

Recombination Kinetics of Electrons and Holes at Isoelectronic Impurities: GaP(Zn,O)

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A model describing the kinetics of electron and hole (exciton) recombination at isoelectronic impurities is presented. The model considers three separate occupation states for the isoelectronic center, i.e., empty, electron (hole) occupied, and exciton occupied. As a result, it generalizes the conventional two-state Shockley-Read-Hall (SRH) model which cannot be applied to recombination at isoelectronic centers. A detailed analysis is given of the time-dependent behavior of the radiative recombination at isoelectronic centers. Included in the analysis are the effects of nonradiative Auger and thermalization process. It is shown that under steady-state conditions the recombination at isoelectronic centers can be described by the SRH model, provided that the temperature is not so high that thermalization of the electron (hole) occupied state becomes important. The radiative decay time is shown to depend at low temperatures on thermal dissociation of excitons bound to the centers, and at high temperatures on Auger processes and thermalization of the electron (hole) occupied state. Using the model, a good fit is obtained to the measured time decay of the red luminescence from *p*-type Zn,O-doped GaP for $0 < T < 440^\circ\text{K}$. On the basis of the agreement between calculated and measured time-decay curves, values are given for the Auger parameters, and for the electron and hole-capture lifetimes of the isoelectronic Zn-O trap.

I. INTRODUCTION

IT has been well established that isoelectronic impurities can act as efficient centers for radiative recombination of electrons and holes in solids.¹ Because these centers can exist in three possible states, i.e., empty, electron (hole) occupied, or exciton occupied, the standard Shockley-Read-Hall (SRH) recombination model,² which allows for only two possible states, fails to give a general description of the recombination kinetics. The kinetic transfer among the three occupation states has an important influence on the transient behavior of the recombination process. In this paper, we present a three-state model for recombination of electrons and holes at isoelectronic impurities. On the basis of the model, we calculate the decay constants for luminescence originating from isoelectronic centers as functions of the strength of excitation and temperature. In addition, we show that SRH kinetics can be applied to isoelectronic centers under steady-state equilibrium conditions, for temperatures sufficiently low that thermalization of the electron (hole) occupied state can be neglected. This provides some justification for applying the SRH model to isoelectronic impurities as done by other workers.³

To compare the predictions of the three-state model with experiment we particularize to *p*-type GaP doped with zinc and oxygen. In this system, a special type of isoelectronic center is formed when an oxygen donor and a zinc acceptor associate to form a nearest-neighbor ion pair. Such Zn-O complexes can form in moderately high concentrations ($\sim 10^{16} \text{ cm}^{-3}$), and have been

shown^{4,5} to be the source for the efficient red luminescence in GaP(Zn,O). This luminescence originates from: (1) pair recombination of a deeply trapped (0.3-eV) electron on a Zn-O complex with a hole bound to a distant Zn acceptor, and (2) radiative recombination of an exciton bound to a Zn-O complex. Cuthbert, Henry, and Dean⁵ (CHD) have measured the time decay of the red luminescence over the temperature range 1.5–300°K, and have explained qualitatively the temperature dependence of the measured time decay above 80°K using a simplified model for the recombination kinetics. In applying our model to GaP(Zn,O), we achieve quantitative agreement with the measured time decay above 80°K and qualitative agreement below 80°K. This is accomplished by taking into account explicitly the temperature dependence of the cross section for capture of holes onto electron-occupied Zn-O complexes. We find that the low-temperature ($< 80^\circ\text{K}$) variation of the decay time is determined primarily by thermalization effects involving the weakly bound (0.03-eV) hole component of the trapped exciton. At higher temperatures, our formulation emphasizes the importance of nonradiative Auger processes from both exciton-occupied and bare-electron-occupied states of the Zn-O complex.⁶ These Auger processes are shown to be the principal sources limiting the decay time and quantum efficiency in the range $80 \leq T \leq 300^\circ\text{K}$. Above 300°K, we find that the decay time and quantum efficiency are controlled by thermalization of the deeply trapped bare electron.

The complete kinetics of minority carrier recombination in *p*-type GaP doped with Zn and O are com-

¹ D. G. Thomas, J. Phys. Soc. Japan Suppl. **21**, 265 (1966).

