# Decay kinetics of the red luminescence of GaP(Zn, O) for quasi-thermal-equilibrium conditions

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(Received 23 August 1972; revised manuscript received 25 April 1974)

The luminescent decay of the red "exciton" emission of GaP(Zn, O) has been analyzed for the case of high-density excitation in the temperature range (40–100) °K. The decay behavior under these conditions has previously been poorly understood. We show that kinetics based on a quasi-thermal-equilibrium model adequately explain the literature data. The crucial step in the analysis resides in the use of proper impurity activation energies. Advantages of the present method of analysis, based on its relative simplicity, are also discussed.

## I. INTRODUCTION

Luminescent-decay data have often been used for an improved understanding of the physical nature of the recombination transitions. Thus, in view of the technological importance of the red emission in GaP(Zn, O), this system has been extensively studied. Early results by van der Does de Bye[1] showing a connection between the time decay and the luminescence efficiency were soon followed by further studies by Bhargava,[2] Jayson et al.,[3] and Dishman et al.[4] Of particular practical importance was the realization by Bhargava[2] and Jayson et al.[3] that a quantitative understanding of the connection could lead to a prediction of phosphor efficiency without measuring the absolute efficiency itself, a difficult measurement. Extensive additional[5–10] work on luminescent decay has followed these original works.

Taken as a whole, the picture which has emerged from these studies[1–10] on the decay is one of considerable complexity. Not only is there a dependence on temperature, but also a dependence on sample and on excitation conditions, as Jayson and Bachrach[7] (JB) have shown by detailed measurements. In view of this complexity, some aspects of the decay behavior are still poorly understood. In the present paper we give in Sec. II a unifying classification of various ranges of decay behavior in terms of the occupancy of the main levels. Secondly, we explain the time decay in the poorly understood range of partly filled hole levels under relatively strong excitation; we show that a rise in decay time observed as the temperature increases beyond $\approx 40$ °K results from thermal release of holes from the exciton hole levels, leaving fewer such centers available for recombination. We employ a convenient quasiequilibrium approach which has not previously been applied to GaP (Sec. III B). Also, the validity of this approach is checked numerically (Sec. III C). The results show that one requires a careful specification of the thermal activation energies for the analysis. This problem,

together with the effect of screening[11] on these energies, is an important aspect which is discussed in Sec. III D. A detailed comparison to the experimental data[7] for GaP as well as a discussion of the present approach are presented in Sec. IV, and conclusions in Sec. V.

## II. CLASSIFICATION OF DECAY RANGES: REVIEW OF PREVIOUS RESULTS

The over-all time decay of a specific luminescence band is determined by the decay times of the relevant process (or processes), modulated by the probability that a particular process can take place. This latter factor depends on the occupancy of the initial and final levels. It is this feature with which we shall concern ourselves in this section. We show in Fig. 1 the impurity levels relevant to the red luminescence of GaP doped with Zn and O. This luminescence takes place[12,13] from the electron (upper) level of a nearest-neighbor Zn-O complex (the "exciton" center) to either the hole level of the complex (with decay time $\tau_{xr}$) or to an isolated Zn acceptor level (with a decay time $\tau_{ar}$). It must be noted that an exciton hole level can exist only for excitons with filled electron levels. Compensating accidental shallow donor impurities (Si, S, etc.) are also present in the material, and can influence the occupancy of the acceptor levels.

We now classify various decay ranges according to the occupancy and thermalization of the electron and hole levels of the exciton. Five distinct ranges can be distinguished, as shown in Fig. 2, a schematic composite of the data in Refs. 2, 3, 7, and 10. The numbering of the ranges in Fig. 2 follows the prescription:

(i) Range 1: both electron and hole levels are essentially fully occupied. This condition requires both low temperatures *and* high excitation densities. We assume the high excitation to fill *all* impurity levels. (Under low excitation, the generated holes will preferentially occupy the deeper Zn levels, and the occupancy of the exciton hole level will be low.) The decay behavior in this range has been accounted
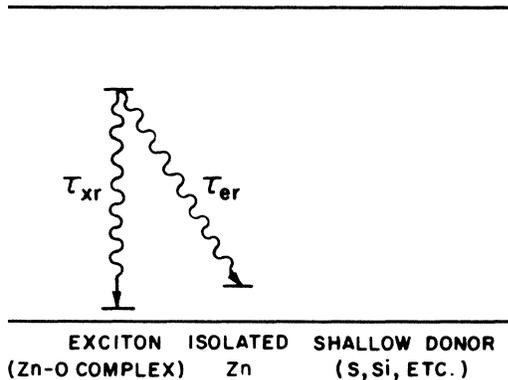
FIG. 1. Schematic of the energy levels of GaP(Zn, O) relevant to the low-temperature decay of the red emission.

for by considering thermalization between the spin sublevels of the exciton.[7]

(ii) Range 2: any electron levels filled by the excitation remain occupied until recombination (no thermal emission into the conduction band). The available hole exciton levels are largely empty. The condition for this range is low temperature (no transfer out of the isolated Zn levels into the valence band) and low excitation density. The few holes generated by the excitation then preferentially fill the deeper and more numerous empty Zn levels (available because of compensating donors). The resultant recombination is largely pair type between the electron exciton levels and the isolated Zn levels.[5,7]

(iii) Range 3: any electron levels filled by the excitation remain occupied until recombination. The hole levels are partly filled. This range occurs at higher temperatures, above cases (i) and (ii), where there is a hole distribution between the exciton and Zn levels and the valence band. Under *low* excitation, results in this range are interpreted[7] by use of the thermal equilibrium occupancy of the hole levels, modified by thermal emission involving the donor levels[7,9] (the latter can be eliminated by use of below-band-gap excitation[9]). In the present paper, we consider mainly the case of fairly *high* excitation, where one no longer has thermal equilibrium, but where the initial hole concentration results from a quasiequilibrium state determined by the occupancy of the donor levels. (We predict an additional decay situation at still higher excitation intensities, where the hole concentration exceeds this value, but this case has not yet been experimentally reported; further discussion is given in Sec. III, especially Sec. III C.) The experimental results in the case of present interest are relatively poorly understood. Although JB did an analysis (Fig. 10 of Ref. 7) for various "$f$-factor" values (where $f$ gives the degree of occupancy of the ex-

citon hole level), they did not obtain the temperature variation of this $f$ factor. In fact, it is precisely the temperature variation of $f$ which determines the decay characteristics in this range. An earlier analysis by Dishman and DiDomenico[6] did calculate $f(T)$, but by use of a carrier capture cross section which has since been shown[7] to be incorrect by several orders of magnitude. Use of the Dishman and DiDomenico[6] parameter values with the proper (JB) cross section does not give a satisfactory temperature dependence.[14] We show that the JB data can be explained by a quasiequilibrium approach with reasonable parameter values, provided one uses appropriate impurity activation energies.

