ABSORPTION AND DISPERSION OF LIGHT

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Abstract

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ABSORPTION AND DISPERSION OF LIGHT IN THE FORMATION OF MOLECULAR EXCITONS

1. The theory of light absorption in molecular crystals with allowance for the creation and annihilation of phonons was developed by A. S. Davydov ([1]) for the model of a one-dimensional molecular crystal and by A. S. Davydov and E. I. Rashba ([2]) for three-dimensional crystals. These studies were qualitative in character and did not take into account the shifts of exciton frequencies caused by interaction with phonons. In ([2]) it was shown that the shape of the light-absorption band in three-dimensional and one-dimensional crystals may be different. The theory of light absorption by ionic crystals (Wannier excitons) was developed in the work of Toyozawa ([3]). The interaction operators of molecular excitons and Wannier excitons with phonons are substantially different. The difference is especially great for interaction with optical phonons ([4]). This difference is due both to the different nature of the optical lattice vibrations of molecular and ionic crystals and to the peculiarities of the two types of excitons.

In the present article, the shape of absorption bands and the dispersion of light in the formation of excitons in three-dimensional crystals are investigated by the method of temperature Green' s functions. Interaction with acoustic and optical phonons is taken into account.

2. Let us consider a molecular crystal of the rhombic system with basis vectors $\mathbf{a}_x, \mathbf{a}_y, \mathbf{a}_z$ ($|\mathbf{a}_x| = |\mathbf{a}_z| = a$).

Let the dipole moment $\mathbf{d}$ of the unit cell of the crystal, corresponding to exciton excitations, be directed along the vector $\mathbf{a}_y$. The exciton energy is determined by the formula*

$$E(\mathbf{k}) = L\{e + \Xi(y, \rho)\}. \tag{1}$$

Here the wave vector $\mathbf{k}$ of the excitons is defined in the cylindrical coordinate system

Fig. 1 and Fig. 2: calculated curves

Figure 1: Fig. 1 and Fig. 2: calculated curves

$$\pi y = k a_y, \qquad \pi\rho = a\sqrt{k_x^2 + k_y^2},$$

$$\varphi \text{ in the region } -1 \le y \le 1, \qquad 0 \le \rho \le 1, \qquad 0 \le \varphi \le 2\pi; \tag{2}$$

$$\Xi(\rho, y) = \frac{1}{2} + \frac{1}{6}(3 - \rho^2 - y^2)\frac{y^2 - \rho^2}{y^2 + \rho^2}, \qquad L = \frac{4\pi d^2}{v}; \tag{3}$$

v is the volume of the unit cell. Transverse excitons with positive effective mass $3\pi^2/a^2 L$ in this zone are characterized by the value $y = 0$. The bottom of the zone is $E_{\min} = eL$. The top of the zone is $E_{\max} = (e+1)L$. Consequently, the total width of the zone is L. The structure of the exciton band (1) resembles the structure of the exciton band in an infinite anthracene crystal calculated in ([5]). Below all energies (frequencies) are expressed in units of the exciton-band width.

The refractive index n and the damping coefficient χ of light having frequency ω, wave vector $\mathbf{Q}$, and electric-field intensity directed along the y axis are determined by the component ε_{yy} of the dielectric-permittivity tensor by means of the formula

$$\varepsilon_{yy}(\mathbf{Q}, \omega) = (n + i\chi)^2. \tag{4}$$

In this case, in the region of exciton-absorption frequencies,

$$\varepsilon_{yy}(\mathbf{Q}, \omega) = \varepsilon_{yy}^0(\omega) - \{G(\mathbf{Q}, \omega) - G^+(\mathbf{Q}, -\omega)\}, \tag{5}$$

* We use a system of units in which $\hbar = 1$.