² W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952); R. N. Hall, *ibid.* **87**, 387 (1952).

³ W. Rosenzweig, W. H. Hackett, Jr., and J. S. Jayson, J. Appl. Phys. **40**, 4477 (1969).

⁴ T. N. Morgan, B. Welber, and R. N. Bhargava, Phys. Rev. **166**, 751 (1968); C. H. Henry, P. J. Dean, and J. D. Cuthbert, *ibid.* **166**, 754 (1968).

⁵ J. D. Cuthbert, C. H. Henry, and P. J. Dean, Phys. Rev. **170**, 739 (1968), hereafter referred to as CHD.

⁶ K. P. Sinha and M. DiDomenico, Jr., Phys. Rev. B (to be published).

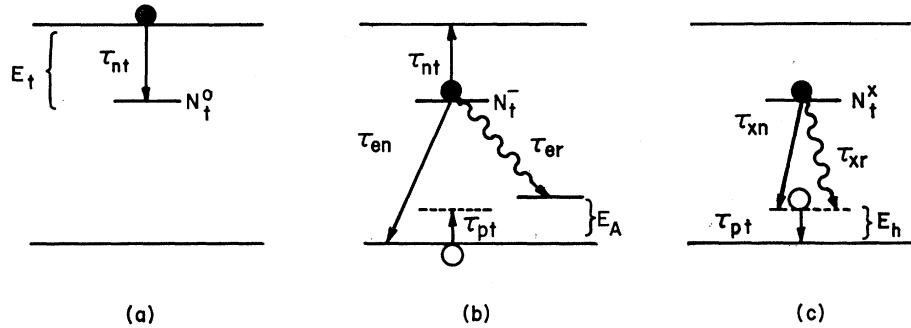


FIG. 1. Schematic representation of electron and hole recombination at an isoelectronic center. (a) Conversion of N_t^0 state into N_t^- state by electron capture (τ_{nt}). (b) Conversion of N_t^- state into N_t^0 state by thermalization (τ_{nt}) and by radiative (τ_{er}) and nonradiative Auger (τ_{en}) recombination. Also indicated is conversion of N_t^- state into N_t^x state by hole capture (τ_{pt}). (c) Conversion of N_t^x state into N_t^- state by hole emission (τ_{pt}). Energy levels E_t and E_h refer, respectively, to the electron and hole-binding energies of the isoelectronic center, and E_A refers to acceptor binding energy.

plicated by the necessity of including at least three recombination paths: one due to isoelectronic Zn-O complexes, a second due to isolated oxygen donors, and a third due to the combined effect of unknown impurity centers. The present paper considers in detail the time-decay processes connected with the Zn-O complexes. In a separate paper,⁷ we present steady-state solutions including the effects of all three paths, and show how the concentration of Zn-O complexes and substitutional oxygen donors can be determined from optical measurements alone.

II. RECOMBINATION KINETICS

The model used in the analysis of the recombination kinetics of electrons and holes at isoelectronic traps is indicated schematically in Fig. 1. Since we wish ultimately to apply the results of the calculations to GaP(Zn,O), we assume at the outset that the isoelectronic center is a deep electron trap in *p*-type material. Under this assumption, we may distinguish between three states of the trap: (1) the neutral unoccupied state (concentration N_t^0), (2) the negatively charged bare-electron state (concentration N_t^-), and (3) the neutral exciton-occupied state (concentration N_t^x). Figure 1(a) indicates how the N_t^0 -type states are converted into N_t^- states by capture of minority carriers within a characteristic time τ_{nt} defined by

$$\tau_{nt} = (v\sigma_{nt}N_t)^{-1}, \quad (1)$$

where v is the thermal velocity, N_t is the total concentration of traps, and σ_{nt} is the cross section for capture of minority carriers into the unoccupied traps. Our

