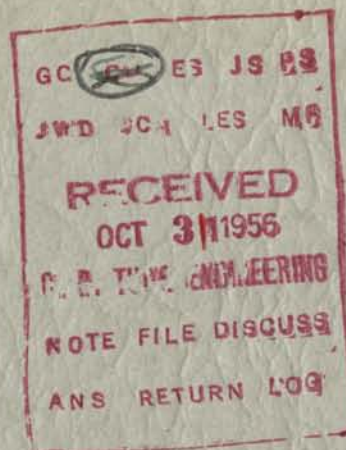LCM

RB-71

ANALYSIS OF PHOTOCONDUCTIVITY
APPLIED TO CdS-TYPE PHOTOCONDUCTORS

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The model of a photoconductor including two different types of recombination centers, filled in the dark, and with trapping centers, empty in the dark, is able to adequately describe such photoconductivity phenomena in *CdS*-type photoconductors as supralinearity, temperature dependence, infrared quenching, and variations in speed of response. Thus the conceptual description of Rose which has been previously shown to have semi-quantitative validity, is put on a more detailed quantitative basis. The application of the theoretical calculations to experimental data for *CdSe* gives self consistent values for the ratio (8×10^5) of the capture cross-section of the "sensitizing" centers for holes to that for electrons, and for the energy difference (0.64 ev) between the level corresponding to this type of center and the top of the valence band. On the basis of the model, the relatively fast response of *CdSe* is associated with the specific location of these levels, which location carries with it the occurrence of supralinearity and large temperature dependence of photosensitivity.

Introduction

Recent investigations of a number of different photoconductivity phenomena (supralinearity, temperature dependence, infrared quenching, speed of response) in *CdS*-type photoconductors [1-4] have shown the semi-quantitative validity of the conceptual model of a photoconductor proposed by Rose.[5-8] The essence of this model is the existence in the photoconductor of two different types of recombination centers, as characterized by their capture cross sections. Illustrative calculations on similar models have been reported by Duboc[9], Dirksen and Memelink[9a], and Schön.[10] Recently almost identical phenomena have been reported for germanium with divalent impurities.[11-12]

It is the purpose of this bulletin to explore in somewhat greater detail the mathematical analysis and the physical interpretation of a representative type of such a model. The insight obtained from a consideration of the model may then be used to analyze data of photocurrent as a function of light intensity, measured at various temperatures, to obtain numerical values for the energy separation between the levels of the low-lying "sensitizing" centers and the top of the valence band, and also the ratio of the capture cross section of these centers for holes to that for electrons.

Additional investigation of photosensitivity and speed of response as a function of temperature for *CdS* and *CdSe* indicates that on the basis of the model, the relatively fast response of *CdSe* is associated with the specific location of these "sensitizing-center" levels, which location (for normal operation based at room temperature) has of necessity connected with it both marked temperature dependence of photosensitivity and speed of response, and supralinear photocurrent vs. light intensity variation.

Theory

The model to be considered is shown in Fig. 1. Three sets of levels are assumed to exist in the forbidden gap; levels of type 1 and 2 are assumed filled in the dark, and levels of type 3 are assumed empty in the dark. The symbols to be used have the following definitions.

N_i — density of states i

n_i — density of filled states i

S_{n_i} — capture cross section of states i for electrons

S_{p_i} — capture cross section of states i for holes

n — density of free electrons

p — density of free holes

S_n'' — recombination cross section between free electrons and free holes

F — density of electron-hole pairs created per second by optical excitation across the band gap

β_{n_i} — product of S_{n_i} and the thermal velocity for an electron

β_{p_i} — product of S_{p_i} and the thermal velocity for a hole

β_n'' — product of S_n'' and the thermal velocity

E_1 — energy difference between levels 1 and top of valence band

E_3 — energy difference between bottom of conduction band and levels 3

P_1 — probability per unit time for thermal ejection of a hole in levels 1 into the valence band

$$P_1 = N_v \beta_{p_1} \; exp \; (-E_1/kT)$$

where N_v is the density of states in the uppermost kT-wide part of the valence band

P_3 — probability per unit time for thermal ejection of an electron in levels 3 into the conduction band

$$P_3 = N_c \beta_{n_3} \; exp \; (-E_3/kT)$$

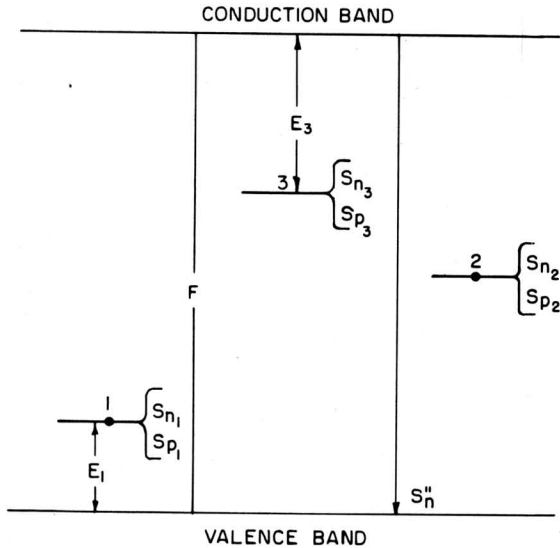where N_c is the density of states in the lowest kT-wide part of the conduction band

Fig. 1 — Energy level scheme for model of a photoconductor.

The equation for charge neutrality is:

$$n + n_3 = p + \sum_{i=1}^{2} (N_i - n_i) \qquad (1)$$

The following five equations express the rate of change of the various densities involved:

$$dn/dt = 0 = F - n \sum_{i=1}^{3} \beta_{n_i} (N_i - n_i) + n_3 P_3 - \beta_n'' np \qquad (2)$$

$$dp/dt = 0 = F - p \sum_{i=1}^{3} \beta_{p_i} n_i + (N_1 - n_1) P_1 - \beta_n'' np \qquad (3)$$

$$dn_1/dt = 0 = (N_1 - n_1) P_1 - \beta_{p_1} n_1 p + \beta_{n_1} n (N_1 - n_1) \qquad (4)$$

$$dn_2/dt = 0 = \beta_{n_2} n (N_2 - n_2) - \beta_{p_2} n_2 p \qquad (5)$$

$$dn_3/dt = 0 = \beta_{n_3} n (N_3 - n_3) - \beta_{p_3} n_3 p - n_3 P_3 \qquad (6)$$

The rates have been set equal to zero in the above equations to give the conditions for the steady state. (Only four of the equations (2) through (6) are independent.)

Solutions for the n_i in terms of n and p can be obtained from Equations (4) through (6):

$$n_1 = N_1 (1 + \beta_{p_1} p / (\beta_{n_1} n + P_1))^{-1} \qquad (7)$$

$$n_2 = N_2 (1 + \beta_{p_2} p / \beta_{n_2} n)^{-1} \qquad (8)$$

$$n_3 = N_3 (1 + (\beta_{p_3} p + P_3) / \beta_{n_3} n)^{-1} \qquad (9)$$

Using Eqs. (7) through (9) together with Eq. (1), p can be expressed in terms of n.

$$p = n - N_1 - N_2 + N_1 (1 + \beta_{p_1} p / (\beta_{n_1} n + P_1))^{-1} + N_2 (1 + \beta_{p_2} p / \beta_{n_2} n)^{-1} + N_3 (1 + (\beta_{p_3} p + P_3) / \beta_{n_3} n)^{-1} \qquad (10)$$

Eqs. (7) through (10) can be substituted into Eq. (3) to give F in terms of n. The actual substitution was not carried out in detail because of the obvious complexity which the results would have, but calculations were made to solve the two equations arithmetically, thus preserving the possibility of understanding the variations physically.

$$F = p \left[\beta_{p_1} N_1 (1 + (\beta_{p_1} p + P_1) / \beta_{n_1} n)^{-1} + \beta_{p_2} N_2 (1 + \beta_{p_2} p / \beta_{n_2} n)^{-1} + \beta_{p_3} N_3 (1 + (\beta_{p_3} p + P_3) / \beta_{n_3} n)^{-1} + \beta_n'' n \right] \qquad (11)$$

