PHYSICAL REVIEW B VOLUME 23, NUMBER 10 15 MAY 1981

Diffusion-limited lifetime in semiconductors

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(Received 27 May 1980)

At high recombination rates, minority carrier recombination at defects in crystals ceases to obey Shockley-Read theory, and diffusion theory should be applied. These theories for neutral plane, line, and point defects are compared and used to interpret experimental results on hole recombination in n-type GaP. The steady-state kinetics and spatial distribution of the recombining carriers are briefly discussed but most attention is placed on the transient lifetime of the carriers for comparison with experiment. With no recourse to disposable parameters, the concentration and temperature dependences for plane sinks (surfaces) and line sinks (dislocations) in n-GaP are in excellent agreement with the diffusion theory. The resulting lifetimes are approximately independent of the sink strength (capture distance) and represent a lower limit to the observable lifetime for a fixed (low) defect concentration. For point sinks such limitation is not predicted and the experimental lifetime data do not agree with the diffusion theory. However, extending the diffusion theory to the case of a negatively charged defect, using a modified "Lax" treatment, produces concentration and temperature dependences in good agreement with experiment, and again a similar lifetime limitation is predicted providing the effective capture radius does not exceed 2×10^{-5} cm ($\sigma\sim10^{-11}$ cm^2).

I. INTRODUCTION

Minority carrier recombination in semiconductors has been the subject of a vast amount of scientific study, which at least in part reflects the fact that recombination processes control the operation of many of the most important semiconductor devices. It is probably true to say that a satisfactory quantitative basis for understanding the recombination of carriers between extended states in semiconductor crystals has been achieved, and that the study of luminescence processes has led to a satisfactory quantitative description of many radiative recombination processes which occur at defect states, especially those shallow states well described under the effective-mass approximation. It is in the area of nonradiative recombination at deep defect states that fundamental ignorance is most evident. Although deep-defect-controlled lifetime in, for example, silicon is fairly well quantified in an empirical sense, no adequate description of the physical processes has emerged. This probably stems from the facts that electron wave functions at deep defect states are seldom well established and that the detailed lattice structures of the defects are seldom known. Notable attempts to quantify the nonradiative processes for shallower states have been made by Lax[1] and later workers,[2] and more recently for deep states by Henry and Lang.[3] Other work on ionic materials has also been successful in a limited number of cases but this is not specifically relevant to covalent semiconductors. Lax[1] treated the diffusion and phonon cascade process occurring between closely spaced, shallow excited states at a charged defect, and Henry and Lang[3] formulated the behavior of a multiphonon emission process to explain the energy dissipation between widely spaced energy levels at a defect. Both descriptions have been qualitatively successful in describing the behavior and temperature dependences of a limited number of experimental systems, but as yet their success is not widely established in a quantitative sense.

This paper relates to the quantitative description of nonradiative recombination at deep defects which control the hole lifetime in the highest quality (longest lifetime) n-type gallium phosphide. However, the work reported does not add much to our understanding of the details of electronic transitions at the deep defects, but attempts to bring attention to the often ignored fact that, regardless of the details of the local recombination process, the experimentally observed recombination in neutral crystals can be wholly controlled by the diffusion rates of the particles toward the recombination sites. Using experimental data we will show that diffusion-controlled kinetics are certainly established for recombination at plane sinks (surfaces) and line sinks (dislocations) in n-type gallium phosphide, and that although for the point sink the simple diffusion limit is not observed, a quantitative case can be established for "Lax-type" recombination at the 0.75-eV deep state which usually controls the lifetime and luminescence efficiency of (LED) light-emitting-diode grade n-type gallium phosphide.[4] This Lax-type recombination is effectively an extension of the diffusion theory and gives rise to a similar limitation of the recombination rate re-

gardless of the local processes occurring at the deep defect states. Some of the work presented here has been the subject of earlier brief publications[5] describing the concentration dependences for line and plane sinks, and other workers have further developed the analysis of such room-temperature recombination including a detailed discussion of the transient and sine-wave responses of the minority carriers.[6,7] Our earlier work is included here with minor improvements in interpretation, so that a complete, self-consistent theoretical and experimental discussion of the diffusion-limited condition can be made. Attention is also drawn to the earlier work of Suzuki and Matsumoto[8] who proposed a one-dimensional model for diffusion-limited dislocation recombination in n-type GaP.

In Sec. II the classical theories used to describe the diffusion processes for neutral sinks are presented. In Sec. III the material studied and the experimental techniques used to measure sink concentration and lifetime are described. In Sec. IV the experimental results giving the quantitative dependence of hole lifetime on sink concentration are compared with the theory, and the temperature dependence of the lifetime data is then used as a positive test of the diffusion theory. The Lax interpretation for the point-sink case is also presented in Sec. IV.

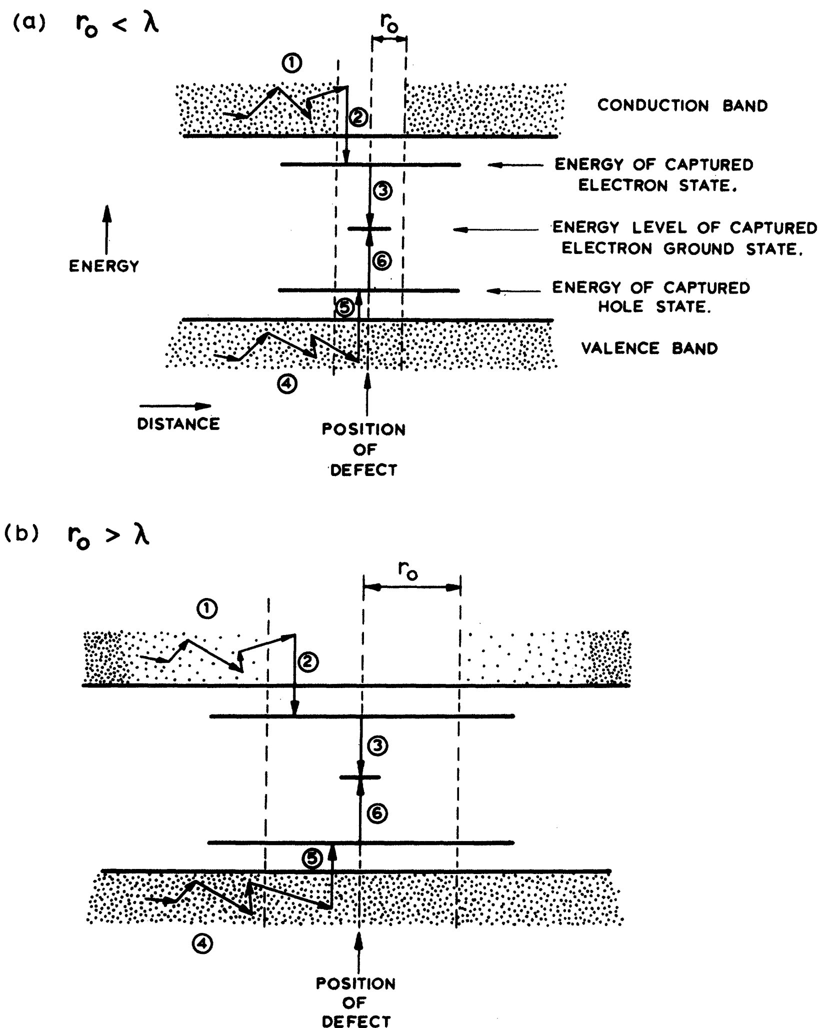

FIG. 1. Schematic diagrams showing a typical, steady-state recombination sequence for minority electrons at deep levels associated with line and point defects. Infinitely short lifetime is assumed inside the capture distance r_0. (a) When r_0 is less than the mean free path (λ) a constant minority carrier concentration is maintained in the crystal. (b) When r_0 is greater than λ the minority carrier concentration becomes locally depressed and diffusion limits the recombination rate. For plane sinks the diffusion limit applies for all values of r_0.

II. THEORY

It is clear that when describing electron-hole recombination in a semiconductor a number of physical events have to be considered. A large number of processes can operate in series or in parallel to determine the recombination kinetics for the minority carriers. In each of the cases to be considered here, the carriers are assumed to recombine at localized deep defect states. If we consider how the minority carrier relaxes to its parent band, we might typically sequence the events as (1) transport to the recombination site, (2) capture at the site, (3) relaxation to the ground state at the site, (4) transport of the majority carrier to the site, (5) capture at the defect, and (6) recombination (see Fig. 1). Any one of these processes may be dominant in determining the minority carrier recombination rate. All of these processes need not occur; for example, radiative recombination could occur without either of the particles being truly captured or indeed at any point of the particles' descent into the capture ground state. Also, the free electron and hole may associate so that only one transport process is involved, as could occur in bound exciton recombination. However, the sequence described is chosen to highlight all of the nonradiative mechanisms for single-particle processes relevant to this paper (multiple-particle processes such as Auger recombination are excluded). In this sequence the assignment of process (6) as the recombination event is arbitrary since the whole sequence from the average free electron to the average free hole is a more proper description of the recombination process. If we ascribe an average time ($\tau_1 - \tau_6$) for each of these processes to occur for single carriers at a defect center, the total recombination time is of course the sum of these times and will be dominated by any one which is significantly longer than the others. Moreover, if we consider the locations of the particles as a space and time average, it is apparent that the longest-time-constant process is a "bottleneck" in the recombination traffic, the largest change in the state occupancy occurring between the terminal states of the dominant process.