(iv) Range 4: electron levels can also empty by thermal emission into the conduction band. The hole levels are partly filled. This is the condition at still higher temperatures ($T \gtrsim 200\,°K$) where the relatively deep exciton electron level can be emptied thermally. This results in an additional recombination path for the released electrons via accidental centers. A fully quantitative treatment here is difficult; equilibrium between more than four levels (the two exciton levels, the isolated Zn level, the shallow donor level, and accidental centers) and both conduction and valence bands are involved, with a resultant large number of parameters. Nevertheless, the qualitative behavior appears to be adequately explained.[2,3]

(v) Range 5: both electron and hole levels are largely empty. This condition requires fairly high temperatures ($\gtrsim 500\,°K$). Now, with both levels empty, the kinetics are largely determined by other accidental centers. A quantitative treatment has been given by van der Does de Bye and Vink.[10]
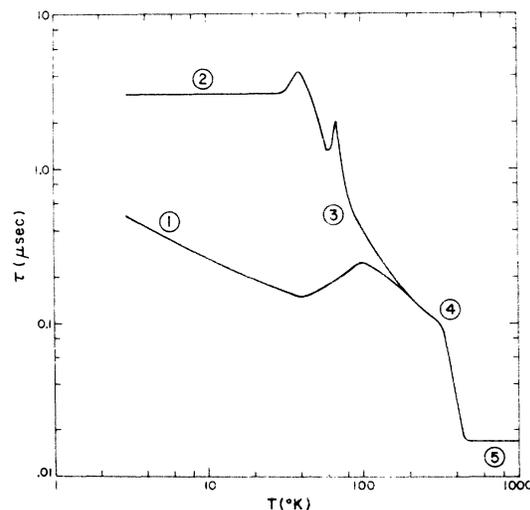


FIG. 2. Decay ranges of the GaP(Zn, O) red emission. The numbering is explained in the text (Sec. II).

### III. THEORY

#### A. Kinetic equations

The decay equations have been derived previously.[3,6] Here we include only those processes considered[15] by Dishman and DiDomenico[6] and by Jayson et al.[3] which are also relevant to the range of present interest. Thus, we neglect (a) transitions between the conduction-band and the exciton-electron levels,[16] and (b) Auger processes involving two holes (the hole concentration is relatively low). With these two simplifications, one obtains[3,6]

$$\frac{dN_t^e}{dt} = -\frac{N_t^x}{\tau_\alpha} - (N_t^e - N_t^x)\frac{f_A}{\tau_{er}} \quad , \tag{1}$$

$$\frac{dN_t^x}{dt} = -\frac{N_t^x}{\tau_\alpha} - \frac{N_t^x}{\tau_{xp}} + \frac{N_t^e - N_t^x}{\tau_{px}} \quad , \tag{2}$$

where

$$(1/\tau_\alpha) = (1/\tau_{xr}) + Bp \quad , \tag{3}$$

$$\tau_{px} = (v\sigma_{px}\, p)^{-1} \quad , \tag{4}$$

$$\tau_{xp} = (N_v\, v\sigma_{px}/D_h)^{-1}\, e^{E_h/kT} \quad , \tag{5}$$

$$f_A \equiv N_A^0/N_A \quad , \tag{6}$$

and where for future reference we also define

$$f \equiv N_t^x/N_t^e \quad . \tag{7}$$

The electroneutrality condition for this system is

$$p + N_D^I = (N_A - N_A^0) + (N_t^e - N_t^x) + n \quad . \tag{8a}$$

Here $N_t^e$ is the concentration of exciton levels filled with electrons (under the present case of strong excitation, this is initially equal to the total concentration of exciton centers); $N_t^x$ is the concentration of filled exciton hole levels; $\tau_{xr}$ and $\tau_{er}$ are the exciton and pair radiative recombination times, respectively; $p$ is the hole concentration; $n$ is the electron concentration; $B$ is the coefficient for exciton hole Auger recombination; $v$ is the hole velocity; $\sigma_{px}$ is the capture cross section into the excitation hole level; $N_v$ is the valence-band density of states; $D_h$ and $E_h$ are the exciton hole level degeneracy and activation energy, respectively; $k$ is Boltzmann's constant; $T$ is the temperature; $N_A$ is the acceptor (Zn) concentration; $N_A^0$ is the concentration of neutral acceptors; and $N_D^I$ is the concentration of ionized shallow donors (Si, S, etc.). For future reference, we also define the acceptor energy and degeneracy $E_A$ and $D_A$. The quantity $\tau_\alpha$ gives the overall electron-hole recombination time at the exciton center, $\tau_{px}$ the capture time of holes into the hole exciton level, and $\tau_{xp}$ the excitation time out of this hole level. The factors $f_A$ and $f$ are the occupancy factors of the Zn and exciton hole levels, respectively.

In the present paper we have analyzed the system of Eqs. (1)–(8) in two ways. First (Sec. III B and Appendix), one can carry out an approximate solution of the full system, as long as the system is in quasiequilibrium (defined in Sec. III B) during the first part of the decay. It is this approach which gives the main physical insight, emphasizes the role of the exciton hole occupancy factor, and is mathematically very convenient. Second (Sec. III C), one can approximate the system of differential equations (neglecting pair and Auger decay) and fairly readily obtain an exact numerical solution; this was carried out with the CSC TRAC program on a Univac 1108. This latter approach also is used to give a correction factor ($\lesssim 25\%$ for the present samples) for the quasiequilibrium method.

#### B. Quasi-equilibrium approach

Under conditions such that the interaction time between a set of impurity levels (donors or acceptors) and the respective band (conduction or valence) is fast compared to the recombination time, a system is either in equilibrium or in quasiequilibrium. Note that since free electrons most likely recombine very quickly, quasiequilibrium can exist only if there is no appreciable free-electron population, i.e., if

$$p + N_D^I \approx (N_A - N_A^0) + (N_t^e - N_t^x) \quad . \tag{8b}$$

This revised electroneutrality condition (8b) follows for excitation conditions such that

$$n < (N_A - N_A^0) + (N_t^e - N_t^x) - N_D^I \quad ,$$

or, in view of Eq. (8b), $N < p$. As will be shown in Sec. III C, the experimental results agree with the use of this condition. Although this is the main justification for its use, we can also show that it is not unreasonable. As is well known, the electron concentration under excitation is given by the product of the excitation intensity and the minority-carrier lifetime. With the laser intensity as given by JB (300 mW) and a 50-$\mu$ absorption length, and assuming some losses (reflection, surface recombination, instrumental) we estimate the intensity as $\sim 10^{25}$ photons/cm$^3$. The low-temperature electron lifetime is not known, but we estimate it[17] at $\lesssim 10^{-10}$ sec. This leads to $n \lesssim 10^{15}$ cm$^{-3}$, which is less than $p$ in the range of interest (Sec. IV). Physically, this result means that the excitation is strong enough to fill all or most donor and exciton levels, thus causing deviation from the thermal-equilibrium case; however, once these levels are filled (a very fast process) and not available as electron traps, the resultant free electrons decay rapidly, so that there is no large-scale buildup of the free-electron population (still higher intensities would be required). The second requirement for a quasiequilibrium case is slow recombination of the hole population, which can be expressed quantitatively as

$$1/\tau_{xp} + 1/\tau_{px} \gg 1/\tau_\alpha \quad . \tag{9}$$

The applicability of this condition can be checked (Sec. IV), and the simplifications discussed below are used only when it holds.

To obtain an approximate solution for the decay, it can be noted that with condition (9) and *steady state* $[(dN_t^x/dt) = 0]$, Eqs. (2) and (7) give

$$f = [1 + (\tau_{px}/\tau_{xp})]^{-1} \quad , \tag{10}$$

and the occupation factor is thus independent of the recombination time. With the aid of Eqs. (4) and (5), this can be expressed as

$$f = [1 + (N_v/D_h p) e^{-E_h/kT}]^{-1} \quad . \tag{11}$$

An analogous result can be obtained for the factor $f_A$. We note that Eq. (11) has already been given by Jayson *et al.*[3] (their Appendix B), but was considered only for thermal equilibrium. Since $p$ is, however, not limited to its thermal-equilibrium value, but under condition (9) can correspond to a quasiequilibrium value, it follows that Eq. (11) has a wider validity range, namely that of the quasi-Fermi-level approach.