In the consideration of the dynamics of the photo-conductivity process, it is frequently convenient to describe phenomena in terms of the quasi-Fermi-levels and the demarcation lines corresponding to the various centers. The location of the quasi-Fermi-levels and demarcation lines for the conditions of low light intensity and high light intensity are indicated schematically in Fig. 2. There are five equations relating the quasi-Fermi-levels and the demarcation lines which it is helpful to keep in mind:

$$E_{Fn} = E_{D_{n_3}} + kT \, ln \, (S_{p_3} p / S_{n_3} n) \qquad (12)$$

$$E_{Fp} = E_{D_{p_1}} - kT \, ln \, (S_{p_1} p / S_{n_1} n) \qquad (13)$$

$$E_{D_{p_1}} = E_{Fn} + kT \, ln \, (S_{p_1} / S_{n_1}) \qquad (14)$$

$$E_{D_{n_3}} = E_{Fp} - kT \, ln \, (S_{p_3} / S_{n_3}) \qquad (15)$$

$$E_{Fp} = E_{Fn} - kT \, ln \, (p/n) \qquad (16)$$
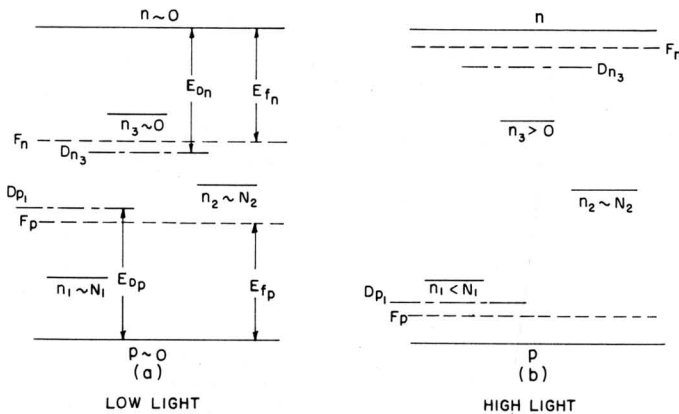

Fig. 2 — Schematic representation of the increase in sensitivity of a photoconductor between low light and high light excitation intensity.

These equations as written above contain the assumption that $N_c = N_v$. They are also based on the definition of the quasi-Fermi-levels:

$$E_{Fn} = kT \, ln \, (N_c/n) \qquad (17)$$

$$E_{Fp} = kT \, ln \, (N_v/p) \qquad (18)$$

The meaning of the demarcation line is the following: When an electron (hole) is located at the electron (hole) demarcation line, it has equal probability of recombining with a free hole (electron) and of being thermally ejected to the conduction (valence) band.

The relation between the quantities of Eqs. (12) through (18) and those of Eqs. (10) and (11) can be illustrated by four examples: (1) when $\beta_{n_3} n$ is equal to P_3, under conditions such that the centers 3 are still in thermal equilibrium with the conduction band as far as capture and ejection of electrons are concerned, the electron quasi-Fermi-level, F_n, is located at the levels 3; (2) when $\beta_{p_3} p$ is equal to P_3, the electron demarcation line, D_{n_3}, for the centers 3 is at the levels 3; (3) when $\beta_{p_1} p$ is equal to P_1, under conditions such that the centers 1 are still in thermal equilibrium with the valence band, the hole quasi-Fermi-level, F_p, is located at the levels 1; (4) when $\beta_{n_1} n$ is equal to P_1, the hole demarcation line, D_{p_1}, for the centers 1 is at the levels 1. It is clear that at least some of the changes in the variation of n with F will occur at concentrations of n and p which are described in these examples.

In order to make the arithmetical calculations on the basis of Eqs. (10) and (11) somewhat less complicated, certain simplifying assumptions were made, as well as the assumption of reasonable numerical values for the various parameters.

$$N_1 = N_2 = 10^{15}/cm^3$$

$$S = S_{p_1} = S_{p_2} = S_{p_3} = S_{n_2} = S_{n_3} = 10^{-15} \, cm^2; \, Sv = \beta$$

$$S' = S_{n_1} = 10^{-19} \, cm^2 \qquad \qquad ; S'v = \beta'$$

$$S''_n = 10^{-20} \, cm^2 \qquad \qquad ; S''_n \, v = \beta''$$

$$(19)$$

$$P_1 = 10^{-1} \, sec^{-1} \, at \, 300°K \, (corresponds \, to \, E_1 = 0.7 \, ev)$$

$$P_3 = 10^{-4} \, sec^{-1} \, at \, 300°K \, (corresponds \, to \, E_3 = 0.9 \, ev)$$

Calculations were carried out for $N_3 = 10^{17}$, 10^{15}, 10^{13}, and $10^7 \, cm^{-3}$. The assumptions used imply principally that centers 2 and 3 are of the same type with about equal cross-sections for capture of either electrons or holes; they could, therefore, be replaced in the model by a single set of centers which are only partially filled in the dark.[*] Centers 1, on the other hand, have a cross-section for holes the same as that of centers 2 and 3, but have a considerably smaller cross section for electrons.

The calculation for the case of $N_1 = N_2 = N_3 = 10^{15} cm^{-3}$ leads to the variation of n and p as a function of F shown

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[*] An equivalent way of considering these states would be to assume a continuous distribution of levels corresponding to centers of type 2 with the dark electron Fermi-level located within this continuous distribution. The only result of the present discussion which would be appreciably altered by such an assumption would be the low-light dependence of n on F.

in Fig. 3. The corresponding variation of n_1, n_2, and n_3 with F are shown in Fig. 4. Most of the essential features of the dependence of photocurrent on light intensity are found in Fig. 3. At low values of F, where the quasi-Fermi-level for electrons and the electron demarcation line for centers 3 lie below the levels 3, (and of course the quasi-Fermi-level for holes and the hole demarcation line for centers 1 lie above the levels 1), the density of free electrons varies as the square-root of the light intensity. In this range of F, the density of trapped electrons in centers 3 is essentially the same as the density of empty recombination centers (centers 2), and the density of free electrons is proportional to the density of trapped electrons.

When βn (and for slightly higher F, βp) exceeds P_3, the centers 3 become about half-occupied, the electrons initially in the centers 2 being equally divided between centers 2 and centers 3. In this range of F, where the density of empty centers 1 is still negligible compared to the density of empty centers 2 and 3, the density of empty recombination centers is essentially constant, and the density of free electrons is proportional to the light intensity.

As the light intensity is increased further, the point will be reached where the photocurrent will begin to rise supralinearly with light intensity if the conditions are suitable. The conditions for the onset of supralinearity can be obtained in the following way. Consideration of Eq. (11) indicates that except for slight changes of the order of two, F will vary linearly with p, and that, therefore, the variation of n with F is determined approximately by the variation of p with n. Examination of Eq. (10) under the conditions which will apply for the onset of supralinearity, i.e., $\beta p \gg P_3$, $\beta n \gg P_3$, and $\beta' n \ll P_1$, gives for $p \ll n$, and $\beta p \ll P_1{}^*$.

$$p = nP_1(n + N_3)\,(n\beta N_1 + (n + N_2 + N_3)\,P_1)^{-1} \qquad (20)$$

In this formulation, the simplifying assumptions of Eqs. (19) have been used, but unequal N_1, N_2, and N_3 are allowed. The n vs. F variation will be sublinear if p varies with a power of n greater than unity, linear if p varies linearly with n, and supralinear if p varies with a power of n less than unity.

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* In the case where $P_3 \gg \beta n$, βp, i.e., the levels 3 lie near the conduction band, supralinearity does not occur. It may be shown that a variation $p\ a\ n^2$ changes to $p\ a\ n$ when $\beta n = \dfrac{N_2}{N_1}\,P_1$.

