Recombination Processes in Insulators and Semiconductors

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The discrete states in the forbidden zone are divided into ground states and shallow trapping states. The major recombination traffic passes through the ground states. The shallow trapping states cause the observed decay time of free carrier concentrations to exceed the lifetime of a free carrier in the conduction (or valence) band. At low rates of excitation (free carrier concentrations less than ground state concentrations) the electron lifetime and hole lifetime are independent and, in general, significantly different. At high rates of excitation the free electron and hole lifetimes are equal. For an insulator having one class of ground states (a class being defined by the capture cross sections for electrons and holes) the high-light lifetime is bracketed by the two low-light lifetimes.

The behavior of a model having one class of ground states can be described relatively simply and quantitatively. The behavior of a model having more than one class of ground states becomes sufficiently complex that only special cases can be treated easily. More than one class of ground states, however, is required to account for infrared quenching, "superlinearity" and the ability of added ground states to reduce the rate of recombination. These phenomena involve a redistribution of electrons and holes amongst the classes of ground states. Such redistributions can give some meaning to the phrases: "filling of traps" or "saturation of centers."

The recombination behavior of a semiconductor is significantly different from that of an insulator. For example, superlinearity can occur in a semiconductor having only one class of ground states. Also, the photocurrents in a semiconductor can be intrinsically more noisy than the photocurrents in an insulator.

1.0 INTRODUCTION

ONE may increase the density of free electrons and free holes in a semiconductor or insulator by bombarding the material with photons, electrons or other high-energy radiations or by injecting extra carriers as in the transistor. In the steady state the rate of generation of holes and electrons must be equal to their rate of recombination. The way in which these carriers recombine is a primary concern in the relatively separate fields of luminescence, photoconductivity, and semiconductor control devices. While the physics of these recombinations is common to all three fields, the models and modes of description reflect three different approaches. The discrete states in the forbidden zone, through which recombination is most likely to take place, have been called activators and poisoners in luminescence, deathnium and recombination centers in semiconductors, and traps or primary centers in photoconductors. To this list of names can be added donors and acceptors; electron traps and hole traps; deep traps and shallow traps; and an extensive list of centers in the alkali halides.

All of the states just enumerated have the common characteristic of being discrete states in the forbidden zone. Beyond this their chief distinctions and their chief contributions to recombination are described by their capture cross sections for free electrons and for free holes. One might expect, accordingly, to achieve some condensation of terminology. This is one of the aims of the present discussion.

A number of other questions are considered. Perhpas the most important is the question of how much can be said simply, quantitatively and unambiguously about recombination models. It is by no means certain that a simple description of recombination is at all possible. In fact, the present discussion concludes that when there is more than one class of recombination centers, the variety of possible behavior allows only certain special cases to be discussed with reasonable clarity. This variety is inescapable since experience with phosphors, photoconductors, and some of the more insulating semiconductors has already defined broad limits of actually realized behavior.

It is appropriate in a generalized treatment of recombination to try to give a more precise meaning to certain words and phrases that are commonly used but not always accurately defined. The word "trap" is one example. The distinction between "shallow traps" and "deep traps" is a second. And the phrases "filling of traps" and "saturation of recombination centers" are further examples of ideas that at least merit re-examination.

Finally, there are three first order observations which on the surface are puzzling and, indeed, are not readily explained. These observations are (1) photocurrent *versus* light curves that have a power greater than unity and are therefore called "superlinear," (2) the enhancement of photoconductivity by the *addition* of recombination centers, and (3) "infrared quenching" or the attenuation of short-wavelength excitation by the addition of long-wavelength excitation.

The first item is particularly interesting. Usually, one can find a number of models to explain a given observation and one tries to eliminate models. Here it is difficult to find even one model to account for superlinearity. The second item is puzzling because one would expect that the addition of more paths for recombination would shorten rather than lengthen the lifetime of a free carrier. The last item has had frequent discussion in the literature, mainly as infrared quenching of luminescence, but more recently as infrared quenching of photoconductivity as well. All three items, to anticipate later discussion, have this in common: a satisfactory model must contain more than one class of recombina-

tion centers.[1] A "class" is characterized by its capture cross sections for electrons and holes and is independent of energy.

2.0 LIMITATIONS OF THE PRESENT DISCUSSION

Capture is assumed to take place between free carriers and discrete states in the forbidden zone in essentially one step. That is, if capture is a two step process, both steps are assumed to be of negligible duration. The physical merits of this assumption are not argued here. Little enough is known of capture processes. For lack of knowledge, the simpler process is assumed and its possibilities explored.

The discrete states in the forbidden zone are assumed to be physically separate both in the sense that they do not interact and in the sense that electrons and holes cannot make transitions directly between discrete states. At sufficiently high densities such interaction and such transitions undoubtedly do take place. State densities below $10^{17}/cm^3$ are likely to satisfy the criteria of separateness.

The excitation or generation process is assumed to be one in which electrons are raised from the filled band to the conduction band. Free electrons and free holes are thus generated at identical rates. They recombine at the same rate via discrete states in the forbidden zone. Excitation from discrete states into the conduction band is known to occur in many photoconductors and is by no means a negligible process. Many of the ideas of the present discussion can be carried over to aid in the understanding of these more complex processes.[2]

A state in the forbidden zone is assumed to have either one electron or one hole in it. The possibility of its having more than one electron or hole is excluded. This exclusion, again, is not for lack of physical evidence but only to explore simpler assumptions first.

With all of the above simplifications, the problem of recombination still retains a large measure of complexity. There is likely more need for points of view that allow semiquantitative judgments than there is for complete and closed mathematical solutions.

The properties of a single class of discrete states will be discussed first since reasonably simple and quantitative statements can be made about the possible recombination processes. A second class of discrete states will then be introduced to account, at least qualitatively for a number of observations that cannot be accounted for by a single class of states.

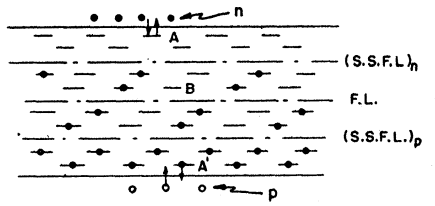


FIG. 1. Model showing that discrete states can be separated for statistical resons into shallow trapping states (A,A') and ground states (B). The ground states are often called recombination centers. $(S.S.F.L.)_n$ is the steady-state Fermi level for electrons.

