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THE THEORY OF ELECTROMAGNETIC WAVES IN A CRYSTAL IN WHICH EXCITONS ARE PRODUCED

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Light waves at frequencies in the region of exciton absorption of light in a crystal are considered. A relationship is obtained between the specific dipole moment of polarization of the crystal and the electric field intensity. This relation is not a direct proportion, as customarily assumed, but is expressed by a differential equation. For this reason, the resultant Maxwell equations are of higher order and have more complicated solutions than the generally known solutions that follow from the simple phenomenological theory. It is shown that in a crystal there exist several waves of the same frequency, polarization, and propagation direction, but with different indices of refraction. This phenomenon differs from double refraction of light and occurs even in isotropically polarizing (cubic) crystals. Strictly-longitudinal electric waves are shown to exist in the crystal. Surface exciton states — analogues to surface electron states — are considered.

1. RELATION BETWEEN THE SPECIFIC DIPOLE MOMENT OF POLARIZATION AND THE ELECTRIC FIELD

LET Ψ^0 represent the ground state of the crystal, $\Psi_{\mathbf{k}}$ an excited exciton state with a quasi-momentum **k**, and Ψ_n, any other excited state of the crystal. By exciton state we mean here any excited state of the crystal, which has among its quantum numbers only one continuous (three-dimensional) quantum number **k**. Such a broad definition of an exciton embraces, for exmaple, Frenkel's exciton,[1] the Wannier-Mott exciton,[2,3] the simple phonon, or a molecular electron-oscillation excitation wave propagating through the crystal.

Further, let H be the energy operator for the crystal, and W operator for the interaction energy between the crystal and an applied electric field. The aforementioned wave functions and operators depend on the coordinates of the electron, as well as on those of the nuclei of the atoms in the crystal.

To investigate a crystal perturbed by a small alternating electric field, we write

$$\Psi = \Psi^0 + \psi + \psi', \quad \psi = \sum_{\mathbf{k}} c_{\mathbf{k}} \Psi_{\mathbf{k}}, \quad \psi' = \sum_n c_n \Psi_n, \tag{1}$$

wherein the entire time dependence is assumed to be contained in the coefficients $c_{\mathbf{k}}$ and c_n, so that $\Psi_{\mathbf{k}}$ and Ψ_n are independent of time. W, ψ, and ψ' will be considered quantities of the first order of magnitude. Then, retaining only first order terms in the Schrödinger time dependent equation, we obtain

$$\left[i\hbar\frac{\partial}{\partial t} - H\right] c_{\mathbf{k}} \Psi_{\mathbf{k}} = W_{\mathbf{k}0}\Psi_{\mathbf{k}}, \quad W_{\mathbf{k}0} \equiv \int \Psi_{\mathbf{k}}^* W \Psi^0 d\Omega. \tag{2}$$

The integral is to be taken over the coordinates of all the particles of the crystal.

Exactly analogous equations are obtained for $c_n\Psi_n$.

Let us suppose that the electric field decreases quite slowly with distance (i.e., it changes only by a small amount over a distance on the order of the lattice constant). Then one can introduce the average specific dipole moment of the dielectric polarization of the crystal **P(r)**, due to the external electric field

$$\mathbf{P}(\mathbf{r}) = \int \Psi^* \Psi \hat{\mathbf{P}}(\mathbf{r})\, d\Omega, \quad d\Omega = \prod dx_i dy_i dz_i. \tag{3}$$

Here

$$\hat{\mathbf{P}}(\mathbf{r}) = \sum_i e_i(\mathbf{r}_i - \mathbf{r}) D(\mathbf{r}_i - \mathbf{r}), \tag{4}$$

where $D = 1$ for $-\frac{1}{2} \leq x, y, z \leq \frac{1}{2}$ and $D = 0$ for other values of x, y, and z. The summation is to be taken over all the particles comprising the crystal; i is the number of the particle, e is its charge, $\mathbf{r}_i$ is its coordinate and $\mathbf{r}$ is the coordinate of the macroscropic point in the crystal, with relation to which the value of the specific dipole moment is determined.

Retaining only first-order terms, we obtain

$$\mathbf{P}(\mathbf{r}) = \mathbf{P}_1(\mathbf{r}) + \mathbf{P}_2(\mathbf{r}) + \mathbf{P}'(\mathbf{r}), \quad \mathbf{P}_1(\mathbf{r}) \equiv \int \Psi^{0*}\psi\hat{\mathbf{P}}(\mathbf{r})\, d\Omega, \quad \mathbf{P}_2(\mathbf{r}) \equiv \int \psi^*\Psi^0\hat{\mathbf{P}}(\mathbf{r})\, d\Omega, \quad \mathbf{P}'(\mathbf{r}) \equiv \int (\Psi^{0*}\psi' + \psi'^*\Psi^0)\, \hat{\mathbf{P}}(\mathbf{r})\, d\Omega. \tag{5}$$

Let $T_\mathbf{m}$ represent the translation operation for all the electrons and for all deformations of the lattice by an integral lattice vector $\mathbf{m} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3$ ($\mathbf{a}_j$ are the lattice constants). In other words, $T_\mathbf{m}$ represents a change in the configuration of the crystal, such that every electron is displaced by the vector $\mathbf{m}$ ($\mathbf{r}_i \rightarrow \mathbf{r}_i + \mathbf{m}$), and every atom (nucleus) of type ℓ in the elementary cell number $\mathbf{n}$ is displaced to the site formerly occupied by the atom of the same type located in cell number $\mathbf{n} - \mathbf{m}$ $\{\mathbf{r}_\mathbf{n}^\ell - \mathbf{n} \rightarrow \mathbf{r}_{\mathbf{n}-\mathbf{m}}^\ell - (\mathbf{n} - \mathbf{m})\}$. As a result of such a coordinate transformation, H remains invariant. Therefore, making use of the well known methods of group theory, one can obtain the following results: the system of eigenfunctions of the operator H can always be chosen such that they posses the property:

$$T_\mathbf{m}\Psi_\mathbf{f} = e^{i\mathbf{f}\mathbf{m}}\Psi_\mathbf{f}, \tag{6}$$

where

$$\mathbf{f} = g_1\mathbf{b}_1 + g_2\mathbf{b}_2 + g_3\mathbf{b}_3, \quad -\pi \leqslant g_1, g_2, g_3 \leqslant \pi,$$

where $\mathbf{b}_i$ are the reciprocal lattice constants. The ground state of the crystal Ψ^0, as is well known, must be real and positive. Therefore $T_\mathbf{m}\Psi^0 = \Psi^0$. An exciton state must satisfy the relation (6), in which the quantum number $\mathbf{f}$ should be identified with $\mathbf{k}$, for, by definition, an exciton state is characterized generally by one (three-dimensional) continuous quantum number $\mathbf{k}$. Examination of concrete models of excitons shows that $\Psi_\mathbf{k}$ and the energy of the crystal $\mathscr{E}(\mathbf{k})$ turn out to be continuous functions of $\mathbf{k}$, i.e., of $\mathbf{f}$, in the region denoted by Eq. (6).