In the case where $\beta p \gg P_1$, an investigation of the conditions for the possible onset of supralinearity show that the assumption of $\beta p \gg P_1$ holds only for $N_3 > N_1$. Supralinearity does not occur; a variation $p\ a\ n$ changes to $p\ a\ n^2$ when $n = (N_3 - N_1)$. If $\beta p \ll P_1$ at the onset of supralinearity, it is, of course, possible for βp to become $\gg P_1$ during the supralinear range (see Eq. 26).
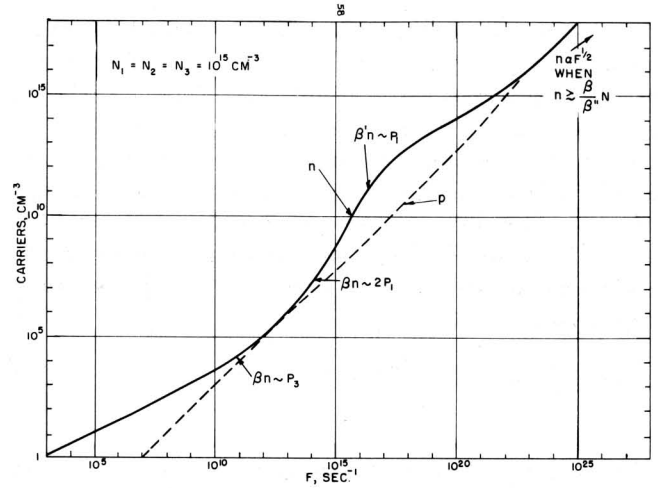

Fig. 3 — Calculated density of charge carriers as a function of light intensity for $N_1 = N_2 = N_3 = 10^{15}/cm^3$.

Under the condition that $n \ll N_1$, N_2, N_3, Eq. (20) reduces to:

$$p = nN_3 p_1\,(n\beta N_1 + (N_2 + N_3)\,P_1)^{-1} \qquad (21)$$

If $(N_2 + N_3)\,P_1 \gg n\beta N_1$, p varies linearly with n, and n varies linearly with F. If, however, $(N_2 + N_3)\,P_1 \ll n\beta N_1$, p is constant and n varies supralinearly with F. Thus the condition for the onset of supralinearity is given by:

$$\beta n = (N_2 + N_3)\,P_1/N_1 \qquad (22)$$

If n is not $\ll N_1$, N_2, N_3, supralinearity may not set in under certain conditions. As one example of such a case, consider $n < N_2$ but $n > N_3$. Then Eq. (20) becomes:

$$p + n^2 P_1\,(n\beta N_1 + N_2 P_1)^{-1} \qquad (23)$$

If $N_2 P_1 \gg n\beta N_1$, p varies as n^2, and n varies as $F^{1/2}$; if $N_2 P_1 \ll n\beta N_1$, p varies as n, and n varies as F. Thus supralinearity does not occur. Supralinearity will not occur in general if $n > N_3$.

It may be shown that the condition for the onset of supralinearity given in Eq. (22) (for $\beta p \gg P_3$, $\beta n \gg P_3$) corresponds to the situation where the density of empty centers 1 is equal to the density of empty centers 2 and 3: $(N_1 - n_1) = (N_2 - n_2) + (N_3 - n_3)$. The general condition for the onset of supralinearity may be stated as follows: supralinearity sets in when the number of electrons removed from centers 1 becomes comparable to the number of holes in centers 2 and 3 below the corresponding electron demarcation lines, provided that the number
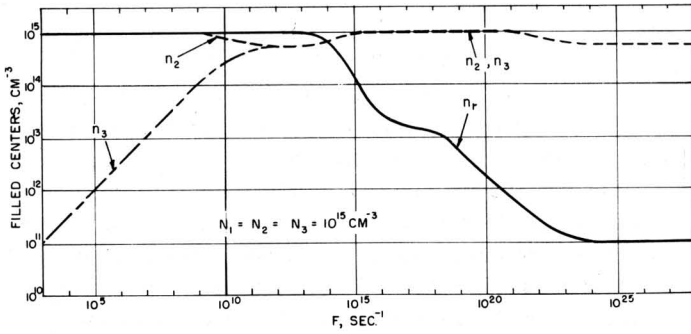
Fig. 4 — Calculated density of filled centers as a function of light intensity for $N_1 = N_2 = N_3 = 10^{15}/cm^3$.

of free electrons at that condition is less than the number of electrons transferred from center 1 to centers 2 and 3.

Eqs. (20) through (23) have been based on the assumption that $p \ll n$. If the case for $p \gg n$ is considered, as will occur if $N_3 \gg N_1$, N_2, it is found that p will vary linearly with n:

$$p = nN_3/(N_1 + N_2) \qquad (24)$$

Supralinearity does not occur for $p \gg n$, the asymmetry being due to the assumption that $S_{n_1} \ll S_{n_2}$, S_{n_3}; $S_{p_1} = S_{p_2} = S_{p_3}$.

Referring back to the calculation summarized in Figs. 3 and 4, it should be noted that recombination of electrons and holes is always dominated by the centers 2 and 3 because of the small value assumed for S_{n_1}, under the other assumptions used. Maximum sensitivity (n/F) occurs for $n = 10^{12}/cm^3$, for which the density of empty centers 1 is almost $10^{15}/cm^3$ and the density of empty centers 2 and 3 is a total of $1.4 \times 10^{13}/cm^3$. But because of the difference in the capture cross sections for electrons, more than 99 percent of the recombination traffic still takes place through centers 2 and 3.

When the light intensity, F, has increased to the point where $\beta' n = P_1$, the hole demarcation line of centers 1 is at the levels 1. It would be expected conceptually that this situation would mark the end of the supralinear range, and a consideration of the appropriate calculations confirms this fact. Under the assumption that $\beta p \gg P_3$, $\beta n \gg P_3$, $p \ll n$, and $n \ll N_1$, N_2, N_3, it may be shown that if $\beta p \ll (\beta' n + P_1)$, (as will occur for $N_3 \ll N_1$, N_2):

$$p = nN_3(\beta' n + P_1)\, (n\beta N_1 + (\beta' n + P_1)\,(N_2 + N_3))^{-1} \qquad (25)$$

or that if $\beta p \gg (\beta' n + P_1)$, (as will occur if $N_3 \approx N_1$, N_2):

$$p = (4\beta n N_1 (N_2 + N_3)\,(\beta' n + P_1))^{\frac{1}{2}}/(2\beta(N_2 + N_3)) \qquad (26)$$

An invariance of p with n (Eq. 25), or a variation of p with $n^{1/2}$, (Eq. 26), for $\beta' n \ll P_1$, both change to a variation of p linearly with n for $\beta' n \gg P_1$.*

As the light intensity is raised further beyond the end of the supralinear range, a range is first encountered where the density of empty recombination centers is approximately constant, and the density of free electrons varies linearly with light intensity. Then for a range of higher light intensities, the density of empty recombination centers increases (from $7 \times 10^{12}/cm^3$ to $7 \times 10^{14}/cm^3$, and hence not discernible in Fig. 4), and the density of free electrons varies sublinearly with light intensity. With continued increase of light intensity, the occupancy of centers 1 drops to that given by the ratio of its capture cross section, i.e., to 10^{-4}, when $n = p$. Similarly, the occupancy of centers 2 and 3 becomes stabilized at 0.5, since the cross sections of these centers for electrons and holes are equal. Until direct recombination between free electrons and free holes becomes important, therefore, the density of recombination centers is constant, and the density of free electrons varies linearly with the light intensity. Finally, when $n > (\beta/\beta'')N$, direct recombination between free electrons and holes becomes the major recombination process, and the density of free electrons varies as the square-root of the light intensity.

Fig. 5 illustrates the case discussed in connection with Eq. (24), with $N_3 \gg N_1$, N_2 and $p \gg n$. Supralinearity is not found.
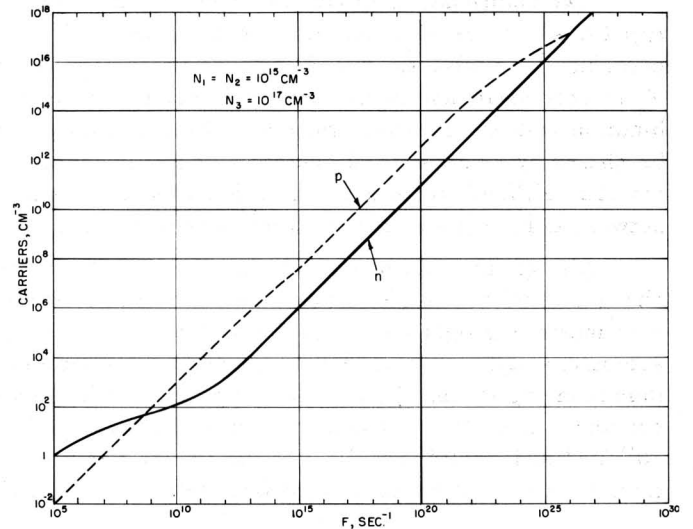

Fig. 5 — Calculated density of charge carriers as a function of light intensity for $N_1 = N_2 = 10^{15}/cm^3$; $N_3 = 10^{17}/cm^3$.