definition of lifetime follows the convention⁸ that the capture rate is given by $(n/\tau_{nt})(N_t^0/N_t)$, where n is the minority-carrier density. Once formed, the N_t^- states can be converted into N_t^0 states and N_t^x states by the processes shown in Fig. 1(b). At sufficiently high temperatures, the electron may be thermally emitted back into the conduction band at a rate $(n_t/\tau_{nt}) \times (N_t^-/N_t)$, where n_t is defined in the conventional way⁸ such that the capture and thermal emission processes balance at thermal equilibrium. Thus,

$$n_t = n_0 \beta_t \exp[(E_g - \phi - E_t)/kT], \quad (2)$$

where n_0 is the thermal equilibrium value of free electrons, β_t^{-1} is the degeneracy of the trap level at energy E_t below the conduction band, E_g is the band-gap energy, and ϕ is the Fermi level measured from the valence band. The electron may also recombine radiatively with a hole trapped on a distant shallow acceptor (e.g., zinc) in a lifetime τ_{er} . Alternatively, the electron may recombine nonradiatively via an Auger process⁶ with a lifetime τ_{en} . All three of these processes transform N_t^- states into N_t^0 states. On the other hand, a hole may be captured into a shallow level of energy E_h by the Coulombic attraction of the charged state with a lifetime τ_{pt} defined analogously to τ_{nt} in Eq. (1) by

$$\tau_{pt} = (v\sigma_{pt}N_t)^{-1}. \quad (3)$$

Here σ_{pt} is the capture cross section of the N_t^- states for free holes. This event transforms N_t^- -type states into N_t^x states. Finally, the N_t^x states may decompose in three ways, as shown in Fig. 1(c). They may be converted back into N_t^- states by thermal emission of the bound holes. Alternatively, they may transform into N_t^0 states, either by radiative recombination of the exciton with intrinsic lifetime τ_{xr} , or by a nonradiative Auger process with lifetime τ_{xn} .

Based on the above considerations, the general

⁷ J. M. Dishman, M. DiDomenico, Jr., and R. Caruso, Phys. Rev. (to be published). This paper gives a detailed study of luminescence and minority carrier recombination in Zn and O doped *p*-GaP. By using an iterative self-consistent fit to the available temperature and Zn-doping dependence of the red luminescence efficiency and time decay, values are obtained for all of the important capture cross sections, time decay parameters and Auger recombination coefficients, as well as the minority carrier lifetime.

⁸ J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Inc., New York, 1962).

differential equations governing the recombination kinetics are given by

$$\dot{N}_t^0 = N_t^x/\tau_\alpha + N_t^-/\tau_\beta - (n/\tau_{nl})(N_t^0/N_t) + (n_i/\tau_{ni})(N_t^-/N_t), \quad (4)$$

$$\dot{N}_t^x = (p/\tau_{pt})(N_t^-/N_t) - (p_h/\tau_{pt})(N_t^x/N_t) - N_t^x/\tau_\alpha, \quad (5)$$

$$N_t = N_t^0 + N_t^x + N_t^-, \quad (6)$$

where p is the free hole density and τ_α , τ_β , and p_h are defined by

$$1/\tau_\alpha \equiv 1/\tau_{xr} + 1/\tau_{xn}, \quad (7)$$

$$1/\tau_\beta \equiv 1/\tau_{er} + 1/\tau_{en}, \quad (8)$$

$$p_h = (p_0/\beta_h) \exp[(\phi - E_h)/kT]. \quad (9)$$

In Eq. (9), p_0 is the thermal equilibrium concentration of free holes and β_h is the degeneracy of the hole state of energy E_h . The quantity p_h is defined analogously to n_t in Eq. (2). Its presence in the second term of Eq. (5) ensures that the thermal emission rate of the bound hole just balances the capture rate at thermal equilibrium. To be completely general, we should also consider time-dependent equations for recombination of the minority and majority carriers n and p . In Sec. III, we shall show that Eqs. (4)–(6) can be solved, apart from such equations, using reasonable approximations for the behavior of n and p .

