

icients will be constant. Substitution in Eq. (3) of Lotgering's value of $\mu = -0.8$ for $x=2$ and the value $\mu = 0.9$ at $x=1.3$ (obtained by extrapolation from $x=1.2$ in Fig. 3) gives $n_3/n_1 = 1.3$ and $n_2/n_1 = 0.31$. Using these values for n_3/n_1 and n_2/n_1 in Eq. (3), curve *c* in Fig. 3 was calculated.

The situation in the region $x=0.3$ to $x=1.3$ is more complicated. To begin with, the equation for μ contains an additional Weiss coefficient, n_4 , for the interaction, $A(\text{Fe}^{3+}) - B(\text{Cr}^{3+})$. Also, since the value of u varies considerably in this region, the interaction coefficients are probably not even approximately constant. Fitting the equation to the experimental curve at three points in this region gives the curve *d* and the values $n_2/n_1 = 1.5$, $n_3/n_1 = 0.19$, and $n_4/n_1 = 1.8$. These values for ratios of Weiss coefficients have little meaning as they represent only some sort of average values for the region.

Using the experimental values for μ in the region $x=0$ to $x=0.3$ and assuming inverse structures lead to $n_3/n_2 = 1.7$. Since $n_3/n_2 = 0.13$ (average) and 4.2 in the regions $x=0.3$ to $x=1.3$ and $x=1.3$ to $x=2$, respectively, this ratio does not show a persistent trend as the structure changes from inverse to normal.

IV. SUMMARY

The oxygen parameters were found for the Fe-Cr spinels and support qualitatively the cation arrangements given by Eq. (1). The magnetic measurements agree with these cation arrangements for $x=0$ to $x=0.3$. For higher values of x (at least for $x > 0.5$) the magnetic measurements indicate that the spins of cations on *B* sites are not all parallel, so that the cation arrangements cannot be inferred directly from them. Estimates of the relative strengths of the magnetic interactions and a prediction of the curve of saturation moment (curve *c*, Fig. 3) in the range $x=1.3$ to $x=2$ were made.

Further magnetic moment measurements are needed on the $x=1.2$ sample at lower temperatures to check its value of μ (because of the uncertainty in its temperature extrapolation) and of the samples in the region $x=1.3$ to $x=2$ to check the predicted curve *c* of Fig. 3.

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Decay of Excess Carriers in Semiconductors

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A discussion is given of the nonlinear differential equations which govern the decay of excess carriers with arbitrary densities. The form of decay is explored for situations where the Fermi level is in the same half of the energy gap as the recombination level; criteria are established for both strong and weak trapping in addition to recombinative action. Analytic results are augmented and illustrated by numerically computed decay curves for a variety of circumstances. The separate solutions for holes and electrons are combined to show various kinds of behavior for photoconductive lifetime.

I. INTRODUCTION

AN important recombination process—one which indeed controls the lifetime in many semiconductors—is that whereby a recombination center can accept electrons and holes alternately. Consideration of the transition probabilities between the recombination level and the conduction and valence bands leads to two coupled first-order equations¹ which can describe the buildup, maintenance, and decay of excess hole and electron populations. Steady-state solutions of these equations, which gave expressions for the effective carrier lifetimes, were demonstrated in the well-known

papers of Shockley and Read² and of Hall³; these solutions gave great impetus to studies of recombination.

The S-R treatment dealt only with steady-state recombination and required that either the recombination-center density or the departure from thermal equilibrium be small. A number of subsequent contributions, for instance those of Rittner⁴ and Rose,⁵

² W. Shockley and W. T. Read, *Phys. Rev.* **87**, 835 (1952), hereinafter referred to as S-R.

³ R. N. Hall, *Phys. Rev.* **87**, 387 (1952).

⁴ E. S. Rittner, in *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954*, edited by R. G. Breckenbridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 215.

⁵ A. Rose, in *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954*, edited by R. G. Breckenbridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 3.

¹ E.g., N. Riehl and M. Schön, *Z. Physik* **114**, 682 (1939).

TABLE I. List of symbols.

n_0	= thermal equilibrium electron density in conduction band
p_0	= thermal equilibrium hole density in valence band
Δn	= excess free electron density
Δp	= excess free hole density
$c = (\mu_n/\mu_p)$	= ratio of electron to hole mobility
$\Delta \bar{n} = (c\Delta n + \Delta p)/(c+1)$	
N_t	= density of traps
n_1	= thermal electron density when the Fermi level is at the energy of a nondegenerate trap
p_1	= thermal hole density when the Fermi level is at the energy of a nondegenerate trap.
$C_n = N_t \langle c_n \rangle = 1/\tau_{n0}$	= probability per unit time that an electron will be captured by any of a set of N_t available sites
$C_p = N_t \langle c_p \rangle = 1/\tau_{p0}$	= probability per unit time that a hole will be captured by any of a set of N_t available sites
f_t	= fraction of traps occupied by electrons
$f_{t0} = (1+p_0/p_1)^{-1} = (1+n_1/n_0)^{-1}$	= value of f_t in thermal equilibrium
$x = \Delta n/p_0$	
$y = \Delta p/p_0$	
$a = n_1/p_0$	
$b = p_1/p_0$	
$\gamma = C_p/C_n = \tau_{n0}/\tau_{p0}$	
$\bar{N} = N_t/p_0$	
$\bar{N} = \bar{N}_t/p_0 = \gamma(1+b)^2/(1-\gamma b)$	
$\tau_0 = \tau_{n0}(1+b)$	
$\tau_\infty = \tau_{n0}(1+1/\gamma) = (\tau_{n0} + \tau_{p0})$	
$\tau_1 = \tau_{n0}(1+b)/\gamma b$	
$\tau_2 = \tau_{n0}(1+b)\{\gamma b + \gamma(1+b)^2/N\}^{-1}$	
$T = t/\tau_{n0}$	= normalized time scale

have discussed the more general problem—which can get very complicated. Mathematically, these complexities arise because general analytic solutions for the nonlinear S-R equations are not known. From a more physical standpoint, complexity is anticipated in that any center which has dealings with both the conduction and valence bands combines the dual functions of trapping and recombination.⁶

