ELECTROMAGNETIC WAVES IN THE REGION OF EXCITON ABSORPTION IN A CRYSTAL

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A theory is developed for the absorption coefficient and the refractive index in the absorption bands corresponding to exciton excitation in molecular crystals at low temperatures. It is shown that the structure of the absorption band can serve as a means of determining the sign of the effective mass of the exciton. Conditions are found for which the index of refraction equals zero at the short-wave side of the absorption band. Electromagnetic waves at these frequencies are completely reflected from the crystal surface, penetrating it to only a small depth. When the temperature is increased this effect vanishes.

INTRODUCTION

Because of the recent work of Pekar,[1] Ginzburg,[2] and Agranovich and Rukhadze[3] attention has been directed to the propagation of light in crystals characterized by spatial dispersion. It has been shown in the work cited above that in frequency regions close to the exciton absorption band the index of refraction can have several values for waves of the same frequency, direction of propagation, and polarization. Only the transparent region of the crystal has been studied in references 1 to 3. However, it is of interest to consider propagation of electromagnetic waves in a crystal at frequencies corresponding to absorption bands.

The reduction in the amplitude of an electromagnetic wave as it passes through matter is due to two effects: (a) scattering, (b) conversion of energy in the electromagnetic wave into the energy of motion of the molecules (true absorption). In this paper we shall be interested only in true absorption at crystal temperatures close to zero.

The molecules of a molecular crystal are neutral; hence an optical wave cannot communicate motion to them directly. However, when the molecules are excited there are additional interaction forces between molecules and these shift the equilibrium positions of the molecules. Thus, true absorption is due to coupling between the internal molecular excitations and the molecular oscillations. This coupling leads to a considerable broadening of the absorption band at absolute zero.

Davydov[4] has shown that excitations of two types can be produced in molecular crystals by optical waves: (a) localized excitations that propagate slowly through the crystal and whose polarization is determined by the orientations of the molecules, which are considered as independent absorption center, (b) exciton excitation, i.e., excitations that propagate rapidly in the form of excitation waves in the crystal. These excitations are responsible for the appearance in the absorption spectrum of sharply polarized "crystallographic" absorption bands, the polarization of which is determined by the crystallographic structure.

The absorption bands corresponding to the localized excitation are roughly Gaussian in shape and do not yield any information as to the detailed structure of the crystal. The absorption bands corresponding to exciton excitations, on the other hand, are very sensitive to crystallographic structure. Consequently, an investigation of the structure of exciton absorption bands is one of the methods of studying crystallographic structure, the energy of the exciton states as a function of the propagation vector of the exciton, and the exciton interaction with the lattice vibrations.

An analysis of the structure of the optical absorption band in a molecular crystal has been given by Davydov,[5] using a one-dimensional crystal; Davydov and Rashba have considered a more general case. However, in this work no account was taken of the self-consistency of the problem: the propagation vector of the optical wave which excites the crystal depends on the refractive index and the optical absorption. This self-consistency may be especially important close to an absorption band where, in certain cases, it leads to spatial dispersion. In the present paper we investigate the passage of light through a crystal in the region of the absorption band using a simple model of the molec-

ular crystal; in this model the molecules can execute translational and rotational oscillations about the fixed equilibrium positions.

1. CRYSTAL WAVE FUNCTIONS IN THE PRESENCE OF OPTICAL WAVES

Let G be some region of a molecular crystal with a cubic lattice in each elementary cell of which there is one molecule. All molecules have the same equilibrium orientation. It is further assumed that the region G is a cube with sides $N_i a_i$ (i = 1, 2, 3) where the a_i are the base vectors of the lattice. Then the position of the center of gravity of the molecule is given by the vector $R = r + n$ where r is the coordinate of the center of region G while $n = \sum n_i a_i$, $n = 0, \pm 1, \pm \ldots \ldots \pm N_i/2$ (i = 1, 2, 3). The total number of molecules in region G, $N = N_1 N_2 N_3$ must be large enough to exhibit the basic interaction effects between molecules; at the same time the dimensions of the region must be smaller than the wavelength of the light.

