Spatial dispersion and additional light waves in the region of exciton absorption in CdS

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Dispersion of the refractive index, absorption of light, and its reflection by a semi-infinite crystal in the vicinity of the extreme long-wave exciton absorption band $A_{n=1}$ is considered. The experimental facts cannot be explained even qualitatively by assuming the existence of a single wave with a given polarization. The results of the measurements can be explained in detail if it be assumed, as the theory predicts, that there exists a second wave with the same polarization.

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The theory of additional light waves in a crystal appeared in 1957.[1-3] Since that time, experimental proof of the existence of these waves was presented in many papers. In most cases, however, the proof was not fully unequivocal. The reason was that in investigations of light in vacuum before and after passage through a crystal plate it is difficult to determine how many waves have propagated inside the plate.

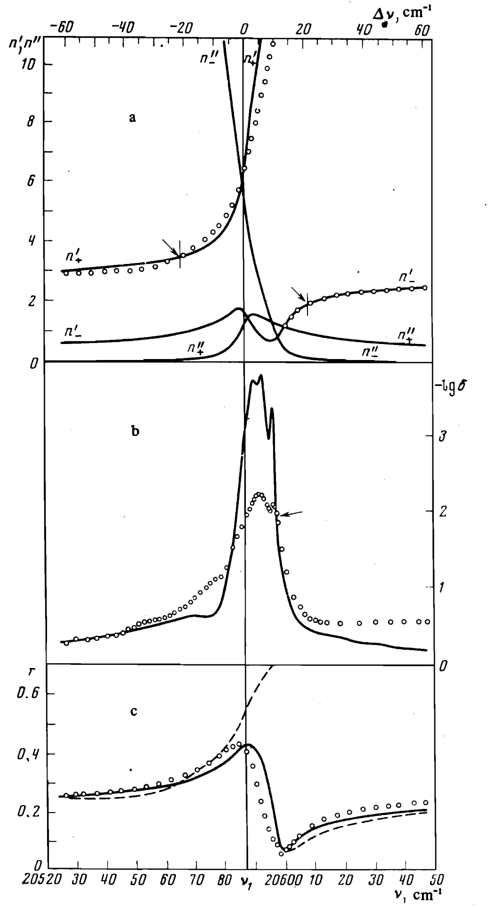
By studying only one selected phenomenon, say only the frequency dependence of the reflection coefficient, it is always possible to interpret the results with the aid of one wave, provided its refractive index is ascribed a corresponding frequency dependence. If one measures only the change of the phase of the wave on passing through the plate and the frequency dependence of this change, then the results can also be interpreted with the aid of a single wave, by ascribing its refractive index to the necessary frequency dependence. If the frequency dependence of the transparency of a plate is determined experimentally at only one value of the plate thickness, then the result can again be interpreted with the aid of one wave. However, when the results of an investigation of these phenomena are compared, it may turn out that in each case it is necessary to assign to the complex refractive index a different frequency dependence. This indeed proves that it is impossible to interpret the experimental results with the aid of only one wave. It is such a comparison of the results of different investigations that is presented in the present paper.

1. RESULTS OF EXPERIMENTAL MEASUREMENTS

We consider below, in single-crystal CdS at T = 4.2°K, in the vicinity of the frequency 20587 cm^{-1}, an exciton band that absorbs light with polarization E ⊥ C (E is the electric field of the wave and C is the hexagonal axis of the crystal), and practically does not absorb light of polarization E ∥ C. The surfaces of the crystal plate are free (not in contact with the substrate) and are parallel to the C axis.

Light of polarization E ⊥ C was incident normally on the plate. In this case the wave is strictly transverse and is described by only one principal value of the dielectric tensor $\epsilon(\omega, k) = \epsilon' + i\epsilon''$ (ω is the frequency and k is the absolute value of the wave vector). The tensor indices of ϵ will therefore be omitted from now on, and the formula for the refractive index $n = n' + in''$ simplifies to

$$n^2=\varepsilon\left(\omega,\frac{\omega}{c}n\right), \qquad (1)$$



Frequency dependences: a) Of the real (n′) and imaginary (n″) parts of the refractive indices of the plus and minus waves in accordance with the additional-wave theory (solid lines) and as obtained by measurements (points); b) of the logarithm of the plate transparency δ (plate thickness 0.18 μ): solid curve—results of additional-wave theory, distorted by the assumption that μ″ is constant; points—experiment; c) of the coefficient r of light reflection from a semi-infinite crystal: dashed curve—calculation assuming one wave, by formula (6) at the measured values of n′ and n″, solid curve—calculation assuming two waves by formulas (7) and (10), points—measured values.