Some transient solutions of the S-R equations have been reported by several authors⁷⁻¹⁰ for certain restrictive cases. In most instances, solutions were limited to the effects of small excess-carrier concentrations (thus removing the nonlinearities in the differential equations). These treatments also imposed severe restrictions on the parameters of the model. But this rendered their conclusions of limited value, since in practice the parameters governing the recombination process (capture constants, trap energy, etc.) vary very widely between one semiconductor and another. Isay's

approach to the problem¹¹ was different from those of the above authors in that the nonlinear terms of the differential equations were retained; but he sought to force a fit in terms of specific types of function—to the detriment of the underlying physical problem.¹²

It is our intention to explore the transient decay of excess-carrier populations (whether these be large or small) for any values of the controlling parameters.¹³ Some insight into the transformation from purely recombinative to purely trapping character comes from such a study. The following sections are based on analytic solutions where applicable, numerical solutions where convenient, and intuition when all else fails. Such a combination of approaches is called for by the nature of the problem. Indeed Rose remarks¹⁴ “. . . 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.”

In Sec. V, characteristic forms of photoconductive decay are synthesized from the behavior of the excess hole and electron densities. This has an important bearing on the validity of carrier lifetimes inferred from photoconductive measurements.

II. GENERAL DECAY EQUATIONS

Using the customary notation for Shockley-Read² recombination via a set of recombination centers (the symbols used are defined in Table I, the rates at which electrons and holes are captured are

$$-(d\Delta n/dt) = C_n[(n_0 + \Delta n)(1 - f_t) - n_1 f_t], \quad (1)$$

$$-(d\Delta p/dt) = C_p[(p_0 + \Delta p)f_t - p_1(1 - f_t)], \quad (2)$$

where f_t is the fraction of recombination sites occupied by electrons. From the neutrality condition we find that

$$f_t = \left[\frac{\Delta p - \Delta n}{N_t} + \frac{p_1}{p_1 + p_0} \right], \quad (3)$$

which reduces at zero modulation to

$$f_{t0} = p_1/(p_1 + p_0) = n_0/(n_0 + n_1).$$

Hence (1) and (2) can be written as

$$-\left(\frac{d\Delta n}{dt}\right) = \frac{C_n}{N_t} \left\{ \Delta n \left[n_0 + n_1 + \frac{N_t n_1}{n_0 + n_1} \right] - \Delta p(n_0 + n_1) + \Delta n^2 - \Delta n \Delta p \right\}, \quad (4)$$

⁶ The terms “recombination center” and “trap” are used interchangeably in this paper.

⁷ D. J. Sandiford, Phys. Rev. **105**, 524 (1957).

⁸ D. H. Clarke, J. Electron. Control **3**, 375 (1957).

⁹ G. K. Wertheim, Phys. Rev. **109**, 1086 (1958).

¹⁰ G. M. Goureau, Zhur. Eksptl. i Teoret. Fiz. **33**, 158 (1957) [translation: Soviet Phys. JETP **6**, 123 (1958)].

¹¹ W. H. Isay, Ann. Physik **13**, 327 (1953).

¹² For example, concepts such as trapping would tend to be lost in this treatment of the problem.

¹³ As discussed a little later, it is convenient to group the work into two papers dealing with the two principal zones of trap energy. A second paper will describe the situations omitted here.

¹⁴ A. Rose, Phys. Rev. **97**, 322 (1955).

and

$$-\left(\frac{d\Delta p}{dt}\right) = \frac{C_p}{N_t} \left\{ \Delta p \left[p_0 + p_1 + \frac{N_t p_1}{p_0 + p_1} \right] - \Delta n(p_0 + p_1) + \Delta p^2 - \Delta n \Delta p \right\}. \quad (5)$$

We shall choose to discuss primarily the case of a p -type semiconductor; then in making a set of substitutions to dimensionless variables it is convenient to use p_0 as the normalizing parameter. In the notation to be used, $x = (\Delta n/p_0)$ and $y = (\Delta p/p_0)$. Further, we denote $N = (N_t/p_0)$, $a = (n_1/p_0)$, $b = (p_1/p_0)$, $\gamma = (C_p/C_n) = (\tau_{n0}/\tau_{p0})$, and use a dimensionless time scale $T = (t/\tau_{n0}) = tC_n$. In this notation, $x' = (dx/dT)$, etc.

When the appropriate substitutions are made, (4) and (5) can be rewritten as

$$-Nx' = (x-y)[x+a(1+b)] + Nx/(1+b), \quad (6)$$

$$-(N/\gamma)y' = (y-x)[y+1+b] + Nby/(1+b). \quad (7)$$

These can be solved simultaneously to get equations for x and y separately:

$$N\{y''(y+1+b) - y'^2(1-1/\gamma)\} + y'\{y^2(1+\gamma) + y[(1+b)(1+a+2\gamma) + N(1+2b)/(1+b)] + [(1+b)^2(a+\gamma) + N(1+\gamma b)]\} + \gamma y\{y^2 + y[(2+b+ab) + Nb/(1+b)] + [(1+b)(1+ab) + Nb/(1+b)]\} = 0, \quad (8)$$

$$N\{x''[x+a(1+b)] - x'^2(1-\gamma)\} + x'\{x^2(1+\gamma) + x[(1+b)(2a+\gamma a+\gamma) + \gamma N(2+b)/(1+b)] + a[(1+b)^2(a+\gamma) + N(1+\gamma b)]\} + \gamma x\{x^2 + x[(1+a+2ab) + N/(1+b)] + a[(1+b)(1+ab) + Nb/(1+b)]\} = 0. \quad (9)$$

Analytic solutions for these nonlinear differential equations are known only for restrictive values of N , b , γ , and a ; or when x and y are either very large or very small. When (8) or (9) are reduced to any of the canonical forms given by Ince,¹⁵ the equations either lose their generality or else fall outside the range of interest. Perturbation methods fail when the variables are similar in magnitude to the normalized trap density N : for then all terms are of comparable importance. Accordingly, some otherwise inaccessible cases were solved numerically on an I.B.M.-650 computer. The more restrictive cases were dealt with by approximate methods.