Since Eq. (11) was derived for the steady state, it remains to be shown that this relation is also appropriate for analyzing the decay. [This follows automatically for a low density of generated carriers, i.e., for approximate thermal equilibrium; under condition (9) one has $dN_t^x/dt \approx - dp/dt$, and at thermal equilibrium, $dp/dt = 0.$] In principle, this now requires simultaneous solution of Eqs. (1) and (2) without use of $dN_t^x/dt = 0$. The validity can be proven for a short (but sufficient) initial decay time. The proof for a particular condition of high interest is given in the Appendix. Here, we briefly present a simpler, less rigorous approach to show the general applicability of the method.

As the first step in the proof, we show that for short time intervals, a constant value of $f$ [and thus specifically a value as derived via Eq. (1)] satisfies Eq. 2. For convenience, substitute Eq. (7) into (1), which gives

$$\frac{dN_t^e}{dt} = - N_t^e \left( \frac{f}{\tau_\alpha} + \frac{(1-f)f_A}{\tau_{er}} \right) \quad . \tag{12}$$

Now assume

$$N_t^e(t) \approx N_t^e(0) e^{-t/\tau} \quad , \tag{13}$$

where

$$1/\tau = f/\tau_\alpha + (1-f)f_A/\tau_{er} \quad . \tag{14}$$

We next check whether Eqs. (13) and (14) satisfy Eq. (12) if $f$ varies with time. Differentiation of Eq. (13), taking $\tau_{er}$ as time independent (as is justified in the early stages of the decay[18]) gives

$$\frac{dN_t^e}{dt} = - N_t^e \left\{ \left[ \frac{1}{\tau} + t \left( \frac{1}{\tau_\alpha} - \frac{f_A}{\tau_{er}} \right) \right] \frac{df}{dt} \right\} \quad . \tag{15}$$

Thus, in general, Eqs. (13) and (14) do not satisfy Eq. (12). However, if $df/dt$ is not excessively large, then for short times, such that

$$t \left( \frac{1}{\tau_\alpha} - \frac{f_A}{\tau_{er}} \right) \frac{df}{dt} \ll \frac{1}{\tau} \quad , \tag{16}$$

Eqs. (13) and (14) are a correct solution of Eq. (12). Moreover, if Eq. (16) is valid, one can show that $dN_t^x/dt \sim N_t^x/\tau_x$, and is thus negligible in Eq. (1) [by condition (9)]; Eqs. (10) and (11) for $f$ are thus obtained for the decay as well as for the steady-state case. Regarding the validity criteria for Eq. (16), it is because of the first one ($df/dt$ not too large) that it is necessary to enforce Eq. (8b); since the free-carrier decay is expected to be rapid[17] compared to the other system decays, presence of such a component would result in a very large initial value of $df/dt$. With the quasi-equilibrium value of $f$ as initial condition [which follows from Eq. (8b)], $df/dt$ is reasonably small. As to the restriction to short decay times, we satisfy this by extrapolating the *initial* decay to the $1/e$ point, rather than using the observed $1/e$ point [this also gives $\tau_{er}$ independent of $t$ (Ref. 18)]. A fuller mathematical analysis of these points for a particular case of high interest ($p \approx N_t^e - N_t^x$), is given in the Appendix (also see Sec. III C).

We still note that Eq. (14) has been derived earlier under condition (9) by both Dishman and DiDomenico[6] and by Jayson *et al.*,[3] but only for thermal equilibrium. It is primarily in the evaluation of the occupancy factor $f$ that the present (quasiequilibrium) treatment differs from the earlier (Refs. 3 and 6) use of Eq. (14). Under the strong-excitation case of present interest one must explicitly consider the dependence of the hole concentration (and thus of $f$) on the occupancy of both the exciton hole and the Zn acceptor levels (and this occupancy also depends on the concentration of ionized donors—see further discussion below). Evaluation of the hole concentration can be carried out by standard statistical methods [from simultaneous solution of Eq. (11), an analogous equation for the Zn level, and Eq. (8b)]. Due to the two levels, the resultant equation is cubic;

$$p^3(D_A D_h/N_v^2) e^{(E_A + E_h)/kT} + p^2[(N_D^I D_A D_h/N_v^2) e^{(E_A + E_h)/kT} + (1/N_v)(D_A e^{E_A/kT} + D_h e^{E_h/kT})]$$

$$+ p\{[(N_D^I - N_t^e)D_A/N_v] e^{E_A/kT} + [(N_D^I - N_A)D_h/N_v] e^{E_h/kT} + 1\} + (N_D^I - N_A - N_t^e) = 0 \quad . \tag{17}$$

As indicated above, it is in the parameter values (and solution) for Eq. (17) that the differences between the present case and the thermal-equilibrium case manifest themselves. At thermal equilibrium, $N_t^e = 0$ and $N_D^I = N_D$, and these conditions are approximately maintained with weak excitation. Under strong excitation, all (or most) donor centers become filled, and the initial $N_t^e$ is given, approximately, by the concentration of Zn-O complexes. The concentration $N_D^I$ is given by its quasiequilibrium value; since we are interested in the range $T < 100\,^\circ$K, this generally gives $N_D^I \approx 0$. (Further discussion of this point is given in Sec. IV.) It is interesting to note that solution of Eq. (17) gives a strong dependence of $p$, and thus $f$, on the value of $N_D^I$. For example, for the parameter values of sample 2 (see Sec. IV), at $T = 40\,^\circ$K one obtains $f = 0.6$ for $N_D^I = 0$ cm$^{-3}$ and $f = 0.002$ for $N_D^I = 1 \times 10^{16}$ cm$^{-3}$. This is, in fact, the main reason why a thermal-equilibrium treatment $(N_D^I = N_D)$ is inadequate for strong excitation.

### C. Numerical solutions and comparision to quasiequilibrium approximation

To obtain numerical solutions of the system of Eqs. (1)–(5) and (8) without excessive computer time, two simplifications were used: first, neglect of Auger and pair recombination; second, use of a constant value for $(N_A - N_A^0)$. The resultant equations could readily be solved on a UNIVAC 1108 by the CSC TRAC program.

The specific equation which was solved for various parameter values was of the form

$$\ddot{N}_t^e = -(\tau_{xr}^{-1} + \tau_{xp}^{-1})\dot{N}_t^e - (N_t^e + \tau_{xr}\,\dot{N}_t^e)$$

$$\times \left[(N_A - N_A^0) + (N_t^e + \tau_{xr}\,\dot{N}_t^e)\right](v\sigma_{px}/\tau_{xr}) \ , \qquad (18)$$

with the initial conditions

$N_t^e(0) = $ assumed concentration of Zn-O centers,

$N_t^x(0) = f(0)N_t^e(0)$ .

