

FIG. 2. Theoretical two-photon LO-phonon-assisted absorption constant versus two-photon energy.

present value was chosen within reasonable bounds as typical to demonstrate the strength of the exciton-phonon interaction.

A more comprehensive study of the parametric sensitivity of the absorption constant will be pursued further. However, at present, it can be stated with reasonable certainty that LO-phonon-assisted transitions play an important part in the

optical spectra of KI, where the theoretical predictions of such an interaction agree favorably with experiment. It can also be said that acoustic phonon broadening is probably smaller than supposed. Mahan previously stated that the $2P$ state was not resolvable because of its closeness to other exciton lines and its large width.³ Since we have resolved this state, its width cannot be as large as believed. What probably causes confusion is the closeness of the LO-phonon-assisted transitions. In the present experiment the instrumental resolution is probably lower than is needed to give an accurate description of the acoustic phonon broadening. For this reason further experiments at even higher resolution are desirable.

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Phonon Sideband in Exciton Absorption: Perturbation Theory*

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The imaginary part of the dielectric response function ϵ_2 is calculated in the second-order perturbation theory for the Fröhlich electron-optical-phonon and hole-optical-phonon interactions. Coulombic attraction between the electron and the hole is included exactly. The interaction produces a maximum near the energy E_{1s} (energy of $1s$ exciton) $+ \hbar\omega_0$ (energy of optical phonon) accompanied by minima on both high-energy and low-energy sides. Positions of the maximum and the minima agree well with the experiment.

Optical absorption associated with optical-phonon-accompanied exciton transitions in polar semiconductors has been observed by many workers.¹⁻⁶ A theory analogous to that of indirect transitions fails to account for the frequency dependence of the imaginary part of the dielectric function ϵ_2 , predicting a smooth threshold at the energy $E_{1s} + \hbar\omega_0$ (E_{1s} is the excitation energy of

the exciton, $\hbar\omega_0$ the energy of the optical phonon) and a maximum at a higher energy.³ Experiments, however, show a maximum at an energy close to $E_{1s} + \hbar\omega_0$ and often slightly shifted to still lower energy. Also a sharp minimum has been observed following the one-phonon maximum in ZnO crystals at 4.2°K² and in BeO at 77°K.¹ Further, a theory in which the absorption due to pho-

non-accompanied transitions is simply added to the purely electron-hole transitions is objectionable on theoretical grounds. It has been shown⁷ that for final-state interactions—i.e., such interactions as do not change the ground state—the following sum rule holds:

$$\int_0^\infty \omega^2 [\epsilon_2(\omega) - \epsilon_2^{(0)}(\omega)] d\omega = 0$$

if the integral converges. ϵ_2 is computed with the final-state interactions (such as electron-hole or exciton-phonon) included, $\epsilon_2^{(0)}$ is the dielectric function as it would be without these interactions. If both the optical-phonon energy and the exciton binding energy are small compared with the gap, the above sum rule approximately reduces to the conservation of the area under ϵ_2 . The theory which adds the indirect transitions to the electron-hole absorption clearly violates the sum rule. It must be emphasized that indirect-transition theory can give useful results if the compensation for the one-phonon maximum takes place in a distant frequency region. This is the case when the energy $E_{1s} + \hbar\omega_0$ is not overlapped by the electron-hole continuum or does not fall into the region of higher excitons. It is not the case, however, with II-VI compounds where the

phonon sidebands have been observed. Here the compensation can, and presumably does, occur at frequencies adjacent to the maximum and thus can modify the line shape profoundly. In other words, indirect transitions and the changes in electron-hole absorption produced by exciton-phonon interaction are equally important, and the configuration interaction between electron-hole states and electron-hole + one-phonon states has to be included in the calculation.

We shall consider a model for a weakly polar semiconductor which proved successful in explaining the low-energy tail of the exciton.^{8,9} It consists of parabolic nondegenerate conduction and valence bands, effective masses being m_e and m_h , respectively. An electron and a hole interact via Coulomb interaction $e^2/r_{eh}\epsilon_s$, where ϵ_s is the static dielectric constant. This leads to formation of a hydrogenlike discrete spectrum and Coulombic scattering in the continuum.