Before proceeding further, we show that under steady-state conditions and for sufficiently low temperatures the isoelectronic trap can be treated as a two-state SRH recombination center with ionization energy E_t . To do this, we define an exciton occupancy factor f as the fraction of the total captured electrons at the isoelectronic center which form bound excitons, i.e.,

$$N_t^x = fN_t^e \quad (10)$$

and, consequently,

$$N_t^- = (1-f)N_t^e, \quad (11)$$

where

$$N_t^e \equiv N_t^x + N_t^-. \quad (12)$$

We can, thus, eliminate N_t^x and N_t^- in terms of f and N_t^e in Eqs. (4)–(6) and obtain

$$\dot{N}_t^e = -N_t^e/\tau_t + (n/\tau_{nl})(1-f)(N_t^e/N_t) - (n_i/\tau_{ni})(1-f)(N_t^e/N_t), \quad (13)$$

$$f\dot{N}_t^e + f\dot{N}_t^x = (1-f)(N_t^e/N_t)(p/\tau_{pt}) - f(N_t^e/N_t)(p_h/\tau_{pt}) - fN_t^e/\tau_\alpha, \quad (14)$$

where τ_t is defined by

$$1/\tau_t \equiv (1-f)/\tau_\beta + f/\tau_\alpha. \quad (15)$$

Except for the factor $1-f$ multiplying the last term, Eq. (13) is just what one would obtain if the isoelectronic trap were a simple two-state SRH center and τ_t were the total lifetime of the N_t^e -type state. An

important distinction is that, for the isoelectronic trap, τ_t depends on N_t^e through f [see Eq. (15)]. For the usual two-state SRH center, only one occupation factor N_t^e is needed to describe the condition of the trap, while for the three-state isoelectronic center two occupation factors N_t^e and f are required. The time dependences of these two factors are coupled through Eq. (14). In steady state, the left-hand side of Eq. (14) vanishes. We then obtain an expression for the steady-state exciton occupancy factor f_0 independent of the value of N_t^e , i.e.,

$$f_0 = (1 + p_h/p + N_t\tau_{pt}/p\tau_\alpha)^{-1}. \quad (16)$$

Thus, in steady state, the parameters τ_t and $(1-f_0)$ appearing in Eq. (13) are independent of N_t^e . For temperatures sufficiently low [e.g., $T < 300^\circ\text{K}$ for GaP(Zn,O)] thermalization of the deeply trapped particle is unimportant and the last term in Eq. (13) can be neglected. For this case, Eq. (13) becomes formally equivalent to the rate equation governing recombination at a two-state SRH center with ionization energy E_t . Under the most general steady-state conditions, however, SRH kinetics do not apply and we must use the full form of Eq. (13) setting $\dot{N}_t^e = 0$. It should be noted that if $N_t\tau_{pt}/p\tau_\alpha \ll 1$, then f_0 approaches the value given by

$$f_0 \rightarrow \{1 + \beta_h^{-1} \exp[(\phi - E_h)/kT]\}^{-1}, \quad (17)$$

which is just the thermal equilibrium occupation probability for a hole bound to the electron occupied Zn-O complex. In general, however, we cannot assume that the bound hole is in thermal equilibrium with the valence band.

III. TRANSIENT SOLUTIONS

In this section, we consider the mathematical details necessary for solving the time-dependent recombination problem at an isoelectronic center. The recombination is governed by Eqs. (4)–(6) and by auxiliary equations for the minority and majority carrier densities n and p . In general, these form a set of nonlinear differential equations whose solution is difficult. Reasonable approximations concerning n and p can be made, however, based on physical arguments. When this is done, solutions to simplified equations are obtained in terms of exponential functions. One approximation implicit in the formulation of the problem should be mentioned at the outset. By assigning a spatially independent lifetime τ_{er} to the Zn-O-to-Zn pair process, we neglect an important physical effect which gives rise to a nonexponential ($\approx t^{-1}$) time decay.⁹ Thus, our solutions will not correctly predict the time variation of the luminescence for intensity changes occurring over many orders of magnitude. However, for the purposes of comparing theory and experiment, it is entirely sufficient to consider only the initial order of magnitude

⁹ D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. **140**, A202 (1965).

in the decay of the luminescence, for which the exponential and nonexponential solutions have very similar time-decay characteristics. We will, therefore, limit ourselves to calculating the parameter $\tau_{1/e}$, which is defined to be the time duration in which the luminescence decays to $1/e$ of its initial value. Of primary interest is the temperature dependence of $\tau_{1/e}$. As shown in Sec. IV, we obtain an acceptable fit to the measured temperature dependence⁵ of $\tau_{1/e}$ for GaP(Zn,O) using exponential solutions, thus, justifying the above approximation.

