Group velocity of light near exciton resonances in CdS crystals

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Analysis of Fabry-Perot modes in CdS crystal plates has been used to determine the group velocity v_g of light and its dependence on frequency in the region of exciton resonances. These modes can be clearly seen in reflection, transmission, and luminescence spectra at different temperatures in a broad spectral range. Excellent agreement has been achieved with the theoretical values of v_g calculated for normal waves (polaritons) in the crystal. Some of the v_g-dependent properties of Fabry-Perot cavities are discussed. The dispersive properties of the crystal are found to depend on exciton concentration, and this is explained in terms of the exchange interaction between the excitons.

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1. The group velocity of light is the velocity of energy transport, so that it determines the cross section for the scattering, amplification, and absorption of light, the cavity mode losses, and so on. In the general case of a medium with small absorption, the group velocity of light is given by (see, for example, Einstein[1] and Agranovich and Ginzburg[2])

$$|\mathbf{v}_g| = c/(n-\lambda dn/d\lambda), \tag{1}$$

where n is the refractive index which is a function of wavelength λ. This formula is based on the following definition of group velocity:

$$\mathbf{v}_g = d\omega/d\mathbf{k}, \tag{2}$$

where $k=(2\pi/\lambda)n(\lambda)$ is the wave vector of the normal light wave in the crystal.[2] The expression commonly found in the literature is

$$v_g = v_f - \lambda dv_f/d\lambda, \quad v_f = c/n. \tag{3}$$

It is readily seen that this expression is obtained when the dependence of k on $n(\lambda)$ is neglected in (2), so that it is valid only in the limiting case when

$$n \gg \lambda |dn/d\lambda|.$$

However, it is precisely the opposite case, i.e., $n \ll \lambda |dn/d\lambda|$, that corresponds to the propagation of light in a crystal in the neighborhood of exciton resonances where photons in the crystal (normal waves, or polaritons[3,4]) differ appreciably from photons in vacuum, and the group velocity of light (polariton) can be written in the form[4]

$$v_g(\omega) \approx \frac{c}{\varepsilon_0^{1/2}}\left[1+\frac{1}{2}\left(\frac{\omega_c}{\omega_0-\omega}\right)^2\right]^{-1}, \tag{4}$$

where ε_0 is the dielectric constant, $\hbar\omega_c$ is the exciton-photon coupling energy which depends on the oscillator strength, and ω_0 is the frequency of a transverse exciton (the effective mass of an exciton is assumed to be infinite). One of our aims was to obtain an experimental verification of (4). In addition, we investigated some of the v_g-dependent properties of Fabry-Perot cavities, both experimentally and theoretically.

2. The simplest and most natural way of determining the dependence of v_g on ω is to analyze the frequency distribution of the Fabry-Perot modes in a crystal with resonating properties. Thus, the spectral interval $\Delta\lambda$ between neighboring longitudinal modes (standing waves) is

$$\Delta\lambda \approx \frac{\lambda^2}{2l(n-\lambda dn/d\lambda)}, \tag{5}$$

where l is the thickness of the crystal plate. Despite the fact that (5) has been known for a long time,[5] its relation to the group velocity has not been considered. Instead of (5), we may write

$$\Delta\omega = \frac{\pi c}{l(n-\lambda dn/d\lambda)} = \frac{\pi v_g(\omega)}{l}$$

3. The experiment was performed as follows. The DRSh-500 mercury lamp and a hot filament lamp were used to record the reflection, absorption, and luminescence spectra of plane-parallel plates of CdS at 1.4° and 77 °K. The plate thickness for which the results are given below was 0.001 cm. Figure 1 shows the reflection spectra in the region of transparency for two excitation levels. The emission of the mercury lamp was not cut off at the top by filters, so that we could investigate the influence of exciton concentration on these spectra.

Clear Fabry-Perot interference was observed. For $\mathbf{E} \perp c$, the mode lines converge to the position of the exciton line A ($n=1$) whilst, for $\mathbf{E} \parallel c$, there is a set of modes converging to the position of the exciton B ($n=1$). Two important features can be noted in both cases: (1) the reduced line spacing is accompanied by a reduction in their widths and (2) the interference structure is