All solutions were carried out for $N_D^I = 0$; extension to other values is trivial. The quantity $(N_A - N_A^0)$ was obtained as the difference between $p$ as given by Eq. (17) and an analogous solution carried out for exciton levels only; i.e., $p$ was split into two parts, with one part (time independent) due to the Zn acceptors $(= N_A - N_A^0)$ and another part (time dependent) due to the exciton centers $(= N_t^e - N_t^x)$. The condition $[(N_A - N_A^0) \approx \text{constant}]$ requires that the pair decay (which changes the concentration of the ionized Zn acceptors) is slow compared to the exciton decay; this condition is met in practice. The computer printout included $\dot{N}_t^e$ (equivalent to $N_t^x$, since $N_t^x = -\tau_{xr}\,\dot{N}_t^e$), and this was plotted semilogarithmically versus $t$ to give $\tau_{1/e}$.

A typical solution of Eq. (18) for the quasiequi-

librium case [i.e., Eqs. (8b) and (9)] is shown as the solid line in Fig. 3. The parameter values are those for one of the samples (No. 1) of JB at 50 $^\circ$K (see Sec. IV). Similar curves were obtained for other parameter values of interest. The results of these various curves were compared with the quasiequilibrium solutions of the equivalent equations; i.e., the equations with neglect of pair and Auger recombinations. It was found that the agreement in the decay times was reasonable (error $\leq 25\%$) in all cases, and excellent in some (see below). The error appears due to the approximation that $f$ remains constant [in the solution of Eq. (2)—see Eq. (16)]. The magnitude of the error was found to depend both on the occupancy factor $f$ and on the "origin" of the holes (from acceptors or from exciton centers). Not surprisingly [in view of Eq. (16)], the error decreased rapidly with an increasing contribution from $(N_A - N_A^0)$ to $p$, and vanished [within the approximation of constant $(N_A - N_A^0)$] for $p \approx N_A - N_A^0$. At the other end of the range, i.e., for $N_A - N_A^0$ negligible and $p \approx N_t^e - N_t^x$, it was found that the error could be well represented by a quadratic dependence on $f$. Defining the decay of the numerical solution by $\tau_N$, and that of the approximate solution by $\tau_A$, the ratio was fitted by

$$\tau_N/\tau_A \approx 1 - 0.31(1 - f) + 0.20(1 - f)^2 \ . \qquad (19)$$

Note that in the range in which Eq. (19) is valid $(p \approx N_t^e - N_t^x)$, there is no need for further computer work for additional samples.

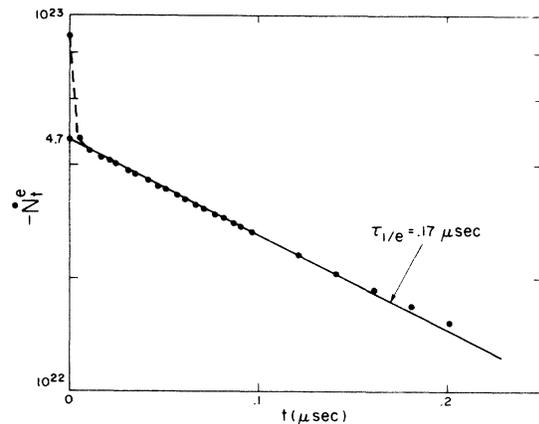As a final step in the use of this computer work,



FIG. 3. Semilog plot of a typical computer printout (dots) of $\dot{N}_t^e$ vs $t$. The solid line is for the quasiequilibrium value of $f$ (from Eqs. (11) and (17)) as initial condition; the dashed line is for $f = 1$ as initial condition. The parameter values of this plot are $T = 50\,^\circ$K, $E_h = 22$ meV, $N_t^e(0) = 1 \times 10^{16}$ cm$^{-3}$ and $N_A - N_A^0 = 0$; these values are those of sample No. 1.

the quasiequilibrium equations (including pair and Auger decay) were corrected. Since the pair and Auger effects were relatively minor in the range of interest, the mathematical error in the solution will be very close to that obtained in the absence of these effects. Thus, if we use the quasiequilibrium decay from the full equations [i. e., $\tau$ as given by Eq. (14)], then the final corrected decay ($\equiv \tau_F$) is given by

$$\tau_F \approx \tau(\tau_N/\tau_A) \ . \tag{20}$$

Since Eq. (18) is in no way restricted to the quasiequilibrium case, we have also carried out a solution assuming a very high excitation intensity; the values of $n$ and $p$ are assumed to be sufficiently large to give $f(0) \approx 1$ as the initial condition. The result, with the other parameter values the same as previously, is shown as the dashed curve in Fig. 3. There is an initial very fast decay due to hole thermalization. This is essentially complete within a time interval ~0.005–0.01 $\mu$sec. There is a second slower decay; this is the decay due to the electron-hole recombination via the exciton centers, and it is the same as that obtained in the quasi-equilibrium case. It can be noted that none of the experimental curves[7,21] show such a very fast component. This is the reason we feel justified in using Eq. (8b) for comparison to the experimental data. Such a fast-decay mode should of course exist; however, until low-temperature values of the minority-carrier lifetime are available, we cannot predict the required excitation levels.

In addition to its use for very high excitation, Eq. (18) can also be solved at low temperatures, where condition (9) is not valid. Although this case is not of main interest here, we did check that the solution in this range gave $\tau_{1/e} = \tau_{xr}$ ; this relation has been used by JB,[7] but was obtained by an approximate analysis.

### D. Activation energies

Evaluation of the hole concentration [Eq. (17)] and of the occupancy factors [Eq. (11)] requires a knowledge of the activation energies at "infinite dilution" (those for an isolated impurity) corrected for screening.[11]

The infinite-dilution energy for the Zn level is known[19] fairly accurately to be 64 meV. For the exciton level a value of 37 meV has been estimated from the energy difference between the peaks of the "pair" and of the "exciton" bands.[13] However, the reliability of this value is uncertain; the peaks are broad, with no structure, and thus without any accurate "landmarks." It is thus quite difficult to *completely* eliminate either the pair or the exciton band when measuring the other. Any mixing obviously decreases the energy difference between the pure peaks and gives a higher apparent activation
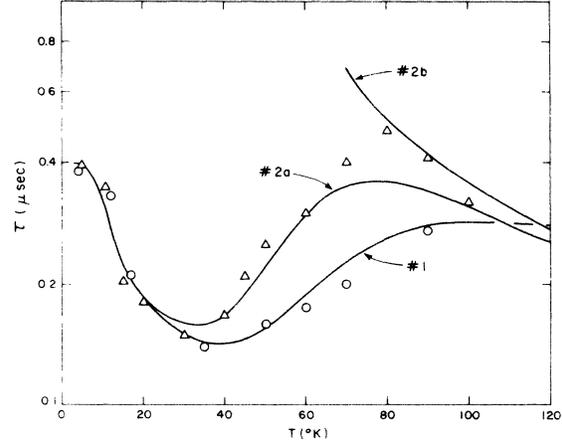


FIG. 4. Fit of the theory (curves) of Eqs. (14) and (20) to the data for JB samples No. 1 (circles) and No. 2 (triangles). Curve No. 1 is for sample No. 1, curves Nos. 2a and 2b for sample No. 2. The parameter values of the curves are as follows: $B = 10^{-10}$ cm$^{-3}$ sec for both samples. Sample No. 1: $E_h = 22$ meV, $E_A = 55$ meV, $N_t^e = 1 \times 10^{16}$ cm$^{-3}$, $N_A = 5 \times 10^{17}$ cm$^{-3}$, and $N_D^I = 0$. Sample No. 2: $E_h = 22$ meV, $E_A = 57$ meV, $N_t^e = 0.3 \times 10^{16}$ cm$^{-3}$, $N_A = 8 \times 10^{17}$ cm$^{-3}$, $N_D^I = 0$ (curve No. 2a), and $N_D^I = 10^{16}$ cm$^{-3}$ (curve No. 2b).

energy. We thus use 37 meV as an upper limit for the exciton hole level and assume that values down to ~10 meV lower would be reasonable. Within this limit, we find (Sec. IV) that 27 meV gives a satisfactory fit to JB's data.