3.0 DEFINITION OF TERMS

Consider the problem shown in Fig. 1. Free electrons and holes are generated at identical rates and recombine via the discrete states. It is clear, from physical grounds, that there are states (A) near the conduction band such that electrons falling into these states are rapidly re-excited thermally into the conduction band. These states are in thermal equilibrium with the electrons in the conduction band. They will be called shallow trapping states. It is clear also that electrons falling into deeper lying states (B) will not be thermally re-excited for a long time. Before thermal re-excitation takes place, such an electron is more likely to capture a free hole. These deeper lying states will be called ground states. The connotation is that electrons and holes falling into these states have completed their life history. The occupancy of ground states by electrons or holes is determined by the purely kinetic processes of recombination. The occupancy of shallow trapping states is determined by the condition of being in thermal equilibrium with the electrons in the conduction band or the holes in the filled band.

While it is clear that there should be shallow trapping states and ground states, it is not immediately clear what the demarcation line should be. If the discrete states are sufficiently uniformly distributed in energy, and this means that their variation with energy is not as rapid as the function $e^{-E/kT}$, one can locate the demarcation line for electrons at that energy level at which an electron is equally likely to be thermally excited into the conduction band and to capture free electrons. Similarly, a demarcation line for holes can be located at the energy level at which a trapped hole is equally likely to be thermally excited into the conduction band and to capture a free electron. Discrete states lying between these two demarcation lines control the rate of recombination. Discrete states lying outside these two demarcation lines have a finite but negligible effect on recombination. Statistically their contribution to recombination decreases as $e^{-E/kT}$, where E is their energetic distance from the demarcation line.

[1] The problem of "superlinearity" in the field of luminescence has been reported and discussed in a number of papers. All of the papers make use of more than one class of ground states. Recent data are to be found in Nail, Urbach, and Pearlman, J. Opt. Soc. Am. **39**, 690 (1949). Analyses that lead to powers higher than 2 are to be found in S. Roberts and F. E. Williams, J. Opt. Soc. Am. **40**, 516 (1950) and in M. Schön, Z. Naturforsch. **6a**, 251 (1951). More extensive analyses are contained in M. Schön, Tech.-wiss. Abhandl. Osram-Ges. **6**, 49 (1953), and in C. A. Duboc, Brit. J. Appl. Phys. (to be published). The writer is indebted to Dr. Schön for a reprint and to Dr. F. Urbach for a preprint of the last two papers. Insofar as one can characterize analyses made with different types of approximation, the writer believes that the two papers just cited and the present paper are in substantial agreement in using the same physical processes to account for "superlinearity."

[2] Reference 4 is essentially a discussion based on excitation from discrete states.

If there is only one class of discrete states and if the numbers of electrons and holes in the ground states are equal, the demarcation lines coincide with the steady-state Fermi levels[3] for free electrons and holes. This still allows the capture cross section of the ground states for free electrons to be different from their capture cross section for free holes. If the numbers of electrons and holes in the ground states are not equal, both demarcation lines are rigidly shifted by kT times the natural logarithm of the ratio of electrons to holes. Since this shift is usually small (a ratio of 100 to 1 at room temperature causes a shift of only 0.1 electron volt) and since the steady-state Fermi levels have an important connotative value, the steady-state Fermi levels are used in this discussion as a sufficiently good and useful approximation to the demarcation lines.

It there is more than one class of discrete states, each class has its own set of demarcation lines shifted from the steady-state Fermi levels by kT times the natural logarithm of the ratio of electrons to holes in its own ground states.

The ground states, then, are mainly those discrete states that lie between the two steady-state Fermi levels defined by the free electron concentration and the free hole concentration. In this sense, the distinction between traps and ground states is purely statistical. As the excitation is increased and the free carriers increase, the two steady-state Fermi levels move apart toward their respective band edges. States that were trapping states now become part of the group of ground states. Conversely, if the excitation is suddenly removed the free carrier densities decay in time towards zero. As the carrier densities decrease, their Fermi levels recede from the band edges and approach each other at the dark or thermal equilibrium value of the Fermi level. States that were ground states during steady excitation now become trapping states and empty their electrons (or holes) via the free bands. The thermal emptying of these deeper-lying states may be regarded as the emptying of deep traps to be contrasted with the emptying of shallow traps at the start of the decay curve.

It is worth restating that the trap character of a discrete state is not derived here from a physical one-sideness such that electrons can enter and leave through the top but cannot leave through the bottom. The trap character is a purely statistical condition such that an electron is more likely to have an opportunity of leaving through the top by thermal excitation than through the bottom by recombination with a hole.

Over and above the statistical basis for regarding some discrete states as traps, there is evidence that discrete states may be traps in the absolute sense of having a zero or near-zero capture cross section for one sign of carrier.[4] The asymmetry of capture cross sections is discussed in the following section.

4.0 CONCERNING CAPTURE CROSS SECTIONS

The capture cross section of a discrete state for a free carrier can range from about 10^{-13} cm^2 to arbitrarily small values. 10^{-13} cm^2 is the largest value that can be reasonably expected, based on the attractive Coulomb field of a charged center. 10^{-15} cm^2 is a frequently observed value and coincides with the dimensions of a lattice site. Arbitrarily small values can arise from selection rules and from potential barriers surrounding the center—that is, a repulsive Coulomb field. Capture cross sections observed in photoconductors have been reported in the range of 10^{-13} cm^2 to about 10^{-22} cm^2 (reference 7).

Any given center is likely to have markedly different capture cross sections for electrons and holes. For example, a singly negatively charged center is likely to have a large cross section for capturing a hole. After capturing a hole it becomes neutral and is likely to have a much smaller cross section for capturing an electron. A doubly negatively charged center should show an even greater disparity in capture cross section since, after capturing a hole, it actually presents a repulsive field at large distances, for capturing an electron. In the case of CdS photoconducting crystals capture cross sections for electrons have been reported as small as 10^{-21} cm^2.[5,6] On the other hand, attempts to detect the motion of free holes suggest that these same centers have cross sections of 10^{-15} to 10^{-13} cm^2 for holes.

5.0 A SINGLE CLASS OF DISCRETE STATES

This section is a generalization and in some ways a simplification of an earlier discussion[7] in which the emphasis was placed on one sign of carrier. Some of the earlier results will be referred to where there is no need for reporducing the arguments.

5.1 CARRIER CONCENTRATION SMALL COMPARED WITH GROUND STATE CONCENTRATIONS

Figure 2(a) shows an insulator in the dark. A set of discrete states has been assumed lying near the Fermi level. Those below the Fermi level are essentially filled with electrons and those above are essentially empty.

[3] The concentration of free electrons is, in the case of thermal equilibrium, given by $n_c = N_c e^{-E_f/kT}$, where E_f is the energetic distance of the Fermi level from the conduction band. This same relation may be used to *define* a steady-state value of the Fermi level when the steady-state concentration of free electrons is given. The steady-state Fermi level was used in reference 7 and has been used in the analysis of transistors by W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950). In the analysis of transistors, it is called a quasi-Fermi level and is a mathematical device to describe the concentration of free carriers. Such use needs no justification other than convenience. The validity of its use in the present paper, however, depends on how faithfully it describes the occupancy of trapping states as well as the occupancy of free states from which it was defined.