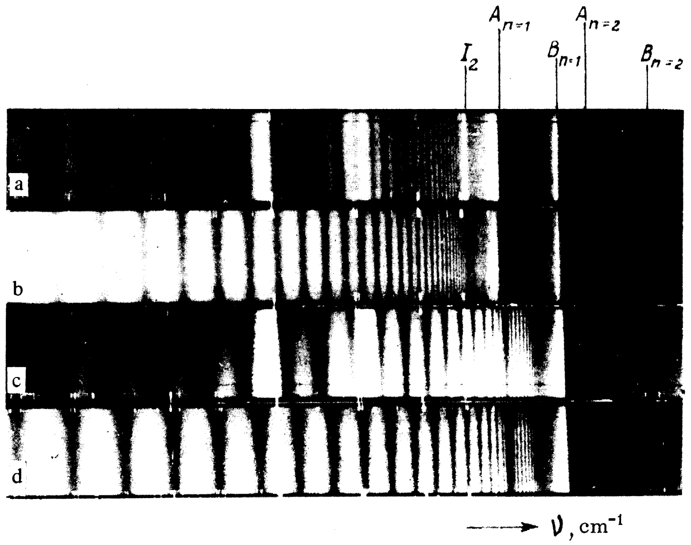

FIG. 1. Reflection spectra of a CdS crystal at $T = 1.4$ °K illuminated by light from a mercury lamp (a, c) and a hot-filament lamp (b, d) with $\mathbf{E} \perp c$ (a, b) and $\mathbf{E} \parallel c$ (c, d). The emission and reflection spectra are complementary. The designations are the same as in our previous paper.[6]

shifted (and this depends on frequency) toward the red as the excitation level is increased in the region of fundamental absorption.

The Fabry-Perot mode structure is also observed in the luminescence spectrum of the CdS crystal excited by the mercury lamp (Figs. 2b and 3). In this case, we used a filter that confined the spectrum of exciting radiation of frequencies smaller than the gap width. The mode frequencies in the relation spectrum obtained under exposure to radiation from the mercury lamp are equal to the corresponding mode frequencies in the luminescence spectrum (Fig. 2).

4. We must now proceed to a more detailed analysis of the experimental data. As noted in Sec. 2, measurements of the intermode spacing enable us to determine the dependence of the group velocity of light on frequency ω. The corresponding results for $c/v_g(\omega)$ are given in Fig. 4, in which the theoretical curves are obtained from (1), taking into account the contribution of the A ($n = 1$) and B ($n = 1$) exciton resonances for $\mathbf{E} \perp c$. Good agreement between theory and experiment is obtained at $T = 1.4$ °K for $\hbar\omega_c = 0.072$ eV (this value corresponds to the observed transverse-longitudinal splitting of 0.002 eV for the exciton A), $\omega_{0A} = 20\,584$ cm^{-1}, $\omega_{0B} = 20\,706$ cm^{-1}, $\varepsilon_0^{1/2} = 3$, and the oscillator strength for the exciton B ($n = 1$)

$$f_B(n=1,\ \mathbf{E}\parallel c) = 18.7\cdot 10^{-4}, \quad f_B(n=1,\ \mathbf{E}\perp c) = 16.7\cdot 10^{-4}.$$

The above value of $f_B(\mathbf{E} \parallel c)$ was obtained by fitting the theoretical expressions to the experimental curves for $\mathbf{E} \parallel c$. The ratio $f_B(\mathbf{E} \perp c)/f_B(\mathbf{E} \parallel c)$, reported by Reynolds *et al.*[7] was used to determine $f_B(\mathbf{E} \perp c)$. It is important to note that the effects of spatial dispersion are negligible in this case.

The values of the refractive index n can be determined from the interference order in the region of weak dispersion and by counting the number of modes in the frequency interval in which we are interested. We have used this method to show that $n = 3$–4.5 throughout the interval under investigation. Consequently, the group velocity turns out to be much less than the phase velocity c/n. For example, at the frequency of the bound exciton I_2, the group velocity is lower by two orders of magnitude than the phase velocity. It is possible to obtain a very approximate estimate for v_g for the much closer neighborhood of the exciton resonances if we use the data of Fabry-Perot interference reported by Reynolds *et al.*,[7] Kysilev *et al.*,[8] and Voight *et al.*[9] for

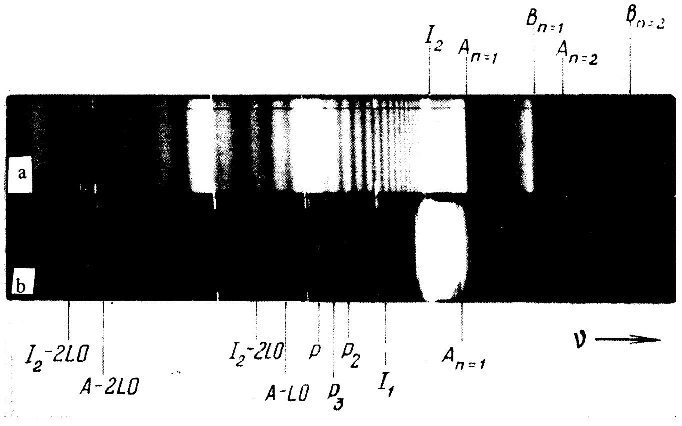

FIG. 2. Luminescence (b) and reflection (a) spectra for $T = 1.4$ K and $\mathbf{E} \perp c$.

