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ON THE CONNECTION BETWEEN THE EXCITON BAND STRUCTURE AND THE NATURAL OPTICAL ACTIVITY OF CRYSTALS

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We have considered the structure of degenerate exciton bands in uniaxial crystals. We have obtained expressions for the dispersion of the optical activity which is caused by the intersection of the exciton energy surfaces.

INTRODUCTION

PEKAR[1] has shown that if account is taken of the spatial dispersion of electromagnetic waves in a crystal in which there are excitons, one is led to new solutions of the Maxwell equations, which are essentially different from the previously known ones in the range of frequencies of the light which are near the exciton absorption frequency. Pekar[1,2] assumed the validity of the following expansion

$$\mathscr{E}(\mathbf{k}) = \mathscr{E}_0 + \frac{\hbar^2}{2}\sum_{ps} M_{ps}^{-1} k_p k_s + \ldots$$

for the exciton energy $\mathscr{E}(\mathbf{k})$ in the neighborhood of $\mathbf{k} = 0$ ($\mathscr{E}_0$ depends on the direction of the vector $\mathbf{k}$); this is always true for non-degenerate exciton bands, but not when degenerate bands intersect in the point $\mathbf{k} = 0$.

When electromagnetic waves are propagated along the principal optical axis of a uniaxial crystal only the exciton states that belong to degenerate bands contribute to the specific polarization.[1]

We shall show in the following, for crystals with symmetry groups D_4^3, D_3^4, D_3^6, ..., that the degenerate energy surfaces intersect at the point $\mathbf{k} = 0$ along the direction of the principal optical axis. These imply that there occur in $\mathscr{E}(\mathbf{k})$ terms linear in $\mathbf{k}$. Account of these terms when the $\mathscr{E}(\mathbf{k})$ surfaces intersect leads to a connection between the specific polarization and the electrical field different from the one given by Pekar.[1,2] This connection is significant in a wide range of light frequencies and causes a rotation of the plane of polarization of light in the crystal.

1. THE STRUCTURE OF A TWO-FOLD DEGENERATE EXCITON BAND OF A UNIAXIAL CRYSTAL FOR THE DIRECTION OF THE PRINCIPAL OPTICAL AXIS

We shall follow reference 1 and call an exciton any excited state of the crystal, the wave function of which is characterized by one continuous quantum number $\mathbf{k}$ and which is transformed upon application of a symmetry operator that commutes with the Hamiltonian according to the single-valued irreducible representation of the space group.

We shall everywhere consider $\mathbf{k} = (0, 0, k)$ to be a dimensionless wave vector within the interval $-\pi \le k \le \pi$.

As an example we shall study the behavior of $\mathscr{E}(k)$ for excitons in crystals with groups D_4^3 and C_{4h}^1. For $k = 0$ the wave functions $\psi_{11}(0)$ and $\psi_{21}(0)$, transforming as $x + iy$ and $x - iy$ respectively, correspond to the same energy $\mathscr{E}(0)$.

The matrices of the irreducible representations of the group D_4^3, obtained from the E representation of the group C_4 and constructed by Seitz' method,[3] are of the form

$$D_{1,2}(u_2) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad D_{1,2}(t) = \begin{pmatrix} \exp(ikt_3) & 0 \\ 0 & \exp(-ikt_3) \end{pmatrix},$$

$$D_1(\hat{4}_{00^1/_4}) = i\begin{pmatrix} \exp(ik/4) & 0 \\ 0 & -\exp(i3k/4) \end{pmatrix},$$

$$D_2(\hat{4}_{00^1/_4}) = -D_1(\hat{4}'_{00^1/_4}). \tag{1}$$

In the group there is an element u_2 which rotates the wave vector. D_1 and D_2 can therefore be brought to a real form.[4] Let $\psi_{11}(k)$ and $\psi_{12}(k)$ transform according to D_1, and $\psi_{21}(k)$ and $\psi_{22}(k)$ according to D_2. One can immediately verify that the functions

$$\xi_j = \frac{1}{\sqrt{2}}[\psi_{1j}(k) + \psi_{2j}(-k)], \quad \eta_j = \frac{i}{\sqrt{2}}[\psi_{1j}(k) - \psi_{2j}(-k)]$$

are transformed through real matrices. It is well known[5] that this leads to

$$\psi_{1j}^*(k) = e^{i\alpha}\psi_{2j}(-k). \tag{2}$$

If $\mathscr{E}_1(k)$ and $\mathscr{E}_2(k)$ belong respectively to the representations $D_1(k)$ and $D_2(k)$, it follows from (2) that

$$\mathscr{E}_1(k) = \mathscr{E}_2(-k). \quad (3)$$

For the group C^1_{4h} (which contains an inversion) the matrices analogous to (1) have the form

$$D'_{1,2}(\sigma) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad D'_{1,2}(t) = \begin{pmatrix} \exp(ikt_3) & 0 \\ 0 & \exp(-ikt_3) \end{pmatrix}$$

$$D'_1(\hat{4}) = \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix}, \qquad D'_2(\hat{4}) = -D'_1(\hat{4}). \quad (4)$$