In the absence of interactions between the exciton excitations and the lattice vibrations, the frequency of the exciton excitations can be written in the form

$$\omega_k = \omega_0 + (\tau/2)(\cos k \cdot a - 1), \qquad (1.1)$$

where $\hbar |\tau|$ is the energy width of the exciton band for excited states. The wave function corresponding to the excitation (1.1) is of the form

$$\psi_k = N^{-1/2} \sum_n e^{i k \cdot n} \varphi_n^f (\rho_n) \prod_{n' \neq n} \varphi_{n'}(\rho_{n'}), \qquad (1.2)$$

where $\varphi_n^f(\rho_n)$ and $\varphi_n(\rho_n)$ are wave functions which determine the excited and ground states of the molecule at n.

For simplicity we assume that the exciton excitations interact only with two kinds of lattice vibrations: translational and rotational oscillations. The frequencies of these oscillations are given by the relations

$$\nu_p^2 = \nu_{max}^2 \sin^2(p \cdot a/2), \quad \Omega_q = \Omega_0 + \frac{\Delta\Omega}{2}(\cos q \cdot a - 1), \quad (1.3)$$

where $|\Delta\Omega|$ is the width of the band of the optical frequency branch. The propagation vectors k, p and q run over N discrete values $\sum (2\pi/N_i) b_i \eta_i$ ($\eta = 0, \pm 1, \pm \ldots \ldots$) if we take cyclical boundary conditions with periodicity $N_i a_i$ as boundary conditions. Here the b_i are the vectors of the reciprocal lattice.

In actual crystals the dependences of ω_k, ν_p, and Ω_q of the propagation vectors can be expressed

by more complicated functions than those given in (1.2) and (1.3). It is important, however, that in the limit of infinitely long waves Ω_q and ω_k approach a finite limit while $\nu_p \to 0$. Usually, in molecular crystals the width of the exciton zone exceeds the width of the zones which correspond to lattice vibrations, i.e., the following inequality holds

$$|\tau| > |\Delta\Omega|, \quad \nu_{max}.$$

Further, let H_0 be the Hamiltonian, whose eigenfrequencies

$$E_{kpq} = \hbar(\omega_k + \nu_p + \Omega_q),$$

and whose eigenfunctions $\Phi_{kpq} = \psi_k \psi_p \psi_q$ correspond to excitation in the crystal of one exciton, one accoustical phonon and one optical phonon. The ground state of the crystal (at basolute zero) will be a state in which none of these excitations are excited. The energy of this state will be taken as zero energy and the wave function will be denoted by Φ_0.

The operator for the interaction of the excitations with the lattice vibrations is

$$H' = H_1 + H_2,$$

where

$$H_1 = N^{-1/2} \sum_{mn} V_{nm}^{(1)} \rho_{n} \cdot \rho_m \{A_p (e^{ip \cdot n} - e^{ip \cdot m}) + A_p^+ (e^{-ip \cdot n} - e^{-ip \cdot m})\},$$

$$H_2 = N^{-1/2} \sum_{mnq} V_{nm}^{(2)} \rho_{n'} \cdot \rho_m \{A_q (e^{iq \cdot n} + e^{iq \cdot m}) + A_q^+ (e^{-iq \cdot n} + e^{-iq \cdot m})\}.$$

Here ρ_n is the ensemble of internal molecular coordinates for molecule n; A_p^+ and A_q^+ are creation operators for the appropriate phonons. When these operate on the function Φ_0 they produce a state with one phonon of the appropriate type. Operators A_p and A_q are annihilation operators for the corresponding phonons.