Eliminating N_i^- between Eqs. (4)–(6), the mathematical problem reduces to two simultaneous differential equations in the unknowns N_i^x , N_i^0 , n , and p :

$$\dot{N}_i^x = -N_i^x(p + p_h)/N_i\tau_{pi} - N_i^x/\tau_\alpha + (1 - N_i^0/N_i)(p/\tau_{pi}), \quad (18)$$

$$\dot{N}_i^0 = N_i^x(1/\tau_\alpha - 1/\tau_\gamma) + (1 - N_i^0/N_i)(N_i/\tau_\gamma) - (N_i^0/N_i)(n/\tau_{ni}), \quad (19)$$

where we have defined

$$1/\tau_\gamma = 1/\tau_\beta + n_i/N_i\tau_{ni}. \quad (20)$$

We can neglect the term involving n in Eq. (19) for two experimentally interesting cases. In the first, we assume that the minority carriers decay to zero much more rapidly than any decay process at the isoelectronic center. Thus, after a very short interval, the last term in Eq. (19) goes to zero. The second case of interest arises from the fact that N_i^- states may be excited directly without the generation of minority carriers using below gap radiation,¹⁰ in which case the last term of Eq. (19) is replaced by G , the excitation rate. Also, in this case, the decay after excitation is described by setting the last term in Eq. (19) to zero. We will henceforth restrict the analysis to these two cases alone.

We can replace p in Eq. (18) by its value determined from charge neutrality in a p -type crystal,¹¹ i.e.,

$$p = p_0 + N_i^- + n. \quad (21)$$

Setting $n \approx 0$ and using Eq. (21) to replace p in Eq. (18), we obtain

$$\dot{N}_i^x = -N_i^x(p_h/N_i\tau_{pi} + 1/\tau_\alpha) + (N_i - N_i^0 - N_i^x)(p_0/N_i\tau_{pi}) + (N_i - N_i^0 - N_i^x)^2/N_i\tau_{pi}. \quad (22)$$

Equations (19) and (22) form a set of simultaneous equations in two unknowns N_i^x and N_i^0 .¹² At this point,

¹⁰ For example, it has been shown that the red luminescence in GaP(Zn,O) can be excited by direct excitation of the N_i^- and N_i^x states (see Refs. 4 and 7).

¹¹ Equation (21) assumes that the occupancies of the dominant acceptor and donor impurities do not change from their thermal-equilibrium values under excitation. The more general case introduces unnecessary complications in the mathematics. We consider one such case in Sec. IV and the Appendix.

¹² There is still an implicit p dependence in these equations due to the Auger terms involved in the definitions of τ_α and τ_γ . We assume Auger recombination is negligible at low temperatures, and at higher temperatures we use the thermal-equilibrium hole density p_0 in the definitions of τ_{zn} and τ_{en} [see Eqs. (33) and (34)].

we digress briefly from the main development to show under what restrictions the last term in Eq. (22), i.e., the nonlinear one, can be neglected.

For a crystal in which the dominant acceptor is present in much larger concentrations than the isoelectronic trap, we have at appropriately high temperatures $p_0 \gg N_i$. Thus, the last term in Eq. (22) may be neglected with respect to the second term. This condition is met for example in GaP(Zn,O), where the zinc-acceptor concentration is necessarily larger than the Zn-O pair concentration. At low temperatures, the physical significance of the nonlinear term can be seen by artificially setting $1/\tau_\alpha$ and $1/\tau_\gamma$ to zero in Eqs. (19) and (22). Then, by taking $p_0 = p_h = 0$, a valid assumption at low temperature, we obtain a simple solution for the system of Eqs. (19) and (22), under the previous constraint of neglecting the last term in Eq. (19). The solutions for N_i^0 and N_i^x are