[4] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953).
[5] R. W. Smith, RCA Rev. **12**, 350 (1951).
[6] R. H. Bube and S. M. Thomsen, J. Chem. Phys. (to be published).
[7] A. Rose, RCA Rev. **12**, 362 (1951).

In Fig. 2(b) an excitation process has been introduced such that the discrete states lie between the two steady-state Fermi levels and therefore qualify as ground states. The excitation is low enough that the free carrier concentrations, n and p, are kept small compared with the ground state concentrations, n_0 and p_0. This is the usual condition under which photoconductors operate.

If the rate of excitation is $f(\text{cm}^{-3}\ \text{sec}^{-1})$,

$$f = vs_n n p_0 = vs_p p n_0, \tag{1}$$

where v is the thermal velocity of a carrier and s_n, s_p are the capture cross sections of ground states for electrons and holes respectively. In words, this says that, in the steady state, electrons must pour out of the conduction band at the same rate as they are poured in; holes must pour out of the filled band at the same rate as they are poured in, and electrons and holes must pour into the ground states at identical rates. All of the above must be true, else charge would accumulate indefinitely in any of the three places.

The important simplifying fact is this: if the concentrations of free carriers are small compared with the concentrations in the ground states, then, to the same approximation the concentrations of electrons and holes in the ground states remain the same after excitation as they were before excitation. The validity of this statement follows readily from the condition of charge neutrality.

Thus, in Eq. (1), n_0 and p_0 are the concentrations of electrons and holes in the ground states that existed in the dark *before* exposure to light. From Eq. (1):

$$n = f/vs_n p_0, \tag{2a}$$

$$p = f/vs_p n_0. \tag{2b}$$

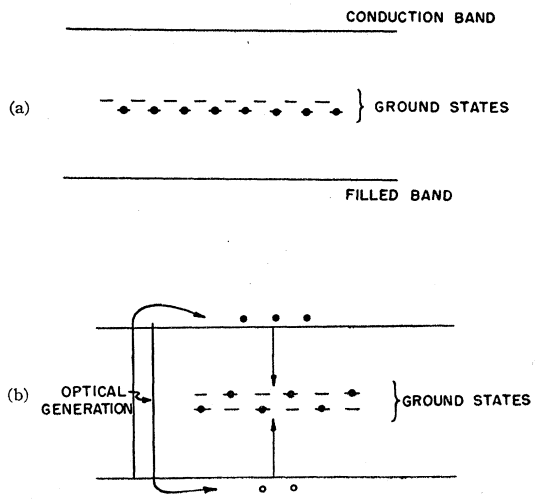
The concentrations of free electrons and holes are determined *independently* by the concentrations and capture cross sections of their respective ground states. From Eq. (2):

$$\text{lifetime of an electron} = (vs_n p_0)^{-1}, \tag{3a}$$

$$\text{lifetime of a hole} = (vs_p n_0)^{-1}. \tag{3b}$$

Because these lifetimes are constants, independent of the number of free electrons, the concentration of free electrons will increase linearly with light intensity or other excitation means. The same is true independently for the concentration of free holes.

When the light is suddenly turned off, the free electron concentration will decay exponentially in time, the concentration falling to e^{-1} of its initial value in $(vs_n p_0)^{-1}$ seconds. The free hole concentration will also decay exponentially and independently at the rate of $(vs_p n_0)^{-1}$ seconds to fall to e^{-1} of its initial value. It is significant here that there are two independent time constants to be associated with a free pair. It is also significant, and to be contrasted with later discussion,



FIGS. 2(a) and (b). Model showing one class of ground states at low excitation rate.

that the lifetime of a free carrier and the observed decay time of its current are one and the same time.

While the numbers of electrons and holes in the ground states remain the same after excitation as before, their distribution does not. Before excitation, the electrons lay below the dark value of the Fermi level and the holes above. After excitation, electrons and holes are uniformly dispersed among the ground states. Any given ground state is occupied on the average $n_0/(n_0+p_0)$ of the time by an electron and $p_0/(n_0+p_0)$ of the time by a hole.

This uniform dispersion of electrons and holes in the ground states can lead to a long-time, low-level tail on the decay curve of photocurrent during which time the thermal distribution of Fig. 2(a) is being re-established. The uniform dispersion also gives some meaning to the phrase "filling of traps." In this case, the upper states that were empty before excitation are now half filled with electrons. Similarly, the lower states that were filled with electrons before excitation, are now only half filled. If the optical excitation had been carried out at a low temperature, this non-equilibrium distribution of electrons and holes would have been "frozen in." Raising the temperature would allow thermal excitation into the free bands and subsequent recombination into the thermal equilibrium distribution of Fig. 2(a). The thermal excitation into the free bands is the seat of the conductivity "glow curve"; the subsequent recombination if radiative is the seat of the luminescence "glow curve."

5.2 BOTH CARRIER CONCENTRATIONS LARGE COMPARED WITH THE GROUND STATE CONCENTRATIONS (FIG. 3)

Let the concentrations of free carriers both be large compared with the concentration of ground states. Then, according to the charge neutrality condition, the

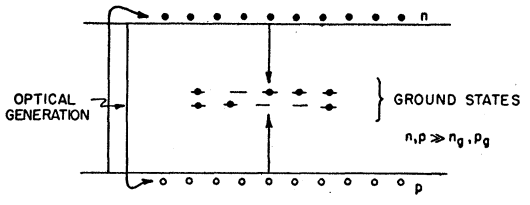


FIG. 3. Model showing one class of ground states at high excitation rate.

concentration of free electrons must be equal to the concentration of free holes—to the approximation given by the ratio of ground states to free carriers. The concentrations of electrons and holes in the ground states need not remain the same after excitation as they were before excitation. Only the sum of the two concentrations is fixed and must, of course, equal the total concentration of ground states. The average occupancy of the ground states by electrons and holes may easily be computed and may bear almost no relation to their initial occupancy.

The rate at which electrons pour into the ground states must equal the rate at which holes pour into the ground states. For this reason and because the concentrations of free electrons and holes are equal, their lifetimes must be equal. (In the previous case of low carrier concentration, the number and lifetimes were, in general, not the same for electrons and holes.) The lifetime is given by:

$$\text{lifetime of electron} = (vs_n p_g)^{-1} = \text{lifetime of hole} = (vs_p n_g)^{-1}. \quad (4)$$

From Eq. (4),

$$n_g = \frac{s_n}{s_n+s_p} N_g, \quad (5a)$$

$$p_g = \frac{s_p}{s_n+s_p} N_g, \quad (5b)$$

where N_g is the total concentration of ground states, n_g+p_g. From Eqs. (4) and (5),

$$\text{lifetime of electron (or hole)} = \left[v\left(\frac{s_n s_p}{s_n+s_p}\right) N_g \right]^{-1}. \quad (6)$$

Equations (5) say that a given ground state will be occupied $s_n/(s_n+s_p)$ of the time by an electron and $s_p/(s_n+s_p)$ of the time by a hole. These are to be contrasted with the corresponding fractions n_g^0/N_g and p_g^0/Ng obtained for the case of low carrier concentrations. n_g^0 and p_g^0 are the initial dark concentrations; n_g and p_g are the concentrations under high light conditions. Only by accident will these two sets of fractions have the same numerical values.

