ANALYSIS OF MIXED AMBIPOLAR
AND EXCITON DIFFUSION IN CdS CRYSTALS *)

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3. Spectral response of the diffusing excitation

One can determine this response in two different ways: (a) by measuring the
photodiffusion curve \( I(x_1) \) several times using each time a different wavelength
of the monochromatic incident light; (b) by measuring the photocurrent as a
function of \( \lambda \) with a constant shadow width \( x_1 - x_0 \). Figures 19 and 20 give some
examples of results obtained in this way. To correct for the variation with
wavelength of the number of absorbed quanta and at the same time for the
variation of photoresponse with overall illumination we plotted the ratio
\( I(x_1)/I_0 \) of the photocurrent through the probes when a finite shadow width
was interposed to that with overall illumination. Because of the easy propaga-

Fig. 19. Photodiffusion curves \( I(x_1) \) of sample \( B_1 \), obtained with monochromatic incident light
of various wavelengths.

(a) Excitation with HP 125 W lamp + filters 3 × BG 12 + GG15 + CuSO4 (\( \lambda = 4360 \) Å); 
\( V = 17 \) volts.

(b) Excitation with tungsten-ribbon lamp + interference filter \( \lambda = 5470 \) Å; \( V = 3.2 \) volts.

(c) Excitation with tungsten-ribbon lamp + interference filter \( \lambda = 4650 \) Å; \( V = 7 \) volts.

(d) Excitation with tungsten-ribbon lamp + interference filter \( \lambda = 7230 \) Å; \( V = 73 \) volts.

tion of long-wavelength light ($\lambda > 5150 \text{ Å}$) as discussed in section 2.4 we can not draw conclusions from the variations of the ratio $I(x_1)/I_0$ for this wavelength region. The variations at both sides close to the fundamental absorption edge, however, might point to a wavelength dependence of the excitation. Balkanski and Broser $^6$ found these variations to be more strongly pronounced at low temperatures, as should be expected. An increase of exciton-type generation farther in the short-wave region beyond the absorption edge has also been found by Apker c.s. $^3$ in their photo-emission experiments on halides. With regard to the fine structures as found by Gross et al. $^2$ it would be useful to repeat the diffusion measurements at liquid-helium temperatures, using monochromatic polarized light.

### 3.1. Quenching and stimulation by long-wave radiation

We often found the photocurrent to be much more strongly quenched by infrared radiation if diffusion through a finite shadow width had taken place than with overall illumination. With the arrangement of fig. 1 infrared light from an incandescent lamp passed through an UG 12 filter ($\lambda > 8500 \text{ Å}$) was projected onto the lower side of the crystal (the black screening at the bottom of the crystal was removed resulting in an overall I.R. excitation). Since the

![Fig. 20. Spectral response of the photodiffusion of sample $B_1$ measured at a constant shadow width $x_1 - x_0$; (a) $x_1 - x_0 = 2.2 \text{ mm}$; (b) $x_1 - x_0 = 5.0 \text{ mm}$. $I_0 =$ response with overall illumination.](image-url)
I.R. can have a much stronger effect when the excitation density is low than when it is high, in the latter case one has to reduce the intensity of the incident light to such a level that the non-quenched photocurrent is equal in the two experiments. But even then it is striking that in the diffusion case the quenching is much stronger than with overall illumination (a factor of 10 and only 1.3, respectively). Part of this may still be due to the difference in excitation depth below the crystal surface in the two cases, but the experiment by Gross, Kaplianski and Novikov (ref. 2), Doklady 1957, in which they found that when irradiating in the "exciton band" (\(\lambda = 4869\) Å) the photocurrent peak could be quenched by I.R. whilst the absorption did not decrease, points to the possibility of a more fundamental effect. Perhaps the infrared changes the occupancy of the centres with which the excitons have to interact in order to give rise to photoconduction (see also Balkanski and Waldron 4)).

We investigated the I.R. quenching of the diffusion as a function of wavelength in the near infrared (0.8 \(\mu - 10\) \(\mu\)), but found no selective quenching in this region; on the contrary, two weak stimulation maxima of the diffusion were found at 1.1 \(\mu\) and at 1.45 \(\mu\).

4. Temperature dependence of the diffusion length

In our former experiments we found that the diffusion length can increase considerably with decreasing temperature, a result which could not easily be understood with ambipolar diffusion 5).