The reduction of the infinite-dilution energies by screening has been calculated in Ref. 11. As discussed,[11] such screening can be caused by either free carriers or ionized impurities. The ionized-impurity screening is important at low temperatures only if the concentration of such impurities is appreciably greater than that of the free carriers. One expects very few ionized impurities under strong excitation, the situation of present interest, and we therefore neglect this contribution. This reduces Eq. (13) of Ref. 11 to the form

$$\frac{E_S}{E_0} \approx 1.00 - 1.81 a_0 \left(\frac{4\pi p e^2}{\kappa k T}\right)^{1/2} + 0.81 a_0^2 \left(\frac{4\pi p e^2}{\kappa k T}\right) \ , \tag{21}$$

where $E_0$ is the ionization energy and $a_0$ is the Bohr radius of the isolated impurity, $E_S$ is the energy of the screened impurity (here applying to either $E_A$ or $E_h$), $\kappa$ is the dielectric constant, and $e$ is the electron charge. It must of course be realized that under different decay conditions (e. g., low excitation) the more complete Eq. (13) of Ref. 11 may be required. In the present case, Eq. (21) is a satisfactory approximation.

TABLE I. Better-known parameters.

| | |
|---|---|
| Exciton radiative decay time $\tau_{xr}$ (sec) | $\dfrac{4 \times 10^{-7} (1 + 0.6e^{-31.4/T})^a}{1 + 6.86e^{-31.4/T}}$ |
| Pair radiative decay time $\tau_{er}$ (sec) | $3 \times 10^{-6 \ a}$ |
| Zn level degeneracy factor $D_A$ | 4 |
| Exciton level degeneracy factor $D_h$ | $2(1 + e^{-0.01 \text{ eV}/kT})^b$ |
| Valence-band density of states $N_v$ (cm$^{-3}$) | $4.12 \times 10^{15} T^{3/2}$ (based on $m^*/m = 0.9$) |

[a]Reference 7.          [b]Reference 5.

## IV. COMPARISON TO EXPERIMENT AND DISCUSSION

We next fit the decay data for JB[7] samples[20] Nos. 1 and 2 from 40 °K up, under the condition of high excitation, by use of Eqs. (14) and (20). [We emphasize this range here, since our quasiequilibrium approach is not applicable below about (30–40) °K. Moreover, the numerical method confirmed JB's approximate solution below 30 °K—see Sec. III C.] The data[7] are shown in Fig. 4. Measurements were taken[7] from 4 °K to (90–100) °K, and within this temperature interval the decay time first decreases, then increases, with another decrease starting at $\approx 80$–100 °K. As discussed in Sec. III B and in the Appendix, the points for the experimental $(1/e)$ values (from 40 °K up) in Fig. 4 have been extrapolated from the initial recombination decay. (For this we used Fig. 1 of Ref. 7 for sample No. 1, and a similar[21] plot for sample No. 2.)

In the use of Eq. (14), substitution of $\tau_\alpha$, $f$, $f_A$, and $p$ [Eqs. (3), (11), and (17)] shows an immediate difficulty: a large number of parameters are involved. We list in Table I those which are relatively well known ($\tau_{xr}$, $\tau_{er}$, $D_h$, $D_A$, and $N_v$), but this still leaves a considerable number to be determined ($B$, $p$, $N_t^e$, $N_A$, $N_D^I$, $E_h$, and $E_A$). Moreover, there is also a second difficulty; the unknown parameters, except for the Auger $B$ coefficient, are interrelated via Eqs. (17) and (21).

In view of these difficulties, we first discuss Eq. (14) qualitatively. First, we note that the first term of Eq. (14) dominates in the range of interest; the pair decay $\tau_{er}$ is always appreciably slower than the exciton decay $\tau_\alpha$ ($\tau_{er} \gtrsim 10\tau_\alpha$), where-

as the hole-occupancy factor remains appreciable ($f \gtrsim 0.2$ for present parameter values—see below). Thus, the decay depends primarily on the hole-occupancy factor $f$, and on the exciton decay $\tau_\alpha$; i.e., $\tau \approx \tau_\alpha/f$. As the next step, we note that at low temperatures, Auger transitions, which are proportional to the hole concentration $p$, are very unlikely, and thus $\tau_\alpha \approx \tau_{xr}$. The equation for $\tau_{xr}$ is given in Table I; evaluation shows that for $T \gtrsim 40$ °K it becomes approximately constant. We thus attribute the rise in $\tau$ for $T \gtrsim 40$ °K (Figs. 2 and 4) to thermal release of holes out of the exciton levels, with a resultant decrease in the quasi-equilibrium hole-occupancy factor $f$. It is for the calculation of $f$ that we use our quasiequilibrium approach (see below). As to the higher temperature decrease in $\tau$ (above $T \approx 80$–100 °K), we agree with earlier work[3,4,6] attributing this largely to an increased importance of Auger transitions.

As to the quantitative evaluation of Eq. (14), we require parameter values (as mentioned, $B$, $p$, $N_t^e$, $N_A$, $N_D^I$, $E_h$, and $E_A$ are to be determined) which fit the data, and which also give self-consistent solutions to Eqs. (17) and (21). In practice, we have not carried out a completely self-consistent approach, but have used the following approximate procedure: Step 1: Assume reasonable values of the parameters $E_h$, $E_A$, $N_A$, $N_t^e$, and $N_D^I$, calculate $p$ [Eq. (17)] and fit the data [via Eqs. (3), (11), (14), and (20), using a reasonable value for the Auger $B$ coefficient]. Several sets of parameters were found to fit the data, since a change in one parameter could be compensated by a change in another one. Step 2: From the values of $p$ for those curves which fit the data, we calculate $E_A$ and $E_h$, with reasonable values of $a_0$ and $E_0$, via Eq. (21). Step 3: Those results are selected which give approximate agreement between $E_A$ and $E_h$ as calculated by Eq. (21); and between $E_A$ and $E_h$ as initially assumed in Eqs. (11) and (17).