* It is of interest to note that Eq. (25) describes the case where the supralinear range occurs for both hole demarcation line for center 3 and hole Fermi-level above the level 3. Eq. (26), on the other hand, describes the case where the supralinear range occurs for the hole demarcation line for centers 3 above the levels 3, but the hole Fermi-level below the levels 3. In the former case, the hole demarcation line passes through the levels 3 before the hole Fermi-level; in the latter case the reverse is true.

Fig. 6 illustrates the case where $N_3 \ll N_1, N_2$, but is still large enough so that Eq. (22) applies and not Eq. (23).

Finally Fig. 7 illustrates the case where N_3 is so much smaller than N_1 and N_2 that Eq. (23) holds and no supralinear region is found.
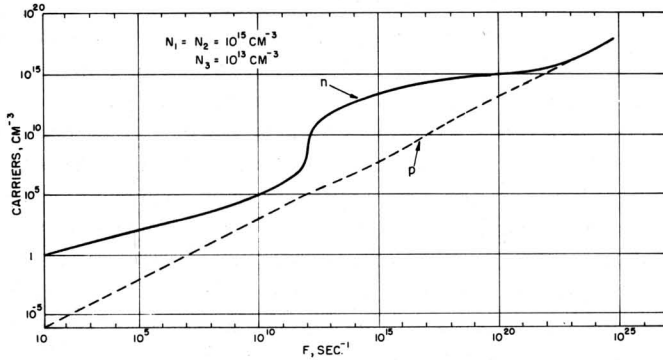

Fig. 6 — Calculated density of charge carriers as a function of light intensity for $N_1 = N_2 = 10^{15}/cm^3$; $N_3 = 10^{13}/cm^3$.

Two additional facts may be noted: (1) the ratio of n/p for any value of F increases continuously with decreasing N_3 relative to N_1 and N_2; (2) in the case where N_3 is very small and supralinearity is not found, recombination traffic for certain ranges of light intensity can be shared by centers 1 and centers 2 and 3; in the limiting case of $N_3 = 0$, recombination traffic is shared equally between centers 1 and centers 2 for moderately high F.

All of the above calculations have shown the changes in photosensitivity possible at fixed temperature with increasing light intensity. Similar changes in photosensitivity can be caused by varying the temperature, thus changing P_1 and P_3, while keeping the light intensity constant. Fig. 8 illustrates the case for $N_1 = N_2 = N_3 = 10^{15}/cm^3$ and $F = 10^{16}$ sec.$^{-1}$. The lifetime of a free electron, t^*, can also be calculated (for $\beta p \gg P_3$, $\beta n \gg P_3$):

$$t^* = (\beta'(N_1 - n_1) + \beta(N_2 - n_2) + \beta(N_3 - n_3))^{-1} \qquad (27)$$

The lifetimes calculated in this way for the case of Fig. 8 are shown by the scale on the right of the Figure; the same curve is applicable to both the variation of n and t^* with temperature.

The variation of photosensitivity with temperature can be summarized by considering three temperatures: (1) a low temperature for which βn, $\beta p \gg P_3$; βn, $\beta p \gg P_1$;

and $\beta'n \gg P_1$; (2) an intermediate temperature for which βn, $\beta p \gg P_3$; βn, $\beta p \ll P_1$; and $\beta'n \ll P_1$; and (3) a high temperature for which βn, $\beta p < P_3$; βn, $\beta p \ll P_1$, and $\beta'n \ll P_1$. For temperatures (1), the crystal is sensitive, with the hole demarcation line for centers 1 lying below the levels 1 and the electron demarcation line for centers 3 lying above levels 3. For temperatures (2), the crystal has passed through a range of temperature quenching and has lost sensitivity; the hole demarcation line for centers 1 lies above the levels 1, but the electron demarcation line for centers 3 still lies above the levels 3. For temperatures (3), centers 3 are being thermally emptied, the electron demarcation line for centers 3 lies below levels 3. Only the range from temperatures (1), through the temperature quenching, to the beginning of temperatures (2) is shown in Fig. 8.

With the assumptions that $p \ll n$, and that $n \ll N$, values of n and p in these ranges can be calculated for the case where $N = N_1 = N_2 = N_3$ as follows:

Low Temperature

$$p = F/(2\beta N) \qquad (28a)$$

$$n = (F/N)(2\beta\beta')^{-\frac{1}{2}}, \text{ for } 2\beta nN \ll F \ll 2\beta N^2 \qquad (28b)$$

Intermediate Temperature

$$p = n/2 \qquad (29a)$$

$$n = 3F/(2\beta N) \qquad (29b)$$

High Temperature $(P_3 \ll N)$

$$p = (\beta n^2)/P_3 \qquad (30a)$$

$$n = (FP_3/N)^{\frac{1}{2}}/\beta \qquad (30b)$$
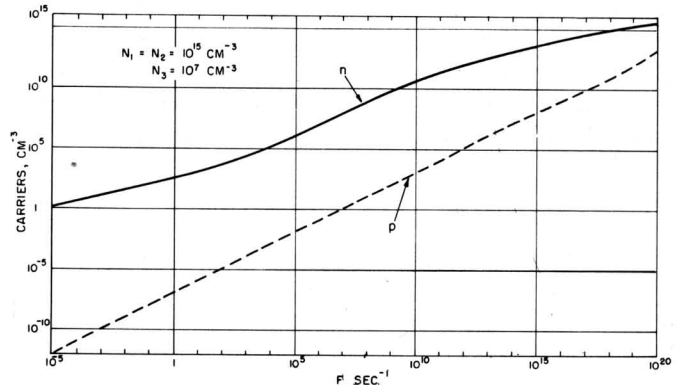

Fig. 7 — Calculated density of charge carriers as a function of light intensity for $N_1 = N_2 = 10^{15}/cm^3$; $N_3 = 10^7/cm^3$.

For the calculation shown plotted in Fig. 8, Eqs. (28b) and (29b) apply; the ratio between n at low temperatures and n at intermediate temperatures is given by:

$$R = (2\beta/(9\beta'))^{\frac{1}{2}} = 47 \qquad (31)$$

Direct Excitation from Imperfection Levels

Thus far only the case of excitation across the band gap, with the creation of both free electrons and free holes, has been considered. Such transitions across the band gap constitute the major contribution to photoconductivity in "pure" materials and in many activated materials with low activator proportions.

Direct excitation from imperfection levels may be important, however, for certain ranges of excitation wavelength for materials with a high impurity concentration. We shall at this point, therefore, briefly consider the changes in the preceding picture which would be necessitated if excitation of centers 1 or centers 2 occurred directly.
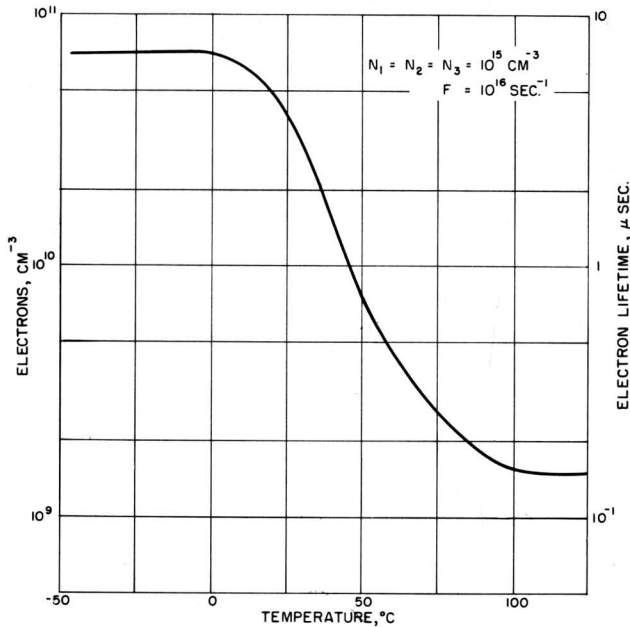

Fig. 8 — Density of electrons and electron lifetime as a function of temperature calculated for $N_1 = N_2 = N_3 = 10^{15}/cm^3$; $F = 10^{16}/sec$.