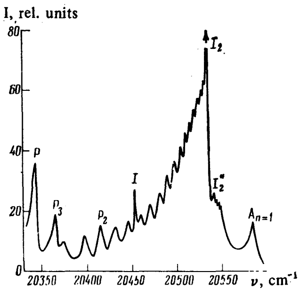

FIG. 3. Luminescence spectrum of a CdS crystal at $T = 1.4$ °K for $\mathbf{E} \perp c$.

CdS crystals much thinner than our plates. In this way, we find that $v_g = 10^{-3}c - 10^{-4}c$.

Let us now consider the observability of the mode structure. It is clear that the condition for the observability of the structure is

$$\Delta\omega > \Gamma, \tag{6}$$

where Γ is the linewidth of an individual mode. In the case of a thin plane-parallel plate, we can neglect diffraction losses and losses due to departure from parallelism of the two reflecting plates. In the transparent region, however, the mode losses are determined exclusively by the escape of radiation from the crystal, and we can write

$$dE = -\frac{E}{2}\frac{v_g dt}{l}(1-R), \tag{7}$$

where E is the energy of the field corresponding to one mode, $v_g dt/l$ is the number of reflections undergone by the light energy in one of the progressive waves reflected from the surfaces in the time interval dt, R is the reflection coefficient, and l is the plate thickness.

Equation (7) differs from the usual expression for the losses (see, for example, Basov *et al.*[10]) in two respects: first, it contains the group velocity v_g instead of c or v and, consequently, the "extra" factor $\frac{1}{2}$, which represents the fact that the energy of the standing wave is shared equally between two progressive waves. Integration yields

$$E(t) = E(0) \exp[-v_g(1-R)t/2l].$$

Consequently, the relaxation time (photon lifetime in the cavity) is

$$t_0 = 2l/v_g(1-R),$$

and this corresponds to

$$\Gamma = 2\pi/t_0 = \pi v_g(1-R)/l.$$

Condition (6) can now be rewritten in the form $\pi v_g/l > \pi v_g(1-R)/l$, or

$$R > 0. \tag{8}$$

Thus, in the region of relative transparency, the Fabry-Perot modes cannot overlap. We note that, if we use (7) without the above factor of $\frac{1}{2}$, we obtain the condition $R > \frac{1}{2}$ instead of (8), and this is in clear conflict with experimental data which show that the modes are clearly observed even in the region where

$$R = [(n-1)/(n+1)]^2 = 25-30\%.$$

Next, if we were to use the phase velocity instead of the group velocity to determine Γ, we would have a still greater conflict with experiment. The mode structure should vanish in the region of sufficiently strong absorption because the additional loss mechanism due to photon absorption leads to an increase in the damping Γ. On the other hand, when the absorption is strong enough, the very concept of group velocity loses its meaning. When the temperature is increased to 77 °K, the group velocity v_g cannot be measured in the region where $c \gtrsim 100 v_g$ because of the temperature broadening of the exciton absorption line. At frequencies close to the bound exciton line I_2, population inversion is reached under illumination by the mercury lamp[11] (negative absorption is produced) and we can observe the mode structure in the luminescence spectrum (Figs. 2b and 3).

Let us now consider the mode shift along the frequency axis as the level of interband excitation is increased. It is clear that, in our case, this shift is due to a change in the refractive index. If we use the above experimental data, we may conclude that the change in the refractive index n occurs as a result of a change in the concentration of free excitons, and is not a temperature effect. In fact, as the temperature increases, the frequencies of the exciton resonances should shift toward longer wavelengths, whereas the observed positions A and B of the excitons are shifted slightly toward shorter wavelengths. Moreover, for some of the specimens, we observed a change in the sign of the shift (shift toward the blue with increasing excitation) after specimen deformation leading to the suppression of exciton luminescence.