The resultant fit to the data is shown in Fig. 4. The various parameter values used in Step 1 above are given in Table II. Together with the values of Table I, these are sufficient for a fit to the data (step 1 above). It can be noted that two values of $N_D^I$ are used for sample No. 2 in the higher-temperature range. At low temperature and high ex-

TABLE II. Parameter values used in Fig. 4.

| | Sample No. 1 | Sample No. 2 |
|---|---|---|
| Auger $B$ coefficient (cm$^3$/sec) | $1 \times 10^{-10}$ | $1 \times 10^{-10}$ |
| Concentration of isolated Zn levels $N_A$ (cm$^{-3}$) | $5 \times 10^{17}$ | $8 \times 10^{17}$ |
| Concentration of exciton levels $N_t^e$ (cm$^{-3}$) | $1 \times 10^{16}$ | $3 \times 10^{15}$ |
| Concentration of ionized donors $N_D^I$ (cm$^{-3}$) | 0 | $0, 1 \times 10^{16}$ |
| Activation energy of Zn level $E_A$ (meV) | 55 | 57 |
| Activation energy of exciton hole level $E_h$ (meV) | 22 | 22 |

TABLE III. Results for sample No. 1.

| $T$ (°K) | $p$ ($10^{15}$ cm$^{-3}$) | $f$ | $\tau$ ($\mu$sec) | $E_A$ (meV) | $E_h$ (meV) |
|---|---|---|---|---|---|
| 40 | 2.5 | 0.75 | 0.14 | | 24 |
| 50 | 4.7 | 0.54 | 0.16 | | 23 |
| 60 | 7.1 | 0.38 | 0.19 | 57 | 23 |
| 70 | 10.4 | 0.28 | 0.23 | 56 | 22 |
| 80 | 16 | 0.24 | 0.26 | 55 | 21 |
| 90 | 23 | 0.22 | 0.28 | 54 | 21 |

citation $N_D^I$ will essentially be zero (all donors filled); however, as the temperature increases, the shallow donors emit electrons into the conduction band, with appreciable[7,9] effect starting at $\approx 60$–$70$ °K. This release appears significant for sample No. 2, and it can be noted that in the 60–100 °K range, the data for this sample fall within the two different $N_D^I$ curves, as expected. The release does not appear significant for sample No. 1, as shown in the next paragraph. The results shown in Fig. 4 have been approximately adjusted for self-consistency (as discussed above). Values of $p$ as calculated in step 1 from Eq. (17) are given in Tables III (sample No. 1) and IV (sample No. 2) in the first column, for the $N_D = 0$ case. The values of $f$ and $\tau$ [Eqs. (11), (14), and (20)] are given in the second and third columns; these results substantiate the assertion made earlier in this section that the variation in $\tau$ depends mainly on that of $f$. The $E_A$ and $E_h$ values were calculated in Step 2 via Eq. (21), using the parameter values $a_0 = 13$ Å, $E_0 = 64$ for the Zn level, and $a_0 = 20$ Å, $E_0 = 27$ meV for the exciton level. The results are given in the fourth and fifth columns of Tables III and IV. (Note that no low-temperature values are given for $E_A$; in this range, $p$ does not depend on $E_A$ and such values are thus irrelevant). It can be seen that the $E$ values in Tables III and IV (step 2) agree with those in Table II (step 1) to within 2 meV in the middle of the temperature range and (except at 100 °K) to within 3 meV in the outer range. In view of this agreement, we have not carried out a fully self-consistent procedure, which would involve inclusion of the temperature dependence of $E_A$ and $E_h$ in step 1. (Some such more elaborate procedure would be required in fitting a wider temperature interval.)

It remains to be shown that the various parameter values used in our fit are reasonable. These *specific* values were each picked from a *range* of values; these ranges, with each followed by its justification, are as follows:

(i) *Auger B coefficient*: $B = (0.5$–$2) \times 10^{-10}$ cm$^3$/sec. By analysis of higher-temperature decay ($\gtrsim 300$ °K), a value of $B = 10^{-10}$ cm$^3$/sec was obtained by Dishman and DiDomenico[6]; values by Jayson *et al.*[3] and by Dishman *et al.*[4] are slightly lower [$\sim (3$–$5) \times 10^{-11}$ cm$^3$/sec], but probably less reliable.[22]

A recent theoretical estimate[23] is $B = 10^{-10}$ cm$^3$/sec.

(ii) *Infinite-dilution impurity radii* (the corresponding activation energies are discussed in Sec. III D). For the Zn level, $a_0 = 12$–$13$ Å; for the exciton level, $a_0 = 17$–$20$ Å. Experimental estimates[24,25] of $a_0 = 10$–$15$ Å have been given for the Zn level. For the exciton level, no experimental values of $a_0$ seem to be available. We have therefore estimated it by use of the relation $1/a_0 \sim \sqrt{E}$, scaling from the Zn level; with an $a_0$ for Zn of 13 Å, this gives values of $a_0$ for the exciton ranging from 17 Å (for $E_0 = 37$ meV—see Sec. III D) to 20 Å (for $E_0 = 27$ meV).

(iii) *Impurity concentrations*: For sample No. 1, $N_A = (4$–$6) \times 10^{17}$ cm$^{-3}$, $N_t^e = (0.5$–$3) \times 10^{16}$ cm$^{-3}$, and $N_D^I = 0$. For sample No. 2, $N_A = (0.8$–$1.2) \times 10^{18}$ cm$^{-3}$, $N_t^e = (0.2$–$2) \times 10^{16}$ cm$^{-3}$, and $N_D^I = (0$–$1) \times 10^{16}$ cm$^{-3}$. The acceptor concentration $N_A$ in sample No. 1 has been given by JB as $5 \times 10^{17}$ cm$^{-3}$, and the doping level for sample No. 2 was twice as high, fairly well delineating the $N_A$ values above. As to the complex concentration $N_t^e$, only estimates are available. The present samples are unannealed, with an $N_A - N_D$ value[7] of $\sim 4.6 \times 10^{17}$ for sample No. 1, and that for sample No. 2 probably $\sim 7$–$8 \times 10^{17}$. There is an estimate[4] of $N_t^e \approx 1$–$4 \times 10^{16}$ for unannealed samples with $N_A - N_D \approx 1.3 \times 10^{18}$. These values are expected to be lower for lower $N_A - N_D$, as in the present samples. Moreover, these[4] estimates are based on use of $\tau_{xr}(p)$ in the analysis; a constant value for $\tau_{xr}$ (Ref. 22), would give a reduction by about a factor of 2. The range $(0.2$–$2) \times 10^{16}$ cm$^{-3}$ thus appears reasonable. As for the ionized donor concentration, this will be essentially zero at low temperatures, but may become significant[7,9] starting at 60–70 °K. We feel that a value of $N_D^I \sim 10^{16}$ cm$^{-3}$ is reasonable for sample No. 2 in the range 60–90 °K. Sample No. 1 appears to have a lower compensation ratio than sample No. 2 (Ref. 26), and thus a significantly lower $N_D$ concentration; we thus expect $N_D^I \ll N_t^e$, with negligible effect on $p$ [see Eq. (17); also note that $(N_D^I/N_v) \ll 1$], and $\tau$.

In addition to the parameter values being reasonable, it must also be shown that the inequality given in Eq. (9), on which the quasiequilibrium treatment is based, is satisfied. This is shown in Table V.

TABLE IV. Results for sample No. 2.

| $T$ (°K) | $p$ ($10^{15}$ cm$^{-3}$) | $f$ | $\tau$ ($\mu$sec) | $E_A$ (meV) | $E_h$ (meV) |
|---|---|---|---|---|---|
| 40 | 1.2 | 0.60 | 0.17 | | 25 |
| 50 | 2.2 | 0.36 | 0.22 | | 24 |
| 60 | 3.5 | 0.25 | 0.29 | 59 | 24 |
| 70 | 7.4 | 0.22 | 0.35 | 57 | 23 |
| 80 | 13 | 0.22 | 0.36 | 56 | 22 |
| 90 | 22 | 0.22 | 0.34 | 54 | 21 |
| 100 | 34 | 0.22 | 0.31 | $52\frac{1}{2}$ | 20 |

TABLE V. Proof of inequality (9) for $T \gtrsim 40\,°K$.

| $T$ (°K) | Sample No. 2 (Parameters as Table IV) p (cm$^{-3}$) | $(1/\tau_{px}+1/\tau_{xp})$ (sec$^{-1}$)[a] | $(1/\tau_\alpha)$ (sec$^{-1}$)[b] |
|---|---|---|---|
| 40 | $1.2 \times 10^{15}$ | $0.9 \times 10^8$ | $0.8 \times 10^7$ |
| 50 | $2.2 \times 10^{15}$ | $3.1 \times 10^8$ | $0.9 \times 10^7$ |
| 60 | $3.9 \times 10^{15}$ | $8.7 \times 10^8$ | $1.1 \times 10^7$ |

[a]From Eqs. (4) and (5), with $\sigma = 10^{-14}$ cm (Ref. 7).
[b]From Table I; $\tau_\alpha \approx \tau_{xr}$.