The free electron and hole concentrations are given from Eq. (6) by

$$n = p = f\left[v\frac{s_n s_p}{s_n+s_p} N_g \right]^{-1}. \quad (7)$$

These concentrations are, again as in the low-light case, proportional to the rate of excitation f, since the lifetime of Eq. (6) is a constant.

It is worth noting that at high rates of excitation there is no "saturation" of the ground states that might give meaning to the phrase, "saturation of recombination centers," referred to at the beginning of this paper. The rate of excitation may, indeed, be arbitrarily high without in any sense clogging the recombination paths.[8]

A comparison of the lifetimes at low light intensities, Eq. (3), with the single lifetime at high light intensities, Eq. (6), shows that the two low-light lifetimes either straddle the high-light lifetime or are equal to it. The latter is a fortuitous occurrence when the two low-light lifetimes are equal to each other. In general then, there is an intermediate region between low light intensities and high light intensities in which the two low-light concentrations, n and p, converge to their common high-light value (see Fig. 4). A photoconductivity measurement favors the longer of the two lifetimes and will have the shape of the upper curve in Fig. 4.

The particular form of the convergence of the n and p curves in the intermediate region of Fig. 4 depends upon the values of s_n, s_p, n_g, and p_g. An example of particular interest to photoconductors is described in the next section.

5.3 CARRIER CONCENTRATIONS INTERLACED WITH GROUND STATE CONCENTRATIONS (FIG. 5)

It would be fortuitous to find the two ground state concentrations n_g and p_g equal within a factor of two. It is more likely that the ratio of these concentrations is

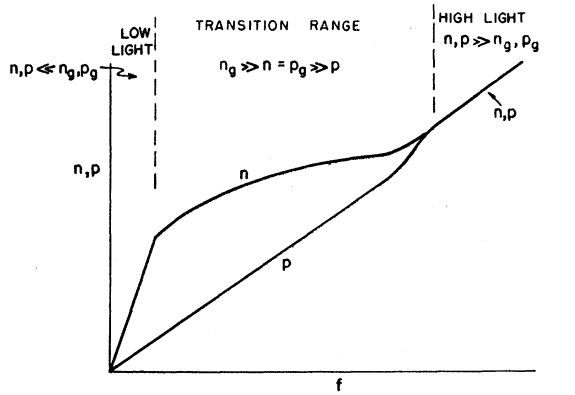


FIG. 4. Schematic description of electron and hole concentrations as a function of rate of excitation. The photocurrents are proportional to these concentrations.

[8] Clogging of the recombination centers could occur if the act of recombination itself occupied a finite time. That time has been assumed to be negligible in this discussion.

measured by factors of ten. This allows the range between high-light intensities and low-light intensities to be described by the conditions:

$$n_g \gg n \doteq p_g \gg p, \tag{8}$$

or the parallel set obtained by interchanging n and p. In Eq. (8), n_g is a constant and equal to its value before excitation. p_g remains approximately equal to n.

The free electron concentration is, since $p_g \doteq n$,

$$n = f/vs_n n, \tag{9a}$$

or

$$n = (f/vs_n)^{\frac{1}{2}}. \tag{9b}$$

It is to be noted that this is the first instance of a bimolecular recombination process. The free electron concentration increases only as the square root of the light intensity (Fig. 4). The lifetime of a free electron $(vs_n n)^{-1}$ is, of course, dependent on the free electron concentration and decreases as the electron concentration increases.

The free hole concentration is, by Eq. (8), small compared with the free electron concentration. The free hole concentration, however, increases linearly with light intensity:

$$p = f/vs_p n_g. \tag{10}$$

As the high-light condition is approached, n_g in Eq. (10) is no longer constant but changes rapidly to its high-light value as shown in Fig. 4.

5.4 EFFECT OF ADDING SHALLOW TRAPPING STATES (FIG. 6)

In the previous sections only ground states and free states were considered. A common characteristic of the recombination processes was that the lifetimes computed for the free carriers were also the observed decay times for photocurrents. The chief effect of the addition of shallow trapping states, as in Fig. 6, is to cause the observed decay time (also rise time) for currents to exceed the lifetime of free carriers by the ratio of trapped to free carriers (see also reference 4). The excitation process must now generate not only the number of electrons in the free states but also those in the shallow trapping states. The rise time in the excitation process is therefore lengthened by the ratio of trapped to free carriers. In the case of some relatively insulating photoconductors, such as are used in the

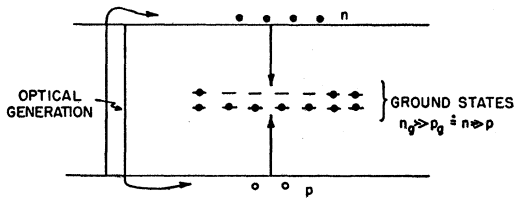


FIG. 5. Model showing conditions for intermediate range of excitations.

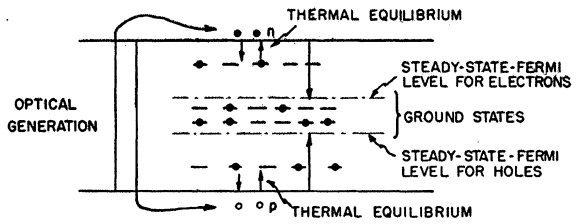


FIG. 6. Model showing both shallow trapping states and ground states.

television pickup tubes of the Vidicon[9–11] type, this ratio may easily exceed 10^6. Similarly, when the excitation is removed, not only must the free electrons recombine into ground states but also the shallow trapped electrons must be emptied via the conduction band into the ground states. This lengthens the decay time of the observed photocurrents by the ratio of trapped to free carriers.

Since the shallow traps are in thermal equilibrium with the free carriers, the ratio of trapped to free carriers is easily computed to be

$$n_t/n = (N_t/N_c)e^{\Delta E/kT}, \tag{11}$$

where N_t is the number of traps at the level ΔE below the conduction band and $N_c = 10^{19}/\text{cm}^3$ at room temperature. This ratio is not dependent upon the light intensity. Accordingly, the rise and decay times of the photocurrents will be a constant multiple of the free carrier lifetime, and independent of light intensity. It must be remembered that at sufficiently high light intensities the shallow trapping states of Fig. 6 will become part of the group of ground states and the problem reverts then to one of those already discussed in Sec. 5.2.[12]

The introduction of the shallow trapping states also gives some meaning to the phrase "filling of traps." The meaning, however, is perhaps not that normally attached to the phrase. For example, the shallow traps are not actually filled, but only partly occupied in accordance with the Fermi distribution function. Nor does the filling affect the steady-state current but only the rise and decay times. Equations (2) are still valid for the steady-state concentrations.