A change in the refractive index n leads to a change in the frequency of the standing wave, given by the expression

$$m\lambda_0 = 2ln(\lambda_0),$$

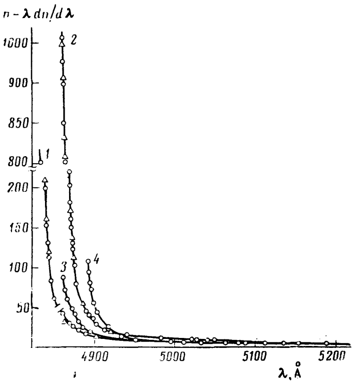

FIG. 4. Dependence of $n - \lambda dn/d\lambda$ on λ: (1) for $\mathbf{E} \parallel c$, $T = 1.4$ °K; (2) for $\mathbf{E} \perp c$, $T = 1.4$ °K; (3) for $\mathbf{E} \parallel c$, $T = 77$ °K; (4) for $\mathbf{E} \perp c$, $T = 77$ °K. ○—experimental, △—calculated. The experimental points for $c/v_g > 600$ are taken from the paper by Reynolds *et al.*[7]

where m is an integer. This shift produces an additional change in n:

$$m\Delta\lambda_0=\left(\Delta n+\frac{\partial n}{\partial\lambda}\Delta\lambda_0\right)2l,$$

where Δn is the change due to the exciton concentration (an algebraic quantity). Consequently, the concentration shift for a single mode is

$$\Delta\lambda_0=\Delta n\lambda_0\bigg/\left(n-\lambda_0\frac{dn}{d\lambda}\bigg|_{\lambda=\lambda_0}\right).$$

In agreement with experiment, $\Delta\lambda_0\sim v_g(\lambda_0)$.

The shift is a maximum in the region of weak dispersion:

$$\lambda_0\Delta n/n\approx\Delta\lambda_0.$$

The observed shift for $\lambda_0=5300$ Å ($\Delta\lambda_0=12$ Å) corresponds to

$$\Delta n/n\approx2.5\cdot10^{-3}.$$

We consider that this phenomenon can be explained by taking into account the exchange interaction of excitons. The exciton polarizability is usually described as the result of the elastic scattering of photons with momentum $\mathbf{K}_{ph}$ due to two phototransitions involving the participation of the exciton state with $\mathbf{K}_{1ex}=\mathbf{K}_{ph}$. In our model of the effect of exciton concentration on dispersion, we take into account the exchange interaction between this (virtual) exciton and one of the excitons that really populate the exciton band (with exciton momentum $\mathbf{K}_{2ex}$), in which case the population of the exciton states is conserved.

We thus obtain

$$\frac{\Delta n(\omega)}{n_{ex}(\omega)}=\frac{M_{\text{exch}}(\rho)}{\omega_{0A}-\omega},\tag{9}$$

where $n_{ex}(\omega)=n(\omega)-\varepsilon_0^{1/2}$, $M_{\text{exch}}(\rho)$ is the matrix element of the exchange interaction which is similar in form to that given by Büttner,[12] and ρ is the average separation between the excitons. The shift calculated with the aid of (9) is in agreement with the observed value if the exciton concentration averaged over the volume of the crystal is of the order of 10^{16} cm^{-3}. We note that, if these excitons were in the state of a Bose condensate, we would have Δn and $\Delta\lambda<0$ because of the negative dispersion produced by excitons with $\mathbf{K}_{ex}=0$. We thus have a new possibility for the investigation of the character of the change in the population of different exciton states. It would be particularly interesting to investigate the mode shift as a function of the level of interband excitation for polarization $\mathbf{E}\parallel c$, since the superlinear dependence on the level of excitation is predicted[6] for the population of the exciton subband B ($n=1$) and for other excited exciton states.

The mode shift due to a change in the plate thickness is also determined by the group velocity v_g. The condition for the observability of mode structure in a crystal with an absolute thickness variation Δl is

$$\Delta l<\lambda/2n(\lambda).$$

Finally, let us consider how the usual expression for the number of modes in a volume V in a spectral interval $\bar{\Delta\omega}$ should depend on the group velocity. We have

$$S=3V\omega^2n^2\left(n+\omega\frac{dn}{d\omega}\right)\bar{\Delta\omega}/\pi^2c^3.$$

where we have used the expression

$$d\omega/d|\mathbf{K}|={}^1/_3|\mathbf{v}_g|.\tag{10}$$

We are greatly indebted to Academician V. L. Ginzburg, V. M. Agranovich, S. M. Ryabchenko, and A. I. Khizhnyak for fruitful discussions of some of the questions considered above.

