1) The analogous dependence $T_1^{-1} \sim \omega_e^{-1/2}$ is also observed in dielectric crystals containing linear chains of localized electron spins.[5] In this case the quantity T_1^{-1} depends on the character of the propagation of the spin excitations in the one-dimensional chain of spins with Heisenberg interaction. For small frequencies ω_e the propagation of the excitations also turns out to be diffusive at sufficiently high temperatures (cf. Ref. 6).

2) A contribution to the three-dimensional diffusion of the spin excitations is also given by the dipole-dipole interaction of the electrons. However, this contribution is two to three orders smaller than the contribution from tunneling of electrons between filaments, even in such strongly anisotropic crystals as TTF-TCNQ In dielectric crystals with spin chains the dipole-dipole interaction of the electron spins makes the principal contribution to the three-dimensional diffusion of the spin excitations of the electron system.

3) In principle we could improve the procedure for determing the parameters t by using, e.g., the least-squares method in the entire range of variation of the magnetic field H. However, without an increase in the accuracy of the experimental measurement of T_1^{-1} this procedure will not give more-accurate values of t, since the experimental points coincide with our calculated curves within the experimental error bars. We note that the most important region for the determination of the parameters t is the region of low fields H, and up to now it is in precisely this region that the experimental errors for T_1^{-1} are rather large.

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Contribution to the theory of spatial dispersion and auxiliary light waves in the exciton absorption region

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The specific polarization of a crystal is expressed in terms of the total electric field in terms of the polarizability tensor $\kappa(\omega,\mathbf{k})$ or in terms of the external field with the aid of the tensor $\beta(\omega,\mathbf{k})$. It is shown that introduction of the dependence on $\mathbf{k}$ in β calls for knowledge of only the effective mass of the exciton, and when this dependence is directly introduced in κ the number of unknown additional parameters becomes much larger. The use of only the general scheme of quantum-mechanical calculation of β by supplementing it with macroelectrodynamic considerations has made it possible to determine $\beta(\omega,\mathbf{k})$ and to use the latter to determine $\kappa(\omega,\mathbf{k})$, the refractive indices of all the light waves, and their polarization in crystals with different symmetry. The dependences of the exciton energies and of the matrix elements of the dipole moment on $\mathbf{s}\equiv\mathbf{k}/|\mathbf{k}|$ are determined in passim as $|\mathbf{k}|\to 0$. The connection between these quantities pertaining to different mutually degenerate excitons is obtained. These general results, deduced without using exciton models, cannot be obtained by direct quantum-mechanical calculation.

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1. TWO FORMS OF CRYSTAL POLARIZABILITY

The macroscopic specific dipole moment $\mathbf{P}$ of a crystal is traditionally expressed in terms of the macrofield $\mathbf{E}$ by the formula

$$\mathbf{P}=\varkappa\mathbf{E},\quad \varkappa(\omega,\mathbf{k})=[\varepsilon(\omega,\mathbf{k})-1]/4\pi,\quad \mathbf{E},\ \mathbf{P}\sim e^{i(\mathbf{kr}-\omega t)},\tag{1}$$

where $\varepsilon(\omega,\mathbf{k})$ is the dielectric tensor of the crystal. The field $\mathbf{E}$ consists of the external field $\mathbf{E}_e$ and the field $\mathbf{E}'$ generated, without a time delay, by the electrons and nuclei of the crystal. The macroscopic field $\mathbf{E}'$, i.e., the field averaged over the cell volume, is the electrostatic field of fictitious dielectric-polarization charges, therefore

$$\mathbf{E}'=\mathbf{E}-\mathbf{E}_e=-4\pi\overline{\mathbf{ss}}\mathbf{P}, \quad \mathbf{s}=\mathbf{k}/|\mathbf{k}|; \tag{2}$$

here and below a common superior bar over two vectors denotes the dyad tensor: $(\overline{\mathbf{AB}})_{xy}=A_xB_y$.