The general problem of electron and hole decay in semiconductors following a burst of generation was divided into two subdivisions. The first of these, Class I, is concerned with semiconductors for which the Fermi level and the recombination level are in the same half of the intrinsic gap; whereas in Class II these levels are in opposite halves of the intrinsic gap. Then, for

¹⁵ E. L. Ince, *Ordinary Differential Equations* (Longmans, Green and Company, London, 1927), p. 317 ff.

example, recombination via levels in the lower half of the intrinsic gap represents a Class II process for an n -type semiconductor, but a Class I process for a p -type semiconductor.

Since it is not necessary to discuss both n - and p -type cases (the solutions for one being derivable from the other by inversion), we have elected to express everything in the formalism of a p -type case. This paper will deal almost exclusively with Class I. Analysis of the Class II process will be published shortly.

In the next two sections, the forms taken by Class I decay processes are discussed as functions of the density and capture asymmetry of the recombination centers. As noted previously, the terms "recombination center" and "trap" are used interchangeably in this paper. For except in a special case we discuss later [where $(\tau_{n0}p_1/\tau_{p0}p_0) = \gamma b = 1$], recombination centers always tend to trap a fraction of either excess majority carriers or minority carriers. The relative importance of trapping *versus* recombination is controlled by the density of centers as well as their asymmetry; but the dual roles are always coexistent.

III. SOME SPECIFIC SOLUTIONS

(a) N Very Small

When N is sufficiently small, many terms in (8) and (9) can be dropped to permit simple solutions for the carrier lifetimes $\tau_n = -\tau_{n0}(x/x')$ and $\tau_p = -\tau_{p0}(y/y')$. How small N must be in order to remove its effect on (8) and (9) depends on the relative magnitude of the various parameters. Thus, for example, in a p -type semiconductor all the terms involving N can always be dropped if $N \ll \gamma$, but the requirement can be much less strict than this if a or b are large enough.

At any rate, when N is small enough for mention of it to be safely expunged from (10), this equation reduces to

$$y'\{y^2(1+\gamma) + y(1+b)(1+a+2\gamma) + (1+b)^2(a+\gamma)\} + \gamma y\{y^2 + y(2+b+ab) + (1+b)(1+ab)\} = 0. \quad (10)$$

Now the solution is simpler than might at first appear since a factor $(y+1+b)$ is common to both the terms of this equation, leaving

$$y'\{(1+b)(a+\gamma) + y(1+\gamma)\} + \gamma y\{1+ab+y\} = 0. \quad (11)$$

The hole lifetime represented by this equation is the familiar

$$\tau_p = -\tau_{p0} \left(\frac{y}{y'} \right) = \tau_{p0} \left\{ \frac{(1+b)(a+\gamma) + y(1+\gamma)}{1+ab+y} \right\} = \left\{ \frac{\tau_{n0}(p_0 + p_1) + \tau_{p0}(n_0 + n_1) + \Delta p(\tau_{n0} + \tau_{p0})}{p_0 + n_0 + \Delta p} \right\}, \quad (12)$$

which is identical with the result of S-R for steady-state hole lifetime when the recombination-center density is small. Application of a similar procedure on (9) gives

the expected result that the electron lifetime is *also* in accordance with S-R for any excess electron density, large or small.

In these cases where N is small and (8) reduces to (11), direct integration is possible to give time as a function of Δp following any disturbance of thermal equilibrium. From (11) we have that

$$T = \frac{t}{\tau_{n0}} = \frac{(1-a)(1-\gamma b)}{\gamma(1+ab)} \ln \left[\frac{y_0+1+ab}{y+1+ab} \right] + \frac{(1+b)(a+\gamma)}{\gamma(1+ab)} \ln \left[\frac{y_0}{y} \right], \quad (13)$$

where y_0 is the normalized excess hole density at the origin of the time scale. This can be written in the more usual notation as

$$t = \frac{(p_0 - n_1)(p_0\tau_{p0} - p_1\tau_{n0})}{(p_0^2 + n_i^2)} \ln \left[\frac{p_0 + n_0 + \Delta p_0}{p_0 + n_0 + \Delta p} \right] + \frac{(p_0 + p_1)(n_1\tau_{p0} + p_0\tau_{n0})}{(p_0^2 + n_i^2)} \ln \left[\frac{\Delta p_0}{\Delta p} \right]. \quad (14)$$

It is interesting to note that if $a=1$ or $\gamma b=1$ this collapses spectacularly to $t = (\tau_{n0} + \tau_{p0}) \ln(\Delta p_0/\Delta p)$. For recombination-center energies near the center of the gap so that both γb and a are less than unity, the decay becomes more rapid as it proceeds; but for levels quite near to one band or the other such that either γb or a is larger than unity, the decay becomes slower as it proceeds.

Our main purpose here is not to discuss these decays for small N which are amenable to exact analytic treatment; but to consider what happens with larger center densities when partial or complete trapping occurs.

We shall consider solutions appropriate for a p -type semiconductor, $ab < 1$, and for much of the discussion assume $ab \ll 1$. Cases where the thermal equilibrium minority carrier density becomes important are noted as they arise.

$$\frac{1}{x} = \frac{\left(\frac{G}{y_0+G}\right)^{1/\gamma} + \left(\frac{y_0}{N}\right) \int_0^T \exp\left(\frac{-T}{1+b}\right) \left[1 - \left(\frac{y_0}{y_0+G}\right) \exp\left(\frac{-\gamma GT}{N}\right)\right]^{1/\gamma} dT}{y_0 \exp\left(\frac{-T}{1+b}\right) \left[1 - \left(\frac{y_0}{y_0+G}\right) \exp\left(\frac{-\gamma GT}{N}\right)\right]^{1/\gamma}}. \quad (20)$$

Equations (19) and (20) contain (15) and (16) as a special case for sufficiently large trap density. When N is large but not infinite, (19) and (20) are important in describing the approach towards low modulation conditions. In particular, for strong minority carrier trapping Sec. IV(d), these equations approximate the behavior for the decay of x and y when x is dropping most steeply.