Under the generally accepted and much used Shockley-Read (SR) theory of recombination,[9] various assumptions are made. From the point of this paper we focus attention on the assumption that the carrier density is uniform throughout the crystal at all times, whether steady-state or transient decay is being considered. As is well appreciated in the field of gas kinetics, when the capture radius (r_0) of an infinitely efficient sink exceeds the mean free path (λ) of the free particle in the gas, the kinetic equations describing the rate of loss of particles change from simple ballistic theory to hydrodynamic flow.[10] This implies that the particle concentration (pressure in the gas case) is significantly reduced in the neighborhood of the capturing center. It is clear that this should also happen in the case of minority carrier recombination in semiconductors, thus violating the SR condition. λ is then the average distance traveled between lattice scattering events. When this condition is well established (i.e., $r_0 \gg \lambda$), the large depression in the free minority carrier concentration is a manifestation of the bottleneck referred to above (see Fig. 1), and regardless of the recombination mechanism at the defect, the lifetime is controlled by the diffusion rate of the carrier to the center.

We will proceed to model the transient kinetic behavior assuming the defect exhibits a capture distance r_0 and that the minority carrier concentration is zero inside this distance. This is precisely the same assumption as is used in the SR theory, and our treatment clearly suffers from the same limitations as the SR theory in that it gives no information as to the details of the local recombination mechanisms. However, in the sense that the diffusion physics are analyzed in detail and can be the dominant process, it may be considered a satisfactory treatment. For example, the temperature dependence of the recombination can be directly predicted in some cases, whereas in the SR case this is never possible unless the details of the local recombination process are known. The treatment due to Lax for charged defects is clearly an intermediate case where the diffusion and phonon cascade processes occurring in the higher-lying excited states of the center are presumed to be the rate-limiting process, and since the Coulomb field is the only parameter required to fully describe the nature of the center, a completely satisfactory description is also obtained.

The situations to be modeled are those pertaining to a regular array of defects in a sample of neutral semiconductor with uniform generation of minority carriers throughout its volume. When the excitation is removed, the concentration of the excess minority carriers decays to its equilibrium value. Small signal conditions are assumed throughout, and it is usually assumed that no recombination processes other than that being analyzed are present. The decay of the total number of minority carriers (holes) in a representative volume is calculated and although this is not strictly an exact exponential function of time, a short time after the excitation an approxi-

mate exponential dependence is deduced. The time constant τ for this exponential is defined as the transient lifetime of the minority carrier. In the three cases of neutral point, line, and plane sinks, the representative volume and the boundary conditions applying to their perimeters are chosen such that the infinite semiconductor is properly described. The experimental conditions for measuring lifetime were chosen to be consistent with these simple cases.

A. Transient lifetime due to plane sink defects

1. Concentration dependence

a. Steady-state lifetime. We will first deal with a steady-state solution to illustrate a number of the basic concepts but after this, no further development of the steady-state conditions will be made. The concentration dependence is equivalent to studying the lifetime as a function of defect spacing. The lifetime observed in an infinite semiconductor with regular parallel defects is clearly the same as that observed in a single filament of thickness equal to the defect spacing. The carrier distribution for uniform steady-state excitation is found from the continuity equation:

$$\frac{\partial p}{\partial t}=G+D\frac{\partial^2 p}{\partial x^2}=0\,, \tag{1}$$

where x is the distance measured from the central plane of the filament, and with boundary conditions

$$p_s S=-D\frac{\partial p}{\partial x}\bigg|_{x=\theta/2} \text{ and } p_s S=D\frac{\partial p}{\partial x}\bigg|_{x=-\theta/2}\,,$$

D is the diffusion coefficient for holes, θ is the filament thickness, p_s is the surface concentration, S is the surface recombination velocity, and G is the volume generation rate of holes. The solution to Eq. (1) is simply found by direct integration and takes the form

$$p=\frac{G}{2D}\left(\frac{\theta^2}{4}+\frac{D\theta}{S}-x^2\right). \tag{2}$$

We can calculate the steady-state lifetime of the minority carriers in a manner consistent with the definition we use for the transient case by integrating the hole concentration in the filament to find the total hole concentration per square centimeter, and then dividing by the total generation rate (cm^2) in the filament:

$$\tau_{SS}=\int_{-\theta/2}^{\theta/2}\frac{G}{2D}\left(\frac{\theta^2}{2}+\frac{D\theta}{S}-x^2\right)dx(G\theta)^{-1}=\frac{\theta^2}{12D}+\frac{\theta}{2S}. \tag{3}$$

Upon inspecting Eq. (3) a number of comments can be made:

(a) The lifetime can either be controlled by $S(S<2D/\theta)$ or the value of $D(S>2D/\theta)$, depending upon which of the two terms Eq. (3) is the larger.

(b) The two terms of Eq. (3) represent a recombination-controlled lifetime ($\tau_{RSS}=\theta/2S$), and a diffusion-controlled lifetime ($\tau_{DSS}=\theta^2/12D$). The former is the time that the carrier moving with velocity S takes to traverse half the filament width, and the latter is the average time the carrier takes to diffuse the same distance, because $D=l^2/3t$ (where l is the rms distance normal to the surface, diffused in time t).

(c) The two lifetimes τ_{RSS} and τ_{DSS} are additive in Eq. (3) indicating that the two processes are in series, whereas parallel processes would in simple cases appear in the typical relationship involving the reciprocals of the lifetimes [e.g., Eq. (10)].

(d) When the lifetime is recombination controlled,

$$p_{x=0}\sim\frac{G\theta}{2S}\sim p_s$$

from Eq. (2), so that no significant depression of the carrier concentration is observed.

(e) When the lifetime is diffusion controlled,

$$p_{x=0}\sim\frac{G\theta^2}{8D}\gg p_s=\frac{G\theta}{2S}\,,$$

so that there is a significant depression of the hole concentration at the surface of the filament as outlined previously. In the absence of any mechanism that accelerates the carriers as they approach the recombination plane, there is in fact a limit to the value of S which is of the order of the mean thermal velocity of the carrier ($\overline{V}$). However, as long as $S\gg 2D/\theta$, the solution for τ_{SS} is not affected so that $S\to\infty$, $p_s\to 0$ will often be taken as general conditions which will define the diffusion-limited case.

(f) If a uniformly distributed bulk recombination process is included in the above calculation the solutions are more complex, partly because the bulk and surface-controlled processes are in parallel. The solutions generally involve hyperbolic functions,[11] but if the bulk diffusion length ($L=\sqrt{D\tau_{BSS}}$, where τ_{BSS} is the steady-state lifetime due to the bulk process) is much greater than the filament thickness the simple treatment above suffices.

b. Transient lifetime. Shockley[12] and McKelvey[13] have treated cases of this kind in detail, including a bulk process with transient lifetime τ_b and they found the solution for the transient behavior of p:

$$p=\sum_{n=0}^{n=\infty}A_n e^{-\nu_n t}\cos a_n x\,, \tag{4}$$

where

$$\frac{a_n\theta}{2}\tan\frac{a_n\theta}{2}=\frac{s\theta}{2D} \qquad (5)$$

and

$$\nu_n=\frac{1}{\tau_b}+Da_n^2, \qquad (6)$$

and the coefficients A_n are chosen such that the correct carrier distribution is obtained at $t=0$. Equation (4) is a series construction for the spatial and temporal decay of the carriers with modes determined by the roots of the transcendental Eq. (5). It is clear that at long times a fundamental mode with the smallest value of ν will persist, and this is defined as the transient lifetime. For the purposes of this work we can set $\tau_b=0$ in Eq. (6) so that only the surface-controlled term is considered. Equation (5) can be solved graphically or numerically and solutions for $a_n\theta/2$ separated by π are obtained, the smallest (fundamental) mode lying in the interval $0\rightarrow\pi/2$. On inspection, two limiting cases can be determined:

$$S\ll 2D/\theta,\ \tfrac{1}{4}a_n^2\theta^2=S\theta/2D,\ \text{yielding}\ \nu_0=2S/\theta=1/\tau_{SR} \qquad (7)$$

from Eq. (6), and

$$S\gg 2D/\theta,\ \tfrac{1}{2}a_n\theta=\tfrac{1}{2}\pi,\ \text{yielding}\ \nu_0=D\pi^2/\theta^2=1/\tau_{SD}\,. \qquad (8)$$

The condition for S is identical to that found in the steady state, and so is the lifetime for the recombination-limited case (τ_{SR}). However, the diffusion-limited lifetime (τ_{SD}) is different and larger than in the steady-state case. This difference can be deduced from qualitative arguments and will be true for diffusion-limited processes in general. The result we require for the diffusion-limited lifetime's concentration dependence is thus Eq. (8):

$$\tau_{SD}=\theta^2/\pi^2D, \qquad (9)$$

and in the presence of a bulk lifetime

$$\tau=(1/\tau_b+1/\tau_{SD})^{-1}. \qquad (10)$$

2. Temperature dependence

Providing the conditions $S\gg 2D/\theta$ and $\tau_b\gg\tau_{SD}$ are maintained, the temperature dependence of the observed lifetime [Eq. (9)] will be determined by that of D and will in no way reflect the temperature dependence of the surface recombination velocity.