In the quantum-mechanical calculation of crystal polarization, the perturbation is the external field $\mathbf{E}_e$, since $\mathbf{E}'$ is already contained in the unperturbed Schrödinger operator of the crystal energy. Such a calculation yields in first-order approximation a linear relation between $\mathbf{P}$ and $\mathbf{E}_e$:

$$\mathbf{P}=\beta(\omega, \mathbf{k})\mathbf{E}_e. \tag{3}$$

Eliminating $\mathbf{E}'$ or $\mathbf{E}_e$ from (2) and (3), we obtain with the aid of (1) the connection between two forms of the polarizability, $\varkappa$ and β. It can be expressed by any of three equivalent formulas:

$$\varkappa=(I-4\pi\beta\overline{\mathbf{ss}})^{-1}\beta, \quad \beta=(I+4\pi\varkappa\overline{\mathbf{ss}})^{-1}\varkappa \;[1]; \tag{4}$$

$$\varkappa=\left(I+\frac{4\pi\beta\overline{\mathbf{ss}}}{1-4\pi\langle\beta\rangle}\right)\beta, \quad \beta=\left(I-\frac{4\pi\varkappa\overline{\mathbf{ss}}}{1+4\pi\langle\varkappa\rangle}\right)\varkappa \;[2], \tag{5}$$

$$\beta^{-1}=\varkappa^{-1}+4\pi\overline{\mathbf{ss}}. \tag{6}$$

Here I is a unit tensor, $I_{xy}=\delta_{xy}$, $\langle T\rangle\equiv(s, Ts)$, and T as a second-rank tensor.

As $|\mathbf{k}|\rightarrow 0$, which corresponds to neglecting spatial disperison, the tensor $\varkappa$ (but not β) acquires favorable properties: it ceases to depend on the direction of s and its principal axes are determined by the crystal symmetry. On the other hand the tensor β, as seen from example from (6), continues to depend on the direction $\mathbf{s}$, and its principal axes, at arbitrary direction of $\mathbf{s}$, do not coincide with the princiapl axes of $\varkappa$. Only if $\mathbf{s}$ is directed along one of the principal axes of $\varkappa$, meaning also $\varkappa^{-1}$, do the principal axes of β and $\varkappa$ coincide even at $|\mathbf{k}|\neq 0$. If $\mathbf{k}$ is perpendicular to one of the principal axes of $\varkappa(\omega, \mathbf{k})$ then, as seen from (6), this will also be a principal axes for $\beta(\omega, \mathbf{k})$, and the corresponding principal values of β and $\varkappa$ coincide then.

However, the aforementioned advantages of the tensor $\varkappa$ notwithstanding, many of the principal problems cannot be solved without the use of the tensor β. These include the separation of the exciton contribution to the polarization, which must be done when the auxiliary boundary conditions are formulated,[3,4] the determination of the dependence of the polarizability on $\mathbf{k}$ (see below), and others.

2. DEPENDENCE OF THE POLARIZABILITY ON k

Using a very general definition of the concept "exciton," taking the exciton to mean any crystal excitation that has a single continuous quantum number–quasimomentum (the remaining quantum numbers are discrete), and without introducing any exciton model whatever, one of us derived quantum-mechanically an expression for $\beta(\omega, \mathbf{k})$.[1,5] If several close-lying exciton energy bands are located far enough from the other energy bands of the crystal, then

$$\beta(\omega, \mathbf{k})=\beta_0(\omega)+\sum_l\frac{V\overline{\mathbf{P}_l\mathbf{P}_l^*}}{\mathscr{E}_l(\mathbf{k})-\hbar\omega}; \tag{7}$$

here l is the number of the exciton band, and $\mathscr{E}_l(\mathbf{k})$ is the exciton energy, assumed close in value to $\hbar\omega$. Next, $\mathbf{P}_l=\langle\psi^0|\hat{\mathbf{P}}|\psi_{l\mathbf{k}}\rangle$, where ψ^0 and $\psi_{l\mathbf{k}}$ are the ground and exciton states of the crystal, $\mathbf{P}$ is the dipole-moment operator per unit volume of the crystal localized at the origin; V is the volume of the principal cyclicity region of the crystal, and $\beta_0(\omega)$ is the "background" value of β, depends little on ω, and includes the contribution from the other excited states of the crystal. To take into account the finite lifetime of the exciton relative to scattering by phonons and relative to a nonradiative transition to other states, it is necessary to add to $\mathscr{E}_l(\mathbf{k})$ the quantity $-i\hbar\Gamma_l$.

The numerators of the fractions in (7) can be expanded in powers of k^2. Examination of the models show that in this case the expansion parameter is $(a/\lambda)^2 \ll 1$, where a is the lattice constant and λ is the wavelength of the light. It is assumed below that the zeroth term of the expansion differs from zero, i.e., the excitonic transition is allowed in the dipole approximation. The terms $\sim\mathbf{k}^2$ in the numerators are then inessential and are discarded.