5.5 EFFECTS OF A CONTINUOUS DISTRIBUTION OF DISCRETE STATES

The models discussed thus far have accounted for linear current-light curves and for observed response times much larger than the actual lifetime of a free carrier in the conduction or filled bands. It is frequently found, however, for the relatively insulating photoconductors in the low-light range, that the photocurrent increases as a fractional power of the light

[9] Weimer, Forgue, and Goodrich, Electronics **23** (1950).
[10] P. K. Weimer and A. D. Cope, RCA Rev. **12**, 314 (1951).
[11] Forgue, Goodrich, and Cope, RCA Rev. **12**, 335 (1951).
[12] The shallow trapping states of Fig. 6 are assumed to have the same capture cross sections as the ground states.

intensity, the fraction lying between 0.5 and 1.0. Further, the observed speed of response becomes faster with increasing light intensity. The rate of change of speed of response with light intensity is more rapid than can be accounted for by the fractional power of the current-light curve. For example, for CdS crystals the photocurrent has been observed to increase as the 0.9 power of the light intensity, while the decay time for the photocurrent varies almost inversely with light intensity.[5]

Both the fractional powers and the change of speed of response with light intensity are readily accounted for in terms of the model shown in Fig. 7. Here a quasi-continuum of discrete states has been assumed. As the light intensity is increased, the steady-state Fermi levels draw apart and embrace a larger number of ground states. The larger numbers of ground states shorten the lifetimes of the free carriers and thereby lead to fractional powers of the current-light curve. A detailed discussion of various discrete state distributions was carried out in reference 4. There it was shown that if the discrete states are distributed below the conduction band in the form $e^{-\Delta E/kT_c}$, the current light curve should have the power $T_c/(T+T_c)$. Here ΔE is measured from the bottom of the conduction band and T_c is a characteristic temperature greater than or equal to the temperature of measurement T.

Inspection of Fig. 7 shows also how the speed of response can vary rapidly with light intensity. The response time is given by $\tau n_t/n$, where τ is the lifetime of a free electron and n_t/n is the ratio of trapped to free carriers. For a uniform, or near uniform, distribution of discrete states, the lifetime τ is substantially constant. The variation with light intensity just discussed is a slow variation. Also, the number of trapped electrons is substantially constant and given by the number of discrete states within kT of the steady-state Fermi level. The number of free carriers, however, increases almost proportional to the light intensity and reduces the response time at the same rate.

Figure 7 leads also to a t^{-1} form for the decay curve rather than an exponential. This matches frequent observations in which a near linear current-light curve, suggesting a monomolecular process, was accompanied by a t^{-1} decay curve normally characteristic of a bimolecular process.

The model of Fig. 7 is properly subject to the criticism that it is elaborate enough to explain any observations. For this reason two statements need to be emphasized. First, no model short of the complexity of Fig. 7, can logically account for the combined observations of a near linear current-light curve and a response time that varies as the reciprocal light intensity. Second, in spite of the complexity of Fig. 7, there are still several first order observations that cannot be accounted for by this model. These observations require the addition of another class of discrete states. The properties of such a model are discussed in the following section.

6.0 TWO CLASSES OF DISCRETE STATES

Figure 8(a) shows schematically a model with two classes of ground states in thermal equilibrium in the dark. The shallow trapping states are omitted to emphasize the significant properties of this model. Figure 8(b) shows the same model under steady excitation. A particular redistribution of electrons and holes in the ground states has been selected.

At low excitation levels (free carrier concentrations small compared with ground state concentrations) the total numbers of electrons and of holes in the ground states must remain substantially the same after excitation as they were before. A redistribution of these electrons and holes amongst the ground states, however, is free to take place.[13] It is this redistribution that can readily account for (1) activation or sensitization of a photoconductor by the addition of discrete states, (2) infrared quenching, and (3) superlinearity.

The particular redistribution to be expected at low light intensities in the model of Fig. 8 can be obtained in a closed mathematical form. It is an involved expression containing eight parameters—four capture cross sections and four ground state concentrations. The solution for the free electron concentration is reproduced here only to show that this is not a simple problem and to suggest caution in trying to reconstruct the proper model from a few experimental data.

$$n=\frac{f}{v\left[(s_{n1}-s_{n2})\dfrac{G_1}{1+rr_1}+s_{n2}P_g\right]}, \tag{12}$$

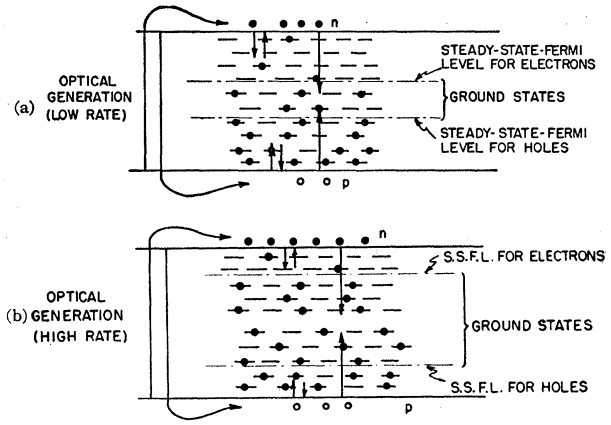
where

$$r=\frac{[N_g(r_1+r_2)-r_1G_1-r_2G_2]\pm\{[N_G(r_1+r_2)-r_1G_1-r_2G_2]^2-4r_1r_2N_gP_g\}^{\frac{1}{2}}}{2r_1r_2P_g},$$

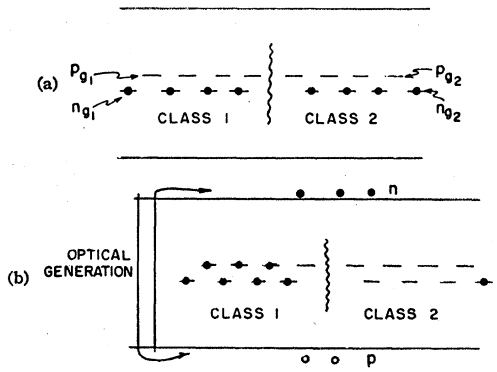
$r_1=s_{n1}/s_{p1}$, $r_2=s_{n2}/s_{p2}$, $G_i=$ sum of ground states in the ith class, $N_g=$ sum of electrons in both classes, and P_g the same sum for holes. The physics of the problem is not readily revealed by this solution.