Now we should combine these states with one phonon, two phonons, etc. and construct the Hilbert space of the model as a direct sum of zero-phonon, one-phonon, etc. spaces. To make the calculations feasible we include only combinations of 1s-exciton and one phonon into the Hilbert space. Now we can write the Hamiltonian

$$H = \mathbf{S}_h |h\rangle E_h \langle h| + \sum_{\vec{q}} |1s, \vec{q}\rangle (E_{1s} + \omega_0 + q^2/2M) \langle 1s, \vec{q}| + i\Omega^{-1/2} \sum_{\vec{q}} \mathbf{S}_h V_q [|1s, \vec{q}\rangle V(h, \vec{q}) \langle h| - \text{h.c.}] \quad (1)$$

Here $|h\rangle$ denotes the hydrogenlike state of the electron-hole pair with zero total momentum; $h = n$, $E_n = E_g - 1/2n^2$ for discrete spectrum and $h = k$, $E_k = E_g + k^2/2$ for the continuum. We consider only states with s character which are the only important ones for the absorption. Continuum states have been chosen as standing s waves. $|1s, \vec{q}\rangle$ is the state with the \vec{q} phonon and 1s exciton moving with the momentum $-\vec{q}$, M is the total mass of the exciton. We adopt here effective atomic units: two effective Rydbergs for energy, reduced effective mass for mass, and exciton radius for length.

The third term in the Hamiltonian (1) describes the configuration interaction between zero-phonon and one-phonon states. It is derived from the Fröhlich interaction¹⁰ between the electron-hole pair and phonons:

$$V = i\Omega^{-1/2} \sum_{\vec{q}} V_q [(e^{i\alpha_h \vec{q} \cdot \vec{r}} - e^{-i\alpha_e \vec{q} \cdot \vec{r}}) e^{-i\vec{q} \cdot \vec{R}} a_{\vec{q}} - (e^{-i\alpha_h \vec{q} \cdot \vec{r}} - e^{i\alpha_e \vec{q} \cdot \vec{r}}) e^{-i\vec{q} \cdot \vec{R}} a_{\vec{q}}^\dagger], \quad (2)$$

$$V_q = q^{-1} [2\pi\omega_0 (\epsilon_s/\epsilon_\infty - 1)]^{1/2}.$$

[In effective atomic units, the bare electronic charge is $(\epsilon_s)^{1/2}$.] Ω is the normalization volume, \vec{r} relative position vector, \vec{R} the position vector of the center of mass of the pair, and $\alpha_{e,h} = m_{e,h}/M$.

To evaluate the matrix elements V we employ the following wave functions of the electron-hole pair in the center-of-mass system:

$$\psi_n(\vec{r}) = (\pi n^3)^{-1/2} e^{-r/n} F(1-n, 2, 2r/n) \quad (3)$$

for the discrete spectrum and

$$\psi_k(\vec{r}) = k^{1/2} [\pi(1 - e^{-2\pi/k})]^{1/2} e^{-ikr} F(i/k + 1, 2, 2ikr) \quad (4)$$

for the continuum. The latter functions are normalized as

$$\int \psi_k(\vec{r}) \psi_{k'}(\vec{r}) d^3\vec{r} = \delta(k - k'). \quad (5)$$

With these functions we get for V

$$V(k, \vec{q}) = V_1(k, \alpha_h q) - V_1(k, \alpha_e q), \quad V(n, \vec{q}) = V_2(n, \alpha_n q) - V_2(n, \alpha_e q), \quad (6)$$

where

$$V_1(k, q) = \langle k | e^{i\vec{q} \cdot \vec{r}} | 1s \rangle = 4 \left(\frac{k}{1 - e^{-2\pi/k}} \right)^{1/2} \frac{1}{q} \text{Im} \frac{(1 - iq + ik)^{i/k-1}}{(1 - iq - ik)^{i/k+1}} \quad (7)$$

and

$$V_2(n, q) = \langle n | e^{i\vec{q} \cdot \vec{r}} | 1s \rangle = 4n^{-3/2} \frac{1}{q} \text{Im} \frac{(1 - n^{-1} - iq)^{n-1}}{(1 + n^{-1} - iq)^{n+1}}. \quad (8)$$

The imaginary part of the dielectric response function is given by the Kubo formula

$$\omega^2 \epsilon_2(\omega) = \text{const} \text{Im} \sum_{\vec{k}, \vec{k}'} \langle \vec{k} | (\omega^+ - H)^{-1} | \vec{k}' \rangle, \quad (9)$$

where $|\vec{k}\rangle$ is a direct Bloch electron-hole pair at the point \vec{k} of the Brillouin zone.

Now we use perturbation theory and expand the Green's function in (9) in powers of the third term in the Hamiltonian (1), denoted as V :

$$\omega^2 \epsilon_2(\omega) = \text{const} [\pi S_h |h(0)|^2 \delta(\omega - E_h) + \text{Im} S_{h,h} h(0) W(h, h'; \omega) h'(0) (\omega^+ - E_h)^{-1} (\omega^+ - E_{h'})^{-1}], \quad (10)$$

$$W(h, h'; \omega) = \langle h | V Q (\omega^+ - H_Q)^{-1} Q V | h' \rangle. \quad (11)$$

Q is the projection operator on one-phonon space, H_Q denotes the second term in the Hamiltonian (1). The expression W can be formally treated as an additional electron-hole scattering. Its diagrammatic representation is shown in Fig. 1. This effective interaction has been first introduced by Toyozawa and Hermanson.^{11, 12} For the special form of the matrix element $V(h, q) = f(h)g(q)$ the problem can be solved exactly.¹³ Here we are concerned with a realistic calculation and therefore do not make any simplifying assumption about the interaction. $W(h, h'; \omega)$ is not local, it is energy dependent and has an analytic singularity at $E_{1s} + \hbar\omega_0$ and an imaginary part for energies above $E_{1s} + \hbar\omega_0$. Thus we must expect an analytic singularity in ϵ_2 at the same energy, but the model calculations¹³ have revealed that the form of this singularity does not resemble a threshold in any way.