Furthermore, from Eq. (4) it follows immediately that the specific dipole moment $\hat{\mathbf{P}}$ at the point $\mathbf{r}$ acquires after the translation the value that it had prior to the translation to the point $\mathbf{r} - \mathbf{m}$: $T_\mathbf{m}\hat{\mathbf{P}}(\mathbf{r}) = \hat{\mathbf{P}}(\mathbf{r} - \mathbf{m})$. By a simple substitution of the variables of integration it can be readily shown that

$$\int T_\mathbf{m}F(\cdots\mathbf{r}_i\cdots)\, d\Omega = \int F(\cdots\mathbf{r}_i\cdots)\, d\Omega.$$

Using the above translation properties of the functions, we obtain

$$\mathbf{P}_{0\mathbf{k}}(\mathbf{r}) \equiv \int \Psi^{0*}\hat{\mathbf{P}}(\mathbf{r})\Psi_\mathbf{k}\, d\Omega = \int T_\mathbf{m}[\Psi^{0*}\hat{\mathbf{P}}(\mathbf{r})\Psi_k]\, d\Omega = e^{i\mathbf{k}\mathbf{m}}\mathbf{P}_{0\mathbf{k}}(\mathbf{r} - \mathbf{m}). \tag{7}$$

Since an external electric field is a smooth function of the coordinates, then, as will be shown below, the main contribution will be made by terms with small values of $\mathbf{k}$. In such a case, the quantity (7) changes only slightly over distances on the order of the lattice constant and one can write in (7) that $\mathbf{m} = \mathbf{r}$ approximately. Then

$$\mathbf{P}_{0\mathbf{k}}(\mathbf{r}) = \mathbf{P}_0 e^{i\mathbf{k}\mathbf{r}}, \quad \mathbf{P}_0 = \mathbf{P}_{0\mathbf{k}}(0) \approx [\mathbf{P}_{0\mathbf{k}}(0)]_{\mathbf{k}=0}. \tag{8}$$

Let us now turn to the calculation of $\mathbf{P}_1(\mathbf{r})$ in (5). In accordance with Eq. (1)

$$\mathbf{P}_1(\mathbf{r}) = \sum_\mathbf{k} c_\mathbf{k} \int \Psi^{0*}\Psi_\mathbf{k}\hat{\mathbf{P}}(\mathbf{r})\, d\Omega = \sum_\mathbf{k} c_\mathbf{k}\mathbf{P}_{0\mathbf{k}}(\mathbf{r}). \tag{9}$$

For simplicity one can choose the energy scale such that the energy of the ground state of the crystal is zero. Then Ψ^0 is time-independent, and on the basis of (8) and (2) one can write

$$\left[i\hbar\frac{\partial}{\partial t} - \mathscr{E}(-i\nabla)\right] c_\mathbf{k}\mathbf{P}_{0\mathbf{k}} = \left[i\hbar\frac{\partial}{\partial t} - \mathscr{E}(\mathbf{k})\right] c_\mathbf{k}\mathbf{P}_{0\mathbf{k}} = \int \Psi^{0*}\hat{\mathbf{P}}\left[i\hbar\frac{\partial}{\partial t} - H\right] c_\mathbf{k}\Psi_\mathbf{k}\, d\Omega = \mathbf{P}_{0\mathbf{k}}W_{\mathbf{k}0}, \tag{10}$$

where $\mathcal{E}(\mathbf{k})$ is the energy of the exciton state.

Summing this expression over $\mathbf{k}$ and taking Eq. (9) into account, we obtain

$$[i\hbar\partial/\partial t - \mathcal{E}(-i\nabla)]\,\mathbf{P}_1(\mathbf{r}) = \sum_{\mathbf{k}} \mathbf{P}_{0\mathbf{k}}(\mathbf{r})\, W_{\mathbf{k}0}. \tag{11}$$

The energy of the interaction between the external electromagnetic field and the crystal can be written in the form

$$W = -\frac{1}{c}\int \dot{\hat{\mathbf{P}}}(\mathbf{r}')\,\mathbf{A}(\mathbf{r}', t)\,d\tau', \quad W_{\mathbf{k}0} = -\frac{1}{c}\int \dot{\mathbf{P}}_{\mathbf{k}0}(\mathbf{r}')\,\mathbf{A}(\mathbf{r}', t)\,d\tau' = -\frac{i\omega_0\mathbf{P}_0^*}{c}\int e^{-i\mathbf{k}\mathbf{r}'}\mathbf{A}(\mathbf{r}', t)\,d\tau', \tag{12}$$

where $\mathbf{A}$ is the vector potential of the field, and $\omega_0 = \mathcal{E}(0)/\hbar$. Here it is seen that with increasing $\mathbf{k}$, $W_{\mathbf{k}0}$ rapidly approaches zero, as a coefficient of the Fourier expansion of a smooth function of the coordinates $\mathbf{A}$. Therefore, in the summation on the right side of Eq. (11), terms with small values of $\mathbf{k}$ dominate, and one can approximately extend the summation over the entire infinite $\mathbf{k}$ space. Then, substituting the results of Eqs. (8) and (12) into (11), and also taking it in account that

$$\sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} = V\delta(\mathbf{r}-\mathbf{r}')$$

(V is the volume of the crystal) we obtain finally

$$[i\hbar\partial/\partial t - \mathcal{E}(-i\nabla)]\,\mathbf{P}_1(\mathbf{r}, t) = -(i\omega_0 V/c)\,\mathbf{P}_0(\mathbf{P}_0^*, \mathbf{A}(\mathbf{r}, t)). \tag{13}$$

Differentiation of this equation with respect to time yields

$$[i\hbar\partial/\partial t - \mathcal{E}(-i\nabla)]\,\dot{\mathbf{P}}_1(\mathbf{r}, t) = ia\mathbf{E}_\perp(\mathbf{r}, t), \quad a_{xy} = \omega_0 V P_{0x} P_{0y}^*, \tag{14}$$

where $\mathbf{E}_\perp = \dot{\mathbf{A}}/c$ is the vortical part of the electric field intensity ($\operatorname{div} \mathbf{E}_\perp = 0$) and a is a tensor of second rank.

The equation for the term $\mathbf{P}_2(\mathbf{r}, t)$, which appears in Eq. (5), is most readily obtained from Eq. (14), if one notes that $\mathbf{P}_2 = \mathbf{P}_1^*$:

$$[i\hbar\partial/\partial t + \mathcal{E}(-i\nabla)]\,\dot{\mathbf{P}}_2(\mathbf{r}, t) = ia^*\mathbf{E}_\perp(\mathbf{r}, t). \tag{15}$$

In most cases $\mathcal{E}(\mathbf{k})$ for small $\mathbf{k}$ has the form

$$\mathcal{E}(\mathbf{k}) = \mathcal{E}_0 + \frac{\hbar^2}{2}\sum_{ps} M_{ps}^{-1} k_p k_s + \ldots; \quad p, s = 1, 2, 3; \quad \mathcal{E}_0 = \mathcal{E}(0). \tag{16}$$

Here M^{-1} is the tensor of the reciprocal effective mass of the exciton. Then Eq. (14) can be rewritten

$$\left[i\hbar\frac{\partial}{\partial t} - \mathcal{E}_0 + \frac{\hbar^2}{2}\sum_{ps} M_{ps}^{-1}\frac{\partial^2}{\partial x_p \partial x_s}\right]\dot{\mathbf{P}}_1 = ia\mathbf{E}_\perp \tag{17}$$

Thus, in a dielectric in which excitons can be generated, the relation between the specific dipole moment and the electric field intensity is given not by the generally well-known "material" Maxwell equations, but rather by the differential equations (17). The latter must be supplemented with initial conditions, i.e., we must specify $\mathbf{P}_1$ and $\dot{\mathbf{P}}_1$ at $t = 0$, and also with boundary conditions, i.e., we must specify the value of $\mathbf{P}_1$, say, on the surface of the crystal. Subsequent sections of the paper are devoted to a formulation of the boundary conditions.

The term $\mathbf{P}'$ in (5) is associated with virtual transitions into non-exciton states Ψ_n. It will not be investigated in detail in this paper, and presumably this term can be taken into account by introducing a conventional phenomenological dielectric constant ϵ' (which is, in general, complex)

$$\mathbf{P}' = (\varepsilon' - 1)\,\mathbf{E}/4\pi, \tag{18}$$

where $\mathbf{E}$ is the electric field intensity. In reality this relation is not always satisfied. This question requires a special investigation.