It is assumed below that at small k we have

$$\mathscr{E}_l(\mathbf{k})=\mathscr{E}_{ls}+\frac{\hbar^2\mathbf{k}^2}{2M_{ls}}+\ldots, \tag{8}$$

where M_{ls} is the effective mass of the exciton in the $\mathbf{s}$ direction. This expansion converges quite rapidly. However, the quadratic term is most significant here, since it is located in the denominator of (7) alongside $\mathscr{E}_{ls}-\hbar\omega$ and in the case of resonance, i.e., when $\hbar\omega \approx \mathscr{E}_{ls}$, discarding the quadratic term would increase β infinitely. Similar fractions are contained in β_0, but since there is no resonance we can put in them $k=0$. Thus, the dependence on k should be preserved only in $\mathscr{E}_l(\mathbf{k})$, and this procedure is justified only because in the essential region the denominator is close to zero. We have thus determined the dependence of β on ω and $\mathbf{k}$.

Similar arguments, which have so greatly simplified the dependence of the polarization on k, would not be valid were we to consider in lieu of β the tensor $\varkappa$ or ε. Thus, for particular exciton models it is possible to transfer the field $\mathbf{E}'$ from the unperturbed energy operator to the perturbation, i.e., regard the total field $\mathbf{E}$ as a perturbation and obtain by direct quantum-mechanical calculation not β, but $\varkappa$ in a form similar to (7). But even if it turns out that in the general case $\varkappa$ and ε have no pole in the vital region of frequencies ω, where the auxiliary waves are essential and β has a pole. By way of example we cite the case of a longitudinal exciton: at resonance, i.e., at $\hbar\omega=\mathscr{E}_{\text{long}}(\mathbf{k})$, a pole exists for β but not for $\varkappa$ or ε. Moreover, in this case the corresponding principal value is $\varepsilon_{ss}(\omega, \mathbf{k})=0$. This equation leads to the dispersion law of the longitudinal wave. If the corresponding principal value $\varkappa_{ss}$ is written in the form

$$\varkappa_{ss}=\varkappa_{0ss}+\frac{Q_{ss}}{K+\hbar^2k^2/2\mathfrak{M}-\hbar\omega}, \tag{9}$$

then the dispersion law of the longitudinal wave takes the form

$$\hbar\omega=K+\frac{\hbar^2k^2}{2\mathfrak{M}}+\frac{4\pi Q_{ss}}{1+4\pi\varkappa_{0ss}}. \tag{10}$$

It is seen from this formula that, if we retain the second term of the right-hand side, there are no grounds for neglecting terms of order $\mathbf{k}^2$ in the numerator Q_{ss} of formula (9) and in the "background" part $\varkappa_{0ss}$. On the other hand neglect of this kind was justified in expression (7) for β.

It can be shown that the resonances of β and $\varkappa$ coincide only when the denominator $\mathcal{E}_l(\mathbf{k})$ of the fraction in (7) is the energy of a strictly transverse exciton.

Case of isolated nondegenerate exciton. This case is realized in crystals of various symmetry. In (7), the sum contains one term, which we shall designate by the index l. Changing from β to $\varkappa$, say by means of formula (5), we get

$$\varkappa=\varkappa_0+\frac{Q^{(l)}}{K_l+\hbar^2\mathbf{k}^2/2M_{ls}-\hbar\omega}, \tag{11}$$

where the second-rank tensors $\varkappa_0$ and $Q^{(l)}$ and the constant K_l are connected with the parameters of β by the following formulas:

$$\varkappa_0\equiv\left(I+\frac{4\pi\beta_0\overline{\mathbf{ss}}}{1-4\pi\langle\beta_0\rangle}\right)\beta_0,\quad \beta_0=\left(I-\frac{4\pi\varkappa_0\overline{\mathbf{ss}}}{\langle\varepsilon_0\rangle}\right)\varkappa_0,\quad \varepsilon_0\equiv I+4\pi\varkappa_0; \tag{12}$$

$$Q^{(l)}\equiv V\overline{\tilde{\mathbf{P}}_l\tilde{\mathbf{P}}_l^*},\quad \tilde{\mathbf{P}}_l\equiv\mathbf{P}_l+4\pi(\mathbf{s},\mathbf{P}_l)\varkappa_0\mathbf{s},\quad \mathbf{P}_l=\tilde{\mathbf{P}}_l-\frac{4\pi}{\langle\varepsilon_0\rangle}(\mathbf{s},\tilde{\mathbf{P}}_l)\varkappa_0\mathbf{s}; \tag{13}$$

$$\mathcal{E}_{ls}=K_l+\Delta_l(\mathbf{s}),\quad \Delta_l(\mathbf{s})=4\pi V\frac{|(\mathbf{s},\mathbf{P}_l)|^2}{1-4\pi\langle\beta_0\rangle}=\frac{4\pi V}{\langle\varepsilon_0\rangle}|(\mathbf{s},\tilde{\mathbf{P}}_l)|^2. \tag{14}$$