The points in the figure, case a, show the results of experimental measurements of the real part of the refractive index n′[4]; $\Delta\nu \equiv 1/\lambda - 1/\lambda_1$, where λ is the wavelength of the light in vacuum; $1/\lambda_1 = 20587$ cm^{-1} is a certain resonant frequency (see below). The values of n′ were determined by an interferometry measurement of the change of the phase of the wave $\omega n' l/c$ which occurs on passing through the plate. The plate thickness l was 0.33 or 0.18 μ.

The points in Fig. b represents measurements of the plate transparency δ, equal to the ratio of the transmitted and incident light intensities, at l = 0.18 μ,[5], while Fig. c shows the values of the coefficient r of light reflection from a semi-infinite crystal[6].

2. ATTEMPT AT INTERPRETATION OF THE EXPERIMENTAL RESULTS ASSUMING ONE WAVE WITH POLARIZATION $E \perp C$.

One wave is obtained if we neglect the spatial dispersion, i.e., if $\epsilon(\omega, k)$ is replaced by $\epsilon(\omega, 0) \equiv \epsilon(\omega)$. The real and imaginary parts of $\epsilon(\omega)$ are connected by the Kramers-Kronig relation

$$\varepsilon'(\omega) = 1 + \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\varepsilon''(x)}{x-\omega}\,dx. \tag{2}$$

Inasmuch as the considered range of ω is narrow in comparison with the transparency regions on the long-wave and short-wave sides of the considered band, the integral in (2) with respect to the other absorption bands yields a constant which is almost independent of ω, and we can rewrite (2) in the form

$$\varepsilon'(\omega) = n'^2 - n''^2 = \varepsilon_0 + \int \frac{\varepsilon''(x)}{x-\omega}\,dx, \tag{3}$$

where ϵ_0 is a constant, and the integral with respect to x is taken only within the limits of the considered band.

If ω is far enough from the absorption center, then it follows from (3) that

$$n'^2 = \varepsilon_0 - A/(\omega - \omega_1), \quad \omega_1 = 2\pi c/\lambda_1, \tag{4}$$

and A is equal to the integral $\int \epsilon''(\omega)d\omega$ over the band. A formula of the type (4) does indeed describe fairly well the measured values of n' if (see the figure) $|\Delta\nu| > 15\ \mathrm{cm}^{-1}$. Using the measured values of n' at $\Delta\nu = +20$ and $-20\ \mathrm{cm}^{-1}$, we obtain the values of the parameters

$$\varepsilon_0 = 7.74, \quad A = 90.1\ \mathrm{cm}^{-1}. \tag{5}$$

In the case of the one-wave interpretation we have $n''^2 < 1$ even at the absorption maximum, and this term can be discarded together with n'^2 in (3). According to (3), the index n' should decrease with increasing ω in the region of significant absorption (anomalous dispersion). Indeed, if ω corresponds to the long-wave edge of this region, the integral in (3) is positive, since $\omega'' \geq 0$, and in the actual integration interval we also have $x - \omega > 0$. On the other hand, when ω corresponds to the short-wave edge of the region of significant absorption, the integral in (3) is negative, since in the actual integration interval we have $x - \omega < 0$. Thus, formula (3) far from the absorption maximum describes the dispersion of n' well, but in the immediate vicinity of ω_1 it contradicts qualitatively the experimental measurements, according to which n' continues to grow with increasing ω also in the region of the absorption maximum, and even on its shortwave side (compare a and b in the figure).

There should hardly be any doubt of the validity of (2). The contradiction should be attributed to the only unjustified step made above, namely the replacement, without checking, of the exact equation (1) by the equation $n^2 = \epsilon(\omega, 0)$, and the consequent neglect of the additional light wave. This will be proved in the next section of the article, where the use of Eq. (1) leads to agreement between theory and experiment.