The diffusion measurements at the temperatures below room temperature were carried out in an evacuated Dewar vessel to prevent condensation on the crystal surface (see fig. 21). Because it is not easy in that case to use the arrange-

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Fig. 21. Dewar vessel used to measure the temperature dependence of the diffusion length. B: parallel beam of incident light; 1: crystal + PbS monitor cell mounted in the arrangement of fig. 9; 2: copper disk (with thermocouple 6) soldered to hollow ferrico block 3; 4: flat window in the glass wall; 5: liquid nitrogen; 7: heating element.
ment of fig. 1, in which the shadow edge is moved along the crystal surface by means of a micrometer screw, we preferred to work with a constant shadow width obtained by a layer of black lacquer painted on the crystal surface. To be able to study at the same time the influence of the internally propagated fluorescence light (the intensity and the spectral distribution of which can vary strongly with decreasing temperature; see fig. 22), we applied a monitor photocell (1') near the probe electrodes in a way analogous to fig. 9. The whole arrangement was stuck together by thin layers of insulating glue. An electrically insulating but good thermal contact to the cooled copper plate was established by inserting thin layers of silicone grease and a polystyrene foil of 10 \( \mu \) thickness. Since the CdS monitor cell had too slow a response at liquid-nitrogen temperature, it was replaced by a PbS cell. The variation with \( T \) of the diffused photocurrent is shown in fig. 23 for the sample \( B_1 \).

Notwithstanding the fairly strong increase of fluorescence intensity at low \( T \)-values, it could be deduced from the PbS-monitor current in the manner described in section 2.5 that at \( T = -196^\circ C \) only 20\% of the diffused photocurrent was due to self-excitation by diffused fluorescence light. In fig. 22 we give the shape of the simulation spectrum \( s \) used in this case. Since the shape of the fluorescence spectrum could now be measured quite accurately, we have here again strong evidence in favour of exciton diffusion and we conclude that the gradual increase of apparent diffusion length with decreasing \( T \) must be explained by an increasing contribution of exciton diffusion at low temperatures.

![Fig. 22. Spectral distribution of the fluorescence of sample \( B_1 \) at various temperatures.](image-url)
The steeper part of the slope of curve a in fig. 23 below \(-130^\circ C\), however, is probably connected with a rather sharp variation of fluorescence with \(T\): the yellow 5700-Å band (also reported by Broser and Warminsky\(^{13}\)) rather suddenly appears if the temperature sinks below \(-120^\circ C\).

Fig. 23. Temperature dependence of the diffused photoconductivity \(I(x_1)\) obtained with a constant shadow width of 3 mm (curve \(a\)) compared with the variation of photocurrent \(I_0\) with overall excitation (curve \(b\)). Curve \(a/b\) shows the apparent variation of the diffusion length with temperature.

In fig. 23 we have also plotted the ratio \(I(x_1)/I_0\) (curve \(a/b\)), in which \(I_0\) is the current with overall illumination of the crystal, as a function of temperature. As may be seen from eqs (8), (9) and (12c) of ref. 5, \(I_0\) will be proportional to \(n_0 = (g + g_e)r\), whereas \(I(x_1)\) is approximately proportional to \(\frac{1}{2}g_e\sigma\exp\left(-\frac{x}{l_{De}}\right)\). Hence

\[
a/b = \frac{I(x_1)}{I_0} = A \exp\left(-\frac{x}{l_{De}}\right)
\]

with \(A = \frac{1}{2}g_e/(g + g_e)\). Because both \(A\) and \(l_{De}\) may depend on temperature, it is impossible to derive the temperature dependence of the exciton-diffusion length \(l_{De}\) from the \(a/b\) versus \(T\) graph. That the quantity \(A\) (i.e. the ratio of exciton and pair generation) does depend on temperature is clearly shown by the fact that from curve \(c\) of fig. 2 we can estimate \(A = 0.05\) at room temperature, whereas the value of \(a/b\) at \(-190^\circ C\) indicates a value of \(A\) of at least 0.4
at that temperature. However, as the upper limit of $A$ is $\frac{1}{2}$, the value of $l_{De}$ at $-190$ °C must at least be 12 mm, i.e. more than four times as large as at room temperature. Although the derivation of an activation energy of $l_{De}$ from the present temperature-dependence curves appears not to be justified, the increase of $l_{De}$ at decreasing temperatures is qualitatively established.

In our previous publication 5) we have ascribed the decrease of $l_{De} = (D\tau_e)^{\frac{1}{2}}$ at increasing temperatures to thermal dissociation of the excitons, i.e. to a decrease of their characteristic lifetime $\tau_e$. One must, however, bear in mind that (a) the total lifetime $\tau_e$ is not only determined by the probability $\tau_{\sigma e} - 1$ for thermal decomposition, but also by the probability for interaction with electrons or holes trapped at impurity centres $(\tau_{\sigma e})^{-1}$, and (b) the diffusion length is also determined by $D_e$ which depends on the interaction of the excitons with lattice vibrations. Besides $\tau_{\sigma e}$, the quantities $\tau_{\sigma e}$ and $D_e$ may both depend on temperature.