As noted above in the discussion of the dependence of β on $\mathbf{k}$, in all the quantities that enter in (12)–(14) we can neglect the terms of order of $\mathbf{k}^2$, and the result is a negligible relative error of order $(a/\lambda)^2$. Thus, these quantities take the same form as in the absence of spatial dispersion. In this case $\varkappa_0, Q^{(l)}, \tilde{\mathbf{P}}_l$, and the constant K_l does not depend on s. Therefore formulas (12)–(14) determine the explicit dependences of the quantities β_0 and $\mathbf{P}_l$ and of the exciton energy $\mathcal{E}_{ls}$ on s as $|\mathbf{k}|\to 0$. A direct quantum-mechanical calculation of this dependence is a complicated matter, calls for a determination of the crystal wave functions, and is therefore impossible without using particular models of the exciton. Above, however, we have used only the general scheme of the quantum-mechanical calculation of β, supplemented by considerations of macroelectrodynamics. The results pertain to the general definition used above for the exciton and were obtained without the use of models.

The dependence of the limiting exciton energy $\mathcal{E}_{ls}$ on s, defined by formula (14), is a generalization of the result obtained by an exclusively quantum-mechanical method,[6] as well as of a result obtained by a reasoning analogous to the one described above[1] (see formulas (35)], but without allowance for the background polarizability ($\varkappa_0=0$). Formula (14) was obtained in Ref. 3 [see formula (24)] for the case of a uniaxial crystal.

Recognizing that the transformations (4)–(6) are exact (and that in β the relative error is of the order of $(a/\lambda)^2$ and will always be neglected), the use of the tensors β (7) and $\varkappa$ (11) leads to perfectly equivalent results. The advantage of the derivation of $\varkappa$ given above is, as can be seen from the derivation, we can leave out of $\varkappa_0$ and $Q^{(l)}$ the terms of the order $\mathbf{k}^2$ which were mentioned following Eq. (10), if we simultaneously set $\mathfrak{M}$ equal to the effective mass of the Schrödinger exciton M_{ls}.

We have so far not used crystal-symmetry considerations. The latter determine in many cases the direction of the vector $\tilde{\mathbf{P}}_l$ which is independent of s. This refines the s-dependences of $\mathbf{P}_l$ and Δ_l. For example, in crystals of rhombic symmetry $\tilde{\mathbf{P}}_l$ is directed along the crystal axes. In uniaxial crystal $\tilde{\mathbf{P}}_l$ for a nondegenerate exciton is directed along the crystal axis.

Case of doubly degenerate exciton bands. This case is realized in uniaxial crystals. The theory of the Schrödinger exciton can be obtained, as is well known, from the macroelectrodynamic theory of light waves by taking the limits for the speed of light $c\to\infty$ and for the wave refractive index $n\to\infty$, such that the wave vector $\mathbf{k}=\omega n\mathbf{s}/c$ remains finite.[7] In a uniaxial crystal one of the light waves—the ordinary ray—is strictly transverse, i.e., its specific-polarization vector is perpendicular to s. It is easy to show that this specific polarization is parallel to $\mathbf{P}_l$.[1,3] The aforementioned limiting transition transforms this wave into an exciton. Let the number of this exciton be $l=1$. We choose the x axis along $\mathbf{P}_1$, i.e., perpendicular to s and to the crystal axis C. We choose the z axis along C. The extraordinary ray is polarized in the (C, s) plane. An analogous limiting transition leads in this case to the second of the two degenerate excitons, $l=2$, whose $\mathbf{P}_2$ lies in the (C, s) plane.

For an isolated doubly degenerate exciton, Eq. (7) is written in the form

$$\beta=\beta_0+\frac{V\overline{\mathbf{P}_1\mathbf{P}_1^*}}{\mathcal{E}_{1s}+\hbar^2\mathbf{k}^2/2M_{1s}-\hbar\omega}+\frac{V\overline{\mathbf{P}_2\mathbf{P}_2^*}}{\mathcal{E}_{2s}+\hbar^2\mathbf{k}^2/2M_{2s}-\hbar\omega}. \tag{15}$$

Changing from β to $\varkappa$ by means of (5), we get

$$\varkappa=\varkappa_0+\frac{Q^{(1)}}{\mathcal{E}_{1s}+\hbar^2\mathbf{k}^2/2M_{1s}-\hbar\omega}+\frac{Q^{(2)}}{\mathcal{E}_{2s}-\Delta_2(\mathbf{s})+\hbar^2\mathbf{k}^2/2M_{2s}-\hbar\omega}. \tag{16}$$

Here $\varkappa_0$ is connected with β_0 by formula (12), while the vectors $\tilde{\mathbf{P}}_l$ and the tensors $Q^{(l)}$ $(l=1,2)$ and Δ_2 are determined by formulas (13) and (14).