These representations can also be brought into real form, but now the functions

$$\frac{1}{\sqrt{2}}[\psi'_{11}(k) + \psi'_{22}(k)], \qquad \frac{i}{\sqrt{2}}[\psi'_{11}(k) - \psi'_{22}(k)], \ldots,$$

will be transformed according to a real representation; hence it follows that

$$\psi'^{*}_{11}(k) = e^{i\beta}\psi'_{22}(k), \qquad \psi'^{*}_{12}(k) = e^{i\beta}\psi'_{21}(k). \quad (5)$$

To the representation $D'_2(k)$ belong the complex conjugate (transposed) functions of the representation $D'_1(k)$, so that

$$\mathscr{E}'_1(k) = \mathscr{E}'_2(k). \quad (6)$$

If thus the group C'_4 is supplemented with a plane perpendicular to the $\hat{4}$ axis, the degenerate bands are not split up when $k \neq 0$.

One can show that Eq. (3) is valid for degenerate exciton bands of crystals which possess other spatial symmetry groups with one axis of order higher than 2, provided that among the symmetry elements that change k to $-k$ there is no inversion or a plane of reflexion. These groups are D^j_n, C^j_n ($n = 3, 4, 6$), and others.

The expansion of the energy of the two-fold degenerate exciton bands in powers of k is for uniaxial crystals of the form

$$\mathscr{E}_1(k) = \mathscr{E}_0 + \sum_n a_n k^n, \qquad \mathscr{E}_2(k) = \mathscr{E}_0 + \sum_n (-1)^n a_n k^n, \quad (7)$$

if Eq. (3) is satisfied.

Equation (3) is valid also for the electron bands of the same crystals if one neglects the spin-orbit interaction (see, for instance, reference 6), since we have used in deriving (3) only the definition of the exciton state, which can include also a spinless electron.

Pekar[1] considered the spatial dispersion of electromagnetic waves in a uniaxial crystal in the approximation $a_1 = 0$. We shall consider the case where $a_1 \neq 0$ and where the bands $\mathscr{E}_1(k)$ and $\mathscr{E}_2(k)$ intersect along the direction $(0, 0, k)$.

2. THE PROPAGATION OF A PLANE ELECTROMAGNETIC WAVE IN A UNIAXIAL DIELECTRIC CRYSTAL IN THE DIRECTION OF THE PRINCIPAL OPTICAL AXIS

Let H be the energy operator of the crystal and W the operator of the interaction energy of the crystal with the electromagnetic field.* We shall take the wave function of a crystal perturbed by the small alternating electrical field of the light wave in the form

$$\Psi = \Psi_0 + \sum_{q,s,k} C_{qs}(k)\psi_{qs}(k) + \ldots, \qquad |C_{qs}(k)| \ll 1, \quad (8)$$

where $\psi_{qs}(k)$ is the exciton-state wave function, q the number of the irreducible representation of the space group, and s the number of the function belonging to the q-th irreducible representation. All other excited states of the crystal will in the following be taken into account phenomenologically.

We shall neglect the difference between the magnetic induction and the magnetic field strength. This neglect enables us to write down the energy of the interaction of the crystal with the electromagnetic field in the form

$$W = -\frac{1}{c}\int \hat{\dot{\mathbf{P}}}(\mathbf{r}')\,\mathbf{A}(\mathbf{r}'t)\,d\tau',$$

$$\mathbf{A}(\mathbf{r}t) = \mathbf{A}_0 \exp\{i(\varkappa z/d - \omega t)\} + \mathbf{A}^*_0 \exp\{-i(\varkappa z/d - \omega t)\},$$

$$\mathbf{A}_0 = (\mathbf{A}_{0x}, A_{0y}, 0), \qquad \varkappa = n\omega d/c, \quad (9)$$

where d is the lattice constant in the z direction. The field $\mathbf{A}(\mathbf{r}, t)$ is assumed to be sufficiently smooth ($d \ll \lambda$). The coefficients $C_{qs}(k)$ are determined from the Schrödinger equation

$$[i\hbar\partial/\partial t - \mathscr{E}_q(k)]\,C_{qs}(k) = -i\omega_q(k)\,c^{-1}V\langle qsk|\mathbf{P}(0)|0\rangle(\mathbf{A}_0\delta_{\varkappa,k}\exp(-i\omega t) + \mathbf{A}^*_0\delta_{-\varkappa,k}\exp(i\omega t)). \quad (10)$$

when we expand $\mathscr{E}_q(\kappa)$ in the power series (7) we retain the linear terms

$$\mathscr{E}_1(\varkappa) = \mathscr{E}_0 + \varkappa\partial\mathscr{E}_1/\partial k, \qquad \mathscr{E}_2(\varkappa) = \mathscr{E}_0 - \varkappa\partial\mathscr{E}_1/\partial k.$$