As mentioned earlier in this section, without use of Eq. (21) several fits were possible. It is therefore instructive to show the dependence of the calculated curves on the various parameters. Figure 5 shows the effect of variation of one parameter at a time. The results are given here without the correction of Eq. (20), which would not change the relative values. One curve (the heavy solid line) is used as "standard" and fits the $N'_D = 0$ case for sample No. 2. The other curves vary from this one by the change of one parameter for each curve. It can be seen that in the low-temperature range (up to $\sim 60\,°K$) the results depend significantly only on $N^e_t$ and $E_h$; however, in the higher-temperature range, all the parameters contribute. Such a result is, of course, to be expected.

## V. CONCLUSION

The present analysis has aimed at a theory as simple as possible, consistent with the obvious complexity of a multicenter system. The approach has been based on hole thermalization; i.e., a quasiequilibrium hole distribution among the various hole levels. Use of the extrapolated initial recombination decay to give the $1/e$ point has been included in the present treatment.

As a general consequence of the present work, we have demonstrated the utility and validity of the quasiequilibrium approach. Due to its great simplicity and resulting ease of parameter variation, one can readily check the sensitivity to change of parameters (Fig. 5), thus also easily carry out a self-consistent analysis, etc. Such work would use extensive computer time if carried out entirely numerically.

In the specific application of our approach to GaP(Zn, O), we show that it is adequate to explain the previously poorly understood case of high excitation in the temperature range of 40–100 °K. One can account (Fig. 4) quite well for the observed temperature and sample dependence of the decay, with reasonable[27] parameter values. Moreover, the analysis has been carried to approximate self-consistency through correlation between fitting the data and using impurity activation energies properly corrected for screening. In view of this self-con-

sistency, I feel that one can also obtain estimates of the accuracy of the values; I judge that $E_h$ has been determined to within 15%, and $N^e_t$ to within about a factor of 2. With $N_A$ reasonably well known, $E_A$ can be obtained to 10%; the Auger $B$ coefficient, from the present temperature range, appears to be determined to within no better than a factor of 2, and with possibly even less accuracy.

Overall, the present treatment is satisfactory and self-consistent. The question of whether it is the only possible explanation is more difficult to resolve. An earlier[6] analysis, using a very small[27] carrier capture cross section, also appeared to fit the data. This cross section has since[7] been shown to be incorrect. This thus highlights the fact that different analyses can give comparable results. In addition, we have neglected a number of factors which may well contribute, such as: (i) multicenter Auger processes[15]; (ii) shallow levels other than those given in Fig. 1. There is some evidence that nitrogen levels, where $N$ is a usual accidental impurity in crystals of the type used here, may contribute to various recombination processes[9,28]; (iii) the so-called $D^-$ or $H^-$ band (two holes on one acceptor for the present $p$-type material), which is known to contribute to conductivity[29] and luminescence[30] at low temperatures; (iv) possible temperature variation of phonon interactions, with resultant changes in $\tau_{xr}$, $\tau_{er}$, and/or $B$.

Further experimental work (simultaneous measurement of fluorescence efficiency, Hall measurements of hole concentration, etc.) would, of course, shed more light on the correctness of the present approach.

*Note added in proof.* Recent results {J. A. W. van der Does de Bye (private communication) and D. V. Lang [J. Appl. Phys. (to be published)]} indicate $\sigma_{px} \sim 10^{-15}$ cm rather than $10^{-14}$ cm used in the present paper. For such a value the quasiequilibrium treatment would apply only for $T \gtrsim 50\,°K$ (see Table V). At 40 °K the present $\tau$ would be somewhat in error. However, this error is not too large, since $\tau$ will be intermediate between the quasiequilibrium values of 0.14–0.17 $\mu$sec (Tables III and IV), and the now fastest system decay of $\tau_{xr} = 0.12\ \mu$sec.
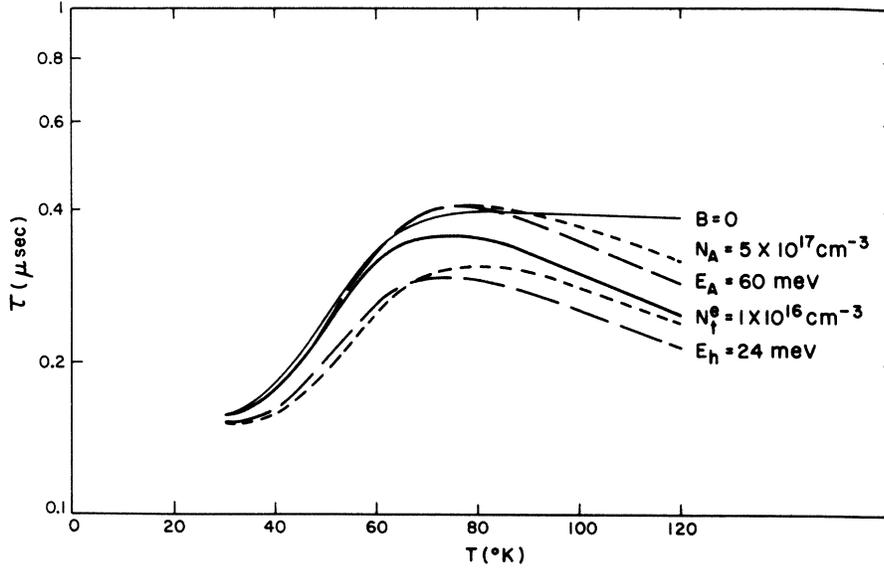
FIG. 5. Effect of parameter variation on the $\tau$ values. These curves are given without the computer correction [Eq. (20)], since relative values will not be greatly affected. The thick solid central curve corresponds to the $N_D^I = 0$ curve of sample No. 2. The parameter values are $E_h = 22$ meV, $E_A = 57$ meV, $N_t^e = 0.5 \times 10^{16}$ cm$^{-3}$, $N_A = 8 \times 10^{17}$ cm$^{-3}$, $B = 10^{-10}$ cm$^3$/sec. The other, dashed and thin solid, curves each have one parameter different, with values as given on the figure.

## ACKNOWLEDGMENTS

The author is grateful to Dr. R. N. Bhargava and Dr. S. K. Kurtz for many helpful discussions and comments, as well as a careful reading of the manuscript. Thanks are also due to Dr. R. Z. Bachrach for a very useful discussion, to Dr. J. S. Jayson for providing additional data, and to S. Herman for assistance in the computer work.

## APPENDIX

The analytical proof (Sec. III B) of the validity of the quasiequilibrium approach hinges on a relatively poorly defined condition of the time rate of change of the occupancy factor $f$ [Eq. (16)]. Here we give a more rigorous proof under simplified conditions: no ionized donors, no contribution to the hole concentration from the Zn acceptors, and no pair and Auger recombination. Although simplified, the above conditions are realistic at the lower temperatures of interest [$\approx$ (40–60) °K].