As $|\mathbf{k}|\to 0$ it is necessary to require that $\varkappa$ be independent of s, and it follows from the symmetry of the uniaxial crystal that $\varkappa_{xy}=\varkappa_{xz}=\varkappa_{yz}=0$; $\varkappa_{xx}=\varkappa_{yy}$. From this we get

$$|\tilde{\mathbf{P}}_2|^2=|\mathbf{P}_1|^2,\quad \tilde{\mathbf{P}}_2\|y,\quad \mathcal{E}_{2s}-\Delta_2(\mathbf{s})=\mathcal{E}_{1s}\equiv K, \tag{17}$$

where K does not depend on s,

$$\varkappa=\varkappa_0+\frac{V|\mathbf{P}_1|^2\overline{\mathbf{xx}}}{K+\hbar^2\mathbf{k}^2/2M_{1s}-\hbar\omega}+\frac{V|\mathbf{P}_1|^2\overline{\mathbf{yy}}}{K+\hbar^2\mathbf{k}^2/2M_{2s}-\hbar\omega}; \tag{18}$$

here **x** and **y** are unit vectors along the axes x and y.

Case of cubic crystals. This case could be treated in analogy with the preceding one by going to the limits $c\to\infty, n\to\infty$. We shall, however, sacrifice the uniformity of the exposition in order to illustrate with this example another analysis method. This enables us to emphasize incidentally some properties of the polarizabilities β and $\varkappa$.

Assume that for an arbitrary specified direction **s** we know β in the form (7). Let the coordinates axes x, y, and z be the principal axes of the tensor β. Their directions, generally speaking can depend on $|\mathbf{k}|$ with **s** fixed.

We consider first the case $|\mathbf{k}|=0$. Any direction in space is then a principal one for $\varkappa$ and $\varkappa^{-1}$. We specify an arbitrary direction of **s** and us (6); we can then easily show the following:

a) The direction of **s** and all the directions in a plane perpendicular to **s** are principal for β^{-1} and β. We choose the z axis along **s**.

b) In directions perpendicular to **s**, the principal values of β are the same, since they coincide with the principal values for $\varkappa$.

c) Since the aforementioned principal axes of β do not depend on ω, they are also principal axes of β_0 and of the numerator of any fraction of (7) having a different frequency dependence, i.e., having different $\mathscr{E}_{ls}$.

d) If the term l in the denominator of (7) contains a nondegenerate energy $\mathscr{E}_{ls}$ (an energy unequal to the energies in the denominators of the other fractions), then the dyad $\mathbf{P}_l\mathbf{P}_l^*$ should have the principal axes indicated in Item a) above; this is possibly only if $\mathbf{P}_l \| \mathbf{s}$.

e) If double degeneracy exists, $\mathscr{E}_{1s}=\mathscr{E}_{2s}$, then the summary numerator $\mathbf{P}_1\mathbf{P}_1^*+\mathbf{P}_2\mathbf{P}_2^*$ must have the same principal axes. This is possible either if $\mathbf{P}_1 \| \mathbf{P}_2 \| \mathbf{s}$, which returns us to Item d) and corresponds to random degeneracy, or if $\mathbf{P}_1$ and $\mathbf{P}_2$ lie in the xy plane. In the latter case, in order for any direction in the xy plane be a principal one for the tensor $\mathbf{P}_1\mathbf{P}_1^*+\mathbf{P}_2\mathbf{P}_2^*$, it is necessary and sufficient to have $\mathbf{P}_1 \perp \mathbf{P}_2$ and $|\mathbf{P}_1|^2=|\mathbf{P}_2|^2$. However, the pair of orthoghal vectors $\mathbf{P}_1$ and $\mathbf{P}_2$ can be arbitrarily oriented in the xy plane.

Degeneracy of higher multiplicity is possible, but it would be accidental, since it would not follow from symmetry requirement. As in the foregoing consideration of crystals of lower symmetry, in the analysis of a cubic crystal we shall also confine ourselves to the minimum number of fractional terms needed in (7) to satisfy the symmetry requirements. As will be shown below, it is necessary for this purpose to introduce three terms in which $\mathscr{E}_{1s}=\mathscr{E}_{2s}\neq\mathscr{E}_{3s}$.