Before leaving the plane-sink case, an important distinction should be made. It will be noted that the transition from the recombination-limited to the diffusion-limited kinetics in a thick layer ($\theta>2D/S$) can only be affected by modulating the strength of the surface recombination. For the line- and point-sink cases this behavior can also be seen, but we will only consider the conditions $S\rightarrow\infty, p_s\rightarrow 0$ in calculating the diffusion-limited case. Under these latter conditions, the effective capture distance (r_0) will be seen to also affect the transition from recombination to diffusion-limited conditions. The concept of varying the capture distance for a plane sink is redundant (providing $r_0\ll\theta$) because it simply varies the effective thickness of the filament by minimal amounts, without materially affecting the diffusion flux.

B. Transient lifetime due to line-sink defects (dislocations)

1. Concentration dependence ($r_0>\lambda$)

We will consider a parallel array of equally spaced line sinks in an infinite semiconductor. As is outlined in a previous letter,[6] using cylindrical coordinates the continuity equation for the transient case, assuming that p is a radially symmetrical function of r, becomes

$$\frac{\partial p}{\partial t}=D\frac{\partial^2 p}{\partial r^2}+\frac{D}{r}\frac{\partial p}{\partial r}. \qquad (11)$$

The representative volume of the crystal associated with each sink is taken as a cylinder radius r_{max} such that the volume of the array is exactly that of the crystal:

$$\rho_D\pi r_{max}^2=1, \qquad (12)$$

with ρ_D being the sink concentration per unit area. We also require from symmetry arguments that the concentration of carriers is a differentiable function at the outer boundary of the volume. To determine the diffusion-limited rate, the concentration is assumed to be zero inside the capture distance (r_0). So the boundary conditions are

$$\frac{\partial p}{\theta r}=0 \text{ at } r=r_{max},$$

$$p=0 \text{ at } r\leqslant r_0 \text{ (i.e., } S\rightarrow\infty),$$

with p being ascribed some arbitrary distribution at $t=0$. Penning[14] has shown that the solution of Eq. (11) under these conditions is of the form

$$p=p_0\sum_{n=0}^{n=\infty}A_nR_n(r)\exp\left(\frac{-t}{\tau_n}\right), \qquad (13)$$

where the coefficients A_n determine the initial distribution and the function $R_n(r)$ is a combination of Bessel functions describing a series of modes ($n=0\rightarrow\infty$), each having a characteristic decay time τ_n. τ_n is found from the roots ($n=0\rightarrow\infty$) of an equation also involving Bessel functions. As in the plane-sink case [Eq. (4)], the decay quickly

settles to its lowest mode, and using a similar treatment, Ham[15] has shown that the characteristic decay time of this ($n=0$) mode is, to a good approximation,

$$\tau_0 \doteq \frac{r_{max}^2}{2D}\left[\ln\left(\frac{r_{max}}{r_0}\right) - \frac{3}{5}\right]. \quad (14)$$

By considering unit volume in the crystal which contains many (ρ_D) sinks it is clear that the total carrier population in a practical sample with no other recombination process, will also settle to this time constant so that the diffusion-limited lifetime observed for a regular dislocation array is

$$\tau_{lD} = \frac{1}{4\pi\rho_D D}\left[-\ln(\pi\rho_D r_0^2) - \tfrac{6}{5}\right], \quad (15)$$

where r_{max} is substituted from Eq. (12).

2. Concentration dependence ($r_0 < \lambda$)

We will now briefly consider the case when r_0 is very small and the recombination ceases to be diffusion limited. A more complete treatment for the point sink will be presented, but because our experimental results for dislocations confirm diffusion limitation, a simplified discussion for the line sink will suffice.

When the capture distance is very much less than the mean free path in the diffusion field, the capture rate per carrier inside the cylinder $0 \leq r \leq r_0$ is determined by the particle velocity and by the probability that the trajectory of the carrier (assumed to be a straight line) intercepts the capture cylinder ($0 \leq r \leq r_0$). If we follow an argument similar to that commonly used in gas kinetic theory,[16] the carrier capture rate can be deduced by considering the volume of the crystal swept in time t by a typical carrier. For a parallel array of sinks we will consider only the component of the carrier velocity lying in the plane normal to the sink axis. This average velocity is clearly less than, but of the same order as, the mean carrier velocity $\overline{V}$ and should be obtained from a proper treatment of the velocity distribution of the particles. However, it would clearly be a constant factor $(K)\times\overline{V}$ regardless of the capture distance assumed or the temperature. We replace the line sinks by point sinks, and then ascribe a rectangular cross section to the particle, parallel with the line sinks. Then considering the portion of the crystal contained between planes normal to the line sinks at, and a distance $l \gg (\rho_D)^{1/2}$ apart, the particles will sweep a volume $2r_0 lK\overline{V}t$ in time t. This volume will contain ρ_D/l sinks per unit volume so the carrier capture rate for a carrier concentration p will be

$$R = 2r_0\rho_D K\overline{V}p. \quad (16)$$

Equation 16 is directly analogous to the standard result for point sinks [Eq. (23)] tending to zero as $r_0 \to 0$, but depending linearly on r_0. We would therefore expect that for small r_0 the carrier density will not be spatially modulated and the transient recombination-controlled lifetime will be

$$\tau_{lR} = \frac{1}{2r_0\rho_D K\overline{V}}. \quad (17)$$

3. Temperature dependence

Equation 15 has only a very weak dependence on r_0, providing it is small compared with the mean dislocation spacing. Therefore the temperature dependence of τ_{lD} is likely to dominated by that of the diffusion coefficient and be exactly equivalent to that observed in the plane-sink case. When r_0 is less than λ, the recombination-limited lifetime τ_{lR} is expected to depend strongly on r_0 and $\overline{V}$.

C. Transient lifetime due to point-sink defects

1. Concentration dependence ($r_0 > \lambda$)

We consider a regular array of point defects with concentration ρ_T per unit volume. The continuity equation expressed in spherical polar coordinates, with p a spherically symmetrical function of r, is

$$\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial r^2} + \frac{2D}{r}\frac{\partial p}{\partial r}. \quad (18)$$

For $r_0 > \lambda$ the boundary conditions are

$$p = 0 \text{ at } r = r_0 (S \to \infty),$$

$$\frac{\partial p}{\partial r} = 0 \text{ at } r = r_{max} = (\rho_T \tfrac{4}{3}\pi)^{-1/3}.$$

Among others, Ham[13] has shown that the solution of Eq. (18) is, then, similar to Eq. (13)

$$p = p_0 \sum_{n=0}^{n=\infty} a_n \psi_n(r)\exp(-t/\tau_n), \quad (19)$$

where $\Psi_n(r)$ describes the spatial dependence and involves trigonometrical functions of r. τ_n is the mode lifetime and a zero-order mode is taken to determine the diffusion-limited lifetime

$$\tau_{PD} = \frac{1}{4\pi D\rho_T r_0}. \quad (20)$$

2. Concentration dependence ($r_0 < \lambda$)

For the case $r_0 < \lambda$ we will present a simple unified treatment to show the connection between the diffusion field and the microscopic kinetics inside the sphere $r = \lambda$. We can assume that the

carrier distribution will settle into a stable mode such that the instantaneous flux into the center will be a constant value for $r_0<r<r_{\max}$, and that this flux is equal to the recombination loss at the center (R). Considering the boundary at $r=r'$, on average, particles at distances greater than λ from this surface do not participate in transport across this surface because they scatter before reaching it.