5. Propagation velocity of diffusing photoconductivity

5.1. Introduction

In the previous sections we have described stationary photodiffusion measurements on CdS single crystals. On one particular sample, in which after careful analysis of various interfering effects — especially the influence of fluorescence light — evidence of exciton diffusion contributing to photodiffusion over distances of several millimetres was found, the velocity of propagation was studied using a sinusoidally modulated local excitation with strongly absorbed light. A theoretical treatment will be given for the phase shift between the diffused photocurrent and the modulated part of the excitation intensity, assuming a mixed ambipolar and exciton-diffusion mechanism.

5.2. Theory of the propagation time

If we accept the existence of mixed photodiffusion, in which both ambipolar and exciton diffusion play a role, we may — for instance with the help of eqs (12) of ref. 5) — obtain numerical values for the two diffusion lengths $l_D$ and $l_{De}$. Each of these diffusion lengths is connected with a product of a diffusion constant $D$ and a lifetime $\tau$, viz. $l_{De} = (D\tau_e)^{\frac{1}{2}}$ and $l_D = (D\tau)^{\frac{1}{2}}$. From stationary photodiffusion experiments alone only the diffusion lengths can be obtained; other experiments are required to find the values of the $D$'s and $\tau$'s separately. Such experiments consist of determining the propagation velocity of diffusing photoconductivity, i.e. the time elapsing between the moment of local excitation and the onset of photoconductance at a distant non-irradiated part of the crystal. From this time lag and the distance, a propagation velocity $v$ can be derived which is of the order of $(D/\tau)^{\frac{1}{2}}$, so that from $l_D$ and $v$ (or $l_{De}$ and $v_e$) the values of the diffusion constants and lifetimes might be found.
In the case of one single type of diffusion like that of injected minority carriers in germanium\textsuperscript{14}, and if trapping of the charge carriers is negligible, the interpretation of time-lag effect is relatively simple. With CdS, however, the situation is complicated by the mechanism of mixed photodiffusion. In this section we shall consider the time-dependent mixed diffusion, starting from the simple equations (7)-(9) of ref.\textsuperscript{5} for exciton and ambipolar diffusion. Next, we shall discuss the effect of a non-linear annihilation rate of the free charge carriers.

5.2.1. Photodiffusion with sinusoidally modulated excitation

The propagation of photoconductivity through the non-excited parts of the crystal may be studied either by exciting a part of the crystal by short pulses and following the propagation of the conductivity wave through the material, or by modulating the excitation periodically and determining the phase shift of the periodical conductivity variation. The first method has been used by Balkanski and Broser\textsuperscript{4,6}), but the interpretation of the results of experiments of the second type seems somewhat more reliable because of the simpler mathematical theory involved. We consider the experimental set-up as depicted in fig. 1 and assume the same boundary conditions as have been indicated in section 2.1 of ref.\textsuperscript{5}). Furthermore, we shall assume the diffusion of the excitons and the excited charge carriers to be governed by the following time-dependent equations:

\begin{align}
\frac{\partial n_e}{\partial t} &= D_e \frac{\partial^2 n_e}{\partial x^2} - \frac{n_e}{\tau_e} + g_e', \\
\frac{\partial n}{\partial t} &= D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} + \frac{n_e}{\tau_e} + g',
\end{align}

where \(n_e\) and \(n\) are the concentrations of excitons and electron-hole pairs, respectively, \(g_e'\) and \(g'\) are the optical generation rates of excitons and pairs, and \(D_e, \tau_e\) and \(D, \tau\) are diffusion constants and lifetimes. It will be further assumed that the non-illuminated region extends from \(x = 0\) to \(x = \infty\), whereas at \(x \leq 0\) a periodically modulated irradiation causes time-dependent generation rates of the form

\[g_e' = G_e + g e^{\text{rot}}, \quad g = G + g e^{\text{rot}},\]

in which \(G_e, G, g_e\) and \(g\) are constants. Introducing eqs (6) into eqs (4) and (5) we obtain two partial differential equations for the concentrations \(n\) and \(n_e\), each of which can be easily separated into an equation for the time-independent parts of \(n\) and an equation for the periodic part of these concentrations. The former equations are identical with those already treated in ref.\textsuperscript{5}), which lead there to the solutions (12). Hence we are left with the following equations for...
the amplitudes of the time-dependent parts of the concentrations, for which the symbols \( n \) and \( n_e \) will henceforth be used:

\[
\begin{align*}
    i\omega n_e &= D_e \frac{d^2 n_e}{dx^2} - \frac{n_e}{\tau_e} + g_e, \\
    i\omega n &= D \frac{d^2 n}{dx^2} - \frac{n}{\tau} + \frac{n_e}{\tau_e} + g
\end{align*}
\]

or

\[
\begin{align*}
    D_e \frac{d^2 n_e}{dx^2} - \frac{n_e}{\tau_e^*} + g_e &= 0, \\
    D \frac{d^2 n}{dx^2} - \frac{n}{\tau^*} + \frac{n_e}{\tau_e} + \dot{g} &= 0,
\end{align*}
\]

where

\[
\tau_e^* = \frac{\tau_e}{1 + i\omega \tau_e}, \quad \tau^* = \frac{\tau}{1 + i\omega \tau}.
\]