The results described above were obtained under the assumption that when the crystal is unperturbed by light it remains in its ground state Ψ^0, and as a result of illumination a slight admixture of excitons, i.e., of states with the same momentum $\Psi_{\mathbf{k}}$, is added to Ψ^0. This assumption is strictly satisfied only at absolute zero. At other temperatures there exist in the crystal many phonons, both in the absence and in the presence of the perturbation by the light. In reality, however, these results will hold approximately for temperatures other than zero, provided that they are still sufficiently low.

2. EFFECT OF THE CRYSTAL SURFACE ON EXCITON STATES; BOUNDARY CONDITIONS ON THE SPECIFIC POLARIZATION DIPOLE MOMENT. SURFACE EXCITONS

To consider the boundary conditions at the crystal surface, it is necessary to make the exciton model more concrete. Let us consider Frenkel's[1] exciton: let us assume that the interaction between the crystal molecules is quite weak and that it is therefore possible to construct the many-electron wave function of the crystal, in the zeroth approximation, according to the method of Heitler-London-Heisenberg (HLH). Let $\Phi_{\mathbf{n}}$ represent the (antisymmetrized) wave function of the crystal, when the electron-oscillation excitation is localized in the n-th elementary cell. Since the excitation can be localized in any cell with equal success and since all such states $\Phi_{\mathbf{n}}$ with the same n are mutually degenerate, then in the zeroth approximation the crystal wave function should be constructed as a linear combination of all $\Phi_{\mathbf{n}}$. One can readily verify that

$$T_{\mathbf{m}}\Phi_{\mathbf{m}} = \Phi_0, \quad \Phi_{\mathbf{m}} = T_{-\mathbf{m}}\Phi_0. \tag{19}$$

Here Φ_0 is the state of the crystal, when the excited cell coincides with the origin of coordinates. If we specify that the above-mentioned linear combination possess the translation properties of Eq. (6), then the coefficients of the linear combination are uniquely determined from Eqs. (6) and (19). Consequently, the wave function in the zeroth approximation has the form

$$\Psi_{\mathbf{k}} = \sum_{\mathbf{n}} a_{\mathbf{n}}\Phi_{\mathbf{n}}, \quad a_{\mathbf{n}} = a_0 e^{i\mathbf{k}\mathbf{n}}. \tag{20}$$

This same zeroth-approximation function is obtained, if instead of the methods of group theory one employs the conventional perturbation method for excited states, by taking into account the interaction between neighboring elementary cells of the crystal as small perturbations. As a result, one obtains for $a_{\mathbf{n}}$ the following system of homogeneous linear equations:

$$(\mathscr{E} - H_0)\, a_{\mathbf{n}} = \sum_{i=1}^{3} H_i\, (a_{\mathbf{n}+\mathbf{a}_i} + a_{\mathbf{n}-\mathbf{a}_i}), \tag{21}$$

where $\mathbf{a}_i$ are lattice constants, and

$$H_0 = \int \Phi_0 H \Phi_0 d\Omega, \quad H_i = H_{0\mathbf{a}_i} = H_{\mathbf{a}_i 0} = \int \Phi_{\mathbf{a}_i} H \Phi_0 d\Omega.$$

One can easily show that the values of $a_{\mathbf{n}}$ from Eq. (20) are solutions of Eq. (21). From this one obtains for the crystal energy the value[1]

$$\mathscr{E}(\mathbf{k}) = H_0 + 2\sum_{i=1}^{3} H_i \cos g_i, \quad \mathbf{k} = g_1\mathbf{b}_1 + g_2\mathbf{b}_2 + g_3\mathbf{b}_3. \tag{22}$$

The solutions (20) and (22), as well as the results of the preceding section are applicable to an infinite crystal. In addition, in obtaining Eqs. (21) and (22) it was assumed that every cell in the crystal had six adjacent cells.

Now let us turn to the consideration of a finite crystal. Let it have the form of an infinite plane-parallel lamina bounded by the surfaces $n_3 = 1$ and $n_3 = G$ (G is a large integer). Thus, junctions between crystal cells occur only at points with vectors **n**, whose third component is included in the interval $1 \leq n_3 \leq G$. If now one sets up the system of equations for $a_{\mathbf{n}}$, then all those equations from the set of Eqs. (21), in which the vector **n** does not belong to surface cells of the crystal, will remain unchanged. At this surface itself Eqs. (21) are changed as follows: for $n_3 = 1$ the term $a_{\mathbf{n}-\mathbf{a}_3}$ of the right side is simply absent, and for $n_3 = G$ the term $a_{\mathbf{n}+\mathbf{a}_3}$ of the right side is absent. In solving such a system of equations it is helpful to keep in mind that the translation symmetry in the direction $\mathbf{a}_3$ is now absent, whereas in the directions $\mathbf{a}_1$ and $\mathbf{a}_2$ it is still there as before. Therefore the wave function should satisfy the relation (6), in which one should put $m_3 = 0$. Finally one obtains

$$a_{\mathbf{n}} = \frac{a_0}{\sqrt{2}}\left[e^{i\mathbf{k}\mathbf{n}} - e^{i\widetilde{\mathbf{k}}\mathbf{n}}\right], \quad g_3 = \pi\frac{\nu}{G+1}, \quad \nu = 1, 2, 3 \ldots G. \tag{23}$$

Here the vector $\tilde{\mathbf{k}}$ represents the specular reflection of the vector $\mathbf{k}$ in the surface plane of the crystal. In other words, $\tilde{\mathbf{k}}$ is uniquely determined from $\mathbf{k}$ by the relations $\tilde{\mathbf{k}}\cdot\mathbf{a}_1 = \mathbf{k}\cdot\mathbf{a}_1$, $\tilde{\mathbf{k}}\cdot\mathbf{a}_2 = \mathbf{k}\cdot\mathbf{a}_2$, and $\tilde{\mathbf{k}}\cdot\mathbf{a}_3 = -\mathbf{k}\cdot\mathbf{a}_3$. In accordance with Eqs. (23) and (20), the exciton wave function in a bounded crystal can be written in the form:

$$\Phi_{\mathbf{k}} = (\Psi_{\mathbf{k}} - \Psi_{\tilde{\mathbf{k}}})/\sqrt{2}. \tag{24}$$

If one denotes the exciton wave incident on the surface by $\Psi_{\mathbf{k}}$, then the wave which is specularly reflected from the surface of the crystal is denoted by $\Psi_{\tilde{\mathbf{k}}}$. In Eq. (24) $\Psi_{\mathbf{k}}$ denotes, of course not the wave function of an infinite crystal, but rather the wave function of the lamina described above, under the condition of periodicity in the direction $\mathbf{a}_3$ with a period $G\mathbf{a}_3$. As a result, $\Psi_{\mathbf{k}}$ also possesses the translation properties of Eq. (6), also in direction $\mathbf{a}_3$. The dependence of the energy on $\mathbf{k}$ is given by Eq. (22) as before.

It is important to emphasize, that the results of the preceding section can be applied also to the case of a bounded crystal. To do so one must change $\Psi_{\mathbf{k}}$ to $\Phi_{\mathbf{k}}$ in Eqs. (1), (2), (9), and (11). Equations (13) through (17) remain precisely the same. Only Eq. (8) is changed and becomes for the bounded crystal

$$\mathbf{P}_{0\mathbf{k}}(\mathbf{r}) = \mathbf{P}_0\,(e^{i\mathbf{k}\mathbf{r}} - e^{i\tilde{\mathbf{k}}\mathbf{r}})/\sqrt{2}, \tag{25}$$

in which the constant $\mathbf{P}_0$ has the previous numerical value.