(b) N Very Large

When N is sufficiently large so that both N and bN are much larger than either x or y , Eqs. (6) and (7) reduce to very simple linear equations with purely exponential solutions (which of course depend on the initial conditions). When excess hole and electron populations are created with a delta function pulse of light, this initial condition is $x=y=x_0$ at $T=0$. Then

$$x = x_0 \exp[-T/(1+b)], \quad (15)$$

$$y = x_0 \exp[-\gamma b T/(1+b)]. \quad (16)$$

Physically, we can see that when N is very large, the fraction of unoccupied traps remains at the thermal equilibrium value of $(1+b)^{-1}$ whether optically created electrons are pouring into the traps or not. Then, independent of the previous history, the probability of electron capture is always $C_n(1+b)$ and of hole capture always $C_nb/(1+b)$, as described by Eqs. (15) and (16). The extent of trapping of electrons or holes is clearly seen to be a strong function of how much γb deviates from unity.

(c) $|Nb/(1+b) - (1+b)| \gg x$

For this apparently specialized case, if the substitution

$$y = -(1+b) + Nu'/\gamma u, \quad (17)$$

is made in Eq. (7), the result is

$$u'' + \left(\frac{\gamma}{N}\right) \left[\frac{Nb}{1+b} - (1+b) - x \right] u' - \left(\frac{\gamma^2 b}{N}\right) u = 0. \quad (18)$$

The condition $|Nb/(1+b) - (1+b)| \gg x$ makes Eq. (18) linear with constant coefficients. The solution for y is then

$$\frac{1}{y} = \left[\frac{1}{G} + \frac{1}{y_0} \right] \exp\left(\frac{\gamma GT}{N}\right) - \frac{1}{G}, \quad (19)$$

where $G = [1+b + Nb/(1+b)]$ and $y = y_0$ at $T=0$.

But when y has this form and a is very small (since this is a necessary condition for Class I), Eq. (6) becomes Bernoulli's equation and has the solution

IV. THE GENERAL CLASS-I SOLUTION

(a) Numerical Solutions

In many physical situations the trap density is too large to permit use of the simple result described in III (a), yet the conditions of III (b) or (c) do not apply. A more general type of solution must then be sought;

though as previously remarked, general analytic solutions to (8) and (9) are not known. Fortunately, Eqs. (6) and (7) are of a kind easily handled by a digital computer, and a number of representative cases were evaluated numerically with an I.B.M.-650 machine. The results of this computation, taken in conjunction with the available analytic solutions, give us a clear picture of the decay forms for either hole or electron trapping.

The numerical solutions illustrated in the following figures were all computed subject to the initial condition $x=y=10$ at time $T=0$. Any other starting condition (i.e., $x=y \neq 10$, or $x \neq y$ at some initial instant) would give solutions different in the initial stages of decay, but which would rapidly coalesce with the above, apart from a trivial change in the origin of the time scale.

(b) Trapping

For a discussion of the results shown in the first few figures it is convenient to return to Eqs. (6) and (7) and note that under the conditions of Class I (that a is very small) these can be written as

$$-\frac{x'}{x} = \frac{1}{1+b} + \frac{x-y}{N} \left[\frac{x+a(1+b)}{x} \right] \quad (21a)$$

$$\approx \frac{1}{1+b} + \frac{x-y}{N}, \quad (21b)$$

and

$$-\frac{y'}{y} = \frac{\gamma b}{1+b} + \frac{\gamma(y-x)}{N} \left[\frac{y+1+b}{y} \right]. \quad (22)$$

Note that the left side of each equation is the reciprocal of the normalized time constant for one type of carrier. For we have, $[-x'/x] = [-(\tau_{n0}/x)(dx/dt)] = \tau_{n0}/\tau_n$, where τ_n is the quantity customarily described as the electron lifetime for the given conditions. It is evident from (21b) that $-x'/x$ will be simply $1/(1+b)$ [i.e., $\tau_n = \tau_{n0}(1+b) = \tau_0$] whenever $(1+b)(x-y)/N$ is small compared with unity. This will be true at the end of a decay, when x and y become sufficiently small.¹⁶ Moreover, this will be true for the initial region of any transient decay which follows a delta function period of illumination. For if the illumination period is sufficiently short compared with the lifetime, $\Delta n = \Delta p$ at the start of this decay; and $-x'/x = 1/(1+b)$ for a short period until Δn and Δp become sufficiently unbalanced to cause a different time dependence. It is not so much that Δn and Δp become different which causes the termination of this initial phase; it is rather that the fraction of empty and available traps shifts from $(1+b)^{-1}$ during this period. When N tends to infinity, the initial phase is indefinitely prolonged Sec. III(b),

¹⁶ Except for the situation of strong minority carrier trapping. Equation (21b) cannot then be used, since terms involving a must be retained no matter how small a may be.