Equations (4b) and (5b) are of the same form as those treated previously, and the solutions will accordingly take the same form as (10) and (12) of ref 5, with the difference that owing to the complex character of \( \tau_e^* \) and \( \tau^* \) some of the parameters of the solutions are complex quantities. Introducing the abbreviations

\[
\begin{align*}
    \lambda_e &= (D_e \tau_e^*)^{-\frac{1}{2}} = \left( \frac{1 + i\omega \tau_e}{D_e \tau_e} \right)^{\frac{1}{2}}, \\
    \lambda &= (D\tau^*)^{-\frac{1}{2}} = \left( \frac{1 + i\omega \tau}{D\tau} \right)^{\frac{1}{2}}, \\
    \lambda_1 &= (D\tau_e)^{-\frac{1}{2}},
\end{align*}
\]

(these are analogous to the real parameters \( \alpha_e, \alpha \) and \( \alpha_1 \) of ref. 5) we obtain for eq. (4b) the solution

\[
\begin{align*}
    n_e &= n_{e0}^* - \frac{1}{2} n_{e0}^* e^{\lambda_e x} (x \leq 0), \\
    n_e &= \frac{1}{2} n_{e0}^* e^{-\lambda_e x} (x \geq 0), \\
    n_{e0}^* &= g_e \tau_e^* = \frac{g_e \tau_e}{1 + i\omega \tau_e}.
\end{align*}
\]

Considering the solution in the dark region of the crystal \((x \geq 0)\) we find that at \( x = 0 \) the exciton concentration shows a phase shift \(-\phi_e\) (with \( \tan \phi_e = \omega \tau_e \)) with respect to the modulated excitation \( g_e' \). Since \( \lambda_e \) is a complex quantity and may be written as

\[
\lambda_e = \lambda_e' + i \lambda_e''
\]
with
\[ \lambda' = (2D_e \tau_e)^{-\frac{1}{4}} \left( \sqrt{1 + \omega^2 \tau_e^2} + 1 \right)^\frac{1}{4}, \]
\[ \lambda'' = (2D_e \tau_e)^{-\frac{1}{4}} \left( \sqrt{1 + \omega^2 \tau_e^2} - 1 \right)^\frac{1}{4}, \]
the solution (8) for \( x \geq 0 \) may be written as
\[ n_e = \frac{1}{2} |n_{e0}^*| e^{-\lambda' x} \exp \left(i(\omega t - \phi_e - \lambda'' x)\right), \] (9)
in which the time-dependent factor \( \exp (i\omega t) \) has been included. The exciton density is accordingly propagated as a damped wave with a damping coefficient \( \lambda' \) and a phase velocity \( v_e = \omega/\lambda'' \). The phase angle with respect to \( g_e' \) is equal to \(-\phi_e - \lambda'' x\) and varies linearly with the distance \( x \).

Because the only measurable concentration is that of the electron-hole pairs, we must also solve eq. (5b) by using the solution (8) or (9). This leads to a solution analogous to (12) of ref. 5), viz.
\[
\begin{align*}
n_+(x) &= \frac{\lambda'^2}{2(\lambda'^2 - \lambda''^2)} \left[ n_{e0}^* e^{-\lambda^* x} + \left( \frac{\lambda^2 - \lambda'^2}{\lambda''} n_{e0} - n_{e0}^* \right) e^{-\lambda^* x} \right] (x \geq 0), \\
n_-(x) &= 2 n_+(0) - n_+(-x) \quad (x \leq 0).
\end{align*}
\] (10)
The complex constant \( n_{e0}^* \) is defined by
\[ n_{e0}^* = \tau^* \left( g + \frac{n_{e0}^*}{\tau_e} \right) = \tau^* \left( g + \frac{\tau_e^*}{\tau_e} g_e \right) = \frac{\tau}{1 + i\omega \tau} \left( g + \frac{g_e}{1 + i\omega \tau_e} \right). \]

According to eq. (10) the periodic part of the concentration \( n_+ \) in the dark region consists of two parts which both take the shape of exponentially damped waves.