Now it is easy to obtain the value of $\mathbf{P}(\mathbf{r})$ at the crystal surface. One of the surfaces of the crystal ($n_3 = 1$) in the macroscopic sense is the plane passing through the origin of coordinates. For points on this surface $\mathbf{r}$ is coplanar with $\mathbf{a}_1$ and $\mathbf{a}_2$ and it can be represented thus: $\mathbf{r} = \mathbf{a}_1 r_1 + \mathbf{a}_2 r_2$. Under these conditions the difference in the indices of the exponentials in Eq. (25) becomes

$$(\mathbf{k} - \tilde{\mathbf{k}}, \mathbf{r}) = (\mathbf{k} - \tilde{\mathbf{k}}, \mathbf{a}_1)\, r_1 + (\mathbf{k} - \tilde{\mathbf{k}}, \mathbf{a}_2)\, r_2 = 0,$$

in accordance with the definition of the vector $\tilde{\mathbf{k}}$. Therefore, on this plane $\mathbf{P}_{0\mathbf{k}}(\mathbf{r}) = 0$. The other surface of the lamina ($n_3 = G$) consists of points whose coordinates are $\mathbf{r} = \mathbf{a}_1 r_1 + \mathbf{a}_2 r_2 + \mathbf{a}_3(G + 1)$. In this case the difference in the exponents of Eq. (25) is [see Eq. (23)]

$$(\mathbf{k} - \tilde{\mathbf{k}}, \mathbf{r}) = (\mathbf{k} - \tilde{\mathbf{k}}, \mathbf{a}_3)\,(G + 1) = 2\,(\mathbf{k}\mathbf{a}_3)\,(G + 1) = 2\pi\nu.$$

Consequently $\mathbf{P}(\mathbf{r}) = 0$ on this surface, too. Then Eq. (9) shows that $\mathbf{P}_1(\mathbf{r}) = 0$ on the surfaces of the crystal. Thus the surfaces of the crystal turn out to be nodal surfaces for exciton waves as well as for the specific dipole moment.

As is well known, in a bounded crystal conduction electrons can exist in surface states as well as in "band" states.[4] In an exactly analogous way, surface exciton states can exist, in which the excitation wave moves only in the layer near the surface of the crystal. In order to obtain these surface excitons in the HLH approximation, let us consider a semi-infinite crystal, whose lattice points are located in the region $n_3 \geq 1$. As before, Eq. (21) is satisfied for all $\mathbf{n}$ not associated with cells adjoining the surface (i.e., for $n_3 \geq 2$). The solution of these equations, just as in the case of the infinite crystal, can be cast in the form of Eqs. (20) and (22). Since the translation symmetry in the directions $\mathbf{a}_1$ and $\mathbf{a}_2$ is strictly conserved, g_1 and g_2, as before, must be real and contained within the interval specified by Eq. (22). But now g_3 can also assume complex values, for Eqs. (21) satisfy Eq. (20) for any complex $\mathbf{k}$, the energy [Eq. (22)] obtained is real, and the wave function remains finite, provided that one puts $g_3 = i\kappa + \ell\pi$ for $\kappa \geq 0$ and ℓ an integer. Thus, Eqs. (21) also have a solution of the form

$$a_{\mathbf{n}} = (-1)^l a_0 \exp\{i(g_1 n_1 + g_2 n_2) - \varkappa n_3\}, \quad -\pi \leqslant g_1,\ g_2 \leqslant \pi,\ \varkappa \geqslant 0; \tag{26}$$

$$\mathscr{E}(\mathbf{k}) \equiv \mathscr{E}(g_1, g_2, g_3) = H_0 + 2\sum_{i=1}^{2} H_i \cos g_i + 2(-1)^l H_3 \cosh\varkappa. \tag{27}$$

Now it is still necessary to satisfy the equation for $a_{\mathbf{n}}$ when $\mathbf{n}$ pertains to cells near the surface of the crystal. These equations differ from (21) in two particulars: (a) for $n_3 = 1$ in the right side of the equation there exists a term $H_3 a_{\mathbf{n}-\mathbf{a}_3}$, (b) the constants H_0 and H_i have a somewhat different value, because of the absence of an adjoining layer $n_3 = 0$. The coefficients, H_i, in the HLH approximation are first-order quantities while their changes near the surface of the crystal are second-order quantities and will therefore be neglected. H_0 is a zeroth order term, and its change near the surface H_0' is a first-order term, and must be allowed for. As a result, when $\mathbf{n}$ pertains to surface cells ($n_3 = 1$), Eq. (21) is replaced by

$$(\mathscr{E} - H_0 - H_0')\, a_{\mathbf{n}} = \sum_{i=1}^{3} H_i \left[a_{\mathbf{n}+\mathbf{a}_i} + a_{\mathbf{n}-\mathbf{a}_i}(1 - \delta_{i3})\right]. \tag{28}$$

We now require that the solutions of the "depth" equations (21), given by (26) and (27), also satisfy the "subsurface" equations (28). This leads to a relation for κ:

$$e^{-\varkappa} = (-1)^l H_3 / H_0'. \tag{29}$$

If a positive value of κ results from this expression, i.e., if $|H_3/H_0'| \leq 1$, then Eqs. (26), (27), and (29) are the solutions of the problem of the semi-infinite crystal. From this one finds that the probability that the excitation will remain in a cell with coordinate $\mathbf{n}$ is given by $|a_{\mathbf{n}}|^2$. This probability does not depend on n_1 and n_2 and decreases exponentially with increasing n_3, i.e., with increasing distance from the crystal surface. The energy of the system, Eq. (27) represents a two dimensional band, because the projection of the vector $\mathbf{k}$ on the direction $\mathbf{a}_3$ remains fixed. For convenience, such states are called surface excitons. If $|H_3/H_0'| > 1$, no surface excitons exist.

The results of the previous section can be extended to include surface excitons. Equations (1) through (5) remain valid even in this case provided that $\Psi_{\mathbf{k}}$ is taken to mean the surface exciton state. Now the validity of Eq. (6) cannot be proven for any arbitrary translation $T_{\mathbf{m}}$ by the methods of group theory, since there is no translational symmetry in the direction $\mathbf{a}_3$. Nevertheless, one can substantiate it as follows. Let us impose a periodicity with a large period $G\mathbf{a}_3$ on the direction $\mathbf{a}_3$ (as we did above when we were considering the plane-parallel lamina. Then Eqs. (19) and (20) yield

$$T_{\mathbf{m}}\Psi_{\mathbf{k}} = \sum_{\mathbf{n}} a_{\mathbf{n}} T_{\mathbf{m}} T_{-\mathbf{n}} \Phi_0 = \sum_{\mathbf{n}} a_{\mathbf{n}} T_{\mathbf{m}-\mathbf{n}} \Phi_0 = \sum_{\mathbf{n}} a_{\mathbf{n}+\mathbf{m}} T_{-\mathbf{n}} \Phi_0 = e^{i\mathbf{km}} \Psi_{\mathbf{k}}, \tag{30}$$

where this relation holds for both real and complex $\mathbf{k}$. In this way, Eqs. (6) through (12) remain valid for surface excitons, but one must remember that the values of $\mathbf{k}$ are restricted by the inequalities (26) and the conditions (29). In Eq. (8) one must now put $\mathbf{P}_0 = \mathbf{P}_{0\mathbf{k}}(0)$ with $g_1 = g_2 = 0$; $g_3 = i\kappa$, and in Eq. (12) one must integrate only over the half-space occupied by the crystal.