The average concentration in the shell, $r'<r<r+\lambda$, is

$$p(r')+\frac{\lambda}{2}\frac{dp}{dr},$$

and the average concentration in the shell $r'-\lambda<r<r'$ is

$$p(r')-\frac{\lambda}{2}\frac{dp}{dr}.$$

Using Joule's approximation that on the average one-sixth of the particles are traveling with velocity V normal to the surface $r=r'$, the net flux across $r=r'$ is

$$R=\frac{4\pi r'^2V\lambda}{6}\left.\frac{\partial p}{\partial r}\right|_{r=r'}. \tag{21}$$

This approximation is crude and V is not to be taken as the mean thermal velocity $\overline{V}$, but is of the same order of magnitude. Integrating this expression we obtain

$$p(r)=p_0-\frac{3R}{2\pi\lambda Vr}, \tag{22}$$

where p_0 is the concentration for $r\to\infty$.

At the center, carriers at $r>\lambda$ are scattered before reaching the center, and using the standard SR argument,

$$R=p(\lambda)\overline{V}\pi r_0^2. \tag{23}$$

Setting $r=\lambda$ and eliminating $p(\lambda)$ in Eqs. (22) and (23) we see how the diffusion field connects to the recombination region at $r=\lambda$ and we obtain

$$p_0/R=\frac{1}{\overline{V}\pi r_0^2}+\frac{3}{2\pi\lambda^2V}. \tag{24}$$

Since the instantaneous average concentration in the volume $r_0<r<r_{\max}$ is approximately equal to p_0 (p is a slow function of r for large r), we can deduce the transient lifetime:

$$\tau_p=\frac{p_0 4\pi r_{\max}^3}{3R}=\frac{p_0}{\rho_T R}=\frac{1}{\pi\rho_T\overline{V}}\left(\frac{1}{r_0^2}+\frac{3\overline{V}}{2\lambda^2V}\right). \tag{25}$$

Since $\overline{V}=3D/\lambda$ and assuming $V=\overline{V}$, we can write

$$\tau_P=\frac{1}{\pi\rho_T\overline{V}r_0^2}+\frac{1}{2\pi\rho_T D\lambda}. \tag{26}$$

This is very similar to the more rigorous treatment due to Ham[15] (p.347) when a "radiation-type" boundary condition at $r=\lambda$ is applied, using the SR theory to define this condition. In fact, halving the second term in Eq. (26) gives exact agreement, and considering the approximations used to obtain Eq. (26) this is very satisfactory. We notice that this term is then precisely Eq. (20) with $r_0=\lambda$, and that the first term (26a) is the standard SR result. The summation indicates that the two processes are in series. So we have, finally,

$$\tau_P=\tau_{PR}+\tau_{PD}(r=\lambda)=\frac{1}{\pi\rho_T\overline{V}r_0^2}+\frac{1}{4\pi\rho_T D\lambda}. \tag{27}$$

Studying Eqs. (20) and (27) we can predict the behavior of the transient lifetime for all values of $r_0<r_{\max}$. The lifetime transfers from diffusion limited to recombination limited as r_0 becomes less than λ and also, when this occurs, the diffusion-controlled term is limited by the value of the mean free path.

3. *Temperature dependence*

The temperature dependences for the two cases are significantly different in that τ_{PR} simply reflects the cross-section and thermal-velocity variation with temperature, whereas for τ_{PD} the cross-section dependence is weaker and compounded with the temperature dependence of the diffusion coefficient. Further, if some hypothetical mechanism reduces τ_{PR} while maintaining $r_0<\lambda$, a temperature-dependence independent of r_0 would emerge that would reflect the diffusion-limited case for $r_0=\lambda$, depending on D and $\overline{V}$ alone.

D. Synopsis

The concentration and temperature dependences obtained in Sec. II are tabulated in Table I where the concentration dependence is expressed in terms of the mean defect spacing, d, for the sake of comparison. The dependences of the transient lifetimes on r_0 for a fixed defect spacing of 10^{-3} cm are compared in Fig. 2. The values for D, λ, and $\overline{V}$ used in Fig. 2 are those for n-GaP at 300 K, selected for comparison with experiment. The relative effects of the various sink geometries can be readily seen. When r_0 becomes sizable with respect to the defect spacing, the lifetimes become depressed and converge because the effective volume of the crystal is being reduced. In the $r_0=d$ limit, of course, the lifetimes all tend to zero. In the absence of this effect (i.e., $d>r_0$), the most significant results are that the diffusion-limited lifetime for plane and line sinks are independent of r_0, and that the familiar SR behavior for point sinks is no longer obeyed. Taking

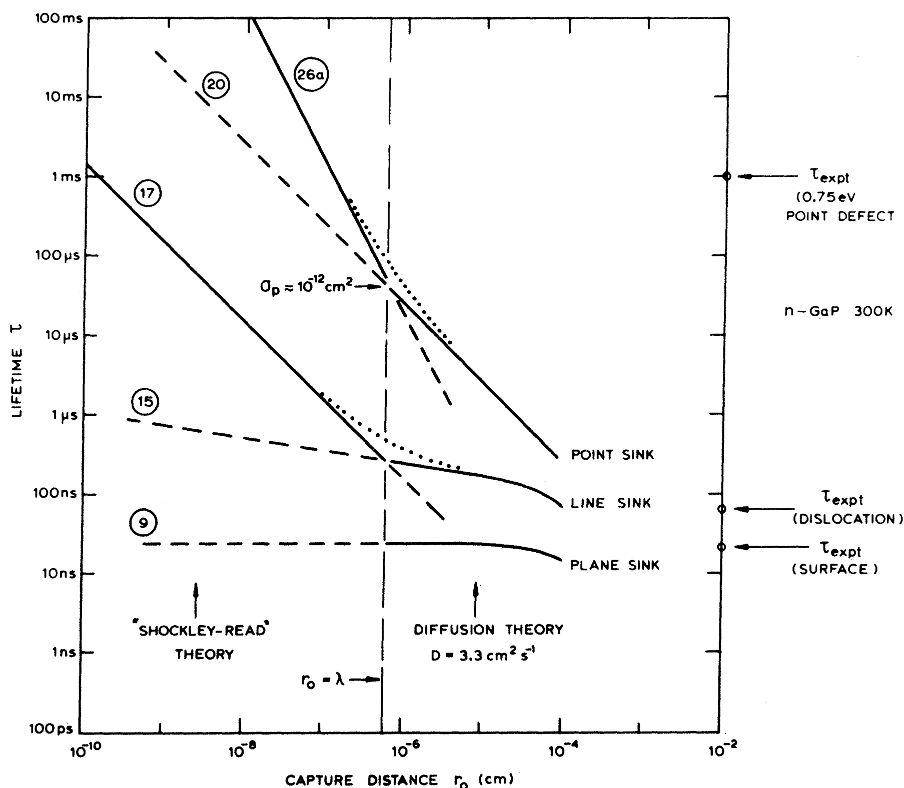

FIG. 2. The dependence of the transient lifetime of minority carriers on the capture distance for neutral plane, line, and point defects in crystals. The encircled numbers apply to the equations in the text, and values for λ, and D and defect spacing have been chosen to be appropriate for hole recombination in n-GaP. The value of K in Eq. (17) has been set to 0.3 so that the lifetimes in Eq. (15) and Eq. (17) are equal at $r=\lambda$. The experimentally observed lifetimes are indicated on the right-hand axis. The dotted portions of the curves give the resultant lifetime in the transition region between SR theory ($r_0<\lambda$) and diffusion-limited theory ($r_0>\lambda$).

TABLE I. Dependence of transient lifetime in semiconductors on defect geometry, defect concentration, and sample temperature. d = average defect spacing, S = surface recombination velocity, r_0 = capture distance, $\bar{V}$ = thermal velocity of minority carrier, and D = diffusion coefficient of minority carrier.

	Concentration dependence		Temperature dependence	
	Recombination limited	Diffusion limited	Recombination limited	Diffusion limited
Plane sink	d	d^2	S^{-1}	D^{-1}
Line sink	d^2	$\sim d^2$	$\bar{V}^{-1}r_0^{-1}$[a]	$D^{-1}[r_0]$[b]
Point sink	d^3	d^3	$\bar{V}^{-1}r_0^{-2}$[a]	$D^{-1}r_0^{-1}$

[a] $S=\infty$ assumed to define r_0.
[b] $[r_0]$ signifies weak dependence.

the line-sink results in Fig. 2, the region where τ is relatively independent of r_0 is not very extensive, but if d were to be increased to 10^{-1} cm (i.e., 10^2 dislocations per square centimeter), an extensive region of relatively constant lifetime would result.