If we write for the factors before the exponential functions \( B_e \exp (-i\psi_e) \) and \( B \exp (-i\psi) \), respectively \( (B_e \) and \( B \) being real), the time-dependent solution takes the form
\[ n_+(x,t) = B_e e^{-\lambda' x} \exp \left(i(\omega t - \lambda'' x - \psi_e)\right) + B e^{-\lambda'' x} \exp \left(i(\omega t - \lambda'' x - \psi)\right). \] (10a)

In this formula the angles \( \psi_e \) and \( \psi \) represent the phase lags of the two components of \( n_+ \) at \( x = 0 \) with respect to \( g \) or \( g_e^* \). For the case that \( |\lambda| \gg |\lambda_e| \) (which is most probably realized with CdS crystals) the phase shifts are simply given by \( \tan \psi = \omega \tau \) and \( \tan \psi_e = \omega (\tau + \tau_e)/(1 - \omega^2 \tau \tau_e) \). For the coefficients \( B \) and \( B_e \) we then obtain \( B = \frac{1}{2} g_e \sqrt{(1 + \omega^2 \tau_e^2)} \) and \( B_e = \frac{1}{2} g \sqrt{(1 + \omega^2 \tau^2)} \) \( (1 + \omega^2 \tau_e^2)^{-\frac{1}{4}} \).

*) We have not assumed a phase shift between the pair-generation rate \( g \) and the exciton-generation rate \( g_e \). If only one of these types of excitation is the primary effect of irradiation, however, the generation of the other one may lag somewhat behind that of the first.
The relation between the amplitude and the phase of each of the parts of eq. (10a) may be visualized in a polar diagram showing each amplitude \( \rho \) (or \( \rho_e \)) as a function of the phase angle \( \phi \). For the last term of eq. (10a) we obtain, by eliminating \( x \) from \( \rho = B \exp (-\lambda'x) \) and \( \phi = -\lambda''x - \psi \), an amplitude

\[
\rho = B \exp \left\{ \frac{\lambda'}{\lambda''} (\phi + \psi) \right\}.
\]

Thus a logarithmic spiral is followed in a clockwise direction with a constant angular "velocity" \( d\phi/dx = -\lambda'' \) when \( x \) is increased. A spiral of the same kind

\[
\left( \rho_e = B_e \exp \left\{ \frac{\lambda_e'}{\lambda_e''} (\phi + \psi_e) \right\} \right)
\]

is described by the first right-hand term of (10a), which must be added vectorially to the first curve to obtain the amplitude-phase relationship of \( n_+ \) (see fig. 24a). If the part of \( n_+ \) determined by ambipolar diffusion dies out much more rapidly than the part governed by the exciton diffusion, i.e. when \( |\lambda| \gg |\lambda_e| \), the total curve is obtained by a translation of

Fig. 24. Polar diagram showing qualitatively the relation between the phase angle \( \phi \) and the amplitude \( |n_+| = \rho + \rho_e \) of the modulated concentration \( n \) of charge carriers (mixed ambipolar and exciton diffusion). Parameter \( x \) = shadow width.

(a) Construction of \( |n_+| \) vs \( \phi \) curve by vectorial addition of the curves \( \rho(\phi) \) (ambipolar contribution) and \( \rho_e(\phi) \) (exciton contribution).

(b) Extension of (a) to the illuminated region \( (x < 0) \).

the former curve until its origin coincides with the starting point of the latter one. It is evident from the second equation (10) that the \( |n| \) vs \( \phi \) curve for \( n_-(x \leq 0) \) is obtained by inverting the curve of \( n_+ \) with respect to the point for \( x = 0 \). In this way the behaviour of \( n(x) \) as shown in fig. 24b is found.

Figure 24 shows that, starting from \( x = 0 \) and with increasing \( x \), the phase angle \( \phi \) will first decrease and pass through a minimum, then reach a maximum value and finally decrease again with \( x \). Unless \( |\lambda_e| \) is very much
smaller than |\lambda|, the amplitude |n_+| will decrease continually, first governed by exp (−λ'x) and afterwards by exp (−λ''x). Under special conditions (g/g_e > (πλ''/λ') exp (πλ'/λ'')) one or more small oscillations may occur in the transition region of the curve of |n_+| vs x (at x = δ). A quantitative example of the behaviour of φ and |n_+| as functions of x is shown in fig. 25.