The operator for the interaction of the electromagnetic wave

$$E = 2E_0 \exp(- \Lambda \cdot R) \cos(\omega t - Q \cdot R)$$

with the molecules of the crystal (when the wave length is much larger than the molecular dimension) can be given by the expression*

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*In computing the exciton excitations, account has already been taken of the dipole-dipole interaction of the molecular electric moments induced by the light wave; hence, in operator (1.4) we introduce the average field rather than the effective field.

$$W = - e\, E_0 \sum_n \rho_n \sum_{\lambda=+,-}' \exp\{(i\lambda Q - \Lambda)\cdot(r+n) - i\lambda\omega t\}. \tag{1.4}$$

In the presence of the light wave, the crystal state is described by the Schrödinger equation

$$(i\hbar\partial/\partial t - H_0 - H_1 - H_2 - W)\, F = 0. \tag{1.5}$$

When the interaction between the excitons and the lattice vibrations is weak, we can use the one-phonon process; hence we seek a solution of (1.5) in the form of a series

$$F = b_0(t)\,\Phi_0 + \sum_{k,p,q} b_{kpq}(t)\,\Phi_{kpq} \exp\left[-i\left(\omega_{kpq} - i\gamma_{kpq}/2\right)t\right], \tag{1.6}$$

with initial conditions

$$b(0) = 1, \quad b'_{kpq}(0) = 0. \tag{1.7}$$

The matrix elements of the operator W are of the form

$$(\Phi_{k'}^* \mid W \mid \Phi_0) \tag{1.8}$$

$$= -N^{-1/2}(E_0\cdot d) \sum_{\lambda=+,-} \exp\left[i(\lambda Q + i\Lambda)\cdot r - \lambda\omega t\right]\delta_{\lambda Q, k'},$$

where $d = (\varphi^f \mid e\rho \mid \varphi)$ is the electric dipole moment excited by the optical wave:

$$\delta_{\lambda Q, k'} = N^{-1} \sum_n e^{-\Lambda n} \exp\left[i\,n\cdot(\lambda Q - k')\right].$$

If $N_1 a\Lambda \ll 1$ the matrix elements in (1.8) are different from zero, only when $k' = \lambda Q$. If the absorption is not very small the matrix elements (1.8) will be different from zero at several values of k' close to λQ. From Eqs. (1.6), (1.8), and (1.5) we find as a first approximation (neglecting H_1 and H_2)

$$b = \frac{(E_0\cdot d)\,N^{1/2}}{\hbar} \frac{\exp\left[i(\omega_{\lambda Q} - \lambda\omega - i\gamma_{\lambda Q}/2)\right] - 1}{\omega_{\lambda Q} - \lambda\omega - i\gamma_{\lambda Q}/2}. \tag{1.9}$$

Thus, in the same approximation the wave function for the crystal (when there is an optical wave of frequency ω present, (at large values of t) can be given by the expression

$$F = \Phi_0 + \frac{(E_0\cdot d)\sqrt{N}}{\hbar} \sum_{\lambda=+,-} \frac{\exp\left[-i\lambda\omega t + i\lambda\,Q\cdot r - \vec{\Lambda}\cdot r\right]}{\omega_Q - \lambda\omega - i\gamma_{\lambda Q}/2} \Phi_{\lambda Q}, \tag{1.10}$$

where $\gamma_{\lambda Q}$ is a complicated function of frequency, the determination of which requires the solution of Eq. (1.5) in the next approximation, which takes account of the interaction of the excitons with the lattice vibrations.

2. CALCULATION OF THE COEFFICIENTS γ

The matrix elements of the operators that determine the coupling between the excitons and the lattice vibrations can be written in the following form:

$$(\Phi_{kp}^* \mid H_1 \mid \Phi_{\lambda Q}) = \mid d\mid^2 V_1 N^{-1/2}\delta_{\lambda Q, k+p},$$

$$(\Phi_{kq}^* \mid H_2 \mid \Phi_{\lambda Q}) = \mid d\mid^2 V_2 N^{-1/2}\delta_{\lambda Q, k+q}, \tag{2.1}$$

where

$$V_1 \approx g_1 \nu_p^{-1/2}\sin(p\cdot a/2)\sin\left[(2\lambda Q - p)\cdot a/2\right],$$

$$V_2 \approx g_2 \Omega_q^{-1/2}\cos(q\cdot a/2)\cos\left[(2\lambda Q - q)\cdot a/2\right].$$