Substituting Eqs. (8) and (12) into Eq. (11) and noting that

$$\sum_{g_1, g_2} e^{i(\mathbf{kr} - \mathbf{k}^*\mathbf{r}')} = G^2 e^{-\varkappa(r_3 + r_3')}\, \delta(r_1 - r_1')\, \delta(r_2 - r_2'), \tag{31}$$

where the new variables r_1, r_2, and r_3 are defined by the relation $\mathbf{r} = \mathbf{a}_1 r_1 + \mathbf{a}_2 r_2 + \mathbf{a}_3 r_3$, we obtain for surface excitons

$$\mathbf{P}_1 = \mathbf{P}_1^{(s)}(r_1, r_2)\, e^{-\varkappa r_3},$$

$$\left[i\hbar \frac{\partial}{\partial t} - \mathscr{E}\left(-i\frac{\partial}{\partial r_1}, -i\frac{\partial}{\partial r_2}, i\varkappa\right)\right] \mathbf{P}_1^{(s)} = -\frac{i\omega_0}{c} G^2 v \mathbf{P}_0 \int_0^{\infty} e^{-\varkappa r_3'} (\mathbf{P}_0^*, \mathbf{A}(\mathbf{a}_1 r_1 + \mathbf{a}_2 r_2 + \mathbf{a}_3 r_3', t))\, dr_3', \tag{32}$$

Here $v = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$, the volume of the elementary cell of the crystal, and $\mathscr{E}(g_1, g_2, g_3)$ is defined by Eq. (27). If $\mathbf{A}(\mathbf{r}, t)$, as a function of $\mathbf{r}$, does not change very much over distances of the order of $1/\kappa$, one can move $\mathbf{A}$ in Eq. (32) outside the integration sign, since it is a smooth function. Finally, differentiation of Eq. (32) with respect to time yields

$$\left[i\hbar \frac{\partial}{\partial t} - \mathscr{E}\left(-i\frac{\partial}{\partial r_1}, -i\frac{\partial}{\partial r_2}, i\varkappa\right)\right] \dot{\mathbf{P}}_1^{(s)} = i a^{(s)} \mathbf{E}_{\perp}(\mathbf{a}_1 r_1 + \mathbf{a}_2 r_2, t), \quad a_{xy}^{(s)} = \frac{\omega_0 G^2 v}{\varkappa} P_{0x} P_{0y}^*. \tag{33}$$

This is the analogue of Eq. (14) for the case of surface excitons.

Within the framework of the HLH approximation one can relate the constants a_{xx} and a_{xx}^{S} to the oscillator strength of a given transition f_x per unit cell of the crystal. For example, for excitons associated with electron excitation one obtains

$$a_{xx} = (e^2\hbar/2m) N f_x, \quad a_{xx}^{(s)} = 2a_{xx}, \tag{34}$$

where N is the number of cells per unit volume and m is the free-electron mass.

In the discussion above we have considered the effect of the surface on the exciton, for which we used Frenkel's model of the exciton. Similar results, however, are obtained for other models of the exciton. For example, in the case of the Wannier-Mott[2,3] exciton, in which the conduction electron and the hole are bound together by Coulomb attraction and perform hydrogen-like motions, it is easily shown that the exciton wave is specularly reflected by the surface. For a plane-parallel lamina one again obtains Eqs. (24) and (25), and g_3 assumes a discrete series of values, as indicated in Eq. (23). Therefore, just as in the case considered above, the surface of the crystal is a nodal surface for exciton waves as well as for the specific dipole moment $\mathbf{P}_1(\mathbf{r}, t)$.

Surface exciton states can also exist for electron-hole excitons. They arise for example, if a conduction hole becomes bound to an electron, located in a surface conduction band, or if, conversely, an electron becomes bound to a hole which is in a surface state. It is also possible for an electron and hole to become coupled, both of them belonging to a surface band. For this case one obtains (32) and (33) again.

If the exciton is an ordinary acoustical phonon, then as is well known for the case of an elastic wave, the displacement vector of the medium does not have a node at the surface, but rather an antinode (the vacuum bounds the surface). However, the specific dipole moment is proportional not to the displacement but rather to the derivative of the displacement with respect to the coordinates, and has therefore, as before, a node at the surface. Surface excitons, in the case of phonons, are Rayleigh surface waves, which have been known for a long time.

In the various models of the bulk exciton considered above, it was found that at the surface of the crystal $\mathbf{P}_1 = 0$, which is a boundary condition for Eq. (14). Now and then, deviations from this rule are observed. For example, in the case of phonons, if the surface of the crystal is fixed (the crystal borders on a more rigid or a heavier medium) the displacements have a node at the surface and the specific polarization, correspondingly, has an antinode.

For surface excitons, one does not obtain any boundary conditions at the surface of the crystal. Equations (32) and (33) are not required for them. For the variables r_1 and r_2 the boundary conditions reduce to conditions of periodicity.

3. PLANE ELECTROMAGNETIC WAVES IN A CRYSTAL

In this section, we shall solve Maxwell's equations for the case when the relation between the specific polarization and the applied electric field has the form of Eq. (16) or Eq. (17). Maxwell's equations can be divided into two groups: the "ideal" equations which are independent of the properties of the crystal

$$\operatorname{curl}\mathbf{E} = -\frac{1}{c}\dot{\mathbf{H}},\ \operatorname{curl}\mathbf{H} = \frac{1}{c}\dot{\mathbf{D}},\ \operatorname{div}\mathbf{D} = 0,\ \operatorname{div}\mathbf{H} = 0, \tag{35}$$

and the "material" equations

$$\mathbf{D} = \varepsilon'\mathbf{E} + 4\pi(\mathbf{P}_1 + \mathbf{P}_2),\quad [i\hbar\,\partial/\partial t - \mathscr{E}(-i\nabla)]\,\dot{\mathbf{P}}_1 = ia\mathbf{E}_\perp,\ [i\hbar\partial/\partial t + \mathscr{E}(-i\nabla)]\,\dot{\mathbf{P}}_2 = ia^*\mathbf{E}_\perp. \tag{36}$$

We shall now look for solutions of these equations in the form of plane waves, thus obtaining $\mathbf{E}$, $\mathbf{H}$, $\mathbf{D}$, $\mathbf{P}_1$, and $\mathbf{P}_2$ proportional to $\exp\{i\omega[n(\mathbf{r}\cdot\mathbf{s})/c - t]\}$. Here ω is the frequency of the wave, n is the index of refraction, $\mathbf{s}$ is a unit vector, normal to a constant phase surface. As a result, it is found that Eqs. (35) are satisfied if the amplitudes of the fields are related as follows

$$n[\mathbf{s}\times\mathbf{E}] = \mathbf{H},\ n[\mathbf{s}\times\mathbf{H}] = -\mathbf{D}. \tag{37}$$

If H is eliminated from these equations, one obtains

$$\mathbf{D} = n^2[\mathbf{E} - \mathbf{s}(\mathbf{s}\mathbf{E})]. \tag{38}$$

Not only Eqs. (37) and (38), but also other relations of ordinary crystal optics, following from the "ideal" equations, remain valid. These relations are to be found, for example, in Born's book[5] (pp. 296—299).