The slopes of the two linearly decreasing parts of φ(x) at x ≥ 0 are given by λ'' and λ_e'' *). From these slopes the respective phase velocities can be obtained as v = ω/λ'' and v_e = ω/λ_e''. At small values of the modulation frequency ω (i.e. ωτ, ωτ_e ≪ 1) the phase velocities are independent of ω. In that case λ'' = \frac{1}{2}ω(τ/D)^\frac{1}{2} and λ_e'' = \frac{1}{2}ω(τ_e/D_e)^\frac{1}{2}, and accordingly

v = 2 \left( \frac{D}{\tau} \right)^{\frac{1}{2}}, \quad v_e = 2 \left( \frac{D_e}{\tau_e} \right)^{\frac{1}{2}}. \quad (11)

Together with the values of the two diffusion lengths l_D = (Dτ)^\frac{1}{2} and l_{De} = (D_eτ_e)^\frac{1}{2}, obtained from a stationary photodiffusion experiment as described in section 2, these values of v and v_e yield the parameters D, D_e, τ and τ_e:

D = \frac{1}{2} l_D v, \quad D_e = \frac{1}{2} l_{De} v_e,

\tau = 2 \frac{l_D}{v}, \quad \tau_e = 2 \frac{l_{De}}{v_e}. \quad (12)

*) For small ω (ωτ, ωτ_e ≪ 1) this is only the case if g_e ≪ g.
With large \( \omega \), i.e. if \( \omega \tau \gg 1 \), the propagation constants \( \lambda' \) and \( \lambda'' \) will be nearly equal and are given by \( \lambda' \approx \lambda'' \approx \left(\omega / 2D\right) \), so that \( v \approx (2D\omega) \) will show a dispersion in this case. The diffusion constant is then equal to \( D = v^2 / 2\omega \) whereas \( \tau = 2\omega / D^2 \). In principle both parameters \( D \) and \( \tau \) (or \( D_e \) and \( \tau_e \)) might then be obtained without reference to stationary measurements by plotting \( v^{-2} \) against \( \omega^2 v^{-4} \), which should yield the straight line \( v^{-2} = \left(\tau / 4D\right) - D\tau (\omega^2 v^{-4}) \).

Apart from the difficulties — to be treated in the next section — with regard to a possible non-linear annihilation rate of electron-hole pairs, there are some effects that may cause deviations from the picture as presented by the formal theory. The first effect is that of scattered exciting or fluorescence radiation which may cause a direct generation of charge carriers in the non-illuminated region of the sample (see section 2.5). Such a contribution to \( n_+ \) will show a negligible increase of phase lag with increasing \( x \) and must accordingly be represented by a straight line through the pole in the polar diagram of fig. 24a. If the attenuation of this contribution, being due to absorption in the crystal, is small with respect to that of the diffusion-dominated parts of \( n_+ \), a constant vector must be added to the original curve. This will affect most strongly the behaviour of the phase angle at large \( x \); the effect will be that, instead of a final linear decrease, \( \phi(x) \) shows at least one other minimum and finally tends to a constant value. The minimum will occur at the point where the diffused conductivity has dropped to about the same value as that of the conductivity induced by scattered radiation.

A second effect is related to the manner of measuring the diffused conductivity. This must be done by means of probe electrodes, which will always have a certain extension in the \( x \)-direction. Even if point electrodes could be used, the spreading of the electric field would cause an effective electrode length of the order of the inter-electrode distance. If the electrode dimension \( d \) is large with respect to the ambipolar diffusion length \( 1/\lambda' \), but small with respect to \( 1/\lambda_e' \), the ambipolar contribution to \( n_+ \) is decreased by a factor \( 1/d\lambda' \) relative to the exciton contribution. Although the variation with \( x \) of the phase angle of the ambipolar vector is not thereby changed, the relative shortening of this vector will diminish the influence of its phase variation on the total phase angle of \( n_+ \). Unless \( g(1 + \omega^2\tau_e^2) \gg g_e d\lambda' \), which is certainly not the case with our experiments on CdS crystals, we can not expect the \( \phi(x) \) curve to show much of a contribution from ambipolar diffusion.

5.2.2. Effect of non-linear pair-annihilation rate

In the previous section it has been assumed that the annihilation of the charge-carrier pairs occurs with monomolecular kinetics, i.e. that its rate can be given by a linear term \( n/\tau \). This is certainly not always the case, which is clear from the fact that the conductivity with overall illumination is not always a linear
function of the excitation density (cf. section 2.6). If the annihilation rate of the pairs is not linear, the phase shift between the generation of free carriers and the photoconductivity depends on the generation rate. This will give rise to an additional phase shift when the shadow width \( x \) is increased and the local generation rate of electrons at the probes decreases accordingly. In order to investigate this effect and the means to neutralize it, if possible, we shall discuss here the solution of the time-dependent diffusion equations with a more general expression for the annihilation rate of the pairs.