Let now $|\mathbf{k}|$ become different from zero but remain small. As a result $\mathscr{E}_l(\mathbf{k})$ are subjected to small perturbations that lift the degeneracy, inasmuch as in (8), generally speaking, $M_{1s}\neq M_{2s}$. In the equations for $\mathbf{P}_l$ we confine ourselves to the zeroth approximation in $|\mathbf{k}|$, an assumption justified in the discussion preceding and following formula (8); the correct choice of the zeroth approximation in the general case, however, is known to be determined by the perturbation. In this case the pair of mutually orthogonal vectors $\mathbf{P}_1$ and $\mathbf{P}_2$ acquires not an arbitrary orientation in the xy plane, but definite directions. If **k** is directed along one of the threefold or fourfold axes, then the degeneracy of $\mathscr{E}_1(\mathbf{k})$ and $\mathscr{E}_2(\mathbf{k})$ is not lifted, and the orientation of the orthogonal vectors $\mathbf{P}_1$ and $\mathbf{P}_2$ remains arbitrary. In the remaining cases, if **k** lies in a mirror-symmetry plane of the crystal, then one of the vectors $\mathbf{P}_1$ or $\mathbf{P}_2$ lies in the same plane, and the other is perpendicular to it. On the other hand if **k** is directed arbitrarily, then the directions of $\mathbf{P}_1$ and $\mathbf{P}_2$ can be determined only by a quantum-mechanical calculation, which can be carried out only for concrete exciton models.

After the degeneracy is lifted, the principal axes of β are not arbitrary dimensions in the plane perpendicular to **s**, but only the directions $x \| \mathbf{P}_1$ and $y \| \mathbf{P}_2$. They in turn are the principal axes of each of the dyads in the numerators of the fractions in (7). Therefore, so long as the introduction of the spatial dispersion consists merely of taking into account the dependence of $\mathscr{E}_l$ on $|\mathbf{k}|$ in the denominators of (7) and of neglecting the dependence of $\mathbf{P}_l$ on $|\mathbf{k}|$, the principal axes x, y, and z do not depend on $|\mathbf{k}|$, i.e., they are the same as in the absence of spatial dispersion.

We proceed now to determine $\varkappa$ in terms of β at $|\mathbf{k}|\neq 0$. The axes x, y, and z are the principal axes of the dyad $\overline{\mathbf{ss}}$. According to (6) they are therefore not principal axes of $\varkappa^{-1}$ and $\varkappa$ likewise at $|\mathbf{k}|\neq 0$, with

$$\varkappa_{xx}=\beta_{xx},\quad \varkappa_{yy}=\beta_{yy},\quad \varkappa_{zz}=\beta_{zz}/(1-4\pi\beta_{zz}). \tag{19}$$

Similar formulas connect $\varkappa_0$ and β_0. If we use for β the expression (7) with $l=1, 2, 4$, where $\mathscr{E}_{3s}$ is the nondegenerate energy and $\mathbf{P}_3 \| \mathbf{s} \| z$ in accord with d), and if we also stipulate $\varkappa_{xx}=\varkappa_{yy}=\varkappa_{zz}$ in the limit as $|\mathbf{k}|\to 0$, then we get ultimately from (19)

$$\varkappa_{xx}=\varkappa_0+\frac{V|\mathbf{P}_1|^2}{K+\hbar^2\mathbf{k}^2/2M_{1s}-\hbar\omega},\quad \varkappa_{yy}=\varkappa_0+\frac{V|\mathbf{P}_1|^2}{K+\hbar^2\mathbf{k}^2/2M_{2s}-\hbar\omega}, \tag{20}$$
$$\varkappa_{zz}=\varkappa_0+\frac{V|\mathbf{P}_1|^2}{K+\hbar^2\mathbf{k}^2/2M_{3s}-\hbar\omega};$$

$$|\mathbf{P}_1|=|\mathbf{P}_2|=\varepsilon_0|\mathbf{P}_3|,\quad \mathscr{E}_{1s}=\mathscr{E}_{2s}\equiv K,\quad \mathscr{E}_{3s}=K+\frac{4\pi V}{\varepsilon_0}|\mathbf{P}_1|^2; \tag{21}$$

K is here independent of **s**.

The results (20) and (21) were obtained without using the exciton model, something impossible to do by a direct quantum-mechanical calculation. These formulas show that in the resonance region cubic crystals can have large optical anisotropy.