III. EXPERIMENTAL

A. Materials

The measurements have been carried out exclusively on n-type liquid-phase epitaxial GaP, either undoped or sulfur doped with carrier concentrations in the range 10^{15}–10^{17} cm^{-3}. Samples were selected such that the lifetime was dominantly controlled by the particular defect under study. For the point-sink case conventional "cool-down" epitaxial layers were used, where it has already been established that τ is controlled by a deep defect level located 0.75 eV from the valence band, independent of the majority electron concentration.[4] The concentration of this state as well as the variation of the hole capture cross section with temperature was measured by Hamilton and co-workers using minority carrier capture (MCC) deep-level analysis.[4] In these samples the role of surface and/or interface recombination and dislocation recombination was ignored because the epitaxial layer thicknesses ($\gtrsim 60$ μm) and dislocation densities ($\sim 10^4/cm^2$) were, respectively, much larger and smaller than the values required to interfere with the point-sink-controlled lifetime (~ 200 ns). For the study of surface and/or interface-controlled lifetime, samples were beveled as described previously[5] to obtain a wedge of varying thickness and lifetime measurements taken in the thickness range 5–40 μm. Again samples were selected such that the dislocation and point-sink-controlled lifetimes were much larger than the surface-controlled value. For this latter study and the study of dislocation-controlled lifetime, material grown by isothermal techniques were included, in which the point-sink (0.75 eV defect) concentration is not detectable (i.e., $< 10^{11}$ cm^{-3}) and very long lifetimes (up to 5 μs) have been observed. When studying the dislocation-limited lifetime, the epitaxial layer thicknesses were >100 μm so that surface-controlled effects were also negligible.

B. Measurement of defect concentrations

For the plane-sink case the thickness measurements were made by cleaving and etching the beveled structures, thus obtaining the wedge angle. For the point-sink case the MCC-determined concentrations were used, which do not vary significantly with position in the epitaxial layers. For the dislocation-limited case the dislocation concentration was measured using cathodoluminescence (CL) techniques in a scanning electron microscope.[17] Areas of the samples were carefully mapped and selected for uniform dislocation density, and then care was taken to measure the lifetime in exactly these locations on the samples.

C. Measurement of lifetimes

The decay time of green CL excited in the samples was used to determine the transient minority lifetime. This technique has been satisfactorily cross-correlated with diffusion-length measurements.[18] A pulsed 70-kV electron beam was focused onto the samples to form a 150-μm diameter spot. Peak currents of ~ 1 μA were used and the pulse lengths of typically 10-μs duration ensured that the steady state was reached before the beam was switched off. The electron beam energy, focused diameter, and current could be varied over wide ranges to check the validity of the measurements. The beam switching was achieved by electrostatic deflection with a switching time of 3 ns. The trailing edge of the light pulse was then measured using a fast photomultiplier and a storage oscilloscope with a sampling amplifier. By applying a logarithmic amplifier to the received signal, the exponentiality of the decay was checked and the exponential decay time determined. The temperature of the samples, mounted in indium on the cold finger of a Dewar containing liquid nitrogen, was controlled using conventional techniques in the temperature range 100–350 K.

It should be emphasized that the experimental conditions used were carefully chosen to be consistent with the theoretically modeled situations, and on occasion this was tested by dramatically changing the experimental parameters. For example, the excited volume has to be large compared with the carrier diffusion length; otherwise, carrier spread can alter the decay kinetics. As another example, the true exponential decay transient ($t \to \infty$) was measured, rather than the initial part of the transient which approximates to the steady-state lifetime. These parameters are not equivalent in the situations modeled and care was taken to isolate the $t \to \infty$ component.

IV. RESULTS AND DISCUSSION

A. Plane sink–diffusion-limited lifetime in filaments

1. Concentration dependence

Earlier work[5] has shown that the free surfaces

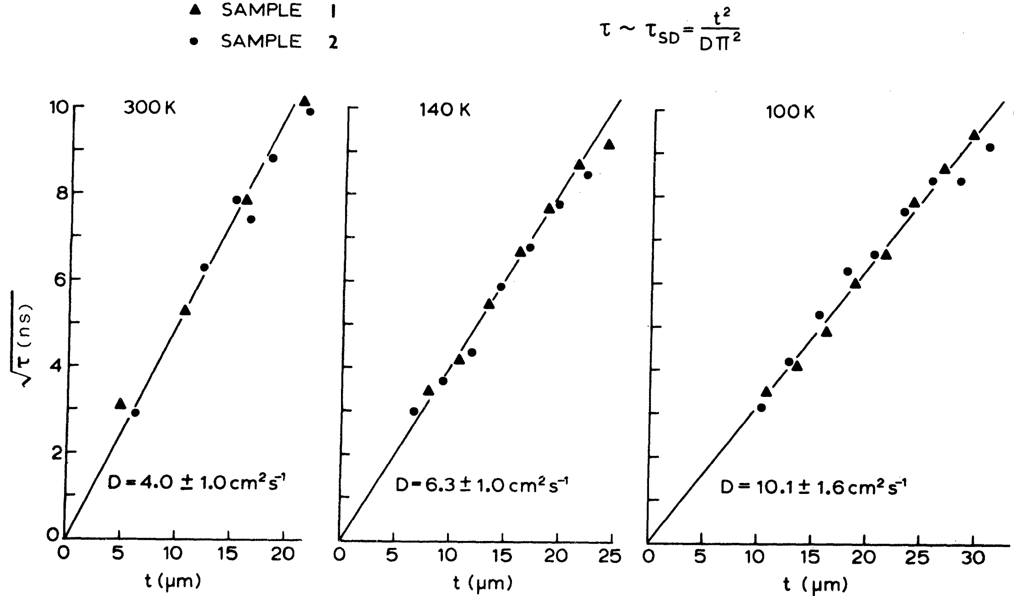

FIG. 3. The variation of transient hole lifetime with filament thickness in n-GaP for three sample temperatures. Values for the hole diffusion coefficient are obtained from the slopes of the fitted lines.

and epitaxy-substrate interfaces of layers give rise to high values of S such that $S \rightarrow \infty$ conditions apply. Two samples were selected for this work and low-angle bevels were produced such that the epitaxy formed a wedge bounded by the lapped surface and the epitaxial interface. Both samples (1 and 2) were grown by the isothermal liquid-phase epitaxy (LPE) technique and at room temperature they exhibited bulk lifetimes of 1500 and 300 ns, respectively. The lifetime was measured, at different points scanning up the wedge so that lifetime (τ) versus thickness (θ) data were obtained. The measurements were made at three temperatures (300, 140, and 100 K). The data are shown in Fig. 3 and as expected for diffusion-limited recombination [Eq. (8)], the square-root dependence of lifetime on thickness is confirmed at all temperatures. The slight departure of the data below the linear relationship at larger thicknesses is due to interference from the bulk lifetime, as was confirmed by extending the measurements to much larger values of θ.

2. *Temperature dependence*

As outlined earlier, the temperature dependence of the diffusion-limited lifetime τ_{SD} depends only on the minority hole diffusion coefficient which can be obtained from the slope of the lines in Fig. 3. But in order to verify these values of D some independent data are required. We can obtain such data from majority carrier mobility measurements.

The scattering processes encountered in such measurements in GaP involve lattice phonons and charged impurity ions, as has been discussed by Rode[19] and Wiley.[20] The minority hole in n-type GaP will be screened by the majority electrons and the ionized impurity scattering will be reduced from that observed in p-type material of the same majority carrier concentration, to a level closer to that observed for electrons. When one adds to this the fact that the ionized donor concentration is progressively reduced by carrier freeze-out as the temperature falls from 300 to 100 K, it becomes reasonable to assume that the ionized impurity scattering of minority holes is negligible in the samples studied (10^{15} cm$^{-3} \leq N_D - N_A \leq 10^{17}$ cm^{-3}). The minority hole mobility can thus be predicted to be controlled by lattice scattering and equivalent to that observed in high-purity p-type material. Casey *et al.*[21] have obtained accurate data for this lattice-limited mobility and find that[20]

$$\mu_h \sim 130(300/T)^{2.2} \text{ cm}^2\, V^{-1}\, \text{s}^{-1}, \qquad (28)$$

where T is the absolute temperature. Using the Einstein relationship the minority hole diffusion coefficient D can be obtained:

$$D \sim 3.3(300/T)^{1.2} \text{ cm}^2 \text{ s}^{-1}. \qquad (29)$$

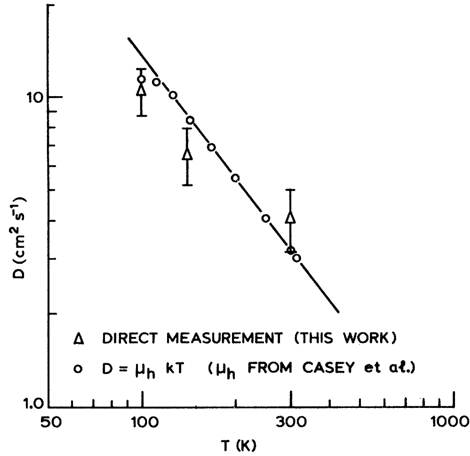

FIG. 4. The variation of hole diffusion coefficient in n-GaP with temperature. The measured values are compared with those deduced from majority hole mobility data.