For the diffusion of the excitons we keep eq. (4), of which the complete solution in the dark region is given by

\[
 n_e = \frac{1}{2} \left( G_e \tau_e e^{-\alpha e x} + g_e \tau_e^* e^{-\lambda e x + i \omega t} \right),
\]

where \( G_e \) and \( g_e \) are given by eq. (6), \( a_e = 1/\lambda D_e = (D_0 \tau_e)^{-1} \) and \( \lambda_e \) has the same meaning as before. The equation (5) for the pair concentration in the dark region is generalized and simplified as follows:

\[
 \frac{dn}{dt} = \frac{n_e}{\tau_e} - F(n),
\]

where we have neglected the diffusion term because of the very small ambipolar diffusion length, and \( F(n) \) is a more general expression for the annihilation rate as a function of the pair concentration. In the monomolecular case \( F(n) = n/\tau \), whereas a bimolecular recombination is expressed by \( F(n) = \beta n^2 \). Writing for the generation rate \( n_e/\tau_e \) of the pairs

\[
 n_e/\tau_e = Q(x) + q(x) e^{i\omega t},
\]

we have to solve the differential equation

\[
 \frac{dn}{dt} = Q + q e^{i\omega t} - F(n).
\]

An exact solution of this non-linear equation is impossible, but in the case of a shallow modulation of the excitation, i.e. if \( |g| \ll |G_e| \) or \( |q| \ll |Q| \), the equation may be linearized by putting as a solution

\[
 n = n_0 + n_1 e^{i\omega t},
\]

with \( |n_1| \ll |n_0| \) and \( n_0, n_1 \) independent of \( t \). The function \( F(n) \) may then be expanded as follows:

\[
 F(n) = F(n_0) + n_1 F'(n_0) e^{i\omega t}.
\]

Inserting (15) and (16) into eq. (14a) we obtain

\[
 i\omega n_1 e^{i\omega t} = Q + q e^{i\omega t} - F(n_0) - n_1 F'(n_0) e^{i\omega t},
\]
\[ \phi(x) = -\lambda_e''x - \arctan \frac{i\omega}{F'(n_0)} \]  

5.3. Measurement of the velocity of propagation

For our measurements of the time lag of photodiffusion — from which the velocity of propagation can be directly determined — we modulated the incident beam by operating the H.P. mercury lamp on a.c. The experimental arrangement is shown in fig. 26. Part of the modulated beam \( B \) (frequency \( f = 2 \times 2500 \) c/s) falls on a monitor photomultiplier, which measures the phase of the modulation without introducing phase delay. Another part of it falls on the partly screened CdS crystal, which is mounted in the diffusion device described in section 2 (see fig. 1). After having passed both currents through 5000 c/s filters, the phase of the diffused photocurrent through the probes (4) on the CdS crystal is accordingly given by

\[ \phi(x) = -\lambda_e''x - \arctan \frac{i\omega}{F'(n_0)} \]

\[ \phi(x) = -\lambda_e''x - \arctan \frac{i\omega}{\beta G_e} e^{i\alpha e x} \]

It follows from eq. (21) that the phase shift, caused by non-linear pair annihilation, will interfere seriously with the linear \( \phi vs x \) dependence (with slope \(-\lambda_e''\)) only if \( \omega/F'(n_0) \) is of the order of unity, i.e. if the apparent decay time \( \tau \) is neither very large nor very small compared with \( \omega^{-1} \). The error, introduced into the measurement of \( \lambda_e'' \) or \( \nu_e \) by the second term of (21), may thus be kept small by a proper choice of the measuring frequency \( \omega \). A more reliable method to neutralize the effect of non-linearity, however, is to keep \( n_0 \) and hence \( \omega/F'(n_0) \) constant. This is achieved simply by varying the exciting intensity in such a way that the d.c. part of the probe current remains constant upon variation of \( x \).
crystal is compared with the multiplier current by means of an electronic switch and an oscilloscope. The intensity of B is increased simultaneously with the shadow width \((x_1-x_0)\) in such a way that the d.c. component of the probe current remains constant (cf. section 5.2.2). From the phase difference \(\Delta \phi\), thus obtained, the apparent diffusion time \(\tau_D = \Delta \phi / 2\pi f\) can be derived, which is plotted in fig. 27 as a function of \(x_1-x_0\). We see that the variations in \(\tau_D\) are only of the order of 10% of the time lag due to the response time of the CdS itself. A time lag of the order of 100 \(\mu\)sec might indeed be expected from the recombination time with overall illumination, as can be deduced from the magnitude of photo-conductivity due to a known excitation density (see section 2.5).