If excitation of centers 2 occurred directly, and the assumption of negligible thermal freeing of holes from centers 2 is retained, the resulting phenomena would be the same as for a simple photoconductor with recombination centers of type 2 only. The phenomena associated with charge-carrier transfer between centers 1 and centers 2 would be absent. Similarly, if excitation of centers 1 occurred directly, and if thermal freeing of

holes from centers 1 were negligible, results characteristic of a simple one-recombination-center photoconductor would be found; in this case the photosensitivity would be larger than the previously mentioned case by the ratio β/β'.

Some interesting changes in the results are obtained if the model previously described is assumed with the only change being a limitation of the excitation process to transitions between centers 1 and the conduction band. To describe this case, Eqs. (2), (3), and (4) may be replaced by the following equations, respectively:

$$dn/dt = 0 = AFn_1 - n\sum_{i=1}^{3}\beta_{n_i}(N_i - n_i) + n_3 P_3 \qquad (32)$$

$$dp/dt = 0 = (N_1 - n_1)P_1 - p\sum_{i=1}^{3}\beta_{p_i}n_i \qquad (33)$$

$$dn_1/dt = 0 = (N_1 - n_1)P_1 - \beta_{p_1}n_1 p + \beta_{n_1}n(N_1 - n_1) - \qquad (34)$$
$$AFn_1$$

where A is the probability of a photon being absorbed by centers 1, and where the terms concerned with direct free-electron-free-hole recombination have been omitted. No changes are required in Eqs. (1), (5), and (6).

The unique feature resulting from this type of excitation is the saturation in n and p which occurs with increasing light intensity. For the simple algebraic assumptions given in Eq. (19), it may be shown that saturation will occur at the following values of the parameters:

$$\left.\begin{array}{l} p = P_1/(2\beta) \\[4pt] n = (2NP_1/(3\beta))^{\frac{1}{2}} \\[4pt] n_1 = (2NP_1/(3\beta))^{\frac{1}{2}}/2 \\[4pt] AF = 2N(\beta' + (3\beta P_1/(2N))^{\frac{1}{2}}) \end{array}\right\} \qquad (35)$$

(These values for n, n_1, and AF are explicitly for the case where saturation occurs when $\beta(n+p) \gg P_3$.)

Direct excitation of centers 1 has the following effects:

(1) Supralinearity. If saturation occurs before the onset of supralinearity, supralinearity will not be found; if saturation occurs in the supralinear range, supralinearity will be terminated at that point; if saturation occurs above the supralinear range, supralinearity will occur as in the band-gap-excitation model.

(2) Rise time. For band-gap excitation, very slow rise of photocurrent with time, following an S-shape

curve, is commonly found, as holes are transferred from centers 2 to centers 1. When centers 1 are excited directly, below saturation, a much more rapid rise will be found, and in fact overshoot on the rise can be very pronounced because of the slow thermal release of holes from centers 1 to be captured by centers 2. Above saturation, the rise will continue fast, but the overshoot will disappear.

(3) Decay time. For a given concentration of electrons, n, in the conduction band, the lifetime for direct excitation of centers 1 will in general be somewhat longer than for band-gap excitation, because a smaller concentration of holes will be in centers 2 and 3 for the same density of free electrons. This difference will increase as the light intensity is increased and saturation is approached.

Direct excitation of electrons from centers 3 or other trapping levels to the conduction band during the course of the decay will decrease the trap-determined decay time regardless of the type of initial excitation. The infrared-quenching transition, from the valence band to centers 1, will also decrease the decay time by decreasing the free electron lifetime.

Application to Luminescence

If either centers 1 or centers 2 are luminescence centers, the dependence of luminescence emission intensity on exciting light intensity and temperature can be determined from the previous calculations. If centers 1 are luminescent centers, the corresponding emission intensity, I_1, will be given by $\beta'n(N_1-n_1)$; similarly if centers 2 are luminescent centers, I_2 will be given by $\beta n(N_2-n_2)$. An illustrative calculation, with the same approximations as used for the determination of the variation of n with F in Figure 3, shows that I_1 will vary supralinearly with F over a very wide range, as $F^{5/3}$ for $10^3 \leq F \leq 10^{11}$, and approximately as F^2 for $10^{11} \leq F \leq 10^{16}$. I_2, on the other hand varies almost exactly linearly with F over the entire range. If both I_1 and I_2 were present simultaneously, I_2 would be orders of magnitude larger than I_1 over the entire F range because $\beta \gg \beta'$.

Discussion of Experimental Results

Photocurrent as a Function of Temperature and Light Intensity

In order to check the above theory and derive from it certain useful values for the parameters involved, measurements were made on the variation of photocurrent
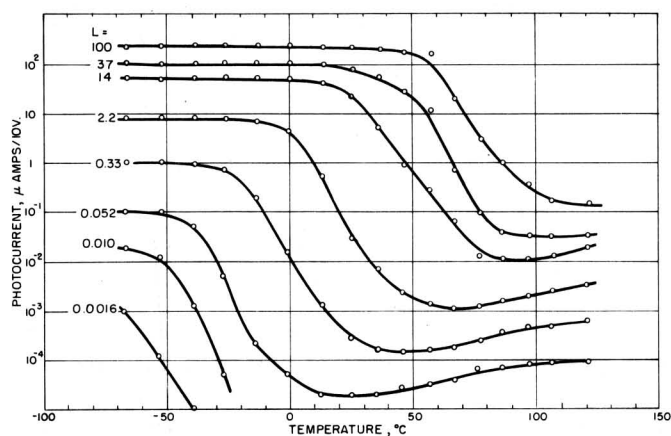

Fig. 9 — Variation of photocurrent as a function of temperature for different relative intensities of excitation for a CdSe:I:Cu crystal.

with incandescent light intensity (giving primarily band-gap excitation) at various temperatures for a single crystal of *CdSe:I:Cu*[13] ($0.92 \times 0.46 \times 0.023$ mm³).The data obtained are presented in two different ways: (1) as the variation of photocurrent with temperature for different intensities of excitation, in Fig. 9; and (2) as the variation of photocurrent with light intensity for different temperatures, in Fig. 10. The experimental points are indicated on Fig. 9 only; the lines on Fig. 10 are drawn through the experimental points particularly to illustrate the break-points from near-linear to supralinear behavior. These data may be used to obtain values for the ratio β/β' of the centers 1, and for E_1, the energy difference between the levels 1 and the top of the valence band.

An approximate estimate of the ratio β/β' can be obtained from the decrease in photosensitivity with
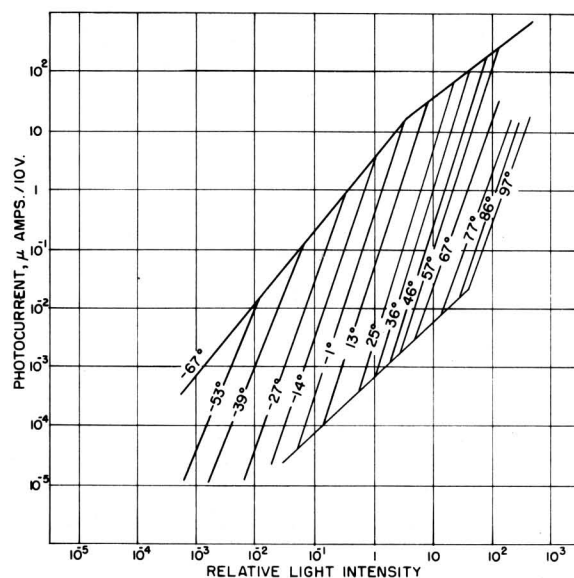

Fig. 10 — Variation of photocurrent as a function of of light intensity for different temperatures for a CdSe:I:Cu crystal.

temperature shown in Fig. 9, using Eq. (31) for the observed value of R of about a thousand. A value of $\beta/\beta' = 10^6 - 10^7$ is obtained from such an estimate.