The purpose of the following discussion is to show qualitatively that the three items just enumerated which could not be accounted for by a model having

[13] The redistribution of electrons and holes in the ground states does not take place directly between these states but rather by the intermediate process of excitation into the filled or conduction bands.



FIGS. 7(a) and (b). Model showing continuous distribution of discrete states. Increased rate of excitation adds more states to the ground state category and thereby leads to shorter lifetimes of the free carriers. This model readily accounts for the current-light curves having noninteger powers between 0.5 and 1.0.



FIGS. 8(a) and (b). Model showing two classes of ground states. The classes are drawn separated but are actually physically interspersed. Class 1, by itself, leads to a high rate of recombination. Class 2, by itself, leads to a low rate of recombination.

one class of discrete states can be accounted for by a model having two classes of discrete states.

6.1 ACTIVATION

In Fig. 8 let the discrete states of Class I be such that by themselves the lifetime of free carriers would be short. That is, Class I by itself would make the photoconductor fast and insensitive. The problem is to show that the addition of other discrete states, those in Class II, can actually slow down the recombination process and extend the lifetime of one of the free carriers so that the photoconductor actually becomes more sensitive.

For convenience of discussion, let the four ground state concentrations in Fig. 8a, n_{g1}, p_{g1}, n_{g2}, p_{g2} be nearly equal, n_{g2} exceeding the others by a factor of 2. Let the capture cross sections of the states in Class I be 10^{-15} cm^2 both for free electrons and for free holes. Let the capture cross section of the states in Class II be 10^{-15} cm^2 for free holes and 10^{-20} cm^2 for free electrons. In the absence of the Class II states, the lifetime of a free electron or hole is $(vs_{n1}n_{g1})^{-1}$ with $s_{n1}=10^{-15}$ cm^2. For $n_{g1}=10^{15}$/cm^3, this time is 10^{-7} seconds. The photoconductor is thus fast and insensitive.

The addition of Class II states has the following effect. Holes falling into Class II states become in a sense "trapped." That is, the Class II states do not readily capture electrons. The immediate consequence is that many of the electrons in the Class II states are transferred[13] to the Class I states, thereby sharply reducing the ability of the Class I states to capture free electrons. Free electrons have difficulty in recombining both because the Class II states have a small capture cross section and because the Class I states have a small number of available places. The lifetime of a free electron now approaches $(vs_{n2}n_{g2})^{-1}$, where $s_{n2}=10^{-20}$ cm^2. This time is about 10^{-2} second. The lifetime for free holes, meantime, has been shortened somewhat owing to the increase in the number of hole-capturing ground states. The sensitivity of the photoconductor has been increased by a factor of 10^5 owing to the long-lived electrons. This increase in sensitivity has been brought about by actually adding recombination paths.

The above example is entirely illustrative. There are obviously many choices of parameters that would lead to the same type of result. Also, there are many other behavior patterns derivable from other choices of parameters. The important fact is that the presence of two classes of ground states permits a significant redistribution of electrons and holes to take place. In this example, the second class was so chosen as to sensitize the photoconductor. Other choices can lead to de-sensitization.

Several basic conclusions can be drawn from the above argument. If one calls the Class II states activators or activating centers, these centers need not be hole traps in the absolute sense—that is, having zero capture cross section for electrons. The states need only have a smaller cross section for electrons than for holes. Second, the Class II states are not to be regarded as the "seat" of the photosensitivity. The light does not have to be absorbed by these states nor, in the steady state, does a significant amount of excitation energy have to migrate to the states.[6] The Class II states contribute to sensitivity by effecting a redistribution of electrons and holes among the ground states which redistribution increases the lifetime of all the free electrons. This conclusion is important for a proper estimate of the noise properties of the photoconductor.

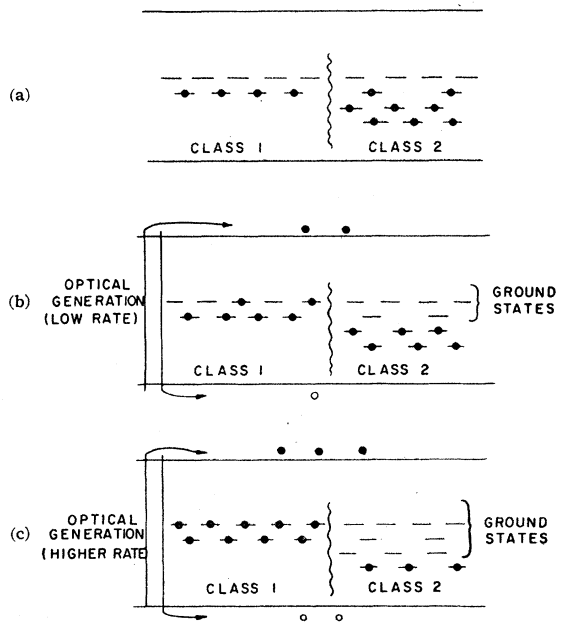
Shulman[14] has shown that the noise properties of a photoconductor with ohmic contacts can be referred back to the noise properties of the incident photon stream. If one argued that activator centers in some way absorbed only part of the incident radiation, the rest of the radiation being somehow "lost" in

[14] Shulman, Smith, and Rose, Phys. Rev. 92, 857 (1953).

insensitive parts of the photoconductor, the photoconductor would be "noisier" than if all of the radiation were effectively used. The present argument leads to the conclusion that activating centers (Class II states) can continuously sensitize the photoconductor by continuously increasing the lifetime of free electrons in such a way that all of the incident photons contribute equally to the photocurrent. The noise properties should then be referred back to all of the incident photon stream even for "partially" activated photoconductors.

The model of Fig. 8 also gives some meaning to the "latent" periods observed by Frerichs[15] and others. Frerichs observed that CdS crystals kept in the dark for a long time and then exposed to a low density of excitation required a long period to develop their photocurrents. The photocurrent *versus* time curve bent sharply upward. (The increase of rise time brought about by shallow trapping states and discussed in Sec. 5.4 still retains the downward curvature of the current *versus* time curve and does not fit here.) The same latent period can often be observed after a CdS crystal has had a strong exposure to infrared quenching radiation.

It is as if the radiation were activating the crystal. Frerichs interprets this observation as a "filling of deep traps." The interpretation to be derived from Fig. 8 is that time is required to transfer electrons from Class II to Class I states. During this time the photoconductor is indeed being activated by the radiation. The simple presence of "deep traps" is not sufficient nor does the phrase "filling of deep traps" completely describe the redistribution taking place in Fig. 8.



FIGS. 9(a), (b), (c). Model showing how two classes of ground states can account for superlinear current-light curves.