The decrease in \(\tau_D\) when the shadow edge is moved from left to right over the probes has a trivial cause. Since the photocurrent is kept constant, the intensity of B is increased because an ever smaller part of the interelectrode region is directly illuminated. Because the recombination is not purely monomolecular, this higher local excitation brings about a faster response of the crystal.
As soon as the shadow edge has passed the electrode edge by some tenths of millimetres, however, we know from the diffusion curves (e.g. fig. 2) that the excitation can now reach the interelectrode region only by diffusion and it will thus be distributed more homogeneously, giving rise to a sharp increase of \( \tau_D \) in the same region where the steep slope of the diffusion curve \( c \) of fig. 2 is observed. The phase shift due to ambipolar diffusion, which is probably too small to be detected in this way (as was pointed out in section 5.2.1), will be completely drowned owing to these electrode effects. The then following linear increase of \( \tau_D \) beyond \( \chi_1 = 1.4 \text{ mm} \) might perhaps be an indication of a finite diffusion time of excitons which according to theory has to increase linearly with the length of the diffusion path through the non-illuminated area. If from the slope of this part of the curve between \( \chi_1 = 1.4 \text{ mm} \) and \( 2.2 \text{ mm} \) we calculate the velocity of propagation we arrive at

\[
v_e = \frac{0.22 - 0.14}{0.8 \times 10^{-5}} = 10^4 \text{ (cm/sec)}.
\]

For the same crystal we have obtained a diffusion length \( l_{De} = (D_{e}\tau_e)^\dagger = 0.3 \text{ cm} \) (section 2.6). As the frequency at which the propagation measurement has been performed was rather high \( (\omega = 3.14 \times 10^4 \text{ sec}^{-1}) \), we must use the correct formula for \( v_e \) instead of the approximation \( v_e = 2(D_{e}/\tau_e)^\dagger \) valid for \( \omega\tau_e \ll 1 \). From the equations of section 5.2.1 we obtain

\[
v_e = \omega/\chi_e'' = \sqrt{2} \omega l_{De} (\sqrt{1 + \omega^2 \tau_e^2} - 1)^{-\frac{1}{2}},
\]

which leads to \( \omega\tau_e = 2.6 \) or \( \tau_e = 80 \mu\text{sec} \). Combining this figure with the diffusion length we find for the diffusion constant of the excitons \( D_e = 1100 \text{ cm}^2\text{sec}^{-1} \). In view of the smallness of the diffusion time-lag with respect to the response time of the photoconduction itself these figures must not be considered as giving exact values for \( D_e \) and \( \tau_e \) but only their order of magnitude.

The increase of \( l_{De} \) at lower temperatures, as experimentally found in section 4, may point to an increase of \( D_e \) or \( \tau_e \) or both. Propagation measurements at low temperatures are needed to find the variation of these quantities separately.

The decrease of \( \tau_D \) at \( \chi_1 \)-values larger than \( 2.3 \text{ mm} \) until the same value as at \( \chi_1 = 1.4 \text{ mm} \) has again been reached may, in accordance with the theoretical predictions of section 5.2.1, perhaps be ascribed to the influence of scattered light outside the crystal, this measurement being performed before we used to apply the anti-reflection layer to our shadow mask (see section 2.3).

To conclude the discussion of these propagation measurements we may point to the results obtained with additional infrared illumination (see fig. 27, dashed curve; overall I.R. excitation at the back of the crystal with \( \lambda > 8500 \text{ Å} \)). The main excitation was increased to such an intensity that the d.c. part of the photocurrent through the probe electrodes always had the same constant value again as that in the experiment without I.R. In accordance with the strong
quenching of the tail of the diffusion curve (section 4), the increase of $\tau_D$ between $x_1 = 1.4$ and 2.2 mm is now totally absent, and $\tau_D$ remains constant at the same value to which $\tau_D$ approached at large $x_1$-values when no additional I.R. excitation was used. With small $x_1$-values (shadow edge above or near the probe-electrodes), $\tau_D$ has essentially the same values as found without I.R., as might be expected. So the difference between the two propagation curves in fig. 27 corroborates the hypothesis of the exciton contribution.

Conclusion

Our analysis of theory and experiments on stationary and on modulated photodiffusion in CdS single crystals has confirmed our former hypothesis that in crystals having very special photoconduction and fluorescence properties excitons can contribute to the diffusion of photoconduction over distances of some millimetres into non-excited parts of the crystal. Special attention has been paid to the influence of scattered and fluorescence light which in our former paper 5) we had studied only qualitatively. It is seen that in many cases this influence can be so large that an exciton contribution, when present, is masked by these interference effects. At present there is considerable divergence in the experimental results obtained with various crystals, even with crystals from one and the same batch. It is very desirable to gain more insight into the nature of the centres from which the excitons can eject photo-electrons, in order that one may be able to activate the crystals in a reproducible way and thus obtain more reproducible results.

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