Probably the best values for β/β' and E_1 can be obtained from the data of Figs. 9 and 10 by considering the values of n for the break from high to decreasing sensitivity, given by the condition that $\beta'n = P_1$. Considering the definition of P_1, this condition can be rewritten as:

$$ln\ n = ln(N_v\beta/\beta') - E_1/(kT) \qquad (36)$$

The log of the photocurrent is plotted against $1/T$ in Fig. 11 for all the values of the break from high to decreasing sensitivity obtained from both Fig. 9 and Fig. 10. From the slope of the straight line drawn through these points, a value of $E_1 = 0.64\ ev$ is obtained. From the intercept of the line for $1/T = 0$, a value of $\beta/\beta' = 8 \times 10^5$ is obtained for a value of $N_v = 10^{19}/cm^3$.
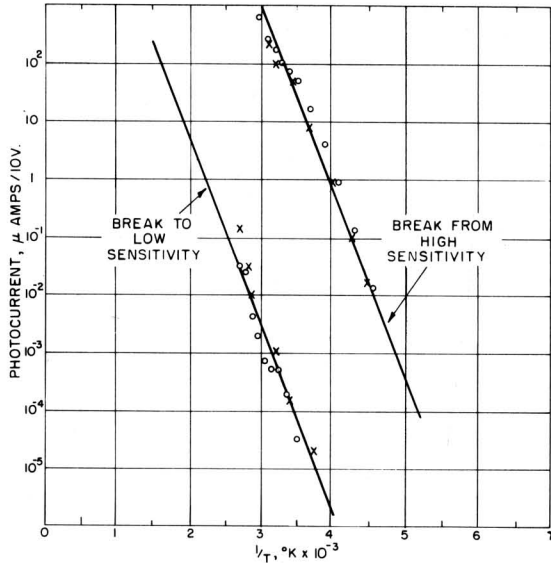

Fig. 11 — Photocurrents at which the break from high sensitivity and the break to low sensitivity occur as a function of the reciprocal temperature. Circles are data from Fig. 10; crosses are data from Fig. 9.

The condition for the break to low sensitivity is given in Eq. (22) and may be rewritten as:

$$ln\ n = ln\ ((N_2 + N_3)\ N_v/N_1) - E_1/kT \qquad (37)$$

Thus if log n is plotted as a function of $1/T$ for the break from decreasing to low sensitivity, a straight line should be found with slope E_1 and intercept $(N_2 + N_3)N_v/N_1$. The data have been plotted and are shown in Fig.

11. The predicted slope of E_1 is found, and from the value of the intercept, again assuming $N_v = 10^{19}/cm^3$, a value of $(N_2 + N_3)/N_1 = 2$ is indicated. Thus the assumption in other calculations of $N_1 \approx N_2 \geq N_3$ seems reasonable.

Another way of analyzing the data is given by the use of the fact that the break from high sensitivity corresponds to a location of the hole demarcation line for the centers 1 at the levels 1. Using Eq. (17) to calculate the location of the quasi-Fermi-level for electrons from the photocurrent at the break, a plot of E_{F_n} as a function of T may be made to test Eq. (14). The results are shown in Fig. 12. Although there is considerable scatter in the points, the best straight line drawn through the points is a fair representation of the data. Such a line has a slope which gives $\beta/\beta' = 10^5$ and an intercept for $T = 0$ of $0.59\ ev$ which corresponds to E_1. A line drawn with slightly higher slope to better match the value of β/β' found in the previous method would also produce a larger value for E_1, in better agreement with the previous method.

Fig. 9 shows that the photosensitivity increases again slightly at high temperatures. Analysis of the data in terms of Eq. (30b) which predicts that $n\ \alpha\ exp\ (-E_3/2kT)$ for the three curves with $L = 2.2$, 0.33, and 0.052, gives for the value of E_3, 0.44, 0.50, and $0.42\ ev$ respectively. An average value of $0.45\ ev$ agrees very well with the major trap peak in $CdSe$ as obtained from thermally stimulated current[1,3] (see Fig. 14).
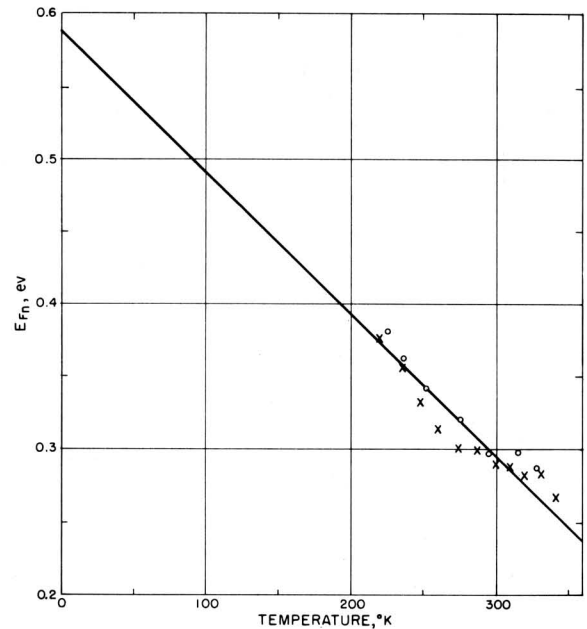

Fig. 12 — Calculated values for the location of the quasi-Fermi-level for electrons at the break from high sensitivity as a function of temperature. Circles are data from Fig. 9; crosses are data from Fig. 10.

Speed of Response as a Function of Temperature and Light Intensity

Measurements of the photocurrent and the decay time (time for photocurrent to decrease to one-half) as a function of temperature for the *CdSe:I:Cu* crystal used in the previous measurements are compared with similar measurements for a *CdS:Cl:Cu*[9] crystal *(0.80 × 0.70 × 0.017 mm³)* in Fig. 13. It is found that the measured decay time has approximately the same temperature dependence as the photocurrent. The chief difference between *CdS* and *CdSe* is that the temperature for which an abrupt decrease in photocurrent and decay time sets in, is around 0 degrees C for *CdSe* and around 100 degrees C for *CdS*. This difference, associated with the greater energy difference between the levels of type 1 from the top of the valence band in *CdS* than in *CdSe,* is also the cause of the faster response of *CdSe* at room temperature.

The decay of photocurrent after the cessation of excitation can be analyzed into the following components, listed in the order of decreasing decay rate:

(1) Direct recombination of free electrons with holes in recombination centers with a large capture cross section for electrons, without any trapping process involved.

(2) Emptying of shallow traps, the freed electrons recombining with holes in the large capture cross section centers.

(3) (a) Transfer of holes from small capture cross section centers to large capture cross section centers, or
(b) Emptying of deep traps.

The importance of each of these components in a measured decay curve will depend strongly on the light intensity used. For very high light intensities, for which the density of free electrons is much larger than the density of trapped electrons, the measured decay time will be equal to the true lifetime as determined by component (1). For
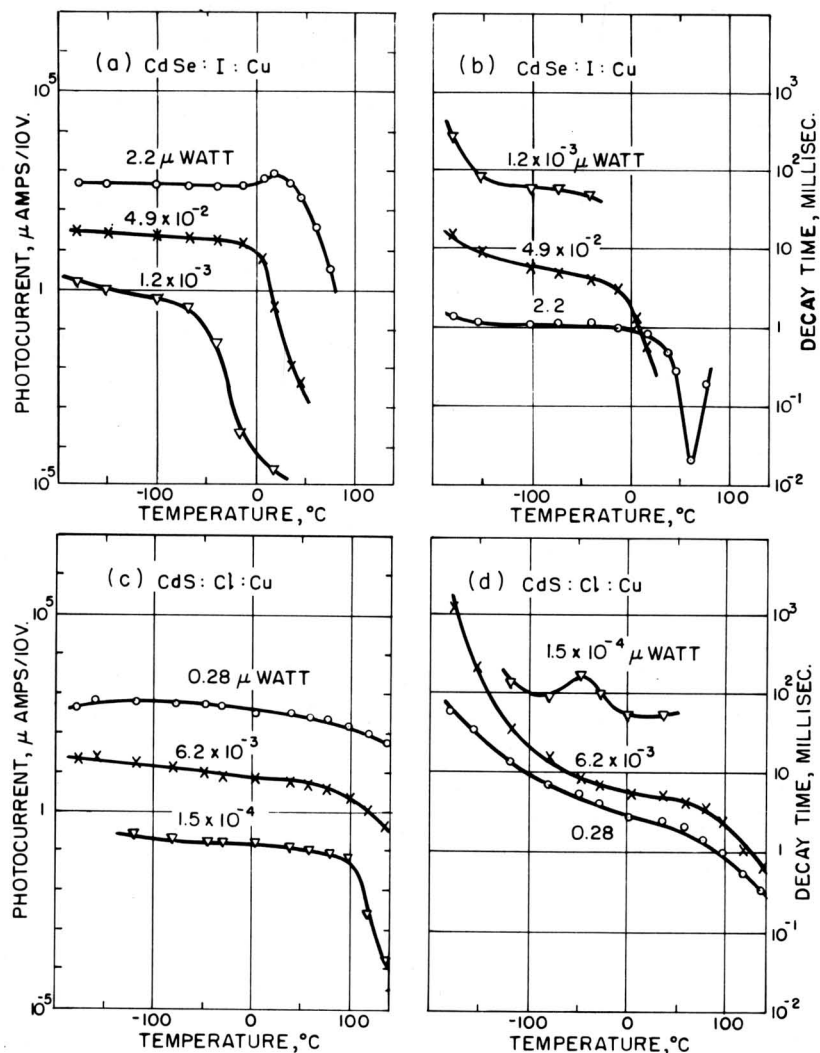