Using Eqs. (2.1) and (1.9), we find $b_{\lambda Q-q, q}$ and $b_{\lambda Q-p, p}$ from Eq. (1.5); then, multiplying (1.5) by $\Phi_{\lambda Q}^*$, we have

$$\gamma_{\lambda Q} = \frac{2\mid d\mid^4}{N} \left\{ \sum_p \mid V_1\mid^2 \frac{1 - \exp\left[-i(\omega_{Q-p} - \lambda\omega + \nu_p)t\right]}{\omega_{Q-p} - \lambda\omega + \nu_p} \right.$$

$$\left. + \sum_q \mid V_2\mid^2 \frac{1 - \exp\left[-i(\omega_{Q-q} - \lambda\omega + \Omega_q)t\right]}{\omega_{Q-q} - \lambda\omega + \Omega_q} \right\}, \tag{2.2}$$

where λ takes values + or −. It follows directly from Eq. (2.2) that

$$\gamma_{-Q} = 0. \tag{2.3}$$

Taking account of (2.3), at large values of t, we can write

$$\gamma \equiv \gamma_Q = \gamma_{tr} + \gamma_{rot}, \tag{2.4}$$

where

$$\gamma_{tr} = 2\mid d\mid^4 N^{-1} \sum_p \mid V_1\mid^2 \zeta(\omega_{Q-p} + \nu_p - \omega), \tag{2.5}$$

$$\gamma_{rot} = 2\mid d\mid^4 N^{-1} \sum_q \mid V_2\mid^2 \zeta(\omega_{Q-q} + \Omega_q - \omega); \tag{2.6}$$

and $\zeta(x)$ is a singular function defined by the relation

$$\zeta(x) = \lim_{t\to\infty} \frac{1 - \exp(-ixt)}{ix} = \pi\delta(x) + i\,P\frac{1}{x}.$$

The imaginary part of this function causes a shift in the energy levels of the system and will not be considered in what follows (cf. reference 7, §16).

In Eq. (2.5) we change the summation to integration and introduce the new variable

$$d\,p = d\sigma d\xi(p)/\mid \text{grad}\,\xi(p)\mid, \quad \xi(p) = \omega_{Q-p} + \nu_p,$$

where $d\sigma$ is a surface element, and $\xi(p) = \text{const}$; thus, we can write

$$\gamma_{tr}(\omega) = \frac{a^3\mid d\mid^4}{4\pi^3} \int_{\xi_1}^{\xi_2} d\sigma d\xi \frac{\mid V_1\mid^2}{\mid \text{grad}\,\xi(p)\mid} \zeta(\xi - \omega)$$

$$= \begin{cases} \dfrac{g_1 a^2\mid d\mid^4}{2\pi^2\sqrt{\nu_{max}}} \displaystyle\int \frac{\sin^2\left([2Q - p]\cdot a/2)\right]\mid \sin(p\cdot a/2)\mid d\sigma}{\mid \tau\sin\left[(Q - p)\cdot a\right] + \nu_{max}\cos(p\cdot a/2)\mid}, & \text{if } \xi_1 < \omega < \xi_2, \\ 0 & \text{if } \omega \text{ is outside the interval } \xi_1, \xi_2. \end{cases} \tag{2.7}$$

The quantities ξ_1 and ξ_2 are respectively the smaller and larger of the values ω_Q and $\omega_{Q-\pi b}$
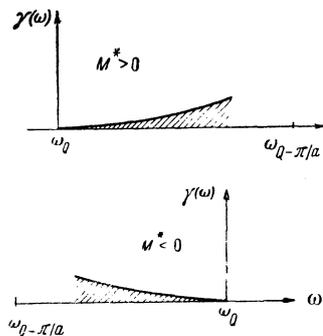
FIG. 1