A cumbersome but elementary calculation leads to the following expression for the average specific dipole moment

$$\mathbf{P}(\mathbf{r}, t) = \int \hat{\mathbf{P}}(\mathbf{r})\,\Psi^*\Psi\,d\Omega.$$

In complex form

$$P_x = \beta_{xx}E_x + \beta_{xy}E_y,$$

$$\beta_{xx} = \beta_{yy} = \frac{a}{\omega_0}\left[\frac{\mathscr{E}_0 - \hbar\omega}{(\mathscr{E}_0 - \hbar\omega)^2 - (\varkappa\partial\mathscr{E}_1/\partial k)^2} + \frac{\mathscr{E}_0 + \hbar\omega}{(\mathscr{E}_0 + \hbar\omega)^2 - (\varkappa\partial\mathscr{E}_1/\partial k)^2}\right],$$

$$\beta_{yx} = \beta^*_{xy} = i\frac{a}{\omega_0}\frac{\partial\mathscr{E}_1}{\partial k}\varkappa\left[\frac{1}{(\mathscr{E}_0 - \hbar\omega)^2 - (\varkappa\partial\mathscr{E}_1/\partial k)^2} + \frac{1}{(\mathscr{E}_0 + \hbar\omega)^2 - (\varkappa\partial\mathscr{E}_1/\partial k)^2}\right],$$

$$\frac{a}{\omega_0} = \frac{V}{4}\left|\int [P_x(0) - iP_y(0)]\,\Psi_0\psi_{11}(0)\,d\Omega\right|^2. \quad (11)$$

We neglected in β_{xy} corrections of the order $(d/\lambda)^2$. In deriving (11) we used the property (2) of the wave functions.

Let the condition $\kappa\partial\mathscr{E}_1/\partial k \ll \mathscr{E}_0 - \hbar\omega$ be satisfied for the frequency ω. We can then neglect

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*Here and in the following we retain Pekar's notation.[1]

the small extra terms in the denominators of (11). We take the other excited states of the crystal into account by introducing ϵ' through $\mathbf{D} = \epsilon'\mathbf{E} + 4\pi\mathbf{P}$.

The specific rotation of the plane of polarization of the light ρ can be obtained from (11) by the well-known equations of crystal optics[7]

$$\rho = \frac{K(\lambda^2+\lambda_0^2)}{(\lambda^2-\lambda_0^2)^2}, \qquad K = \frac{4\pi}{\hbar^2 c^2}\frac{a}{\omega_0}\frac{\partial\mathscr{E}_1}{\partial k}\lambda_0^2 d, \qquad \frac{\lambda}{\lambda_0} = \frac{\mathscr{E}_0}{\hbar\omega}. \tag{12}$$

Expression (12) differs from the analogous equations obtained semi-phenomenologically by Agranovich and Rukhadze[8] and from Chandrasekhar's empirical formula,[9] because λ_0^2 appears in the numerator.

The classical analysis[8] of the optical activity disregards the extra terms of ρ, obtained by expanding the exciton transition frequency $\omega_q(k)$ (which occurs in the quantum mechanical expression for the oscillator strength) in powers of d/λ [$\omega_q(k)$ is defined here by (10)]. Equation (12) is thus a natural way of making the equations obtained in reference 8 more exact.

Agranovich[10] obtained a dispersion relation of the form (12) without taking into account the intersection of the exciton bands. Equation (12) differs therefore from the corresponding dependence (12.2) of reference 10 not only in the meaning of the constants occurring in K but also in the range of applicability. In the case of uniaxial crystals, Eq. (12.2) of reference 10 is, for instance, applicable only for directions of the propagation of light which are different from the direction of the principal optical axis.

Chandrasekhar's formula[9] describes the dispersion of the optical activity of quartz well, but differs strongly from the experimental dependence $\rho(\lambda)$ in the wavelength range $\lambda \sim 0.4\mu$ for benzyl crystals.

Chandrasekhar's empirical formula is thus not universal, and can be applied only when λ_0 corresponds to an isolated absorption band. Equation (12) can also be applied when λ_0 corresponds to an isolated exciton absorption band, provided all other absorption bands are removed from the wavelength region under consideration.