Fig. 13 — Temperature dependence of photocurrent and measured decay time for various excitation intensities for a CdSe:I:Cu crystal and a CdS:Cl:Cu crystal.

very low light intensities, the measured decay time will be determined almost completely by the faster of the (3) components alone.

The measured decay time in *CdSe* is less than in *CdS* at room temperature for two reasons, the difference in decay times becoming more pronounced as the light intensity is lowered. First, the true lifetime of a free electron in *CdSe* at room temperature decreases with decreasing light intensity; i.e., because of the supralinearity found in *CdSe* at room temperature, the sensitivity and the lifetime decrease with decreasing light intensity. Second, transfer of holes from small capture cross section centers to large capture cross section centers occurs at a faster rate than the emptying of at least some of the deeper traps in *CdSe* (i.e., component (3a) dominates the decay rate), whereas in *CdS* the transfer of holes occurs at a much slower rate than the emptying of deep traps (i.e., component (3b) dominates the decay rate.). In order for the rate of thermal ionization of holes from centers 1 (lying 0.64 ev above the valence band) to be greater than the thermal ionization of electrons from those traps in *CdSe* lying 0.45 ev below the conduction band,

$$(N_1 - n_1) \ S_{p_1}/(n_3 S_{n_3}) \ > \ 2 \times 10^3 \qquad (38)$$

which is a reasonable relationship when it is considered that N_1 is probably larger than N_3 and that S_{p_1} (the cross section for the capture of a free hole by a singly or doubly negative center) may well be considerably larger than S_{n_3}. Additional evidence for a relatively small value for S_{n_3} is given in the next section.

The above arguments have been made with the implicit assumption that the difference in the speed of response between *CdS* and *CdSe* does not depend on a significant difference in the density or distribution of trapping centers available. A first glance at the thermally stimulated current curves for the two crystals discussed in this bulletin, shown in Fig. 14, might indicate that there are far fewer traps in *CdSe* than in *CdS*. That the difference between *CdSe* and *CdS* is much less than this can be shown by a consideration of the actual conditions present as these curves were measured. All of the electrons freed from traps and contributing to the thermally stimulated current for the *CdS* crystal (except for temperatures above about 50 degrees C) have the lifetime of the sensitive *CdS* crystal. This lifetime will in fact increase to some extent with increasing temperature, as the electrons freed from traps are captured by the large cross section centers and hence the number of empty large cross section centers for subsequent electrons freed from traps becomes less. Hole transfer from the centers 1 to the centers 2 and 3 in *CdS* does not occur at an appreciable rate below temperatures of 50 degrees C. To illustrate this fact, the calculated values of the
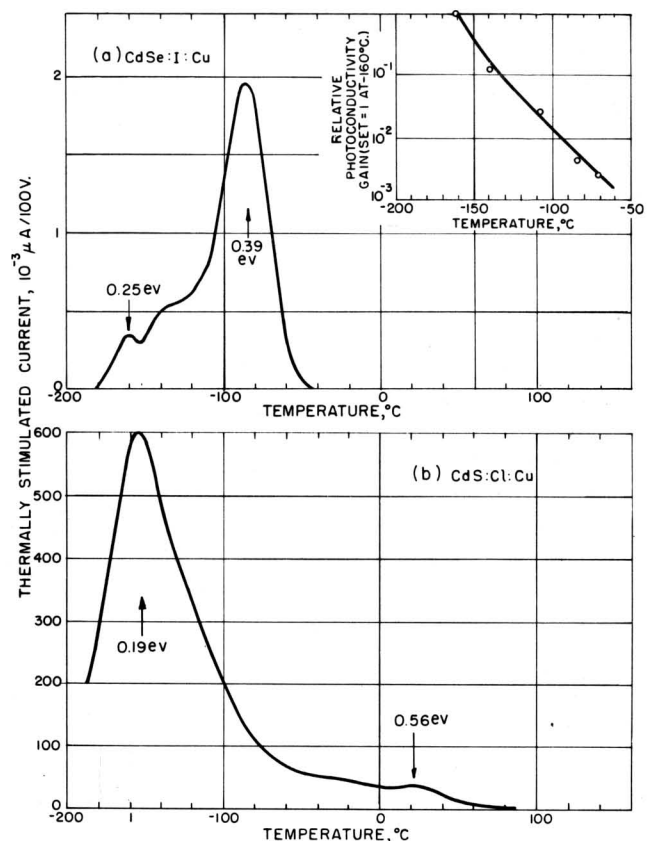

Fig. 14 — Thermally stimulated current curves measured at 0.77°/sec. for a CdSe:I:Cu crystal and a CdS:Cl:Cu crystal. Inset in (a) shows the estimated variation of photoconductivity gain (see text) as a function of temperature.

quasi-Fermi-level for electrons are listed on the curve; a quasi-Fermi-level 0.60 ev from the conduction band in *CdS* corresponds to a location of the hole demarcation line for centers 1 at levels 1 (see Eq. 14). On the other hand, hole transfer in *CdSe* from centers 1 to centers 2 and 3 sets in at about −160 degrees C (the demarcation line for centers 1 being at levels 1 is indicated in *CdSe* by a quasi-Fermi-level for electrons 0.3 ev from the conduction band). An estimate of the decrease in free electron lifetime with increasing temperature because of this hole transfer process in *CdSe* is given in the insert of Fig. 14-a. The photoconductivity gain, determined from steady-state measurements under illumination, for a photocurrent equal to the thermally stimulated current at the temperature of the thermally stimulated current, is plotted as a function of temperature. The gain, and hence the approximate contribution to the current of an electron thermally freed from a trap, decreases by a factor of about 10^3 between −160 degrees and −50 degrees C because of the hole transfer process. This factor can be much larger than the increase in the lifetime of an electron freed from a trap because of the filling of recombination centers by previously freed electrons. The abrupt cut-off on the high-temperature side of the thermally-stimulated current

peak for *CdSe* is thus principally caused by the rapid decrease in the lifetime of electrons freed from traps with increasing temperature, and not by the trap density or distribution.

Rise and Decay Transients

Previous publications[1,2,3] have pointed out how the slow rise of photocurrent frequently observed in *CdS* and *CdSe* can be correlated with the sensitization of the crystal with time, the concentration of holes in centers 1 being increased, and the concentration of holes in centers 2 being decreased. That the reverse process during decay is a much quicker one (i.e., the transfer of holes from centers 1 to centers 2 after the cessation of excitation), as indicated in the discussion of the previous section, is shown also by the fact that the drop in photosensitivity with decreasing light intensity in the supralinear range occurs substantially simultaneously.

If the light intensity is suddenly lowered, either to zero or to a low value within the supralinear range, the photosensitivity may indeed undershoot its long-time equilibrium value. Such undershoot will occur prominently only when the density of holes in centers 2 is equal to or larger than the density of free plus trapped electrons. It is, therefore, not found until measurements are made at a sufficiently high temperature so that most of the holes are located in centers 2 rather than centers 1 at the low light intensity. Under these conditions, the free and very shallow trapped electrons are drained off very rapidly by recombination, the rate of recombination ultimately falling below the rate of electron ejection from traps. When this occurs, the density of free electrons increases to the equilibrium value. An over-rise is found under similar circumstances when the light intensity is increased suddenly to a high value from the dark or from a low light intensity.

