\mathbf{k}}^{(0)}(j) E_{\mu}(\mathbf{k})}{E^2 - E_{\mu}^2(\mathbf{k})} e^{i\mathbf{k}(n-m)}, \quad (2.11)$$

where  $E_{\mu}(\mathbf{k})$  is the energy of the exciton  $\mu\mathbf{k}$ .

Upon solving Eq. (2.9a) for the quantities  $a(ni)$ , we find that for a local excited state (whose energy we shall denote by  $E_0$ ),

$$a(ni) = a(pf) \sum_{mj} G_{ni, mj}(E_0) \tilde{V}_{mj} (0fj0). \quad (2.12)$$

Then if we substitute this relationship into (2.9b), we get an equation that determines the value of the energy  $E_0$ :

$$E_0^2 - \Delta_f^2 = \sum_{n, imj} \tilde{V}_{pn} (0fi0) G_{ni, mj}(E_0) \tilde{V}_{mj} (0fj0). \quad (2.13)$$

The last term in (2.13) proves to be substantial only for impurity molecules whose excitation energies are close to the energy of an exciton. In the converse case, the resonance interaction of the impurity molecules with their environment is hardly significant, so that  $E_0 \approx \Delta_f$ . Without taking up here the details and results of calculating the energy of a local excited state (on these, see, e.g., <sup>[2]</sup>), we shall proceed directly to calculating the matrix element of the transition moment.

If this transition arises under the influence of a light wave propagating through the crystal with the wave vector  $\mathbf{k}$ , then evidently its intensity will be proportional to the square of the projection of the matrix element of the operator

$$\hat{P} = \sum_s \mathbf{p}_s e^{i\mathbf{k}s},$$

onto the  $l$ -direction of the transverse component of the macrofield  $\mathbf{E}^l(\omega, \mathbf{k})$ . Here  $\mathbf{p}_s$  is the dipole-moment operator of the molecule  $s$  and the summation over the sites  $s$  also includes the impurity molecule. When represented in terms of operators for creation and annihilation of molecular excitations, the operator  $\hat{P}$  has the following form:

$$\hat{P} = \sum_{\alpha i} p_{\alpha}^{0i} (B_{\alpha i}^* + B_{\alpha i}) e^{ik_{\alpha}}$$

Thus, if  $\nu = \nu_0$  in the summation of (2.4) corresponds to the excited state of a local center, then the sought matrix element

$$\langle 0 | P | \nu_0 \rangle = \langle 0 | P B_{\nu_0}^* | 0 \rangle \equiv P^{0\nu_0}$$

is determined by the following relationship, in view of (2.4):

$$P^{0\nu_0} = \sum_i \sqrt{\Delta_i} a_{\nu_0}(i) p_{\alpha}^{0i} e^{ik_{\alpha}}$$

Now if we use Eq. (2.12), we find that

$$P^{0\nu_0} = \sqrt{\Delta_j} a_{\nu_0}(pf) |p^{0j} + 2 \sum_{nmij} \sqrt{\Delta_i \Delta_j} G_{nimj}(E_0) V_{mp}(0j|f0) p^{0i} e^{-ik_{\alpha}}. \quad (2.14)$$

If then we take account of the fact that, in accord with (2.11),

$$\sum_n e^{-ikn} G_{nimj}(E_0) = \sum_{\mu} \frac{a_{\mu k}^{(0)}(i) a_{\mu k}^{*(0)}(j) E_{\mu}(k)}{E_0^2 - E_{\mu}^2(k)} e^{-ikm},$$

and introduce the notation

$$p_{\mu}(k) = \sum_i a_{\mu k}^{(0)}(i) p^{0i} \sqrt{\Delta_i},$$

we can write the second term within the square brackets of Eq. (2.14) in the form

$$2 \sum_{\mu} \frac{P_{\mu}(k) E_{\mu}(k)}{E_0^2 - E_{\mu}^2(k)} A_{\mu k}(pf), \quad (2.15)$$

where

$$A_{\mu k}(pf) = \sum_{mj} \sqrt{\Delta_j} a_{\mu k}^{*(0)}(j) V_{mp}(0j|f0) e^{-ikm}. \quad (2.16)$$

In order to give the final formulas the simplest and most lucid form, we shall account only for the dipole-dipole interaction in the energy  $V_{nm}$ . In the dipole approximation, the quantity  $A_{\mu k}(pf)$  equals the interaction energy of a dipole  $p^{0j}$  lying at the point  $p$  with a net of dipoles lying at the lattice sites  $n$ , and varying according to the law  $p_{\mu}(k)e^{-ik \cdot n}$ . This means that

$$A_{\mu k}(pf) = -p^{0j} E_{\mu}(k),$$

where  $E_{\mu}(k)$  is the electric field at the point  $p$  produced by the net of dipoles. According to [3], the components of this field are determined by the relationship

$$E_{\mu}^x(k) = -\frac{4\pi}{v} \frac{(p_{\mu}^x k_x)}{k^2} + \sum_y Q_{xy}(k) p_{\mu}^y,$$

where  $v$  is the volume of the unit cell and  $Q_{xy}$  is the internal-field matrix. Thus

$$A_{\mu k}(pf) = \frac{4\pi}{v} \frac{(p_{\mu}^x k) (p^{0j} k)}{k^2} - \sum_{xy} Q_{xy}(k) p_{\mu}^y (p^{0j})^x, \quad (2.17)$$

so that the  $x$  component of the vector within the square brackets of (2.14) can be represented as follows:

$$[\dots]_x = (\delta_{xy} + g_{xy}) (p^{0j})^y,$$

where

$$g_{xy} = \frac{8\pi}{v} \sum_{\mu} \frac{E_{\mu}(k) p_{\mu}^x}{E_0^2 - E_{\mu}^2(k)} \left[ \frac{(p_{\mu}^x k) k_y}{k^2} - \frac{v}{4\pi} \sum_{\beta} Q_{y\beta}(k) p_{\mu}^{\beta} \right].$$