Fig. 1. Results of calculations of $\varepsilon'(\xi)$ (solid curves) and $\varepsilon''(\xi)$ (dashed curves) for temperatures 20°K ($L/70$) and 100° ($L/14$). A $-g_{\text{ak}} \ll g_{\text{op}} = 0.1$; B $-g_{\text{ak}} \ll g_{\text{op}} = 0.01$; V $-g_{\text{ak}} = g_{\text{op}} = 0.01$

Fig. 2. Curves calculated from formula (4), characterizing the dispersion of the refractive index (solid curves) and the attenuation coefficient (dashed curves) of light in the crystal. The adopted values of g are the same as in Fig. 1 A, B, V, respectively

where $\varepsilon_{yy}^0(\omega)$ is a smooth function determined by all electronic states of the crystal except the exciton band under consideration;

$$G(\mathbf{Q},\omega)=\{\omega-E(\mathbf{Q})-M(\mathbf{Q},\omega)\}^{-1} \tag{6}$$

is the Fourier image of the retarded two-time Green' s function for excitons interacting with phonons; $M(\mathbf{Q},\omega)$ is the mass operator of the ex-

exciton, determined by the integral equation

$$M(Q,\omega)=$$

$$=\frac{v}{(2\pi)^3}\sum_s\int d^3q\,|F_s(Q,q)|^2\left\{\frac{v_s(q)+1}{\omega-E(Q+q)-\Omega_s(q)-M[Q+q,\omega-\Omega_s(q)]+i\eta}+\frac{v_s(}{\omega-E(Q+q)+\Omega_s(q)-i}\right. \tag{7}$$

where $v_s(q)$ is the mean number of phonons of frequency $\Omega_s(q)$ with wave vector q.

In view of the fact that $Qa\ll 1$, the calculation of (7) is carried out for $Q=0$. The interaction with optical phonons corresponding to rotational vibrations of the molecules, and with longitudinal acoustic phonons whose wave vector lies in the xz plane, is taken into account. The phonon dispersion law is taken in the form $\Omega_{\text{op}}(q)=\Omega_{\text{op}}$, $\Omega_{\text{ak}}(q)=\rho\Omega_{\text{ak}}$. The exciton-phonon coupling functions were chosen in the form

$$|F_{\text{ak}}(0,q)|^2=g_{\text{ak}}(1-\rho^2)^2\rho,\qquad |F_{\text{op}}(0,q)|^2=g_{\text{op}}(1-\rho^2)^4.$$

The real and imaginary parts of the mass operator $M(0,\omega)=\Delta\omega-i\gamma(\omega)$ determine, according to (5) and (6), the real and imaginary parts of the dielectric permittivity

$$\varepsilon'_{yy}(\xi)=\varepsilon^0_{yy}(\xi)+\frac{\Delta(\xi)-\xi}{[\xi-\Delta(\xi)]^2+\gamma^2(\xi)};\qquad \varepsilon''_{yy}(\xi)=\frac{\gamma(\xi)}{[\xi-\Delta(\xi)]^2+\gamma^2(\xi)},$$

where $\xi=\omega-e$.

3. The results of calculations of $\varepsilon'(\xi)$ and $\varepsilon''(\xi)$ are presented in Fig. 1. In the calculations the values $\varepsilon^0_{yy}=4$; $\Omega_{\text{op}}=0.05$; $\Omega_{\text{ak}}=0.03$; $L=10^3$ cm^{-1} were used.

The imaginary part of the dielectric permittivity ε'' determines the absorption of light. According to Fig. 1, the dependence of ε'' on ξ at low temperatures and small g_{ak} and g_{op} has the form of a sharp maximum with a slight structure located on the high-frequency side. As the temperature is increased, the height of the principal maximum decreases, while the absorption on the high-frequency

side of the principal maximum broadens and increases. If the interaction with acoustic phonons plays a small role (Figs. 1A and B), then the half-width of the principal maximum depends on the available (at the given temperature) number of optical phonons. As the temperature approaches zero, the principal maximum turns into a delta function. The interaction with acoustic phonons broadens the short-wavelength part of the principal maximum, increasing its asymmetry (Fig. 1B). The asymmetry of the curves $\varepsilon''(\xi)$, i.e., their deviation from Lorentzian curves, is due to the dependence of Δ and γ on frequency. In Toyozawa' s work[3] such a dependence was not taken into account, and therefore curves of Lorentzian type were obtained. To obtain asymmetric curves of exciton absorption in ionic crystals, Toyozawa, in a subsequent work[6], had to take higher approximations into account in the theory. In doing so, only the interaction with acoustic phonons was considered.

Figure 2 shows curves calculated from formula (4), characterizing the dispersion of the refractive index and of the attenuation coefficient of light in the crystal.

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Note: Figure translations are in progress. See original paper for figures.