APPENDIX

Optical properties of bound excitons

We shall now consider the absorption (amplification) of light and the radiative lifetime of bound excitons. It follows from the foregoing discussion that, at the bound-exciton frequency, the main contribution to dispersion is provided by free excitons (states), and absorption is relatively weaker. There is then no doubt as to the validity of the concept of group velocity, and we have to consider how existing expressions describing the interaction between two-level molecules (in our case, bound excitons) and light in a highly dispersive medium have to be modified.

It is well known that the absorption coefficient K is given by

$$K(\omega)=W/v_g(\omega),\tag{11}$$

where W is the probability of absorption of a photon in a mode with frequency ω per unit time. The amplification coefficient β can be expressed in a similar way. Quantization of the light field in a dispersive medium, i.e., a medium characterized by $\varepsilon(\omega)$, can be carried out by analogy with the situation in a nondispersive medium if we use the well-known classical expression for the mean field energy

$$\bar{u}=\frac{1}{8\pi}\left[\frac{d}{d\omega}(\varepsilon\omega)\mathbf{E}_0^2+\mu\mathbf{H}_0^2\right],$$

where $\mathbf{E}_0$ and $\mathbf{H}_0$ are, respectively, the electric and magnetic field amplitudes. If we suppose that $\mu=1$, we have $H_0=\varepsilon^{1/2}E_0$. Since the normalizing factor in the expansion for the vector potential operator $\hat{\mathbf{A}}$ over the modes is

$$\left(\frac{2\pi\hbar c^2}{V\omega n(n+\omega dn/d\omega)}\right)^{1/2},$$

we have

$$W\sim\frac{c^2}{n(n+\omega dn/d\omega)}\equiv vv_g.$$

Consequently, according to (11), the amplification and absorption coefficients are independent of v_g. Before we can directly calculate the absolute values of these coefficients, we must know the damping of the bound exciton state (homogeneous linewidth). However, in the case of bound excitons, this cannot be known because the line broadening is radiative in character. In fact,

$$\frac{\Delta\omega}{2\pi}\equiv\tau_R=b_eS\equiv b_eS^{\cdot}2\pi\tau_R^{-1},$$

$$b_e=\frac{1}{2\pi S^{\cdot}}\equiv\frac{\pi c^3}{6V\omega^2n^2(n+\omega dn/d\omega)},$$

where b_e is the probability of emission of a photon by one bound exciton per unit time and τ_R is the radiative lifetime.

The total amplification coefficient β in the case of homogeneous broadening of the bound exciton line is

$$\beta=Nb_e/v_g=N\pi v^2/V6\omega^2,$$

where N is the number of bound excitons.

The quantity β does not, in this case, depend on the parameters of the bound excitons. The amplification (absorption) cross section for one bound exciton is

$$\sigma=\pi v^2/6\omega^2,$$

i.e., this cross section depends only on the square of the wavelength in the medium. When $\omega=3\times10^{15}$ sec^{-1} and $n=4$, we have

$$\sigma\approx\pi\cdot10^{-12}\,\text{cm}^2,$$

which is roughly equal to the geometric cross section of the bound exciton if its "radius" is estimated from the binding energy of the exciton-impurity complex. In the case of the homogeneously broadened bound-exciton line, the amplification or absorption coefficients can be very high. For example, for $N/V=10^{15}$ cm^{-3}, we have $\beta=10^3$ cm^{-1} (it is assumed that all the corresponding impurity centers are populated by excitons). The maximum value of β can now be determined from the coefficient K for the unexcited crystal. When the concentration of neutral donors is about 10^{15} cm^{-3}, absorption at the line I_2 does not exceed 10^2 cm^{-1}. In the above example, this means that the inhomogeneous width of the line I_2 exceeds the homogeneous width by an order of magnitude. The radiative lifetime is independent of both the magnitude and character of the line broadening and can, therefore, be calculated directly with the aid of (10):

$$\tau_R=\pi mc^3/9e^2\omega^2fn, \qquad (12)$$

where f is the oscillator strength per bound exciton.[11] Estimates for I_2 yield $\tau_R\approx2\times10^{-9}$ sec. However, the expression given by (12) does not take into account the reabsorption of the emitted radiation nor the fact that the radiation can leave the crystal only within the solid angle $\sim n^{-2}$. Inclusion of the last factor yields $\tau_R\sim n$.

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