We examine now the coefficient of light reflection from the surface of a semi-infinite crystal. Neglecting the additional wave, this coefficient is given by

$$r_0 = \frac{(n'-1)^2 + n''^2}{(n'+1)^2 + n''^2}. \tag{6}$$

If we substitute here the measured values of $n'(\omega)$ and $n''(\omega)$, then formula (6) is in fair agreement with experiment far from the resonant frequency ω_1. But as ω approaches ω_1, the value of (6) begins to differ even qualitatively from the measured value of r. Thus, in Fig. c the dashed line represents formula (6) while the points represent the experimentally-measured values of the reflection coefficient. This contradiction will also be eliminated in the next section of the article by taking into account the additional wave.

3. COMPARISON OF EXPERIMENTAL RESULTS WITH THEORY IN WHICH THE ADDITIONAL WAVE AND SUPPLEMENTARY BOUNDARY CONDITIONS ARE TAKEN INTO ACCOUNT

One of the present authors has predicted theoretically the existence in a crystal, near the exciton-absorption band, of light waves other than the two usual birefringence waves[1]. Owing to the increase of the number of waves it was necessary to increase also the number of boundary conditions, so as to be able to express the amplitudes of all the waves produced in the crystal in terms of the amplitude of the wave incident from the vacuum. Supplementary boundary conditions were therefore also formulated in[1]. The results of that theory are shown in the figure by solid lines. The arrows indicate three points at which the theory was made to fit the experimental data in order to determine the three parameters of the theory.

If the crystal surface is parallel to the C axis and the incidence is normal, then, in accord with the aforementioned theory, two waves are produced in the crystal, with identical polarization $E \perp C$ and with identical frequency, but with different refractive indices. The latter are determined from Eq. (1), which turned out, after specifying concretely the right-hand side (see Eq. (13) below), biquadratic in n. Its solution is[1,2]

$$n_\pm^2 = {}^1/_2(\mu + \varepsilon_0) \pm [{}^1/_4(\mu - \varepsilon_0)^2 + b]^{1/2}, \tag{7}$$

where ϵ_0 has the same meaning as in the preceding section of the article, $\mu = \mu' + i\mu''$,

$$\mu' = \frac{2Mc^2}{\hbar\omega_0^2}(\omega - \omega_0), \quad \omega_0 = \frac{\mathscr{E}(0)}{\hbar}, \quad b = \frac{4\pi c^2 e^2}{\hbar\omega_0^3}\frac{M}{m}Nf, \tag{8}$$

M is the effective mass of the exciton, e and m are the charge and mass of the free electron, $\mathscr{E}(0)$ is the energy necessary to excite the exciton with zero quasimomentum, c is the speed of light in vacuum, f is the oscillator strength of the crystal unit cell, and N is the number of cells per unit volume.

At $\mu'' = 0$ there is no true light absorption (release of heat) in the crystal, in spite of the fact that the refractive index n_- is pure imaginary in a certain range of ω, and the minus wave attenuates in space. The true absorption is determined by the nonstationary character of the exciton state—its scattering by impurities in phonons, its decay with conversion of energy into heat, etc. This nonstationary behavior leads to the appearance of an imaginary increment of $\mathscr{E}(0)$[3], i.e., to the appearance of a term $\mu''(\omega) > 0$.1)

Formulas (7) and (8) were obtained from rather general assumptions also without the exciton model. But the dependence of μ'' on ω can be obtained only by specifying the model of exciton and a concrete mechanism for its scattering or decay. For example, the $\mu''(\omega)$ connected with the scattering of a Frenkel exciton by acoustic photons was determined in[7,8]. However, the considered exciton in CdS is more readily of the Wannier-Mott type. The scattering of a polariton by acoustic phonons in CdS was investigated in[9] on the basis of a Wannier-Mott exciton. We have decided, however, not to use the expression obtained there for the scattering probability, for the following reasons:

1) The method used in[9] has made it possible to consider the scattering of a polariton (optical exciton) with only real wave vector. This means that on the long-wave side of the longitudinal-exciton frequency, where allowance for both waves is most important, since their amplitudes are comparable, the results of[9] make it possible to take into account the scattering of only one plus wave.