Substituting the exponential solutions into the second and third of Eqs. (36) yields

$$\mathbf{P}_1 = \frac{a}{\omega}\,\frac{\mathbf{E}_\perp}{\mathscr{E}(\omega n\mathbf{s}/c) - \hbar\omega},\ \mathbf{P}_2 = \frac{a^*}{\omega}\,\frac{\mathbf{E}_\perp}{\mathscr{E}(\omega n\mathbf{s}/c) + \hbar\omega},\quad \mathbf{E}_\perp = \mathbf{E} - \mathbf{s}(\mathbf{s}, \mathbf{E}) \equiv \eta\mathbf{E}, \tag{39}$$

where η is a tensor of the second rank: $\eta_{xy} = 1 - s_x s_y$. Here we can use for $\mathscr{E}$ the quadratic expansion

$$\mathcal{E}(\omega n s/c) = \mathcal{E}_0 + \hbar^2\omega^2 n^2/2M_s c^2 + \cdots, \tag{40}$$

since it is assumed that the wavelength of the light is much greater than the lattice constant. M_s depends on the direction of s and we shall henceforth refer to it as the effective mass of the exciton in the direction s. M_s can be easily related to the tensor of the reciprocal effective mass, calculated in Eq. (17). In Eq. (39) $\mathbf{P}_2 \neq \mathbf{P}_1^*$, but if subsequently one constructs a linear-combination solution in which the condition that the field is real if preserved (this is done by adding together exponentials with different signs in front of ω), then one obtains $\mathbf{P}_2 = \mathbf{P}_1^*$.

If the frequency of the light wave, ω, lies outside the region of absorption by excitons, i.e., if it differs appreciably from $\omega_0 = \mathcal{E}_0/\hbar$ then one can replace $\mathcal{E}(\omega \mathbf{n} \mathbf{s}/c)$ by $\mathcal{E}_0$ in Eq. (39). In this case, the "material" equations of Maxwell preserve their customary well known form, and one obtains the results of ordinary crystal optics. But in the vicinity of the region of exciton absorption such a substitution can be made only in the expression for $\mathbf{P}_2$; in the expression for $\mathbf{P}_1$ one must take into account the functional dependence of $\mathcal{E}$ on n. As a result one can neglect $\mathbf{P}_2$ in comparison with $\mathbf{P}_1$ and the "material" Eqs. (36) can be formally written in the customary way $\mathbf{D} = \epsilon\mathbf{E}$. However, the tensor ϵ is now given by

$$\varepsilon = \varepsilon' + B\eta/(n^2 - \mu), \tag{41}$$

where

$$B = 8\pi M_s c^2 a/\hbar^2\omega^3, \quad \mu = (2M_s c^2/\hbar\omega)(1 - \mathcal{E}_0/\hbar\omega).$$

Thus, ϵ is now a function not only of the frequency ω, but also of s and of n. Consequently, to every direction of propagation of the light wave and every direction of its polarization there corresponds a specific ϵ tensor with its own direction for the principal axes of polarization.

Eliminating D from the material equations and from Eq. (38), we finally obtain

$$\varepsilon\mathrm{E} = n^2[\mathrm{E} - \mathrm{s}(\mathrm{sE})]. \tag{42}$$

Equations (41) and (42) are equivalent to the initial Maxwell equations, Eqs. (35) and (36), if the solution is given in the form of plane exponential waves.

Equations (42) represent a system of three linear, single-valued equations for the components of the amplitude of the electric field. Setting the determinant of this system equal to zero, we obtain the equations for n:

$$(\mathrm{s},\varepsilon\mathrm{s})\,n^4 + [(\mathrm{s},\varepsilon^2\mathrm{s}) - (\mathrm{s},\varepsilon\mathrm{s})\,\mathrm{Sp}\,\varepsilon]\,n^2 + \Delta(\varepsilon) = 0, \tag{43}$$

where $\Delta(\epsilon)$ is the determinant of the tensor ϵ. In the well-known ordinary crystal optics, ϵ is not a function of n, and Eq. (43) is quadratic in n^2. The two roots of this equation determine for a given s two values of $|\mathrm{n}|$, and accordingly two plane waves, for which the D vectors have mutually perpendicular directions. However, it was shown above that near the exciton absorption region, when μ is not large, it is necessary to take into account the dependence of ϵ on n, in accordance with Eq. (41). If (41) is substituted into (43) and for simplification we introduce the symbols

$$\overline{\varepsilon'} = (\mathrm{s},\ \varepsilon'\mathrm{s}),\ \overline{\varepsilon'^2} = (\mathrm{s},\varepsilon'^2\mathrm{s}),\ \overline{B\eta} = (\mathrm{s},B\eta\mathrm{s}),\ \overline{(B\eta)}^2 = (\mathrm{s},(B\eta)^2\mathrm{s})$$

and analogous symbols for the tensor $\epsilon' \mathrm{B}\eta$, then Eq. (43) can be rewritten

$$\left(\overline{\varepsilon'} + \frac{\overline{B\eta}}{n^2-\mu}\right)n^4 + \left[\overline{\varepsilon'^2} - \overline{\varepsilon'}\,\mathrm{Sp}\,\varepsilon' + \frac{\overline{\varepsilon' B\eta} + \overline{B\eta\varepsilon'} - \overline{\varepsilon'}\,\mathrm{Sp}\,B\eta - \overline{B\eta}\,\mathrm{Sp}\,\varepsilon'}{n^2-\mu} + \frac{\overline{(B\eta)^2} - \overline{B\eta}\,\mathrm{Sp}\,B\eta}{(n^2-\mu)^2}\right]n^2 + \Delta\left(\overline{\varepsilon'} + \frac{B\eta}{n^2-\mu}\right) = 0. \tag{44}$$

In terms of n^2, this already is an equation whose order is higher than the second. Therefore, for a given s it determines, generally speaking, more than two values of $|\mathrm{n}|$ and correspondingly more than two plane waves. It will be shown below that the order of Eq. (44) depends on the crystal structure and on the direction of s.

We shall consider as examples, rhombic, tentragonal, and cubic crystals. In these crystals, the calculations are simplified because the principal axes of ϵ' and B coincide with the second or fourth order crystal axes, and consequently the directions of the principal axes are independent of ω, s, or n. In these cases, it is convenient to use the principal axes of ϵ' and B as Cartesian coordinate axes, as is done below.

Rhombic Crystals

In these crystals only one element of the tensor a does not vanish. To show this, we note that from among the three components of the vector $\mathbf{P}_0$ only one can differ from zero. In fact, in accordance with Eq. (8).

$$\mathbf{P}_0 = \int \Psi^{0*}\hat{\mathbf{P}}(0)\, \Psi_0 d\Omega. \tag{45}$$

Let us consider first crystals of the symmetry group D_2. Let $\hat{C}_x$, $\hat{C}_y$, and $\hat{C}_z$ be the operations of rotating all the electrons of the crystal and deforming the lattice through 180° around the second-order crystal axes, i.e., around the axes x, y, and z. The application of any one of these operators to any of the functions in the integrand in Eq. (45) is equivalent to changing the sign of some of the variables of integration and therefore does not change the value of the integral. Application of the well-known methods of group theory shows that only those components of the matrix element in Eq. (45) can be non-vanishing, for which the integrand is invariant for any transformation C. To determine how the integral transforms as a result of the rotations described above, let us consider how each of its three terms transforms.

The function Ψ^0, as the wave function of the ground state of the crystal, must be completely symmetrical, and consequently, invariant under all three rotations. The component of $\hat{\mathbf{P}}(0)$ on the rotation axis stays invariant, while the other components change signs. Since the point symmetry group of a rhombic crystal has only first order irreducible representations, Ψ_0 (and Ψ^0) are certainly eigenfunctions of all three operators $\hat{C}$:

$$\hat{C}_x\Psi_0 = C_x\Psi_0,\ \hat{C}_y\Psi_0 = C_y\Psi_0,\ \hat{C}_z\Psi_0 = C_z\Psi_0.$$

Since $\hat{C}_x^2 = \hat{C}_y^2 = \hat{C}_z^2 = 1$, the eigenvalues C_x, C_y, and C_z can have either one of two values, ± 1. Applying to Ψ_0, on both the left and right sides, the well-known operator equation $\hat{C}_x\hat{C}_y = \hat{C}_z$, we obtain $C_xC_y = C_z$. Hence, it follows that all three eigenvalues of $\hat{C}$ are equal to + 1, or else one is + 1 and the remaining two are − 1.