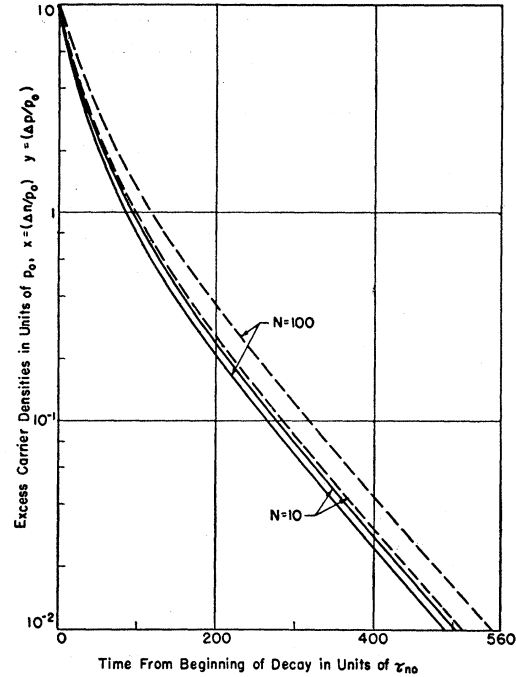


FIG. 1. Excess carrier decays illustrating majority hole trapping are given for the following values of the parameters: $a(1+b) = 10^{-6}$, $b = 100$, $\gamma = 0.05$ when $N = 10$ and $N = 100$. Solid curves for hole decay, dashed curves for electron decay.

since the capture probability is then not affected by prior trapping.

Corresponding to this situation for the electrons, the early stages of hole decay satisfy $-y'/y = \gamma b/(1+b)$. When $\gamma b < 1$, the minority electrons are depleted the more rapidly, i.e., minority electron trapping occurs. Conversely, when $\gamma b > 1$, it is the majority holes which become trapped while the electrons enjoy the longer initial time constant.

(c) Majority Hole Trapping

Of the two trapping alternatives, the simpler is that of majority hole trapping, which, as remarked above, occurs if $(\tau_{n0}p_1/\tau_{p0}p_0) = \gamma b > 1$. It will readily be seen from Table I that when this is so, $\tau_1 < \tau_\infty < \tau_0$; accordingly, the hole decay becomes slower as it proceeds.

Figure 1 illustrates the decay of x and y with time for two numerical examples of majority carrier trapping, following an initial disturbance $x_0 = y_0 = 10$. The time scales for the following figures are given in terms of the dimensionless variable $T = t/\tau_{n0}$. This has the effect of eliminating differences between curves for different trap densities which result purely from the reciprocal dependence of τ_{n0} and τ_{p0} on N_t . Thus consider the two curves for electrons in Fig. 1. In terms of actual time, the decay is *speeded up* by a factor of almost 10 when the normalized trap density is raised from $N = 10$ to $N = 100$. But the figure plots one curve in horizontal

units ten times larger than for the other, to illustrate that electron decay is *slowed* when many traps are present, compared with the functional form of (13) or (14) for very few traps. The curve for (13) with the appropriate values of γ and b does in fact lie neatly between the two inner curves for $N=10$, and the figure demonstrates the progressive departure from this behavior as N increases. The fact that the electrons initially have a larger time constant (τ_0) than the holes (τ_1) leaves an indelible mark on the entire decay scheme for both carriers (although the initial period for which the electron lifetime is anywhere near as large as τ_0 is too small to show clearly in this figure).

Ultimately the ratio $(x/y)=\Delta n/\Delta p$ becomes constant, since in the final stages of the decay both carrier populations have the same time constant. This statement can be confirmed by noting from (21b) that the electrons eventually have the lifetime $\tau_0=\tau_{n0}(1+b)$ again, while Eq. (8) for hole decay simplifies to

$$y''+y'\left[\frac{1+\gamma b}{1+b}+\frac{\gamma(1+b)}{N}\right]+\gamma y\left[\frac{1}{N}+\frac{b}{(1+b)^2}\right]=0, \quad (23)$$

when y is sufficiently small. This well-known equation

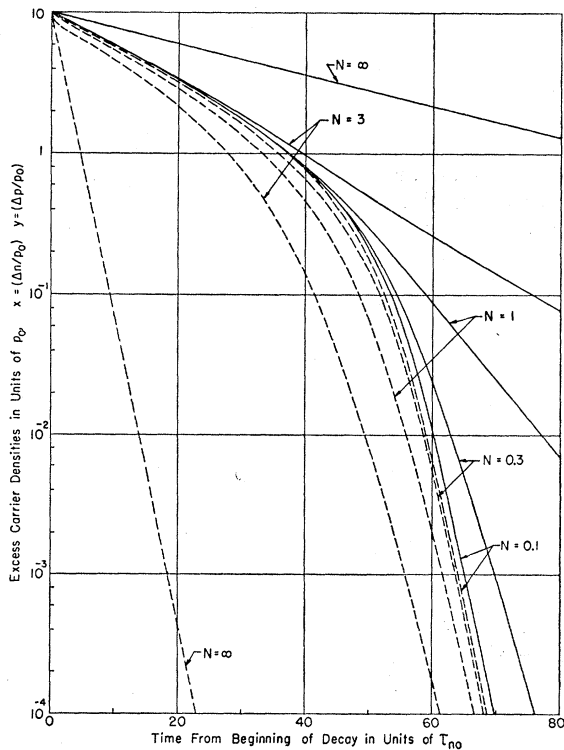


FIG. 2. Electron and hole decay showing minority electron trapping for the following values of the parameters: $a(1+b)=10^{-6}$, $b=1$, and $\gamma=0.05$. The values of N are indicated on the graph. Solid curves for hole decay, dashed curves for electron decay.

has the solution

$$y=\alpha \exp\left\{\frac{-T}{1+b}\right\}+\beta \exp\left\{\frac{-T}{1+b}\left[\gamma b+\frac{\gamma(1+b)^2}{N}\right]\right\}, \quad (24)$$

which, for the hole trapping situation of $\gamma b>1$, is dominated by the first term at sufficiently long times, giving a lifetime equal to that of the electrons.

The ratio of excess electron to hole densities during this final decay is found from (22) and the above result to be

$$\lim_{x \rightarrow 0, y \rightarrow 0} \left(\frac{x}{y}\right) = 1 + \frac{N(\gamma b - 1)}{\gamma(1+b)^2} = 1 - \frac{N}{\bar{N}}. \quad (25)$$

This ratio is greater than unity in hole trapping cases since the quantity we define as $\bar{N}=\gamma(1+b)^2(1-\gamma b)$ is then negative.