2) The experimental data used in the present paper were obtained at $T = 4.2°K$, i.e., in the region of extremely "high" temperatures in accordance with the criterion of[9]. In that reference they consider only the opposite limiting case $T = 0$.

3) It follows from Voigt's work[16] that μ'' varies strongly from sample to sample. This means that at such low temperatures μ'' is determined not by the properties of an ideal crystal but by defects or impurities.

Important proof of the existence of an additional wave in CdSe was obtained in[17].

Fortunately, the frequency dependences of $n_{\pm}^2$ and r are practically insensitive to the values of μ'', with the exception of a very narrow frequency region near $\Delta\nu = 10\ \text{cm}^{-1}$. In this narrow region of frequencies we have taken $\mu''(\omega)$ to be constant. Its value $n'_-(\omega) = 1$.

As ω moves away from ω_0 to the long-wave side, formula (7) for $n_+'^2$ goes over asymptotically into (4). When ω moves from ω_0 to the short-wave side, formula (7) for $n_-'^2$ goes over into (4). Then

$$A=b\hbar\omega_0^2/2Mc^2, \quad \omega_1=\omega_0+\varepsilon_0\hbar\omega_0^2/2Mc^2. \tag{9}$$

In order for formula (7) in these asymptotic regions to approximate correctly the experimental values of n', it is necessary to leave the values of the parameters ϵ_0 and A the same as in the preceding section of the article (see (5))[2)]. The position of the narrow sharp spike on the theoretical curve of Fig. b coincides with the experimental value if one puts $1/\lambda_1 \equiv \omega_1/2\pi c = 20587\ \text{cm}^{-1}$.

To decrease the approximating ability of the theoretical formulas we did not regard M as a free parameter, but put $M = 0.9m$, recognizing that in CdS the mass of the conduction electron in the light-propagation direction is $m_e = 0.2m$, and that of the hole is respectively $m_h = 0.7m$.[10,11]. Actually, however, the effective mass of a Wannier-Mott exciton can be even smaller for the following reasons: 1) The two cited mass values actually pertain to electron and hole piezopolarons that execute hydrogenlike motion, with higher values of the principal quantum number $n = 2, 3, \ldots$ [10], whereas we are interested only in the lowest state of the exciton with $n = 1$, in which, owing to the greater proximity of the electron and hole, the polaron effects are smaller and consequently their effective masses are smaller. 2) The popular hydrogenlike model of the Wannier-Mott exciton does not take into account the resonant mechanism of the exciton translational motion due to annihilation of an electron and a hole in one lattice site and their production in another. The contribution from this mechanism to the reciprocal effective mass of the exciton is determined by the oscillator strength of the phototransition[12]. As a result, the effective mass of the Wannier-Mott exciton can be smaller than the sum of the effective masses of the electron and the hole. At $M < 0.9m$ in Fig. a, in the vicinity of ν_1 and to the right of it, the n'_+ curve would increase less steeply and come even closer to the experimental points.

The theoretical expression for the reflection coefficient of light from a semi-infinite crystal $r(\omega)$[1,2] is

$$r=\left|\frac{n_+-1-q(n_--1)}{n_++1-q(n_-+1)}\right|^2, \quad q\equiv\frac{\varepsilon_0-n_+^2}{\varepsilon_0-n_-^2}=-\frac{E_-}{E_+}, \tag{10}$$

where E_+ and E_- are the amplitudes of the plus and minus waves produced in the crystal. The solid line in Fig. c represents the results of substitution of $n_{\pm}$ from (7) into (10).

The theoretical expression for the plate transparency $\delta(\omega)$ was obtained earlier in[2], and formulas (60) and (61) of[2] are valid also at $\mu'' \neq 0$, while formula (62) is valid only at $\mu'' = 0$. We present below a generalization of formula (62) to the case $\mu'' \neq 0$:

$$\delta=4|G|^2/|(1+iF)^2+G^2|^2, \tag{11}$$

where

$$F=\frac{n_+}{1-q}\operatorname{ctg}k_+l+\frac{n_-}{1-1/q}\operatorname{ctg}k_-l, \quad k_\pm=\frac{\omega}{c}n_\pm, \qquad G=\frac{n_+}{(1-q)\sin k_+l}+\frac{n_-}{(1-1/q)\sin k_-l} \tag{12}$$

Expression (11) takes into account the appearance of two waves in the crystal and their multiple reflection from the plate surfaces.