+ ν_{max}; the integration in Eq. (2.7) is carried out for all values of P which satisfy the condition

$$\omega = \omega_{Q-P} + \nu_{max}.$$

We now assume that the frequency ω inside the absorption band approaches ω_Q, then $p \rightarrow 0$ and it follows from Eq. (2.7) that $\gamma_{tr} \rightarrow 0$. In Fig. 1 is shown the dependence of γ_{tr} on ω close
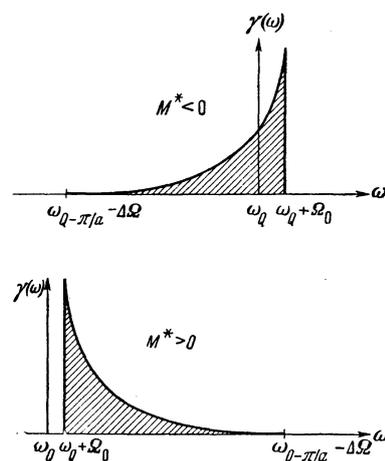
FIG. 2

to the frequency ω_Q for positive and negative effective exciton mass. Carrying out a similar transformation of Eq. (2.6), we have

$$\gamma_{rot}(\omega) = \begin{cases} \dfrac{g^2 a^2 \, |\,d\,|^4}{2\pi^2} \displaystyle\int \dfrac{\cos^2\,[(2Q-q)\cdot a\,/2]\,\cos^2\,(qa/2)\,d\sigma}{\{\Omega_0 + (\Delta\Omega/2)\,(\cos q\cdot a - 1)\}^{1/2}\,|\,\tau\sin(Q-q)\cdot a - \Delta\Omega\sin q\cdot a\,|}, & \text{if } \zeta_1 < \omega < \zeta_2 \\[4mm] 0, & \text{if } \omega \text{ is outside the interval } \zeta_1,\,\zeta_2, \end{cases} \tag{2.8}$$

where ζ_1 and ζ_2 are respectively the smaller and larger of the values. $\omega_Q + \Omega_0$ and $\omega_{Q-\pi b} + \Omega_0 - \Delta\Omega_0$. The integration in Eq. (2.8) is carried out over all values of q which satisfy the relation $\omega = \omega_{Q-q} + \Omega_q$. In Fig. 2 is shown the dependence of γ_{rot} on frequency for positive and negative effective exciton mass.

If the crystal temperature is not zero, the integrands in Eqs. (2.7) and (2.8) will contain the factors $(\tilde{n}_p + 1)$ and $(\tilde{n}_q + 1)$ respectively where $\tilde{n}_p$ and $\tilde{n}_q$ are the mean numbers of phonons at a given temperature. At high temperatures $(\tilde{n} + 1)$ and γ are proportional to temperature. When the temperature is increased, in addition to the increase in γ, which corresponds to the emission of phonons, there are additional terms which correspond to the absorption of phonons by excitons. Both of these increase γ_{tr} and γ_{rot} and cause considerable expansion of the frequency region in which these quantities are different from zero.

We have considered above the interaction between exciton excitations with two branches of the lattice vibrations. However, a larger number of branches take part in the interaction. Because the different oscillations are independent, each makes an additive contribution to γ; consequently

$$\gamma(\omega) = \sum_i [\gamma_{tr}^i(\omega) + \gamma_{rot}^i(\omega)].$$

In Fig. 3 is shown a possible form for the dependence of γ on ω at absolute zero. As the temperature increases the curve $\gamma(\omega)$ expands in both directions about the frequency ω_Q. In computing $\gamma(\omega)$, we consider only the interaction of exciton excitations with lattice vibrations. However, to this value of $\gamma(\omega)$ it is necessary to add the natural width (Γ) of the internal molecular level associated with the finite lifetime of the excited state of the free molecule (radiative and nonradiative transitions). In luminescent crystals $\Gamma \ll \gamma(\omega)$ inside the absorption band so that these corrections need not be introduced.
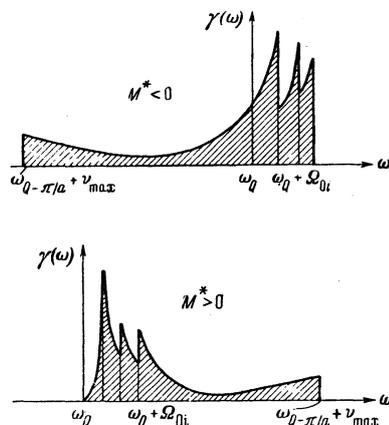
FIG. 3