[15] R. Frerichs, Phys. Rev. **76**, 869 (1949).

6.2 INFRARED QUENCHING

In terms of Fig. 8(b), the effect of infrared in reducing or quenching the photoconductivity already established by shorter wavelength radiation can readily be understood. Infrared can excite electrons from the filled band into the substantially empty Class II states, the the free holes being captured by Class I states. In this way infrared tends to shift the distribution in the ground states from the sensitive form of Fig. 8(b) to the insensitive form of Fig. 8(a). In brief, its effect on the ground states is exactly counter to the effect of short-wavelength radiation.

After exposure to infrared, a latent period is likely to be encountered during which the short-wavelength radiation re-establishes the favorable distribution in the ground states.

If the Class I states represent radiationless transitions and the Class II states radiation transitions, the infrared quenching model holds also for luminescence.

6.3 SUPERLINEARITY

A model for superlinearity can be derived from Fig. 8 by distributing the Class II states over a range of energies. This is shown in Fig. 9. Figure 9(a) shows the distribution of electrons and holes in the ground states in the dark. Figure 9(b) shows the distribution for a small amount of excitation and Fig. 9(c) for a larger amount of excitation. Essentially, as the excitation is increased the steady-state Fermi levels move apart and include more of the Class II states in the ground state category. This allows steadily more electrons to be transferred from the Class II states to the Class I states. Such transfers tend to sensitize the photoconductor in the manner already described by increasing the lifetime of free electrons. Since the sensitization increases with light intensity the current-light curve is superlinear.

6.4 HIGH EXCITATION

The discussion of the recombination properties of two classes of ground states has thus far been confined to the range of low excitations for which the free carrier concentrations are small compared with the ground state concentrations. Under these conditions the ground states interact with each other in the sense of exchanging their electrons and holes, subject to the condition that the total numbers of electrons and of holes are *separately* maintained constant. At high-light intensities, for which the carrier concentrations are large compared with the ground state concentrations, only the sum total of electrons and holes in each class of ground states remains constant and, of course, equal to the sum of the ground states in that class. At high-light intensities, also, the free carrier concentrations are equal. The consequence is that there

is no longer interaction between the ground states. Each ground state acts independently to adjust its behavior to the free carrier concentration. In particular, each ground state will contain an electron $s_n/(s_n+s_p)$ of the time and a hole $s_p/(s_n+s_p)$ of the time. These occupancy fractions are not affected by the presence of other ground states. A photoconductor cannot be sensitized as it was in the low-light range by the addition of ground states. The addition of ground states must shorten the lifetime of both carriers and desensitize the photoconductor.

The foregoing argument means that the photoconductor of Fig. 8 that was made 10^5 times more sensitive in the low-light range by the addition of Class II states reverts at high light intensities to its initial low sensitivity. The current-light curve will actually appear to saturate at high light intensities because of this low sensitivity. In the intermediate range, the current will have a very low power dependence on light intensity. This power may approach close to zero and give the current-light curve a distinct appearance of saturation. In this intermediate range the free electron concentration is exceeding the concentration of Class II states. In this sense, the Class II states are being saturated. Strictly, however, the saturation of the current-light curve is a reflection of the shift in ground state occupancy from the low-light conditions to the high-light conditions.

7.0 SEMICONDUCTORS

A special problem will be discussed, partly to show how the semiconductor problem differs from the insulator problem and partly to demonstrate the present method of analysis.

Figure 10 shows a semiconductor having one level of ground states N_g below the thermal equilibrium value of the Fermi level.[16] The concentration of thermally produced electrons n is taken to be large compared with the concentration of ground states.[17] The concentration of thermally produced holes is assumed to be negligible. This semiconductor differs from the insulator models already discussed in two significant respects. First, there is a large concentration of free electrons ready to pour into any holes in the ground state. Second, the ground states, prior to generation of additional carriers, are substantially filled with electrons.

7.1 LOW LIGHT EXCITATION

Let the carriers n and p added by excitation be small compared with the ground state concentration

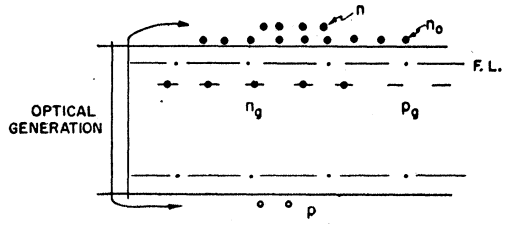


FIG. 10. Semiconductor with one class of ground states. See text for the meaning of the lower dashed line.

N_g. Then

$$f=vs_n(n+n_0)p_g=vs_ppn_g \doteq vs_nn_0p_g \doteq vs_ppN_g. \quad (13)$$

From Eq. (13),

$$p/p_g=n_0s_n/N_gs_p. \quad (14)$$

Since s_n and s_p may be chosen arbitrarily, this ratio may be greater or less than unity. If $p \gg p_g$, then $n \doteq p$ and

$$\text{lifetime of electron} = \text{lifetime of a hole} = (vs_pN_g)^{-1}. \quad (15)$$

If $p_g \gg p$ (this requires $s_p/s_n \gg n_0/N_g$), then since at all times $n=p+p_g$, it follows that

$$n/p \doteq p_g/p. \quad (16)$$

Equation (16) says that the lifetime of the added electrons will be p_g/p times the lifetime of the added holes.[18] From Eq. (13),

$$\text{lifetime of hole} = (vs_pN_g)^{-1}. \quad (17)$$

From Eqs. (17), (16), and (14),

$$\text{lifetime of electron} = (vs_nn_0)^{-1}. \quad (18)$$

Here, then, the electron and hole concentrations are independently determined by the parameters in Eqs. (17) and (18).

7.2 HIGH-LIGHT EXCITATION

Let the extra carrier concentrations n and p be large compared with the ground state concentration N_g and the thermally produced electrons n_0. This immediately duplicates the high-light insulator problem, namely $n=p$ and

$$\text{electron lifetime} = \text{hole lifetime} = \left(v\frac{s_ns_p}{s_n+s_p}N_g\right)^{-1}. \quad (19)$$

A comparison of the high-light lifetime [Eq. (19)] with the possible low-light lifetimes [Eqs. (15), (17), (18)] shows that the high-light value is always greater than or equal to the low-light values. That is, the semiconductor can be more sensitive at high-light intensities than at low-light intensities. This is to be contrasted

[16] The problem of recombination in a semiconductor having one level of discrete states has been treated more extensively by R. N. Hall, Phys. Rev. **87**, 387 (1952) and W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).

[17] Under these conditions, the demarcation line for holes separating shallow trapping states from ground states is located the same distance from the filled band as the dark Fermi level is from the conduction band plus the correction term $kT \times \ln(s_p/s_n)$.