The values of D obtained from Fig. 3 are compared with this relationship in Fig. 4, where the data points from Casey's work have been reproduced. The uncertainty in our measured values are rather high because the diffusion coefficient appears as a square root in the analysis of the slopes in Fig. 3. Also the precision of locating the zero-thickness points in the data is not high, adding further to the uncertainty. However, the agreement is very satisfactory and we conclude that (1) the diffusion-limited case has been verified and (2) that the values of D predicted

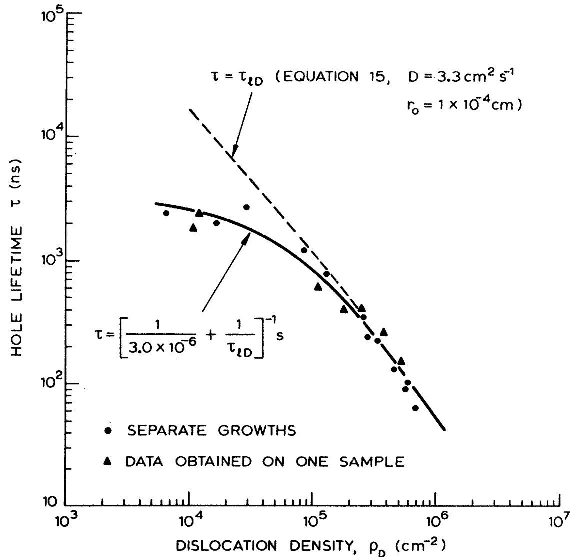

FIG. 5. The dependence of transient lifetime (300 K) on dislocation density in n-GaP. The data are fitted using the diffusion-limited theory [Eq. (15)], with a residual (bulk) lifetime of 3.0 μs.

from mobility can be applied in the analyses that follow. (We choose to do this because of the greater precision of the mobility data.)

B. Line sink–diffusion-limited recombination

1. Concentration dependence

Room-temperature data taken from a range of isothermal LPE samples have been previously published[5] and are reproduced in Fig. 5. Data obtained on one sample which showed a wide variation of ρ_D across its surface are included and the dislocation densities were counted in carefully defined 500-μm diameter regions on this sample. In Fig. 3 the dislocation density varies in the range 1×10^4–1×10^6 cm^{-2}, and at high dislocation densities the lifetime follows Eq. (15) for τ_{lD}, the diffusion-limited lifetime.

A good fit is obtained by setting $r_0 = 1\times10^{-4}$ cm and using the value of $D = 3.3$ cm^2 s^{-1} obtained in Sec. IV A, but it should be noted that a ±20% change in D with a concurrent 30% change in r_0 can be accommodated without materially affecting the fit. At low dislocation densities the lifetime ceases to be dislocation controlled and a value of 3.0 μs for this residual lifetime (τ_r) has been used to fit the data, following the expression for parallel processes:

$$\tau = \left(\frac{1}{\tau_r} + \frac{1}{\tau_{lD}}\right)^{-1} . \tag{30}$$

This value for τ_r is presumed to be set by the concentration of residual point defects, because sample thicknesses ($\gtrsim 300$ μm) predict a surface-controlled lifetime of about 20 μs using Eq. (9). The large value of r_0 is indicative of defect atmosphere around the dislocation core, and it is important to note that the downward curvature in the data at the highest dislocation densities results from the fact that r_0 is becoming significant with respect to the mean dislocation spacing. This value of r_0 is also much greater than the mean free path ($\sim 6\times10^{-7}$ cm) and is therefore consistent with the diffusion-limited kinetic theory. These D, r_0, and τ_r values are altered from those deduced in the earlier publication[5] which included a few data points taken from other workers' publications. (We have chosen to analyze only our data in the present treatment.)

2. Temperature dependence

Having established all of the necessary parameters from the room-temperature data and other independent sources we can now use the temperature dependence as a positive test of the theory. The sample with well defined regions of uniform

but different dislocation densities (see Fig. 5) was used for these measurements. The lifetime was carefully measured in two regions on this sample, one where the lifetime was dislocation controlled ($\rho_D = 3.8 \times 10^5$ cm^{-2}) and the other where the residual lifetime was becoming dominant ($\rho_D \lesssim 1 \times 10^4$ cm^{-2}), and the sample temperature was varied in the range 100–350 K. The data are shown in Fig. 6 plotted on the axes often used to deduce activation energies. It is clear that the residual lifetime remains much larger than that from the highly dislocated region throughout the temperature range studied. Assuming that the interference from the residual lifetime in the dislocated region is negligible (which seems reasonable on inspecting Fig. 5), values for τ_{lD} were obtained from the high-dislocation-density region. The values of D, obtained from Fig. 4, and $r_0 = 1.0 \times 10^{-4}$ cm were inserted into Eq. (15) for τ_{lD} and are compared with the experimental data in Fig. 7. Because the data point for the measurement at 300 K (τ = 255 ns, $\rho_D = 3.8 \times 10^5$) does not lie exactly on the fitted line in Fig. 5, the lifetime data in Fig. 7 been normalized to the 300-K lifetime, and the agreement is excellent. We have therefore confirmed the diffusion-limited theory.

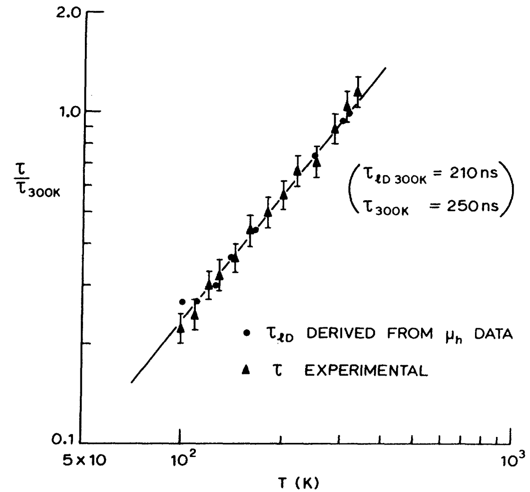

FIG. 7. The temperature dependence of transient, dislocation-controlled lifetime in n-GaP compared with the diffusion-limited theory (τ_{lD}).

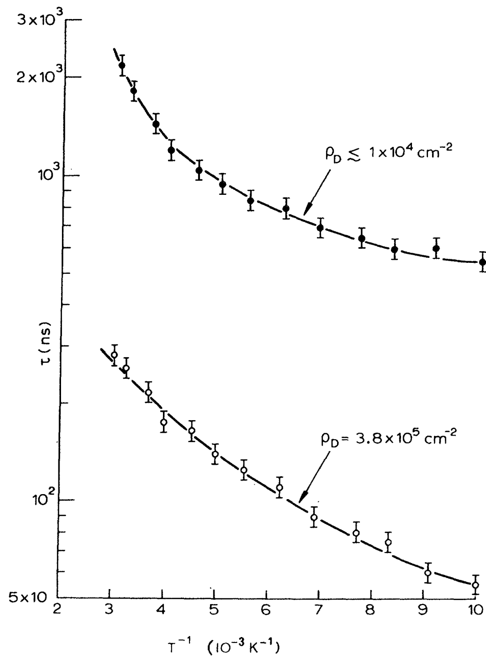

FIG. 6. The variation of transient lifetime with temperature in n-GaP for low and high dislocation density material. The data were obtained at different locations on the sample shown in Fig. 5 (▲). The low dislocation density data give the behavior of the residual lifetime and the high dislocation density data are used to test the diffusion-limited theory.

Figure 7 is plotted on logarithmic axes and demonstrates that the power law is precisely obeyed. One could reasonably fit the data of Fig. 6 to find an exponential activation energy which is clearly an erroneous procedure. This highlights the danger of the common practice of assuming exponential temperature dependences. A very wide range of temperatures or very precise data are necessary to establish such behavior.

If we consider the residual lifetime data in Fig. 6, some comments can be made: The data do not fit the power-law dependence expected for surface- or dislocation-controlled lifetime, nor do they fit the power-law dependence obtained for the 0.75-eV hole trap (see Sec. IV C). One might consider that it could be fit by a combination of these processes but this is also not possible because of the shape of the dependence, i.e., fitting the low-temperature region to a $T^{+1.2}$ dependence is not consistent with obtaining *longer* 0.75-eV point-sink-controlled lifetime near room temperature. We therefore suggest that in this sample the residual lifetime is controlled by unknown, probably point defect recombination in the bulk of the sample.