The foregoing results show that by introducing in (7) three fractional terms we were able to satisfy all the symmetry requirements in a cubic crystal. Were we to introduce a smaller number of terms, say two, we would obtain a particular case of the theory expounded above, which can be easily obtained by setting one of the $\mathbf{P}_l$ equal to zero. But then the first relation of (21), which follows from symmetry, shows that the remaining two $\mathbf{P}_l$ also vanish, i.e., the polarizabilities are equal to β_0 and $\varkappa_0$. This means that in the considered spectral region there are no dipole-allowed excitons at all. The number of fractional terms in (7) can exceed three. This does not follow from symmetry requirements, but is possible as a result of an accidental landing of other dipole-allowed exciton levels in the considered spectral region. From symmetry considerations, however, it can be shown that the additional exciton levels and the corresponding fractions in (7) can appear only in the form of analogous triplets, and two levels within each triplet are degenerate. The appearance of each such triplet produces in each of the formulas of (20) an additional fractional term.

Proceeding from consideration of cubic crystals to a general discussion, we note that in (8) we have assumed that $\mathscr{E}_l(\mathbf{k})$ can be expanded in powers of $|\mathbf{k}|^2$ at a fixed $\mathbf{s}$. The possibility of such an expansion for crystals with inversion center was proved for all exciton bands, and for crystals without an inversion center for many exciton bands by calculating the exciton models. To be able to expand the energy (8) in powers of k_x, k_y, and k_z with expansion coefficients that do not depend on $\mathbf{s}$ it is necessary that M_{ls} have the following dependence on $\mathbf{s}$:

$$\frac{1}{M_{ls}}=g_0+\sum_{i,j}g_{ij}s_is_j,\quad i,j=x,y,z. \tag{22}$$

However an examination of the models show that for the overwhelming majority of the crystal classes substantial deviations from (22) are obtained.[8-10] Consequently, $\mathscr{E}_l(\mathbf{k})$ can in general not be expanded in powers of k_x, k_y, and k_z. Therefore in the region of resonance ε^{-1} can likewise not be expanded in powers of k_x, k_y, and k_z.

We note in conclusion that cases when the expansion of the exciton energy in powers of $|\mathbf{k}|$ contains a linear term are rarely encountered (the crystal classes C_3, D_3, C_4, D_4, C_6, D_6). It is the necessary to replace (8) by a linear expansion, but in all the remaining respect the method developed above remains in force, since relations (4)–(6), as well as the requirement that $\varkappa$ be independent of s at $|\mathbf{k}|=0$, remain in force.

3. REFRACTIVE INDICES OF LIGHT WAVES

The refractive indices can be defined in terms of the tensor β. The corresponding form of the Fresnel equation is shown in Ref. 3. In the present article we shall define them in terms of the tensor $\varepsilon=1+4\pi\varkappa$ using the known Fresnel relation

$$n^4\langle\varepsilon\rangle+n^2[\langle\varepsilon^2\rangle-\langle\varepsilon\rangle\operatorname{Sp}\varepsilon]+\det|\varepsilon|=0. \tag{23}$$

Neglecting the spatial dispersion ($\mathbf{k}=0$ in ε), this is a quadratic equation in n^2. Given $\mathbf{s}$, this equation yields two values of n (ordinary birefringence). When account is taken of the dependence of ε on $\mathbf{k}=\omega n\mathbf{s}/c$, the degree of Eq. (23) and the number of its roots increase—additional light waves appear.

Crystals with rhombic symmetry. In these crystals there exist only nondegenerate exciton bands. We confine ourselves to the case when $\mathbf{s}$ lies in the mirror-symmetry plane of the crystal—the yz plane. The coordinate axes x, y, and z are chosen along the twofold crystal axes. They are not the principal axes of the tensors $\varkappa_0$ and $Q^{(l)}$ in (11). Equation (23) reduces to

$$(n^2-\varepsilon_{xx})[n^2-\varepsilon_{yy}\varepsilon_{zz}/\langle\varepsilon\rangle]=0. \tag{24}$$

Only one of the diagonal elements of the dyad $Q^{(l)}$ differs from zero.