3. EQUATIONS FOR THE ABSORPTION COEFFICIENT AND THE REFRACTIVE INDEX

To obtain equations for the absorption coefficient and the refractive index for a molecular crystal, we use Eq. (1.10) to compute the average value of the electric moment (per unit volume of the crystal) induced in region G by the light wave

$$P_{ex} = \frac{d\,(E_0 \cdot d) 2N_0 \omega_Q\,[(\,\omega_Q^2 - \omega^2) + i\,(\gamma/2)\,(\omega_Q + \omega)]}{(\omega_Q^2 - \omega^2)^2 + (\gamma/2)^2\,(\omega_Q + \omega)^2} \quad (3.1)$$
$$\times \exp\,[-\Lambda \cdot r + i\,(Q \cdot r + \omega t)] + \text{compl. conj.}$$

where N_0 is the number of molecules per unit volume.

In finding the approximate solution (1.10) of Eq. (1.5), we have taken account only of those states that correspond to a definite internal molecular excitation. The absorption of light, when this state is excited, does not depend on the existence of other molecular levels having some other energy. However, these states introduce an additional term $\{\epsilon_0\}$ in the real part of the dielectric permittivity tensor: $\{\epsilon_0\}$ is relatively insensitive to frequency. For simplicity we shall assume that ϵ_0 is a scalar. Then, the total electric moment produced in the crystal can be written in the form

$$P = P_{ex} + \frac{\epsilon_0 - 1}{4\pi}\,E, \quad (3.2)$$

where P_{ex} is defined by Eq. (3.1)

An electromagnetic wave which propagates in the crystal must satisfy the equations

$$\text{curl}\,E = -\dot{H}/c, \quad \text{curl}\,H = \dot{D}/c, \quad \text{div}\,D = 0, \quad \text{div}\,H = 0,$$
$$D = E + 4\pi P. \quad (3.3)$$

We seek a plane-wave solution for these equations, assuming that E, H, and P are proportional:

$$e^{-\Lambda r}\exp\,[i\,(Q \cdot r - \omega t)], \quad Q = \frac{\omega}{c}\,\mu s, \quad \Lambda = \frac{\omega}{c}\,\varkappa s,$$

where s is a unit vector in the direction of propagation of the wave. From the above it is easy to obtain the relation

$$E + 4\pi P = (\mu + i\varkappa)^2\,[E - s\,(s \cdot E)]. \quad (3.4)$$

We now orient the coordinate system xyz in such a way that the x axis lies along the equilibrium direction of the induced electric moment of each molecule (in our crystal all molecules have the same orientation); thus $d = \{d, 0, 0\}$.

If the electric field of the light wave is parallel to the x axis, P is collinear with E; then, from Eq. (3.3) it follows that E and D are also collinear and, consequently, that s is perpendicular to E. Substituting Eq. (3.2) in Eq. (3.4) and separating

real and imaginary parts, we have

$$\mu_{xx}^2 - \varkappa_{xx}^2 = \epsilon_0 + \frac{4\pi\,(e^2/m)\,fN_0\,(\omega_Q - \omega)}{(\omega_Q + \omega)\,[(\omega_Q - \omega)^2 + \gamma^2/4]} \equiv A\,(\omega), \quad (3.5)$$

$$2\mu_{xx}\varkappa_{xx} = \frac{2\pi\,(e^2/m)\,fN_0\gamma}{(\omega_Q + \omega)\,[(\omega_Q - \omega)^2 + \gamma^2/4]} \equiv B\,(\omega), \quad (3.6)$$

where $A\,(\omega)$ is the real part and $B\,(\omega)$ the imaginary part of the dielectric permittivity. In obtaining (3.5) and (3.6) we have expressed d^2 in terms of the oscillator strength f, corresponding to the internal molecular transition, using the relation $d^2 = e^2\hbar f/2m\omega_Q$ where m is the mass of the electron. The other two principle elements of the refractive-index tensor and the absorption tensor are

$$\mu_{zz}^2 = \mu_{yy}^2 = \epsilon_0, \quad \varkappa_{zz} = \varkappa_{yy} = 0.$$