The explicit expression for W reads

$$W(h, h'; \omega) = 2M\omega_0 \left(\frac{\epsilon_s}{\epsilon_\infty} - 1 \right) \frac{1}{\pi} \int_0^\infty dq \frac{V(h, q)V(h', q)}{2M(\omega^+ - E_{1s} - \omega_0) - q^2}. \quad (12)$$

From expression (10) we see that the imaginary part comes not only from the imaginary part of W above the energy $E_{1s} + \hbar\omega_0$ but also from the denominators whenever they vanish. This second contribution is not included in indirect transitions theory.

Formula (10) has been evaluated for CdTe using an IBM 360 computer. The light frequency ω ran along a straight line parallel to the real axis, at the distance 0.4 Ry*. This value was estimated from the width of the 1s exciton. No adjustable parameters have been used. Choosing a value for the constant in Eq. (10) is equivalent to taking the experimental value for the momentum matrix element. The degenerate valence bands in CdTe were simulated by one band with the effective mass $0.5m_0$. This is the upper limit for the hole mass⁹ and gives the strongest effect in ϵ_2 . The other parameters were taken as $\epsilon_\infty = 6$, $\epsilon_s = 10$,

$m_e = 0.11m_0$, $E_B = 0.01$ eV (binding energy of 1s exciton), and $\hbar\omega_0 = 0.021$ eV. The result of the calculation is shown in Fig. 2. For comparison

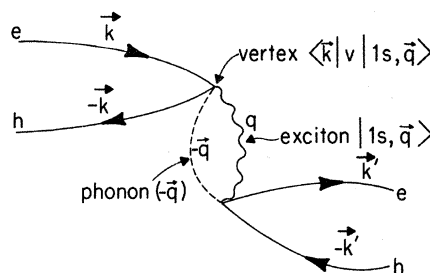


FIG. 1. Additional effective electron-hole interaction. It is real and attractive for energies below the spectrum. At the energy $E_{1s} + \hbar\omega_0$ it has a singularity and has an imaginary part for higher energies. The real part becomes repulsive for sufficiently high energies.

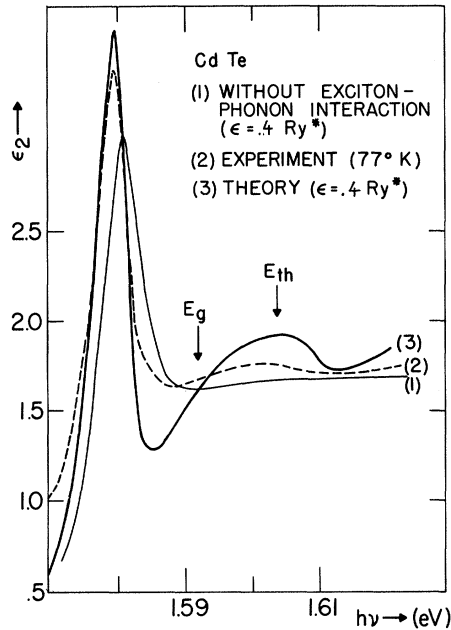


FIG. 2. Dielectric function ϵ_2 . The experimental curve is taken from the work of Dillinger *et al.* (Ref. 3). The theoretical calculations are described in the text.

the curve 1 is shown which was computed according to Elliott theory with phenomenological broadening 0.4 Ry^* .

The positions of the maximum and the minima are in good agreement with experiment, but the theory predicts a stronger effect than is seen in the experiment. The reason for this is not clear but two comments may be in place. First, CdTe shows a very weak effect in comparison with other materials. E.g., CdSe has material constants close to those of CdTe ($\epsilon_s = 10$, $\epsilon_\infty = 7$, $E_B = 0.015 \text{ eV}$, $\hbar\omega_0 = 0.026 \text{ eV}$) but the intensity of the sideband is 3 times as large. Secondly, there is a considerable uncertainty in the hole mass. As has been already mentioned, we took $m_h = 0.5m_0$,

the upper limit.⁹ Since the strength of the pair-phonon interaction increases with the difference in the masses $m_h - m_e$ (it vanishes for $m_e = m_h$) we can expect that, say, $m_h = 0.4m_0$ would give a better agreement for the intensity of the sideband.

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