If $Q^{(l)}_{xx}\neq 0$, then ε_{yy} and ε_{zz} have no spatial dispersion and by equating the square bracket in (24) to zero we obtain one unknown wave polarized in the yz plane. Equating on the other hand the round bracket in (24) to zero and taking (11) into account, we obtain to waves equally polarized along the x axis with refractive indices

$$n_\pm{}^2=\frac{1}{2}(\mu_{ls}+\varepsilon_{0xx})\pm\left[\frac{1}{4}(\mu_{ls}-\varepsilon_{0xx})^2+b_{ls}\right]^{1/2},\quad E\|x, \tag{25}$$

where

$$\mu_{ls}=\frac{2M_{ls}c^2}{\hbar\omega}\left(1-\frac{\mathscr{E}_{ls}}{\hbar\omega}\right),\quad b_{ls}=\frac{8\pi M_{ls}c^2V|\mathbf{P}_l|^2}{\hbar^2\omega^2}. \tag{26}$$

If $Q^{(l)}_{zz}\neq 0$, then ε_{xx} and ε_{yy} have no spatial dispersion and by setting the round bracket in (24) equal to zero we obtain one known wave polarized along the x axis. On the other hand, equating the square bracket to zero and taking (11) into account, we obtain two waves polarized in the yz plane with refractive indices

$$n_\pm{}^2=\frac{1}{2}(\mu_{ls}+\varepsilon')\pm\left[\frac{1}{4}(\mu_{ls}-\varepsilon')^2+\frac{\varepsilon_{0yy}{}^2}{\langle\varepsilon_0\rangle^2}b_{ls}s_y{}^2\right]^{1/2},\quad \varepsilon'\equiv\frac{\varepsilon_{0yy}\varepsilon_{0zz}}{\langle\varepsilon_0\rangle}. \tag{27}$$

If $Q^{(l)}_{yy}\neq 0$, then the result can be obtained from (27) by the substitution $y\rightleftarrows z$.

Uniaxial crystals. In this case we consider an arbitrary direction of $\mathbf{s}$. Choosing the z axis along $\mathbf{C}$, and the x axis perpendicular to the $(\mathbf{C},\mathbf{s})$ plane, so that these axes coincide with the principal directions of the tensors $\varkappa_0$ and $Q^{(l)}$, we arrive again at Eq. (24). If $\hbar\omega$ approaches the energy of the nondegenerate exciton, then only one component $Q^{(l)}_{zz}$ of the tensor $Q^{(l)}$ differs from zero. The vanishing of the round bracket in (24) leads then to one ordinary wave polarized along the x axis. The vanishing of the square bracket in (24) when account is taken of (11) leads to two waves polarized in the yz plane and having refractive indices determined by a formula such as (27).

If $\hbar\omega$ approaches the energy of the doubly degenerate exciton bands, then $\varkappa$ is given by (18). In this case ε_{xx} and ε_{yy} have spatial dispersion, but ε_{zz} does not. Equating the round bracket in (24) to zero, we obtain two waves with like polarization along x and with refractive indices determined by formulas (25) in which we must put $l=1$. Equating the square bracket in (24) to zero, we obtain two waves polarized in the yz plane. Their refractive indices are determined by a formula such as (27), in which we must put $l=2$ and make the substitution $y\rightleftarrows z$ everywhere.

Cubic crystals. Specifying the arbitrary direction $\mathbf{s}$, we choose the coordinates x, y, and z along the principal directions of the tensor $\varkappa$ and of ε, as indicated in the corresponding subsection of the preceding section (see the text preceding formula (19)]. In this case $z\|s$, $\langle\varepsilon\rangle=\varepsilon_{zz}$ and Eq. (23) takes the form

$$\varepsilon_{zz}(n^2-\varepsilon_{xx})(n^2-\varepsilon_{yy})=0. \tag{28}$$

The tensor $\varkappa$ is determined by formula (20), which shows that all three principal values of $\varkappa$ have spatial dispersion.

Equating to zero the factor ε_{zz} in (28), we obtain a longitudinal wave with a refractive index

$$n^2 = \frac{2M_{3s}c^2}{\hbar\omega}\left(1 - \frac{\mathscr{E}_{3s}}{\hbar\omega}\right), \tag{29}$$

where $\mathscr{E}_{3s}$ is given by (21); it does not depend on s.

Equating to zero the second factor in (28), we obtain two waves with like polarizations along the x axis. Their refractive indices are determined by formulas (25) and (26), in which we must put $l=1, \varepsilon_{0xx}=\varepsilon_0$. Finally, equating to zero the third factor in (28), we obtain two waves identically polarized along the y axis. Their refractive indices are given by (25) and (26), in which we must put $l=2$ and $\varepsilon_{0xx}=\varepsilon_0$.

We note that the number of auxiliary waves (on top of the two waves of ordinary birefringence) is equal to the number of excitons that enter into resonance, i.e., to the number of fractional terms in (7). Thus, one additional wave appears in the region of the nondegenerate exciton, two in the region of the double degenerate one, and three in cubic crystals. This is understandable, since the additional wave is produced from the exciton wave as a result of the electromagnetic wave that accompanies the exciton wave and as a result of the time delay.

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