The problem is thus to obtain an approximate analytical solution of Eq. (18) in the case of $n = 0$, $N_D^I = 0$, $N_A - N_A^0 = 0$. The electroneutrality condition (8b) thus reduces to

$$p \approx N_t^e - N_t^x = N_t^e(1 - f) \ . \tag{A1}$$

We now assume an approximate solution of the form

$$N_t^e(t) \approx A e^{-t/\tau_1} + B e^{-t/\tau_2} \ . \tag{A2}$$

As a first step, we evaluate $A$ and $B$ from the initial conditions. Thus,

$$A + B = N_t^e(0) \ . \tag{A3}$$

Use of $N_t^x(0) = f(0)N_t^e(0)$ [and of Eq. (1) without pair and Auger contributions] gives

$$f(0)N_t^e(0) = A(\tau_{xr}/\tau_1) + B(\tau_{xr}/\tau_2) \ . \tag{A4}$$

Solution gives

$$A = N_t^e(0)\left(\frac{\tau_1}{\tau_{xr}}\right)\left(\frac{f(0)\tau_2 - \tau_{xr}}{\tau_2 - \tau_1}\right) \ , \tag{A5}$$

$$B = N_t^e(0)\left(\frac{\tau_2}{\tau_{xr}}\right)\left(\frac{\tau_{xr} - f(0)\tau_1}{\tau_2 - \tau_1}\right) \ . \tag{A6}$$

We now assume

$$A \approx 0 \ , \tag{A7}$$

(to be proven later), and impose the additional condition that we do not follow the decay too long, i.e.,

$$t \lesssim \tfrac{1}{3}\tau_2 \ , \quad e^{-t/\tau_2} \approx 1 \ . \tag{A8}$$

Use of condition (A7) with substitution of Eq. (A2) into Eq. (18), and using the symbol $\sigma$ instead of $\sigma_{px}$, gives

$$\frac{1}{\tau_2^2} \approx \frac{1}{\tau_2}\left(\frac{1}{\tau_{xr}} + \frac{1}{\tau_{xp}}\right) - \frac{\sigma v B}{\tau_{xr}}\left(1 - \frac{\tau_{xr}}{\tau_2}\right)^2 e^{-t/\tau_2} \ . \tag{A9}$$

With additional use of condition (A8), one obtains

$$\frac{1}{\tau_2^2}(1 + B\sigma v\tau_{xr}) - \frac{1}{\tau_2}\left(\frac{1}{\tau_{xr}} + \frac{1}{\tau_{xp}} + 2B\sigma v\right) + \frac{B\sigma v}{\tau_{xr}} \approx 0 \ . \tag{A10}$$

With use of Eq. (A7) it also follows that $B \approx N_t^e(0)$. With this, condition (9) [recalling that $p \leq N_t^e(0)$], and the definition

$$\tau_2 \equiv \tau_{xr}/f \ , \tag{A11}$$

one obtains

$$f^2 - f\left(\frac{1}{\tau_{xp}N_t^e(0)\sigma v} + 2\right) + 1 \approx 0 \ . \tag{A12}$$

With use of $f = f(0)$, this result is, in fact, Eq. (11) in a different form, as can be seen by substitution of Eqs. (4), (5), and (A1) into Eq. (11). Moreover, it can now readily be seen by substitution of $\tau_{xr} = f(0)\tau_2$ into Eq. (A5) that one indeed obtains $A \approx 0$; i.e., assumption (A7) is valid. Thus, the more detailed treatment of this Appendix leads to the same results as Sec. III C, but with a more quantitative condition, Eq. (A8), on the observation time. It can thus be checked that use of the initial slope of the decay to give the $1/e$ point is indeed a satisfactory procedure.

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[14] Use of JB's experimental cross section leads to our quasiequilibrium approach (Table V). For this case, it can then be seen from our Fig. 5 that even the slight shift of $E_h$ from 22 to 24 meV gives an appreciable shift of the theoretical curve to higher temperatures. Use of Dishman and DiDomenico's 36 meV (Ref. 6) would give a very large shift. In principle, such a shift could be counteracted by decreasing $N_t^e$ (Fig. 5), but unreasonably small values would be required for a proper fit of a 36 meV curve.

[15] We follow the earlier analyses (Refs. 3 and 6) in neglecting multicenter Auger processes. These were considered by E. E. Loebner, "Study of Nonradiative Recombination Processes in Semiconductors," Final Report, Contract No. N00014-67-C-0440 (1968) (unpublished) and subsequently by J. M. Dishman, Phys. Rev. B 3, 2588 (1971), for the GaP(Zn, O) infrared luminescence. In principle, they could also play a role in the red luminescence. However, we obtain a reasonable fit to the data without such processes.

[16] The range of interest (Range 3) is defined as being below temperatures at which there is significant thermal excitation *out* of these electron levels. Moreover, we also assume that there is no contribution to the decay from capture *into* these levels. This requires either direct excitation into the levels (below-band-gap radiation) or an electron decay time which is fast compared to the various system recombination times. Since JB concludes from rise-time measurements that the electron lifetime is short, we assume that this latter condition is satisfied.

[17] The minority-carrier lifetime at low temperature is not known. Room-temperature values for similar samples are in the range of 5 nsec [see, for example, J. S. Jayson, R. Z. Bachrach, P. D. Dapkus, and N. E. Schumaker, Phys. Rev. B 6, 2357 (1972)]; since lifetime should decrease with temperature (more shallow recombination levels will capture, and hold, carriers), a low-temperature lifetime of $\lesssim 10^{-10}$ sec does not appear unreasonable. A low lifetime, but with no values given, is also estimated by JB.

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[20] Additional samples measured by JB had higher impurity concentrations; impurity-band Auger processes, not considered in the present theory, are expected to be important in this range. Thus, sample No. 3 is likely to have $N_A \approx 1.5 \times 10^{18}$ cm$^{-3}$; sample No. 4 is likely to have even higher amounts. For S-doped samples, J. C. Tsang, P. J. Dean, and P. T. Landsberg, [Phys. Rev. 173, 814 (1968)], obtain strong concentration quenching starting at just about this concentration. Moreover, the concentration quenching for our Zn case (Bohr radius $\approx 13$ Å) is expected to be quite comparable to the S case (for which they estimate a Bohr radius of 12 Å).

[21] The required data for sample No. 2 was kindly provided by Dr. J. S. Jayson.

[22] References 3 and 4 assume that $B$ and/or $\tau_{xr}$ depend on free-carrier concentration. This was based on taking $\tau_{xr}$ and $B$, which are functions of the Bohr radius $a$, as dependent on activation energy through $a = (\hbar^2/2m^* E)^{1/2}$ [with $E$ given as a function of $p$ by an *ad hoc* equation (Ref. 4)]. It can, however, be shown (G. F. Neumark, unpublished) that the above relation for $a(E)$ does not hold for screened impurities, and that there is very little dependence of $a$ on $p$ in the range of present interest.

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[27] The carrier capture cross section used in the earlier (Ref. 6) analysis, quite aside from subsequently being shown to be incorrect (Ref. 7), is also unduly small for a Coulomb attractive center. This was first pointed out to the author by R. N. Bhargava (private communication).

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