C. Point sink—lifetime controlled by recombination at 0.75-eV deep level centers

1. Concentration dependence

The dependence of lifetime on the concentration of 0.75-eV defect states has been established in

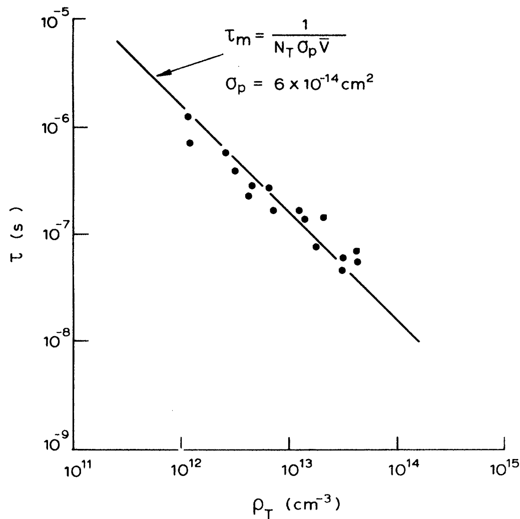

FIG. 8. The variation of transient hole lifetime (300 K) in n-GaP with the concentration of 0.75 eV deep-level (point) defects. A value of 6×10^{-14} cm^2 is obtained from the fitted line (SR theory).

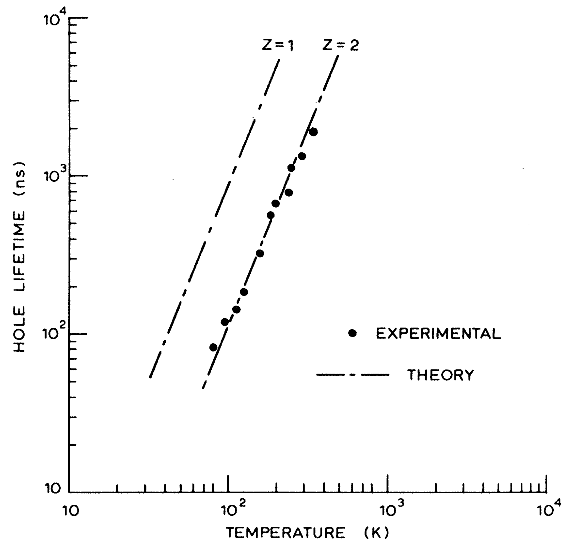

FIG. 9. The temperature dependence of point defect-controlled, transient lifetime in n-GaP. The concentration of 0.75 eV deep-level defects was 10^{-12} cm^{-3} and the temperature dependence is that obtained from hole-capture cross section data. The "modified Lax" theory recombination at negatively charged defects is shown for the singly ($Z=1$) and doubly charged ($Z=2$) state.

earlier work.[4] The experimental results for cool-down LPE materials are reproduced in Fig. 8 and the expected inverse dependence is observed. From these data and independent MCC analysis a value of about 6×10^{-14} cm^2 ($r_0=1.4\times10^{-7}$ cm) has been deduced for the hole capture cross section (σ_p) at 300 K, under SR kinetics. This value of r_0, although fairly close to the value of λ (6×10^{-7} cm), is significantly small for the SR kinetic arguments to be valid, and the diffusion-limited kinetics of Sec. II should not apply.

2. *Temperature dependence*

The experimental results showing the temperature dependence have been presented in earlier publications.[4,22] Three sets of measurements were in fair agreement: (1) direct measurements using the CL decay technique, (2) values deduced from diffusion-length measurements, and (3) values calculated using σ_p data obtained from MCC measurements under SR theory.

Earlier attempts to analyze the temperature dependence[22] sought exponential dependences by the usual ln versus reciprocal-temperature plots, but relatively poor fits were obtained (see Fig. 4, Ref. 22). In order to obtain the most precise temperature-dependence data for the purposes of this paper, we have selected the value of τ (300 K) obtained from Fig. 8 for a point defect concentration of 10^{12}/cm^3 and ascribed to it the temperature dependence measured using the MCC techniques. The reasons for this selection are as follows: (1) Since this paper attempts to analyze the lifetime observed in neutral crystals, the 300-K data of Fig. 8 are most appropriate. (2) The direct assessment of the temperature dependence of τ was compromised by an additional de-trapping component in the luminescence decay signal at lower temperatures, so these were rejected. There were also considerable uncertainties in the diffusion length data, so the more precise σ_p measurements obtained by deep-level analysis (Fig. 5, Ref. 4) represent the best experimental data on the temperature dependence.

Figure 9 shows the temperature dependence of lifetime obtained in this way, plotted on logarithmic axes. A clear power-law dependence is observed ($\tau \propto T^{+2.4\pm0.1}$) and taking $m^*=0.6m_0$ to calculate the thermal velocity, σ_p has been set to 5.5×10^{-14} cm^2 at 300 K, in good agreement with the average value obtained by the direct MCC measurements (6×10^{-14} cm^2). It is tempting to try to analyze the power-law dependence using diffusion theory. Clearly the simple theories for neutral defects presented in Sec. II will not predict

a $T^{2.4}$ dependence in the diffusion limit. Also a brief consideration of the simple diffusion limit for a negatively charged defect does not produce a tenable interpretation. [I.e., as follows: If one considers that the particle is accelerated by the Coulomb field at the defect ($r_0 < r < \lambda$) and that the diffusion field is largely unaltered, one could argue that the velocity at the recombination site is significantly increased above the thermal velocity, and using Eq. (27) the recombination could become limited by the diffusion term. This lifetime is too short to agree with experiment and the temperature dependence ($T^{+2.9}$) also disagrees with the observed behavior. The above case ignores the fact that the particle is losing energy as it diffuses toward the charged center and later in the text we turn to the Lax theory to quantify the behavior when this energy loss is included.]

A number of quantitative treatments of nonradiative recombination are available, which are epitomized by those due to Lax[1] and Henry and Lang.[3] The latter authors predict temperature dependences for multiphonon transitions to the ground states of deep defects [i.e., processes (3) or (6) in Fig. 1] which contain exponential functions of temperature and are inconsistent with the present data. On the other hand, Lax considers phonon cascade processes through the very closely spaced high excited states of a Coulomb-attractive center [i.e., processes (2) and (5) in Fig. 1] and predicts a power-law temperature dependence. Recently, Abakumov and Yassievich[2] have presented a simpler treatment of the Lax theory and have pointed out errors in the original author's treatment. They produce an expression for the capture cross section based on the interaction of low-energy acoustic phonons with the recombining carrier:

$$\sigma = \frac{8}{3}\left(\frac{e^2 Z}{e_0 kT}\right)^3 \frac{m^* E_v^2}{\rho \hbar^4} \tag{31}$$

where eZ ($Z = 1$) is the electronic charge on the defect, e_0 is the dielectric constant (11.1), m^* is the averaged effective mass for the recombining carrier ($0.6m_0$), ρ is the crystal density (4.1g/cc), and E_v is the deformation-potential constant of the valence band for acoustic mode vibrations (?eV). The values in parentheses are those judged to be most reliable for holes in GaP. The choice of E_v deserves some discussion because many authors have suggested widely different values, usually in attempts to analyze majority carrier mobility in GaP. Casey *et al.*[21] propose a value of 1.0 eV, Wiley[20] 3–8 eV, Diguet[23] 12.7 eV, Somogyi[24] 18 eV, Cohen and Bedard[25] 21.7 eV, and Haga and Kimura[26] 55 eV.

We could be assisted in our choice by noting that the sum of the valence-band and conduction-band deformation-potential constants is equal to the change in the band gap per unit strain, which is small (~1.0 eV[21,27]). This implies that the two deformation-potential constants are no more than 1.0 eV different from each other. For the conduction band of GaP we can take a value of 13 eV following Rode[19] and, noting that Koscis[28] deduces a value (8–10 eV), in fair agreement. We could thus select a value of ~13 eV for E_v, but would have to put a very large uncertainty on it. We will avoid this problem by making an assumption which is very much in keeping with the theme of this paper. If we assume that the low-energy phonon-interaction mechanisms embodied in Eq. (31) are approximately quantified in the minority carrier mobility data we have deduced from Casey's work, the deformation-potential constant can be obtained from the standard equation for carrier mobility due to acoustic-phonon scattering.[21,23]

$$\mu_h = \frac{\sqrt{8\pi}\, e \hbar^4 \rho C^2}{3(m^*)^{5/2}(kT)^{3/2}E_v^2} = \frac{5.8\times 10^7}{(m^*/m_0)^{5/2}E_v^2 T^{3/2}}, \tag{32}$$

in units of $\mathrm{cm^2\, V^{-1}\, s^{-1}}$ where C is the longitudinal velocity of sound (6.2×10^5 cm/s, Ref. 19) and the other parameters have been defined earlier. This assumption is directly justified if the hole mobility is dominated by acoustic-phonon processes, but of course the expected $T^{-1.5}$ dependence is not observed in the experimental data. However, some authors (Wiley,[20] Diguet[23]) agree that this *is* the case at temperatures near 100 K, and we will make the same assumption. So inserting $\mu_{100} = 1500\ \mathrm{cm^2 V^{-1} s^{-1}}$ at $T = 100$ K (Ref. 20) in Eq. (32), we can obtain a value of $E_v = 11.8$ eV in reasonable agreement with the earlier estimate, and insert it in Eq. (31) to obtain

$$\sigma = 1.0\times 10^{-7}/T^3, \tag{33}$$

in units of $\mathrm{cm^2}$.