In Eq. (3.5) and (3.6) the frequency ω_Q is a function of the refractive index

$$\omega_Q = \omega_0 + \frac{\tau}{2}\left[\cos\left(\frac{\omega}{c}\,\mu\,s_1 \cdot a\right) - 1\right], \quad (3.7)$$

where s_1 is a unit vector perpendicular to the x axis; hence, in the region $\omega \approx \omega_0$ the second term in Eq. (3.7) can be of some importance in (3.5) and (3.6). In this frequency region these equations can, in general, lead to the appearance of several values of μ_{xx}^2 at the same frequency.

This situation has already been noted by Pekar, Ginzburg,[2] and Agranovich and Rukhadze.[3] In references 1 to 3, however, absorption was not taken into account, and it was assumed that μ can take on very large values; this tends to overemphasize the role of spatial dispersion. Actually, as has been shown by measurements carried out by Obreimov, Prikhot'ko and their colleagues,[8] at low temperatures, where the absorption bands are relatively narrow, the refractive index for molecular crystals rarely exceeds 10. With $\mu \approx 10$, the ratio $(\omega\mu a/c)^2 \sim 10^{-3}$ so that Eq. (3.7) can be replaced by the approximate expression

$$\omega_Q = \omega_0 - {}^1/_4\tau\,(\omega\mu a/c)^2.$$

In this case

$$A\,(\omega) = \epsilon_0 + \frac{4\pi\,(e^2/m)\,fN_0\,[\omega_0 - \omega - \tau\,(\mu\omega a/2c)^2]}{(\omega_0 + \omega)\,\{(\omega_0 - \omega - \tau[\mu\omega a/2c]^2)^2 + \gamma^2/4\}},$$

$$B\,(\omega) = \frac{2\pi\,(e^2/m)\,fN_0\gamma\,(\omega)}{(\omega_0 + \omega)\,\{(\omega_0 - \omega - \tau\,[\mu\omega a/2c]^2)^2 + \gamma^2/4\}}.$$

Now, assuming that in molecular crystals the majority of absorption bands correspond to excitation of excitons of negative effective mass

$$\tau\,(\mu\omega a/c)^2 < \gamma^2\,(\omega), \quad (3.8)$$

we can make a fairly accurate determination of the

absorption coefficient κ and the refractive index μ using the formulas

$$\mu = 2^{-1/2}[A_0 + \sqrt{A_0^2 + B_0^2}]^{1/2},$$

$$\kappa = 2^{-1/2}[-A_0 + \sqrt{A_0^2 + B_0^2}]^{1/2}, \tag{3.9}$$

where

$$A_0(\omega) = \varepsilon_0 + \frac{4\pi(e^2/m)fN_0(\omega_0 - \omega)}{(\omega_0 + \omega)[(\omega_0 - \omega)^2 + \gamma^2/4]}, \tag{3.5a}$$

$$B_0(\omega) = \frac{2\pi(e^2/m)fN_0\gamma(\omega)}{(\omega_0 + \omega)[(\omega_0 - \omega)^2 + \gamma^2/4]}. \tag{3.6a}$$

The inequality (3.8) is not satisfied at very low temperatures for a small frequency region at the long-wave edge of the absorption band; this region corresponds to excitation of excitons with positive effective mass (cf. Fig. 3). In this region Eq. (3.9) cannot be used; to compute μ and κ it is necessary to take account of the second term of Eq. (3.7). However, when the temperature increases, the value of $\gamma(\omega_0)$ increases rapidly even in bands which correspond to the excitation of excitons with positive effective mass. In this case Eq. (3.8) is satisfied and Eq. (3.9) can be used for all frequencies. True absorption (energy dissipation) occurs only in the frequency region in which $B(\omega)$ is different from zero. As follows from Eqs. (3.5) and (3.6) this region of true absorption coincides with the frequency region in which $\gamma(\omega)$ is different from zero. Frequency regions in which $B(\omega) = 0$ are called transparent regions. If $A_0(\omega) > 0$ in the transparent regions, from Eq. (3.9) we have $\kappa = 0$, $\mu = \sqrt{A_0}$, i.e., the light wave is not attenuated in passage through the material.