(d) Minority Electron Trapping

Decay for this case is rather more complicated, particularly in the final stages when two categories of behavior appear; these we call weak trapping and strong trapping. Before going deeply into this, it is preferable to note the behavior during the earlier stages of decay.

When the initial condition is $x=y$ at $T=0$, the holes enjoy an initial decay lifetime τ_1 and the electrons τ_0 [from (21) and (22)] as in the hole trapping case; but now since $\gamma b<1$ we have $\tau_1>\tau_\infty>\tau_0$. Electrons are rapidly trapped from the first instant, but hole decay is slow until the recombination centers have built up enough negative charge to encourage more vigorous recombination. This can be seen at the very beginning of the curves in Fig. 2.

Following this initial adjustment, the hole and electron densities follow paths roughly straddling the route of Eq. (13) if N is not unduly large. At first sight it might appear likely that the decay of both carrier populations would become monotonically faster until both enjoyed the lifetime τ_0 . This does happen when weak trapping is the final result, and is exemplified by the curves labelled $N=0.1$ in Fig. 2. The final behavior of the excess holes when their density becomes small is, as remarked in the previous subsection, determined by (23) with its solution (24). In contrast to the hole trapping case, however, there are now possibilities of the final stages of decay being controlled by either the first or the second term of (24). The dominant term depends on the magnitude of $[\gamma b+\gamma(1+b)^2/N]$ compared with unity; the critical value of N being

$$\bar{N}=\gamma(1+b)^2/(1-\gamma b). \quad (26)$$

When $N<\bar{N}$, both hole and electron populations finally have the lifetime τ_0 and the ratio (x/y) assumes the definite value of Eq. (25); this ratio is now less than unity. But for larger values of N the final hole lifetime is not τ_0 but τ_2 and now the progression of time constant

during the decay is not monotonic. This is the case of strong trapping.

It is intuitively obvious that the ratio (x/y) must remain finite even for this situation, but such a destiny does not appear too likely from the divergent behavior of pairs of curves for strong trapping in Fig. 2. However, the general electron equation (9) reduces to one with a solution of the form (24) when the electron density becomes so small that $x \ll a(1+b)$. When this happens the electron decay slackens to conform with a new final lifetime τ_2 , just as for the hole decay. This process is illustrated in Fig. 3(a) for a semiconductor in which $a(1+b) = 10^{-6}$, a not unlikely value for an extrinsic semiconductor such as silicon at 300°K. And so the headlong collapse of the excess electron density is checked, but not until it has become exceedingly small compared with the excess hole density. The final ratio is in fact

$$\lim_{x \rightarrow 0, y \rightarrow 0} \left(\frac{y}{x} \right) = \frac{\gamma [N/\bar{N} - 1]}{a \bar{N}}, \quad N > \bar{N}. \quad (27)$$

Sandiford⁷ remarked that both electrons and holes decay according to (24) *when their densities are small*: but he did not remark on how small these densities must be to make this form of solution valid. Certainly so far as the minority carriers are concerned, the range of validity for (24) is observationally inaccessible when strong trapping occurs (except for a semiconductor which is almost intrinsic). On the other hand, Eqs. (19) and (20) give a good approximation to the strong trapping decay from the moment x becomes smaller than γ .

The preceding discussion has emphasized that the progression of time constants during a strong trapping process is far from simple. This is amply borne out by the curves of Fig. 3(b).

(e) Result of Varying Trap Density

The most obvious result of varying the trap density is that the parameters τ_{n0} and τ_{p0} vary in the inverse manner. For a case of majority hole trapping, this is the predominant fact, and recombination speeds up more or less in step with the center concentration. The same holds true for cases of weak minority electron trapping, where the final decay is characterized by the lifetime τ_0 . As remarked before, this gross dependence of decay rate on N is masked by the use of T as the abscissa in the first few figures, a variable which is itself proportional to N .

A change occurs in the above-mentioned trend for the strong trapping case of $N > \bar{N}$. The final hole lifetime is now τ_2 which at first decreases more slowly than τ_0 for increasing N . This happens since

$$\tau_2 = \frac{N\tau_0}{N\gamma b + \gamma(1+b)^2}. \quad (28)$$

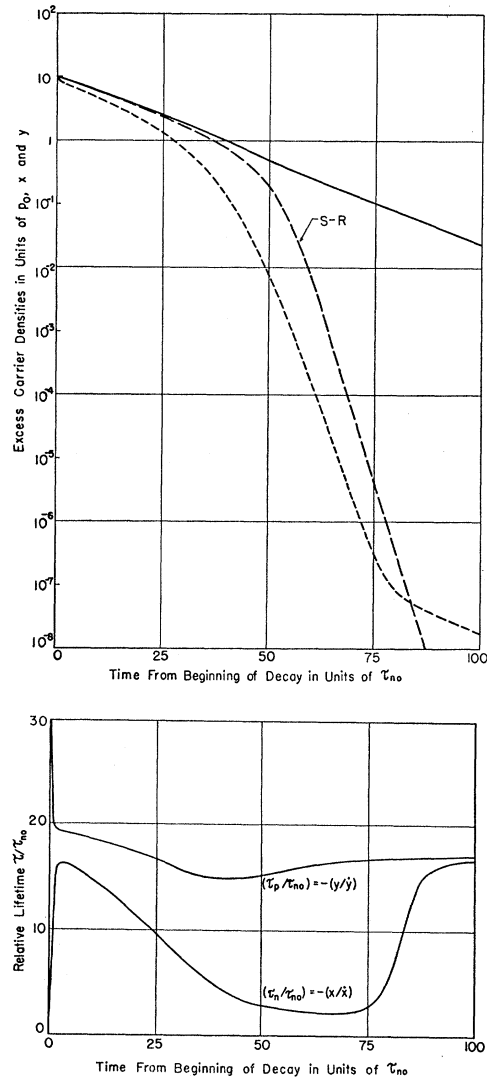


FIG. 3. (a) Decay of holes (solid curve) and electrons (dashed curve) for strong trapping case of $a(1+b) = 10^{-6}$, $b=1$, $\gamma=0.05$, $N=3$, continued to show final modes of decay. Curve of S-R decay [Eq. (13)] shown for comparison. (b) Variation of normalized time constants during this decay.