As (12) is somewhat different from Chandrasekhar's expression, the parameters K and λ_0 in (12) will, of course, be different from the corresponding quantities in reference 9. One can, for instance, obtain for quartz satisfactory agreement with experiment if one chooses $K = 7.1$, $\lambda_0 = 0.081\,\mu$ (ρ is expressed, as usual, in degrees per milimeter, and λ in μ). The parameter λ_0 must also occur in the formula for the dispersion of the refractive index $n_0(\lambda)$ of quartz. If we put $a = 3 \times 10^4$ and assume $\epsilon' = 1$ in (11), the expression for $n_0(\lambda)$, obtained from (11) by the usual methods $[n_0^2 - 1 = 1.4\lambda^2/(\lambda^2 - \lambda_0^2)]$, as well as the expression for $\rho(\lambda)$, will differ by less than 1 or 2% from the experimental values, in a wide range of wave lengths $\lambda < 1\,\mu$.

The slight difference between the proposed expressions for ρ and n_0 and the experimental ones may be caused by the fact that we have not taken into account virtual transitions to exciton states with λ_0' lying within the infrared region, $\lambda_0' \sim 8.8\,\mu$ and $20\,\mu$. Taking these into account is especially important for $n_0(\lambda)$ when $\lambda > 1\,\mu$. We have also neglected other contributions to n_0 and ρ, connected with virtual transitions to nonexciton states, and also the contributions to the rotation, which were considered by Agranovich.[10]

Taking into account the approximate character of our expressions, we can use the numerical values of K and a only for an estimate of the width of the exciton band $\Delta\mathscr{E}$ in quartz, replacing $\partial\mathscr{E}/\partial k$ in (12) by $\Delta\mathscr{E}/2\pi$. We obtain as a result $\Delta\mathscr{E} \approx 0.8$ ev.

In the range of light frequencies near ω_0 one can neglect the terms with $\mathscr{E}_0 + \hbar\omega$ in the numerators of (11).

The refractive indices for left-hand and right-hand circularly polarized waves, $E_y^{(r)} = iE_x^{(r)}$ and $E_y^{(l)} = -iE_x^{(l)}$, are determined from

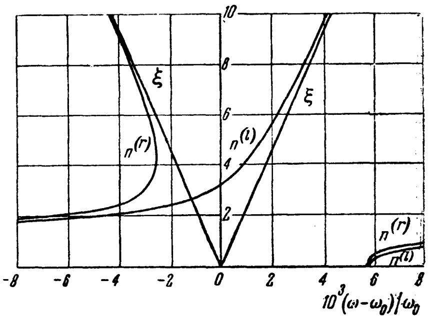
$$(\varepsilon' - n^2)(\xi \pm n) - \frac{4\pi ac}{\omega_0^2\, d\partial\mathscr{E}_1/\partial k} = 0, \qquad \xi = \frac{\hbar c}{d\partial\mathscr{E}_1/\partial k}\frac{\omega-\omega_0}{\omega_0}, \tag{13}$$

where the upper and lower signs correspond to $n^{(r)}$ and $n^{(l)}$ (with $\partial\mathscr{E}_1/\partial k > 0$).

We show in the figure the frequency dependence of real and positive $n^{(r)}$ and $n^{(l)}$ for the following values of the parameters (cf. reference 1)

$$\hbar\omega_0 = 2\,\text{ev}, \qquad \varepsilon' = 2, \qquad \partial\mathscr{E}_1/\partial k = (2\pi)^{-1}\,\text{ev}, \qquad d = 5.29\ \text{A},$$
$$a = (e^2\hbar/2m)Nf, \qquad N = 6.76\cdot 10^{21}\,\text{cm}^{-3},$$

Such a behavior of the dependence $n(\omega)$ is qualitatively the same as the phenomenological dependence $n(\omega)$ obtained by Ginzburg[11] for a gyrotropic medium.



In the frequency range $\omega' < \omega < \omega''$ with

$$(\omega_0 - \omega')/\omega_0 \approx 2.51 \cdot 10^{-2};$$
$$(\omega'' - \omega_0)/\omega_0 \approx 5.75 \cdot 10^{-3}$$

only the l wave has a real positive index of refraction, while the r waves have a complex index, $n_1^{(r)} = n_2^{(r)*}$. In an infinite medium the amplitudes of these two waves must be set equal to zero. In a semi-infinite crystalline medium $(z > 0)$ the r wave is exponentially damped when moving away from the surface. In the enantiomorphous modification of the crystal $(\partial \mathscr{E}_1/\partial k < 0)$, on the other hand, only the r wave will be propagated.

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