The necessary conditions for the existence of undershoot may be determined by considering the equation for the rate of change of the density of free electrons in the absence of excitation:

$$dn/dt = n_3 N_c S_{n_3} v \, exp(-E_3/kT) - nv S_{n_3} (N_3 - n_3) - \qquad (39)$$
$$nv S_{n_2} (N_2 - n_2)$$

The charge neutrality equation may be written as:

$$(n - n_o) + (n_3 - n_{3_o}) = (n_{2_o} - n_2) \qquad (40)$$

where the subscript zero indicates the densities in the dark or at a low light intensity. It has been assumed that all the holes corresponding to the free and trapped electrons are located in the centers 2 at the start of the decay. This will still be substantially true in those regions where a rapid transfer of holes from centers 1 to centers 2 occurs practically simultaneously with the cessation of excitation.

The condition for a minimum in the variation of n with t can be found by setting Eq. (39) equal to zero and solving for n. If the calculated value for $n_{min.}$ is less than n_o, then undershoot will occur.

It can be shown that $n_{min.}$ is given by:

$$n_{min.} = N_c \, exp \, (-E_3/kT) \, (S_{n_3}/S_{n_2}) \, (1 + \qquad (41)$$
$$(N_2 - n_{2_o})/N_3)^{-1}$$

under the conditions that n_o and n_{3_o} are both much less than N_3 and that n_3 is about equal to N_3 at the minimum in n.

Since we can express n_o:

$$n_o = N_c \, exp \, (-E_{F_{n_o}} /kT) \qquad (42)$$

The condition for undershoot, $n_{min.} < n_o$, will, therefore, be met if:

$$(S_{n_3} /S_{n_2}) < exp \, (-(E_{F_{n_o}} - E_3)/kT)(1 + (N_2 - n_{2_o})/N_3) \quad (43)$$

If in the dark or at the low light intensity, the density of holes in centers 2 is substantially less than the density of centers 3, the last term in the above equation will drop out.

A plot of $n_{min.}/n_o$, (actually $\Delta i_{min.}/\Delta i_o$), as a function of temperature for a single crystal of "pure" *CdSe*, for a sudden change in light intensity by a factor of 300, is shown in Fig. 15. As long as the lower light intensity lies above the supralinear range, no undershoot is observed. When the lower light intensity lies in or below the supralinear range, undershoot is found which increases approximately linearly with temperature in magnitude, until a temperature is reached such that the condition of Eq. (43) no longer applies. From the values of current and temperature for which the undershoot ceases, a value of S_{n_2}/S_{n_3} of about $10^3 - 10^4$ can be estimated. That S_{n_3} be somewhat smaller than the other cross sections under discussion is in agreement with the condition for rapid hole transfer of Eq. (38). The small numbers in parentheses below each point in Fig. 15 are the approximate times in minutes required for the current to increase from $n_{min.}$ to n_o.

These results are similar to those reported by Boer[14] for *CdS* at elevated temperatures above 100 de-
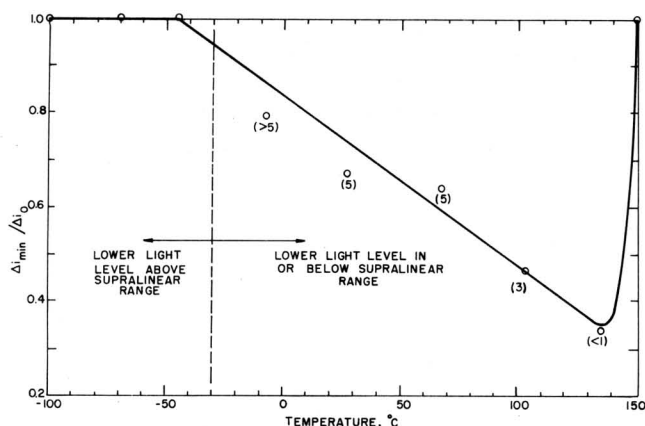
Fig. 15 — Fractional undershoot of photocurrent for a 'pure' CdSe crystal with a sudden decrease in light intensity, as a function of temperature. The small numbers in parentheses are the approximate times in minutes required for the photocurrent to increase from its minimum value to its low-light equilibrium value.

grees C, and attributed by him to possible photochemical reactions in CdS. That the effect should be found in CdS only above 100 degrees C is in agreement with the previous mechanism being the cause of Boer's effects; most of the holes will not be concentrated in centers 2 in CdS until temperatures over 100 degrees C are reached. The fact that the same type of phenomena can be obtained in CdSe below 0 degrees C and can be explained by purely electronic processes, argues strongly against the necessity for photochemical reactions to achieve such effects.

Conclusions

A model of a photoconductor with two different types of recombination centers (one with a much smaller capture cross section for electrons than the other), and trapping centers, is able to provide the mechanism for supralinear photoconductivity, for the temperature dependence of photosensitivity and speed of response, and hence by inference, for infrared quenching (the raising of electrons from the valence band to levels 1 when the crystal is in a sensitive state).

A consideration of the onset and cessation of supralinearity, in the light of the theoretical concepts, leads to the determination from experimental data on CdSe of a ratio of 8×10^5 for the capture cross section of the low-lying "sensitizing" centers for holes to that for electrons. It was also determined that the levels corresponding to these centers lie 0.64 ev above the valence band. The range of photocurrents and light intensities for which supralinearity is found was demonstrated to lie

between (1) that condition for which the density of empty levels with small electron capture cross section is comparable to the density of empty levels with large electron capture cross section, and (2) that condition for which the hole demarcation line for the small cross section centers is located at the level corresponding to these centers. Thus it is shown that a range of supralinearity does not necessarily imply a distribution of "sensitizing" centers in energy.

Assuming the same value of the cross section ratio of the "sensitizing" centers in CdS as in CdSe, results (according to Eq. 14) in a location of the levels corresponding to these centers about 1.0 ev above the valence band. Such a value is in good agreement with the spectral distribution of infrared quenching.[2]

Since the phenomena of supralinearity, and its associated characteristics, occur in crystals of CdSe and CdS to which no impurities have been added, it is indicated that the levels located at 0.64 ev above the valence band in CdSe and 1.0 ev above the valence band in CdS are associated with crystal defects. These crystal defects are probably cation vacancies with one or two trapped electrons, which are, therefore, singly or doubly negative with respect to the rest of the crystal. Supralinearity has been found in CdS at room temperature in samples with a high proportion of Cu impurity[15]; such results suggest that the Cu^+ level lies at about 0.6 ev above the valence band and also acts as a center with much larger cross section for holes than for electrons. Measurements of transmission through CdS sintered layers with small proportions of Cu have revealed only a small absorption at 1.4 ev corresponding to the defect levels 1.0 ev above the valence band. Measurements of transmission and excitation spectrum for luminescence on CdS sintered layers with high Cu proportion[16] indicate high absorption and impurity-excitation of luminescence at about 1.8 ev, corresponding to a level 0.6 ev above the valence band.

The following tentative conclusions about band-gap-excited photoconductivity in CdS-type photoconductors can be made insofar as the model is valid.

(1) Almost all of the properties of interest to photoconductivity in these materials are associated with the presence of a set of small capture cross section imperfection levels, which may or may not act effectively as recombination centers, depending on the temperature and light intensity.

(2) In particular, the speed of response of CdSe is caused by the specific location of these defect levels, which location (for normal operation based at room temperature) has of necessity associated with it both marked temperature dependence of photosensitivity and speed of response, and supralinear photocurrent vs. light intensity variation.

(3) The speed of response in all materials, especially at low excitation intensities, is limited ultimately by trapping phenomena.

(4) Materials fall into three general categories according to their properties at room temperature; (a) sensitive materials with slow response, small temperature dependence, and linear or sublinear photocurrent vs. light variation; (b) materials sensitive at high light intensities, with faster response than type (a) materials (particularly at low light intensities), large temperature dependence, and supralinear photocurrent vs. light variation; and (c) less sensitive or insensitive materials with intermediate or fast response, small temperature dependence, and linear or sublinear photocurrent vs light variation.

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