If $A_0(\omega) < 0$, from Eq. (3.9) we have $\mu = 0$ and $\kappa = \sqrt{-A_0}$.

It follows from Eq. (3.5a) that when $\gamma(\omega) = 0$ the condition $A(\omega) < 0$ is satisfied for frequencies which satisfy the relation

$$\omega_0 < \omega < \omega_0 + \frac{4\pi e^2 fN_0/m}{\varepsilon_0(\omega + \omega_0)}, \tag{3.10}$$

where ε_0 is the value of the dielectric constant in regions far from the absorption band. If the frequencies are measured in reciprocal centimeters $[\nu]$ the relation is (3.10) can be written in the form

$$[\nu_0] < [\nu] < [\nu_0] + \frac{e^2 fN_0}{2\pi c^2\varepsilon_0[\nu_0]m}.$$

Taking $N_0 = 4 \times 10^{21}$, $f = 0.2$, $[\nu] = 25,000$ cm^{-1} and $\varepsilon_0 = 2$, we have

$$e^2 fN_0/2\pi c^2\varepsilon_0[\nu_0]m \approx 73 \text{ cm}^{-1}.$$

In view of the nature of the dependence of γ on ω (Fig. 3), it is easy to show that in the region $\gamma(\omega) = 0$ the condition in (3.2) is satisfied only at very

low temperatures and at the high-frequency side of the absorption band, which corresponds to exciton zones with negative effective mass because the frequencies of the limiting rotational oscillations are usually less than 100 cm^{-1} and the true absorption falls off sharply on the high-frequency side. As the temperature is raised, the absorption band expands and it is impossible to satisfy the condition $\gamma = 0$ and (3.10) simultaneously. If the absorption corresponds to the excitation of excitons of positive effective mass the absorption bands have a considerably greater extent on the high-frequency side of ω_0 even at very low temperatures; thus, the condition $\gamma(\omega) = 0$ and (3.12) are not satisfied as a rule.

If (3.10) is satisfied, total reflection obtains at normal incidence of the light on the surface of a thick crystal. In this case, even though there is no true absorption, the light wave is attenuated rapidly inside the crystal. At small crystal thicknesses, when $z\omega\kappa/c < 1$, part of the light wave passes through the crystal. Since the absorption coefficient is usually deduced from the attenuation of light which passes through a layer of material, the effect indicated above [total or partial reflection of light in the frequency regions which satisfy a (3.10)] may introduce considerable distortion into the measurements.

As has been noted above, if the condition $\gamma(\omega) = 0$ and (3.10) are both satisfied, the index of refraction $\mu(\omega) = 0$. Thus, a measurement of the index of refraction on the shortwave side of the absorption band can give evidence as to the existence of the total reflection effect noted above. Such measurements can be used to determine the need for introducing corrections in the measurements of absorption made by the transmission method.*

We may note further that at frequencies for which the dielectric permittivity (3.5) vanishes in the transparency region, the induction D also vanishes identically. In this case, Maxwell's equations (3.3) allow the existence of longitudinal electric waves in the crystal ($H = 0$, curl $E = 0$). The condition $\epsilon = A(\omega) = 0$ can be satisfied at low temperatures on the short-wave side of the absorption band; this is the region of excitation of excitons of negative effective mass.

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*It should be kept in mind that in determining κ by the transmission method it is necessary to introduce corrections for scattering; these can be significant for narrow absorption bands (at low temperatures).

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