In Fig. b, the solid line represents the result of substitution of $n_{\pm}$ from (7) in (11). In contrast to $n_{\pm}$ and r, the quantity δ depends strongly on μ'' in a wide range of ω. Therefore the foregoing replacement of μ'' by a constant independent of ω distorts $\delta(\omega)$ greatly. Consequently, the theoretical curve in Fig. b cannot claim to be in quantitative agreement with experiment.

It is interesting to note that a sharp spike is obtained on the theoretical curve, in agreement with experiment, although the theory has started from the assumption of the simplest exciton band and of strictly normal incidence of the light, at which the longitudinal exciton is not excited. The distance from the spike to the principal maximum also agrees with experiment.

Figure a shows theoretical curves for n''_+ and n''_-, calculated from formula (7). They show that at $\nu < 20595\ \text{cm}^{-1}$ only a plus wave passes mainly through the plate. Therefore the values of n' determined experimentally from the change of the phase in this region should be compared with the n'_+ curve. At $\nu > 20600\ \text{cm}^{-1}$, both waves attenuate weakly in the plate and are capable of passing through it. In this region, however, we have $|q| \gg 1$ and consequently the minus wave predominates in the amplitude. Therefore the experimental values of n' pertain to the minus wave and should be compared with the n'_- curve.

In cases a and c of the figure, the difference between the calculated and measured values of $n'_{\pm}$ and r are of the order of the measurement errors. Thus, the agreement between theory and experiment is good. There are none of the qualitative contradictions noted

	Present work	B [13]
ε_0	7.74	8.3
ω_0	20586.56 cm^{-1} (2.55236 eV)	20586.89 cm^{-1} (2.5524 eV)
A	90.1 cm^{-1} (0.01117 eV)	133.9 cm^{-1} (0.0166 eV)
M	$0.9m$	$0.9m$
μ''	35.8	0
γ	2.05 cm^{-1}	0

in the preceding section of the article, in which the additional wave was ignored.

Permogorov, Travnikov, and Sel'kin[13,14], have carried out a thorough investigation of the dependence of the coefficient of light reflection from a crystal surface on the frequency and incidence angle (T = 1.8 and 4.2°K). The result of the experimental measurements agree well with the same theory, which takes into account the additional wave[1,2].

Comparison of Fig. 3 of[13] with Fig. b of the present paper shows that in the case of normal incidence our theoretical curve comes closer to experiment than in[13]. The reason is the different choice of the parameters of the theory. Both in[13] and in the present study, the employed principal value of the dielectric tensor (right-hand side of (1)) is of the form

$$\varepsilon(\omega,k)=\varepsilon_0+\frac{A}{\omega_0+\hbar k^2/2M-\omega-i\gamma},\quad \gamma=\mu''\frac{\hbar\omega_0^2}{2Mc^2}. \tag{13}$$

The table shows a comparison of the parameters used in this paper and in[13].

Our value of ω_0 corresponds to a wavelength 4856.2 Å in air. At our values of the parameters, formula (9) yields b = 1578. Further, from formula (8) we can determine the average oscillator strength f of the phototransition per molecule. If the number of molecules per cm^3 is $N = 2\times 10^{22}$, then f = 0.0021. Thomas and Hopfield[15] cite for the oscillator strength of the phototransition a value f = 0.0025. It was determined from the light-reflection spectrum.

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[1] We emphasize that in the considered theory, in contrast to the classical Kramers-Kronig theory, the dispersion of $n'_\pm$ is not connected directly with the absorption, and can be large even at $\mu''=0$, corresponding to a non-absorbed optical exciton (polariton).

[2] Now, of course, $A\neq\int\epsilon''d\omega$, and A can be large also at $\epsilon''=0$.

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