[18] This case is apparently not treated in reference 16. It would account for the fact that the photoconductive decay time does not always give the lifetime of a free pair. The photoconductive measurement gives the longer of the two lifetimes; the lifetime of a free pair is by definition the shorter of the two lifetimes.

with the insulator problem, where a single class of recombination centers could not lead to superlinearity. Two classes were required.

If, in Fig. 10, the single level of discrete states had been located above the Fermi level instead of below it, Eq. (19) for the high-light lifetime would not be altered. However, the low-light lifetime could be made arbitrarily long as the level of discrete states is raised above the Fermi level. The effectiveness of these states for recombination decreases at room temperature by about a factor of 100 for every tenth of a volt above the Fermi level owing to the low thermal density of electrons in them. This is very much the same argument already used in this paper to separate discrete states into shallow trapping states and ground states. Those states lying outside the Fermi limits lose their effectiveness for recombination at the same rate cited above.

If the level of discrete states had been located above the Fermi level, it would then be possible for the high-light lifetimes to be smaller than the low-light lifetimes. Other factors tending in the same direction are discussed in the next section.

7.3 MORE THAN ONE CLASS OF GROUND STATES

If a second class of ground states is added to the semiconductor, its effect in the high-light range (Sec. 7.2) can only be that of adding more recombination paths and of *shortening* the lifetime of both carriers. This statement is independent of the capture cross sections and energy distribution of the Class II states.

The addition of a second class of ground states in the low-light range (Sec. 7.1) can have more varied effects. If the free electron and hole concentrations remain equal after the addition of the Class II states, the lifetime of both carriers is shortened just as it is for the high-light case. This follows from the fact that the addition of more states must shorten the lifetime of a hole, since they provide more places into which a hole can jump. The lifetime of the electron, being equal to that of a hole, must likewise be reduced.

If, in the low-light range, the free electrons and free hole concentrations are not equal, the addition of Class II states must still shorten the lifetime of the minority carrier, but it may either increase or decrease the lifetime of the majority carrier. For example, let an n-type semiconductor have most of its optically created holes in ground states. Under these conditions the number of optically created electrons is essentially equal to the number of holes in ground states. (The conditions of Fig. 10 are assumed here, that is, negligible trapping states between the Fermi level and the conduction band.) There is now a one-to-one correspondence between extra electrons in the conduction band and holes in the ground states. This was not true for the insulator problem discussed in Sec. 5. The addition of Class II states means that some of the holes will be diverted from Class I states to Class II states. If the Class II states have the same capture cross section for electrons as the Class I states, the electron concentration will not be affected. If this capture cross section is greater, the electron concentration will be reduced. Conversely, and this is the significant possibility, if the Class II states have a very small capture cross section for electrons, a large number of holes will congregate in the Class II states and give rise to a large number of extra free electrons. The effect of these states will have been to sensitize the semiconductor as a photoconductor by increasing the free electron concentration. At the same time the lifetime of free pairs has been decreased, since the lifetime of free holes has been decreased.

The type of sensitization just discussed has a fundamental bearing on the noise properties of a photoconductor. In Sec. 5 it was pointed out that a photoconductive insulator could be continuously sensitized by the addition of Class II states without destroying the ability of the photoconductor to reproduce the noise properties of the incident photon stream. In other words, all incident photons make an equal contribution to the photocurrent. In the present instance it becomes possible for the photoconductor to be noisier than the photon stream owing to the addition of sensitizing Class II states. The reason is that it is now possible for only a small fraction of the incident photon stream to contribute holes to the Class II states. At the same time, since the number of holes in the Class II states and their corresponding free electrons are greater than those for the Class I states the observed current will be chiefly that associated with the Class II states. This current must be noisier than the incident photon stream since only a small fraction of the incident photon stream is used in producing the current. (The term "is noisier than" is used here as a shorthand way of saying, "has a smaller signal-to-noise ratio than.")

The fact that Class II states can sensitize a photoconductor in the low-light range and, at the same time, must desensitize it in the high-light range means that the current-light curve of a sensitive semiconducting photoconductor will appear to saturate at high lights. Effects of this kind have been observed for semiconducting crystals CdS.[19] The term "saturation of recombination centers" takes on here a very simple meaning since the number of holes in the ground states must be essentially equal to the number of added electrons in the conduction band. Accordingly, a given class of ground states can support only as many free electrons as there are states in this class. As the number of added free electrons exceeds the number of states in a given class, that class is saturated and other less sensitive classes are forced to take part in the recombination process.

[19] R. H. Bube and R. W. Smith (unpublished).

SUMMARY

In the terms of the present discussion various recombination problems are identified by choosing one characteristic in each of the following categories:

material:	insulator, semiconductor;
excitation range:	low, intermediate, high;
character of ground states:	one class, more than one class
lifetime:	electron, hole, free pair.

Over thirty problems are defined by this table. It is not appropriate here to try to summarize these problems individually but rather to see what general remarks can be made.

(1) In the "high-light" range, electron, hole, and free pair lifetimes are all equal.
(2) In the "high-light" range, the addition of discrete states has only one effect, namely, to reduce the lifetime of both electrons and holes.
(3) In the low-light range, electron and hole lifetimes are independent, as are their concentrations. This is always true for insulators and almost always true for semiconductors. The exception occurs for semiconductors in which the capture cross sections allow electron and hole concentrations to be equal (Sec. 6.1).
(4) In the low-light range the addition of discrete states may reduce the lifetimes of both electrons and holes or may reduce the lifetime of one carrier and increase the lifetime of the other carrier. The latter possibility constitutes the activation process whereby a photoconductor is made more sensitive.
(5) In the low-light range the addition of discrete states always reduces the lifetime of a free pair, since the lifetime of a free pair takes on the shorter of the two carrier lifetimes.
(6) In the high-light range, the carrier concentrations always increase linearly with increase in rate of excitation.
(7) In the low-light range the power of the carrier concentration *versus* excitation curve may take on any values greater than 0.5. Values between 0.5 and 1.0 are derivable from distributions in energy of a single class of discrete states. Values greater than unity are derivable from a distribution in energy of more than one class of discrete states.
(8) If an insulator or semiconductor has been highly sensitized in the low-light range by the addition of more than one class of discrete states, then (see Fig. 4) the majority carrier concentration *versus* excitation curve is likely to have a power less than or equal to 0.5 in the intermediate range.
(9) In the intermediate range, the power of the minority carrier concentration *versus* excitation curve is likely to be greater than unity.
(10) The capture cross sections of discrete states for electrons and for holes are likely to be markedly different owing to the presence of an attractive Coulomb field for one sign of carrier and a zero or repulsive Coulomb field for the opposite sign of carrier.
(11) An ideal photoconductor is a noiseless transformer of photon current into photocurrent. A photoconducting insulator is more likely to retain this property during activation than is a photoconducting semiconductor.

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