Taking into account the above transformation properties of the terms in the integrand of Eq. (45), it is easy to obtain the following results:

1. The case $C_x = C_y = C_z = 1$. All components of Eq. (45) vanish.

2. The case when one of the eigenvalues C (to be specific let this be C_x) is equal to 1, and the other two are equal to − 1; $C_x = 1$, $C_y = C_z = -1$. Then $P_{0x} \neq 0$, $P_{0y} = P_{0z} = 0$. Therefore, in accordance with Eqs. (14) and (41), the only non-vanishing components of the tensors a and B are a_{xx} and B_{xx}, which is what we needed to demonstrate. The same results are obtained also in rhombic crystals with symmetry groups C_{2v} and D_{2h}.

Thus in crystals with rhombic symmetry for any direction of the E vector, the right side of the vector equation (14) and $\mathbf{P}_1$ will be directed along the x axis. This does not necessarily mean that there is a fundamental difference between this axis and the other principal axes of the crystal. This result was obtained because the discussion above was restricted to one exciton band whose wave functions are oriented along the x axis. But in the same crystal there exist other (not considered at this time) exciton bands, oriented preferentially along the y and z directions. The presence of several exciton bands can be taken into account, by introducing into Eq. (1) several ψ-like terms. The result is that in the right hand side of Eq. (5) several $\mathbf{P}_1$-like vector terms appear, among which there are terms directed along the y and z axes. However, in rhombic crystals several of the exciton bands described above will not be degenerate in energy, and therefore, if the frequency of the light falls in the exciton absorption region of one of these bands, it will turn out to be outside the exciton absorption region of the other bands, and the existence of the latter can be taken into account simply by changing the constants ϵ' [see the remarks after Eq. (41)].

Let $b = B_{xx}$ denote the one non-vanishing component of the B tensor. When $\mathbf{s}$ is parallel to $\mathbf{P}_0$, i.e., when $s_x = 1$, $s_y = s_z = 0$, the tensor $B\eta$ vanishes and therefore Eq. (44) assumes exactly the same form which it would have in ordinary crystal optics, when all polarizations can be simply characterized by the ϵ' tensors. In this case, no new answers are obtained; there exist two plane waves, polarized in the directions of the y and z axes with indices of refraction essentially equal to $\sqrt{\epsilon'_{yy}}$ and $\sqrt{\epsilon'_z}$.

However, for other directions of $\mathbf{s}$, for example, if $s_x = s_y = 0$ and $s_z = 1$, Eq. (44) becomes

$$(n^2 - \varepsilon'_{yy})\,[n^2 - \varepsilon'_{xx} - b/(n^2 - \mu)] = 0. \tag{46}$$

In this case the system of equations (22) has these three solutions

$$E_x = E_z = 0, \quad E_y \neq 0, \quad n = \sqrt{\varepsilon'_{yy}}; \tag{47}$$

$$E_y = E_z = 0, \quad E_x = \begin{cases} E_+ \quad n_+^2 = {}^1/_2\,(\mu + \varepsilon'_{xx}) + \sqrt{{}^1/_4\,(\mu - \varepsilon'_{xx})^2 + b}, & (48) \\ E_- \quad n_-^2 = {}^1/_2\,(\mu + \varepsilon'_{xx}) - \sqrt{{}^1/_4\,(\mu - \varepsilon'_{xx})^2 + b}. & (49) \end{cases}$$

Equation (47) is identical with the corresponding solution of ordinary crystal optics, but Eqs. (48) and (49) are new kinds of solutions. In order to satisfy the boundary condition $\mathbf{P}_1 = 0$ at the crystal surface (let this be the $z = 0$ surface) it is necessary to make up the following linear combination of Eqs. (48) and (49)

$$E_x(z,\ t) = E_+\left(e^{i\omega n_+ z/c} - q e^{i\omega n_- z/c}\right) e^{-i\omega t}, \quad q = (n_-^2 - \mu)\,/\,(n_+^2 - \mu). \tag{50}$$

It is readily shown that, depending on whether ω deviates from the exciton photoabsorption band on the red or on the violet side, q becomes much less or much greater than unity. Thus in Eq. (50) the amplitude of one of the waves becomes vanishingly small compared with the amplitude of the other. The wave with the dominant amplitude goes over into the well known solution of ordinary crystal optics. However, in the vicinity of the exciton absorption band, both waves have amplitudes of the same order of magnitude and the solution is essentially different from the results of ordinary crystal optics. It should be noted, for example, that the solutions turn out to be superpositions of two waves with different indices of refraction, but the same polarization. As can be seen from Eqs. (48) and (49), none of the indices of refraction exhibit the customary hyperbolic discontinuity as functions of ω in the region of the exciton photoabsorption. Other theoretical formulae are also changed substantially. For example, the reflection coefficient for light on the surface of the crystal, for normal incidence along the z axis, is given by

$$R = \left|\frac{1 - q - n_+ + q n_-}{1 - q + n_+ - q n_-}\right|^2. \tag{51}$$

As one moves away from the exciton absorption region, when $q \ll 1$ or $q \gg 1$, Eq. (51) transforms into the formula of ordinary crystal optics.

Tetragonal Crystals

Let the x axis coincide with a fourth-order crystal axis, i.e., the lattice constants in the x and y directions are equal. An investigation of exciton states of such a crystal by the methods of group theory, which proceeds in a similar way to that used above for rhombic crystals, leads to the following results. The exciton bands can be subdivided into two types:

a) Non-Degenerate Exciton Bands. For these the vector $\mathbf{P}_0$ is directed along the x axis. If ω approaches the photoabsorption region of an exciton of this type, the tensor B has only one non-vanishing component, namely $B_{xx} = b$. Therefore, the same solutions of Eqs. (42) and (41) are obtained for such excitons as for rhombic crystals.

b) Doubly Degenerate Exciton Bands. One of them corresponds to the vector $\mathbf{P}_0$ directed along the y axis and the second to a vector $\mathbf{P}_0$ of the same magnitude but directed along the z axis. Let us denote these vectors by $\mathbf{P}_0^{(2)}$ and $\mathbf{P}_0^{(3)}$ respectively. To consider this case, it is necessary to introduce two ψ-like terms into the right side of Eq. (1). This leads to an equation similar to Eq. (14), in which, however,

$$a_{xy} = \omega_0 V\left(P_{0x}^{(2)} P_{0y}^{(2)*} + P_{0x}^{(3)} P_{0y}^{(3)*}\right).$$

As a result

$$a = \omega_0 V\,|\,P_0^{(2)}|^2 \begin{vmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}, \quad B = \begin{vmatrix} 0 & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & b \end{vmatrix}, \quad \varepsilon'_{yy} = \varepsilon'_{zz} \equiv \xi. \tag{52}$$

Consider a wave, for which $\mathbf{s}$ lies in the yz plane. Equation (44) changes into

$$(n^2 - \varepsilon'_{xx})\,[n^2 - \xi - b\,/\,(n^2 - \mu)] = 0. \tag{53}$$

Now the system (42) has three solutions:

$$E_y = E_z = 0, \quad E_x \neq 0, \quad n = \sqrt{\varepsilon'_{xx}}; \tag{54}$$

$$\mathbf{E} = \begin{cases} \mathbf{E}_+ \quad n_+^2 = {}^1\!/_2\,(\mu + \xi) + \sqrt{{}^1\!/_4\,(\mu - \xi)^2 + b}; & (55) \\ \mathbf{E}_- \quad n_-^2 = {}^1\!/_2\,(\mu + \xi) - \sqrt{{}^1\!/_4\,(\mu - \xi)^2 + b}, & (56) \end{cases}$$

where $\mathbf{E}_+$ and $\mathbf{E}_-$ coincide in direction, must lie in the yz plane, and must be perpendicular to **s**. If the surface of the crystal is perpendicular to **s**, its equation is $\mathbf{s} \cdot \mathbf{r} = 0$. In order to satisfy the boundary condition $\mathbf{P}_1 = 0$ on this surface, one must, in accordance with Eqs. (55) and (56), form the linear combination

$$\mathbf{E}\,(\mathrm{r},\ t) = \mathbf{E}_+\,[e^{i\omega n_+(\mathbf{s},\mathbf{r})/c} - q e^{i\omega n_-(\mathbf{s},\mathbf{r})/c}]\, e^{-i\omega t}. \tag{57}$$

The properties of this wave are completely analogous to the properties of the solutions of Eq. (50).