Now the numerator of this expression is independent of N , while only the first term of the denominator encourages any dependence of lifetime on trap density. This dependence will not be very marked when N first exceeds \bar{N} ; though as N further increases to become large compared with $(1+b)^2/b$, τ_2 once again becomes simply inversely proportional to $1/N$ and identical with the quantity τ_1 . This becomes the situation described in Sec. III(b), that for very large N both electron and hole decays follow simple exponentials all the way, with time constants τ_1 for holes and τ_0 for electrons. The transition between weak trapping and this limiting behavior is demonstrated by the curves for $N=0.3, 1, 3$, and ∞ in Fig. 2.

(f) Effects of Temperature on Excess Carrier Decay

Any of the parameters characterizing the decay may be a function of temperature, but as a first approach to the problem it may be supposed that the dependence of b is the most important in a Class I process. This ratio is

$$b = p_1/p_0 = (N_v/p_0) \exp[(\epsilon_v - \epsilon_t)/kT], \quad (29)$$

when the recombination level is nondegenerate, and differs by a constant factor when there are multiple spin choices for center occupancy.

In Fig. 4 the progression of excess carrier decay is shown (with $N=0.1$ and $\gamma=0.05$) as b is increased from 0.1 to 100 (corresponding physically with rising temperature). In the same sequence, the character changes from strong to weak trapping of electrons to no trapping and finally to exceedingly mild hole trapping. For these values of N and γ the transition from strong to weak trapping occurs at $b=0.40$, and there is no trapping when $b=20$.

The boundary between electron and hole trapping corresponding to the condition $\gamma b=1$ is a most interesting one because this makes Eqs. (6) and (7) exactly solvable, leading to the simple exponential solutions

$$x = y = x_0 \exp[-T/(1+b)]. \quad (30)$$

This solution is applicable for both Class I and Class II semiconductors at any level of modulation. Trapping is completely absent and the solution is independent of both a and N , except for the indirect appearance of N in the normalizing time constant τ_{n0} .

It is interesting to note how the low-level lifetime varies with b , and curves illustrating this are shown in

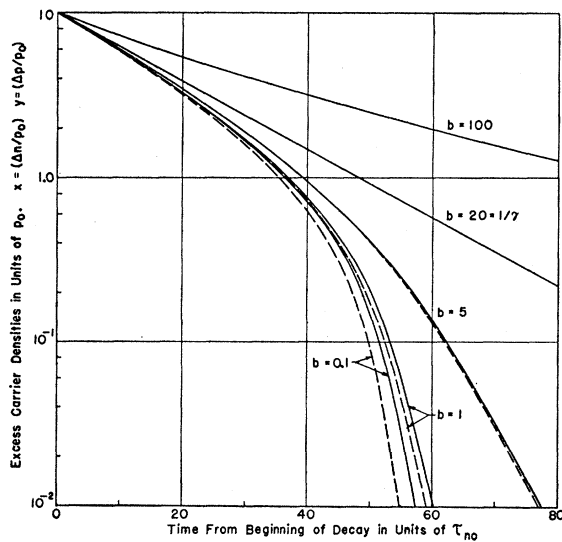


FIG. 4. Dependence of excess carrier on b for $\gamma=0.05$ and $N=0.1$. Physically, increasing b corresponds to higher temperatures.

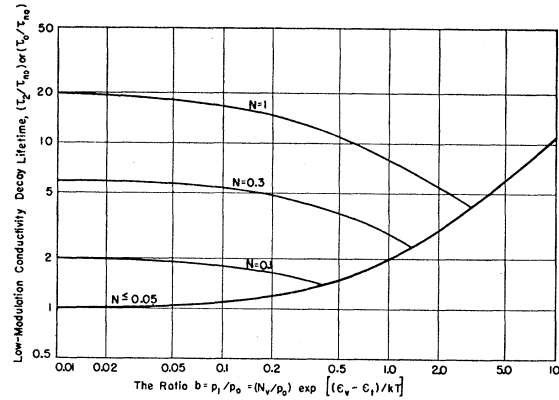


FIG. 5. Low-modulation conductivity decay lifetime as a function of b when $\gamma=0.05$. The descending curves for small b and large N all join the common curve $(1+b)$ as b increases sufficiently to make $N < \bar{N}$.

Fig. 5. (For these curves γ is set at 0.05 in order to conform with the previous numerical decay curves, but similar principles would of course apply for any other value.) When $N \leq \gamma$ strong trapping cannot occur no matter how small b is: the low-modulation lifetime is then the monotonic function $\tau_0 = \tau_{n0}(1+b)$ of b . But for any larger value of N such that $N > \gamma$, strong trapping will occur at the lowest temperatures when b is small. The low-modulation decay will then be controlled by a lifetime τ_2 which is larger than τ_0 , but which decreases as b increases. Three examples of this kind of behavior are shown in Fig. 5. For each of these in turn, b reaches a value appropriate for $N = \bar{N}$, $\tau_2 = \tau_0$; the behavior when b becomes still larger is set by the curve for τ_0 .

Clearly, considerations such as the above will have an important bearing on the interpretation of photoconductive decay in a semiconductor. The problems of photoconductivity are discussed in the next section.

V. PHOTOCONDUCTIVITY

Attempts are often made to compare experimentally determined photoconductive decay lifetimes with theory, principally the S-R theory.¹⁷ Now this is impossible if trapping is appreciable since neither Δn , Δp , nor their lifetimes can be measured. Instead a composite measure of the carrier modulation is obtained from the conductivity equation and its time constant

$$\Delta\sigma = e(\mu_n \Delta n + \mu_p \Delta p) = e(\mu_n + \mu_p) \Delta \bar{n}, \quad (31)$$

$$\tau_{\bar{n}} = -\Delta\sigma / \Delta\sigma' = -\Delta \bar{n} / \Delta \bar{n}'. \quad (32)$$

When Δp and Δn are widely separated, as we have seen can happen, measured values of $\tau_{\bar{n}}$ will not be very revealing about the behavior of either the holes or the electrons.