If the impurity atom (or molecule) lies at the center of the unit cell, then as  $k \rightarrow 0$ , the tensor  $Q_{\alpha\beta}(k)$  is reduced to the scalar  $Q_{\alpha\beta}(0) = (4\pi/3v)\delta_{\alpha\beta}$ . Moreover, according to [12] the relation holds that

$$\frac{8\pi}{v} \sum_{\mu} \frac{E_{\mu}(k) p_{\mu}^{\alpha} p_{\mu}^{\beta}}{E_0^2 - E_{\mu}^2(k)} = \delta_{\alpha\beta} - \epsilon_{\alpha\beta}(E) + \frac{(\delta_{\alpha\gamma} - \epsilon_{\alpha\gamma}) k_{\gamma} (\delta_{\beta\sigma} - \epsilon_{\beta\sigma}) k_{\sigma}}{\epsilon_{rt}(E) k_r k_t},$$

where  $\epsilon_{ij}$  is the dielectric tensor of the crystal, which

takes on the following form for cubic crystals with neglect of spatial dispersion:

$$\frac{8\pi}{v} \sum_{\mu} \frac{E_{\mu} p_{\mu}^{\alpha} p_{\mu}^{\beta}}{E_0^2 - E_{\mu}^2} = \delta_{\alpha\beta} - \epsilon_{\alpha\beta} + \frac{(1-\epsilon)^2 k_{\alpha} k_{\beta}}{\epsilon k^2}.$$

Thus we find that the projection of the vector (2.14) onto the direction of polarization of the transverse macrofield  $\mathbf{l} (\mathbf{l} \cdot \mathbf{k} = 0)$  is

$$l P^{0\nu_0} = \sqrt{\Delta_j} a_{\nu_0}(pf) \frac{\epsilon(E_0) + 2}{3} (p^{0j}). \quad (2.18)$$

For sufficiently deep traps, the quantity  $\tilde{u}_{\nu_0}(pf) \equiv \sqrt{\Delta_j} a_{\nu_0}(pf)$  is close to unity (see also Chap. 4 of the main text). Under these conditions, as we see from (2.18), the effect of the environment is reduced to replacing the transition dipole moment in the isolated impurity molecule with its effective value  $[(\epsilon + 2)/3] p^{0j}$ . One also gets exactly the same result by using the Coulomb gauge for substitutional molecules [13], and of course, it does not depend at all on the choice of gauge (cf. Chap. 2 of the main text, where the Lorentz gauge was used). Thus, in contrast to the treatment in [18], which was based on using the model of Onsager, the acting-field correction has a Lorentzian form even when the properties of the impurity substantially differ from those of the molecules of the main substance. However, the comparison that we have made with the results of the macroscopic model of Onsager indicates simply that it is inapplicable for describing the intensities of transitions at impurity centers (Mahan [19] has also come to an analogous conclusion in calculating the interaction energy in a medium of two static dipoles).

<sup>1</sup>At the same time, of course, the molecules can have static moments of higher multipole character, both in the ground and in the excited state. In general, these moments differ for the ground and excited states. The energies of interaction of a molecule with its environment also come to differ in these states. This leads to a certain frequency shift of the intramolecular transitions with respect to the transition frequencies in vacuo. We shall assume henceforth that the tensor  $a_{ij}(\omega, \mathbf{k})$  differs from the corresponding tensor for a molecule in a vacuum only by taking of this shift.

<sup>2</sup>This treatment using the tensor  $a_{ij}(\omega, \mathbf{k})$  is in no way more phenomenological than the theory of excitons of small radius, where instead of the tensor  $a_{ij}(\omega, \mathbf{k})$  one also assumes the wave functions and energies of the isolated molecule to be known (assigned). However, the structure of the tensor  $a_{ij}(\omega, \mathbf{k})$  in the region of certain resonances of the molecule can be treated by using point-group theory.

<sup>3</sup>The results existing here are reflected in very general form in Khokhlov's article. [4] References to the earlier studies are also found there.

<sup>4</sup>For the accuracy of this approximation, see below in Chap. 4.

<sup>5</sup>The tensor  $\epsilon_{ij}(\omega, \mathbf{k})$  has been calculated within the framework of Frenkel's exciton theory in [1]. In this regard, see also [4].

<sup>6</sup>Of course, a knowledge of the tensor  $\epsilon_{ij}$  (see (24) and (26)) permits us to find the position of absorption lines for arbitrary polarizations and directions of propagation of the light, and also to account for spatial-dispersion effects.

<sup>7</sup>The fact that we are dealing with effects that differ in nature becomes especially evident when we consider that the size of the acting field at the site of the impurity is practically independent of the properties of the impurity (see Appendix 2).

<sup>8</sup>Thus, dispersion measurements in a region of transparency can be used for analyzing the composition of a mixture. A knowledge of this composition is necessary in interpreting results on concentration broadening and comparing them with theory.

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