Let us now consider a wave, for which **s** is oriented along the x axis. Equation (44) then assumes the form

$$[n^2 - \xi - b\,/\,(n^2 - \mu)]^2 = 0. \tag{58}$$

The solutions of Eq. (42) then become

$$\mathbf{E}\,(x,\ t) = \mathbf{E}_+\,[e^{i\omega n_+ x/c} - q e^{i\omega n_- x/c}]\, e^{-i\omega t}, \tag{59}$$

if the crystal surface is the plane x = 0. Here $\mathbf{E}_+$ is an arbitrary vector lying in the yz plane, and n_+ and n_- have the same meaning they had in Eqs. (55) and (56).

We can also consider the case, for which **s** is an arbitrary direction in space. Then Eq. (44) is an ordinary fourth order equation in n^2. It can be solved if the components of the vector **s** are specified numerically.

Cubic Crystals

In these crystals the matrix element $\mathbf{P}_0$ is non-vanishing only for transitions in triply degenerate exciton bands. Three such bands correspond to vectors $\mathbf{P}_0$, equal in magnitude and oriented along the x, y, and z axes. Let us denote these vectors by $\mathbf{P}_0^{(1)}$, $\mathbf{P}_0^{(2)}$, and $\mathbf{P}_0^{(3)}$. Introducing three ψ-like terms into the right side of Eq. (1), corresponding to the three degenerate bands, we obtain Eq. (14), in which, however,

$$a_{xy} = \omega_0 V \sum_{i=1}^{3} P_{0x}^{(i)} P_{0y}^{(i)*}.$$

Consequently, taking the directions of $\mathbf{P}_0^{(i)}$ into account, we obtain

$$a = \omega_0 V\,|\,P_0^{(1)}\,|^2 \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}, \quad B = b \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}, \quad \varepsilon'_{xx} = \varepsilon'_{yy} = \varepsilon'_{zz} \equiv \xi. \tag{60}$$

Thus the tensors B and ϵ' can be simply replaced by the numbers b and ξ. Then for any direction of **s** Eq. (44) assume the form of Eq. (58), and consequently, n_+ and n_- are given by Eqs. (55) and (56). The solution of (42) can be written

$$\mathbf{E}\,(\mathrm{r},\ t) = [\mathbf{E}_+ e^{i\omega n_+(\mathbf{s},\mathbf{r})/c} + \mathbf{E}_- e^{i\omega n_-(\mathbf{s},\mathbf{r})/c}]\, e^{-i\omega t}, \tag{61}$$

where $\mathbf{E}_+$ and $\mathbf{E}_-$ must be normal to **s** but in other respects can have arbitrary orientations. Therefore, Eq. (61) contains four linearly independent waves. All of these represent new kinds of solutions. If the crystal surface is normal to **s** and coincides with the plane $\mathbf{s} \cdot \mathbf{r} = 0$, then the boundary condition $\mathbf{P}_1 = 0$ yields a relation between $\mathbf{E}_+$ and $\mathbf{E}_-$ and Eq. (61) transforms into

$$\mathbf{E}(\mathbf{r},\ t) = \mathbf{E}_+ \left[e^{i\omega n_+(\mathbf{s},\mathbf{r})/c} - q e^{i\omega n_-(\mathbf{s},\mathbf{r})/c}\right] e^{-i\omega t}. \tag{62}$$

Here $\mathbf{E}_+$ is any vector normal to **s**. The reflection coefficient for light at the crystal surface is given by Eq. (51).

If the crystal surface is not perpendicular to **s**, then in order to satisfy the boundary conditions, it is necessary to construct a linear combination of particular solutions with various values of **s**. This remark is also applicable to the other crystal types which have been considered above.

Longitudinal Waves

All the solutions of Maxwell's equations described above were obtained under the assumption, that in Eq. (39) the denominator of the expression for $\mathbf{P}_1$ does not vanish. There exist, however, other exponential plane wave solutions of another type, in which n is determined just from the condition that this denominator should vanish, i.e., from the equation

$$\mathcal{E}(\omega n \mathbf{s}/c) = \hbar\omega. \tag{63}$$

In fact, in this case $\exp\{i\omega\,[n(\mathbf{s}\cdot\mathbf{r})/c - t]\}$ is a solution of the second of Eqs. (36), without the right side, i.e., with $\mathbf{E}_\perp = 0$. Then it follows from Eq. (38) that $\mathbf{D} = 0$, and the system of equations (35) will be satisfied, if one puts also $\mathbf{H} = 0$. It is still necessary to satisfy Eq. (36). As a result of solving the system of equations (35), Eq. (36) becomes

$$\mathbf{E}(\mathbf{r},\ t) = \mathbf{E}_0 e^{i\omega\,[n(\mathbf{s},\mathbf{r})/c - t]};\ \ \mathbf{E}_0 \parallel \mathbf{s};\ \ \mathbf{P}_1 = -\frac{1}{4\pi}\varepsilon'\mathbf{E};\ \ \mathbf{P}_2 \approx 0;\ \ \mathbf{E}_\perp = \mathbf{D} = \mathbf{H} = 0. \tag{64}$$

For rhombic, tetragonal, and cubic crystals, it is easy to find linear combination solutions which satisfy the boundary condition $\mathbf{P}_1 = 0$. They have the following form:

$$\mathbf{E}(\mathbf{r},\ t) = \mathbf{E}_0 \left[e^{i\omega n(\mathbf{s},\mathbf{r})/c} - e^{i\omega n(\tilde{\mathbf{s}},\mathbf{r})/c}\right] e^{-i\omega t}. \tag{65}$$

Here $\tilde{\mathbf{s}}$ is the specular reflection of **s** at the crystal surface. The waves represented by Eqs. (65) and (63) are also new solutions, not encountered in ordinary crystal optics. In the absence of exciton states in a medium such strictly-longitudinal waves cannot exist. It can be shown, that such waves cannot pass out of the crystal into the vacuum, which obviously make it difficult to detect them experimentally. Hence, such waves are a kind of natural polarization oscillations of the crystal. They represent macroscopic electric fields acting on the exciton. Their group velocity coincides with the group velocity of the exciton [this is readily obtained from Eq. (63)]. Since for such waves $\mathbf{D} = 0$, while $\mathbf{E} \neq 0$, their dielectric constant must be equal to zero. The simplest obvious case of such waves is the longitudinal optical oscillation of ions in the crystal. However, according to the theory presented above, similar waves should exist for all kinds of excitons.

In subsequent papers the necessary generalizations of crystal optics and methods of detecting the new waves experimentally will be investigated in detail.

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