¹⁷ E. g., R. L. Watters and G. W. Ludwig, J. Appl. Phys. 27, 489 (1956); R. G. Shulman and B. J. Wyluda, Phys. Rev. 102, 1455 (1956).

On the other hand, when Δn and Δp are known separately (e.g., from numerically computed curves such as we have discussed above), the information on these can be combined to demonstrate the corresponding course of behavior for $\tau_{\bar{n}}$. We have done this to illustrate the dependence of $\tau_{\bar{n}}$ on photoconductive modulation for various types of carrier trapping. It is not particularly necessary to do this for the case of majority hole trapping since, except for exorbitantly large N , the differences between τ_n , τ_p , and $\tau_{\bar{n}}$ are unimportant. Thus the figures discussed below relate to the important minority electron trapping situation, firstly for weak trapping. The coordinates for Fig. 6 are chosen such that when N is sufficiently small [i.e., the behavior satisfies the S-R model of Eq. (12)], the results should lie on a straight line with slope $(1+1/\gamma)$ and intercept $(1+b)$. This line is indicated on the figure, and also the behavior which occurs for two finite values of N . One notes that the "photoconductive lifetime" increases at first more rapidly with modulation than expected from an S-R model. It is obvious from the nature of $\Delta\bar{n}$ that the initial slope may approach but not exceed $(1+c)(1+1/\gamma)$.

Curvature of the characteristic between photoconductive lifetime and modulation has been seen in practice¹⁸; though such curvature can arise from causes other than pronounced weak trapping.¹⁹ Obser-

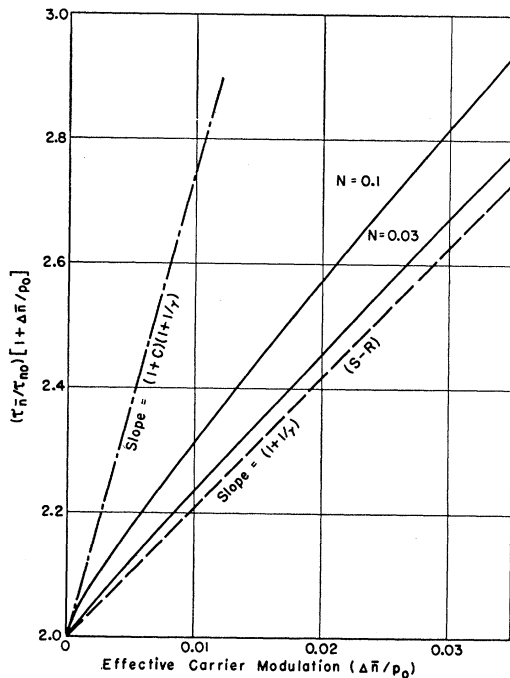


FIG. 6. Photoconductive lifetime as a function of $\Delta\bar{n}$ for weak electron trapping. $\gamma=0.05$ and $b=1.0$, while $N < \bar{N}=0.210$.

¹⁸ E.g., M. S. Ridout, *Report of the Meeting on Semiconductors* (The Physical Society, London, 1956), p. 33.

¹⁹ J. S. Blakemore, *Phys. Rev.* **110**, 1301 (1958).

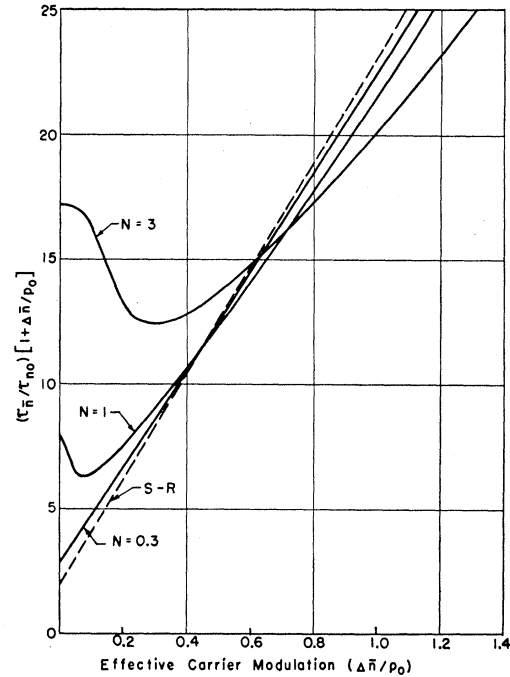


FIG. 7. Typical photoconductive lifetimes for strong electron trapping when $\gamma=0.05$, $b=1.0$, and $N > \bar{N}=0.210$.

vation that the curvature becomes less prominent as temperature increases (lowering the ratio N/\bar{N}) would be important confirmation of weak trapping as the cause of the curvature.

The variation of $\tau_{\bar{n}}$ with modulation deviates much more significantly from the S-R behavior when $N > \bar{N}$ and strong trapping supervenes. The results demonstrate the need for a large-signal theory since departures from the S-R line are still very pronounced at quite considerable levels of modulation. Typical results are shown in Fig. 7 for values of γ , b , a , and N corresponding with three cases for which decays were shown in Fig. 2. A mobility ratio $\mu_n/\mu_p=c=2.6$ is supposed, which makes the form of $\tau_{\bar{n}}$ strongly influenced by the minority electrons for heavy modulation; however as low-modulation conditions are reached the majority holes exert an almost exclusive control over $\tau_{\bar{n}}$. This is the reason for a minimum in these curves (a not very obvious one when $N=0.3$) since $\tau_{\bar{n}}$ must approach τ_2 as the minority density becomes imperceptibly small.

Once again, the propriety of associating experimental results with a model such as this should be confirmed from the temperature dependence. As temperature increases, one should go from strong trapping to weak trapping (and eventually towards hole trapping).

VI. ACKNOWLEDGMENTS

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