We now need to develop this result to obtain the lifetime. There is a critical radius (r_c) embodied in Eq. (31) at which the rate limitation occurs. This radius (~2000 Å) can be calculated by assuming that excited states of depths $\sim m^* u^2$ (~0.2 meV), where u is the velocity of sound, play the principal role as suggested by Abakumov and Yassievich.[2] In the absence of a Coulomb field, a constant minority carrier concentration might be assumed for r greater than r_c. However, as has been recognized by earlier workers in the field of gas kinetics[29] and semiconductor recombination theory,[30] the attractive field generates a local increase in the minority carrier concentration, and following Pekar[30] the recombination

rate per cc should be enhanced by a factor $\exp[-eV(r_c)/kT]$, where $V(r_c)$ is the potential at r_c. r_c is so large in our case that this concentration factor is negligible in the temperature range 100–300 K, so we can simply obtain, in seconds,

$$\tau = \frac{1}{\rho_T \overline{V} \sigma} \doteq 8.5 \times 10^{-12} T^{2.5} , \qquad (34)$$

which is the SR expression for a defect concentration of 10^{12} cm^{-3}, taking $\overline{V} = 2\times 10^7$ cm/s at 300 K. Equation (34) is reproduced in Fig. 9 and it is seen that the temperature dependence is in good agreement and the absolute magnitude of the lifetime is predicted to within one order of magnitude. This is considered to be a tolerable agreement in view of the assumptions embodied in Eq. (31). The agreement would be very close (see Fig. 9) if a double negative charge on the defect were assumed ($Z=2$) in Eq. (31). This would imply a very small majority carrier capture cross section because of Coulomb repulsion. This electron cross section has been measured to be ~2×10^{-17} cm^2 (300 K) and it could be that this is small enough to be consistent with a Coulomb repulsive center, so this interpretation is preferred.

V. CONCLUSIONS

We have presented a complete theoretical treatment for the analysis of recombination at neutral defects in semiconductors with particular reference to large recombination-rate limits. When the capture distance exceeds the mean free path of the minority carrier, the recombination kinetics become controlled by diffusion, the concentration and temperature dependences change, and the SR kinetic theory is violated. Using experimental data on the temperature dependence of lifetime in n-GaP as a positive test of the theory, a completely satisfactory agreement has been obtained in the case of plane and line defects. The experimental values for the 300-K lifetime for a defect spacing of 10 μm are indicated in Fig. 2. In the point-defect case the capture distance is a little less than the mean free path and the diffusion limit for neutral defects does not apply. If the point defect is assumed to be doubly negatively charged, however, a good agreement is found in both the magnitude and temperature dependence of the lifetime, using a modified "Lax theory".[2] We can deduce that in the plane- and line-sink cases, the observed behavior represents a fundamental lower limit to the observed lifetime regardless of the strength of the recombination center. For the charged point defect at 300 K a capture distance of ~15 Å is measured. So (following the simple theory on which this paper is based), for larger capture distances which do not exceed the distance at which the "bottleneck" occurs (~2000 Å), the recombination is governed by the "diffusion" kinetics in the Coulomb field around the defect, and a similar lifetime limitation applies. Although we have obtained very good agreement for the doubly charged point sink and the resulting interpretation appears sounder than previous analyses of the 0.75-eV state in n-GaP, a further positive test is needed before the results can be viewed with the same confidence as those obtained for plane and line sinks. Failing this, we require a more rigorous treatment for the modified Lax theory, incorporating a complete description of all of the relevant phonon interactions in the n-type GaP material, which might be obtained from an improved analysis of the mobility data.

A cursory survey of the literature on plane- and line-sink recombination in other semiconductors indicates: (1) Diffusion-limited conditions are observed for plane sinks in high-quality material, especially for large values of the defect spacing, but temperature-dependence data are seldom reported. (2) Diffusion-limited lifetime is not observed for line sinks in Si where the sinks appear to be very weak.[31] (3) For dislocations in Ge the sink strength is much larger, and two publications[32,33] present a power-law temperature dependence for the dislocation-controlled lifetime in p-type Ge for the temperature range 100–300 K. The lifetimes observed in the control samples in their work have a very similar temperature dependence and might be interpreted under the diffusion-limited theory for plane sinks, as in the present work. However, the Ge data cannot be brought into quantitative agreement with the diffusion theory unless very speculative assumptions are made about the behavior of the minority electron diffusion coefficient and its temperature dependence. (4) Recombination at dislocations in p-type GaAs seems to be diffusion limited[31] but the temperature dependence has not been reported.

ACKNOWLEDGMENTS

We are indebted to A. R. Peaker and M. L. Young for valuable contributions to this work.

[1]M. Lax, Phys. Rev. 119, 1502 (1960).
[2]V. N. Abakumov and I. N. Yassievich, Zh. Eksp. Teor. Fiz. 71, 657 (1976) [Sov. Phys.—JETP 44 345 (1976)]. (1976)].
[3]C. H. Henry and D. V. Lang, Phys. Rev. B 15, 989 (1977).
[4]B. Hamilton, A. R. Peaker, and D. R. Wight, J. Appl. Phys. 50, 6373 (1979).
[5]D. R. Wight, I. O. P. Conference on Materials and Processing Effects in Semiconductor Devices, March, 1976 [J. Phys. D 10, 431 (1977)]. Also, W. Harding, I. D. Blenkinsop, and D. R. Wight, Electron. Lett. 12, 503 (1976); and I. D. Blenkinsop, W. Harding, and D. R. Wight, Electron. Lett. 13, 14 (1977).
[6]C. Van Opdorp, A. T. Vink, and C. Werkhoven, Int. Symp. on GaAs and Related Compounds, Sept. 1976, I. O. P. Conference Series 33(a), p. 317 (1977).
[7]C. Werkhoven, C. Van Opdorp, and A. T. Vink, Int. Symp. on GaAs and Related Compounds, Sept. 1976, I. O. P. Conference Series 33(b), p. 317 (1977).
[8]T. Suzuki and Y. Matsumoto, Appl. Phys. Lett. 26, 431 (1975).
[9]W. Shockley and W. T. Read, Jr., Phys. Rev. 87, 835 (1952).
[10]J. Jeans, *Kinetic Theory of Gases* (Cambridge University Press, London, 1948), p. 60.
[11]J. P. McKelvey, *Solid State and Semiconductor Physics* (Harper and Row, New York, 1966), p. 351.
[12]W. Shockley, *Electrons and Holes in Semiconductors* (Van Nostrand, New York, 1950), p. 323.
[13]J. P. McKelvey, *Solid State and Semiconductor Physics* (Harper and Row, New York, 1966), p. 354.
[14]P. Penning, Philips Res. Rep. 14, 337 (1959).
[15]F. S. Ham, J. Phys. Chem. Solids 6, 335 (1958).
[16]J. B. Hasted, *Physics of Atomic Collisions* (Butterworths, London, 1972), p. 9.
[17]J. M. Titchmarsh, G. R. Booker, W. Harding, and D. R. Wight, J. Mater. Sci. 12, 341 (1977).
[18]M. L. Young and D. R. Wight, J. Phys. D 7, 1824 (1974).
[19]D. L. Rode, *Semiconductors and Semimetals* (Academic, New York, 1975), Vol. 10, p. 1.
[20]J. D. Wiley, *Semiconductors and Semimetals* (Academic, New York, 1975), Vol. 10, p. 91.
[21]H. C. Casey, Jr., F. Ermanis, and K. B. Wolfstirn, J. Appl. Phys. 40, 2945 (1969).
[22]R. M. Gibb, G. J. Rees, B. W. Thomas, B. L. H. Wilson, B. Hamilton, D. R. Wight, and N. F. Mott, Philos. Mag. 36, 1021 (1977).
[23]D. Diguet, Solid-State Electron. 13, 37 (1970).
[24]K. Somogyi, Phys. Status Solidi A 37, 653 (1976).
[25]M. M. Cohen and F. D. Bedard, J. Appl. Phys. 39, 75 (1968).
[26]E. Haga and H. Kimura, J. Phys. Soc. Jpn. 19, 658 (1964).
[27]R. Zallen and W. Paul, Phys. Rev. 134A, 1628 (1964).
[28]S. Koscis, Phys. Status Solidi A 28, 133 (1975).
[29]H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952), p. 330.
[30]S. I. Pekar, *Research in Electron Theory of Crystals* (in Russian) 1951, U. S. Atomic Energy Commission Ref. AEC-pr-5575 (1963), English translation.
[31]D. R. Wight, J. Phys. D 10, 431 (1977).
[32]L. I. Kolensnik, Fiz. Tverd. Tela 4(6), 1449 (1962) [Sov. Phys.–Solid State 4, 1066 (1962)].
[33]G. K. Wertheim and G. L. Pearson, Phys. Rev. 107, 694 (1957).