$$\begin{aligned} N_i^0 &= \text{const}, \\ N_i^x &= N_i^x(0) + N_i^-(0) - N_i^-(0)N_i\tau_{pi} \\ &\quad \times [N_i\tau_{pi} + N_i^-(0)t]^{-1}, \end{aligned} \quad (23)$$

where $N_i^x(0)$ and $N_i^-(0)$ are values of N_i^x and N_i^- at $t=0$. The solution given by Eq. (23) indicates that N_i^x increases from its initial value to a value $N_i^x(0) + N_i^-(0)$ under the action of the nonlinear term. Since $p \approx N_i^- = N_i - N_i^0 - N_i^x$ and $N_i^0 = \text{constant}$, the free-hole density p and the bare-electron concentration N_i^- decay to zero nonexponentially from their initial value $N_i^-(0)$ with a time constant of order τ_{pi} . Thus, at low temperature, the nonlinear term represents the rapid (bimolecular) capture of free holes by the electron occupied traps to form bound excitons. This term is the dominant term in Eq. (22) immediately after the excitation ceases, and until all the holes are captured by the traps. Since N_i^x increases under its influence, we expect that the excitonic radiative recombination (N_i^x/τ_{xr}) increases for a short duration after the excitation is turned off. This is to be compared with the observation of CHD⁵ of a 15-nsec post-excitation increase in the red luminescence from GaP(Cd,O) at low temperature. Since, at low temperature, the lifetime τ_{pi} for this capture process is expected to be much shorter than any other decay process out of the trap, we can solve for the decay at times longer than τ_{pi} by neglecting the nonlinear term.

Having justified the omission of the last terms in each of Eqs. (19) and (22), we can now obtain solutions in terms of simple exponential functions, i.e.,

$$N_i^x = A_1 e^{-t/\tau_+} + A_2 e^{-t/\tau_-} \quad (24)$$

and

$$N_i^0 = B_1 e^{-t/\tau_+} + B_2 e^{-t/\tau_-} + N_i. \quad (25)$$

The decay times τ_+ and τ_- are given by

$$\begin{aligned} 1/\tau_{+,-} &= \frac{1}{2} [1/\tau_\alpha + 1/\tau_\gamma + (p_0 + p_h)/N_i\tau_{pi}] \\ &\quad \pm \frac{1}{2} \{ [1/\tau_\alpha - 1/\tau_\gamma + (p_0 + p_h)/N_i\tau_{pi}]^2 \\ &\quad - (4p_0/N_i\tau_{pi})(1/\tau_\alpha - 1/\tau_\gamma) \}^{1/2}, \end{aligned} \quad (26)$$

where the $+$ sign refers to τ_+ and the $-$ sign to τ_- . The total locally generated luminescence l_r due to radiative recombination at the isoelectronic center is obtained from

$$l_r = N_t^x / \tau_{xr} + N_t^- / \tau_{er}, \quad (27)$$

where we have included contributions of both excitonic and pair emissions. Expressing the coefficients A_1 , A_2 , B_1 , and B_2 in terms of initial conditions for N_t^x and N_t^- , we obtain a complete expression for l_r :

$$l_r = \frac{\{N_t^x(0) + \gamma_- [N_t^x(0) + N_t^-(0)]\} \left(\frac{\gamma_+}{\tau_{xr}} - \frac{(1 + \gamma_+)}{\tau_{er}} \right)}{(\gamma_+ - \gamma_-)} \times e^{-t/\tau_+} + \frac{\{N_t^x(0) + \gamma_+ [N_t^x(0) + N_t^-(0)]\}}{(\gamma_+ - \gamma_-)} \times \left(-\frac{\gamma_-}{\tau_{xr}} + \frac{(1 + \gamma_-)}{\tau_{er}} \right) e^{-t/\tau_-}, \quad (28)$$

where

$$\gamma_{+,-} = (1/\tau_\gamma - 1/\tau_{+,-}) / (1/\tau_\alpha - 1/\tau_\gamma). \quad (29)$$

Equation (28) represents the luminescence time decay one would observe experimentally if the excitonic and pair emissions occurred in the same spectral region, e.g., as in the case of the red luminescence from GaP(Zn,O). We expect Eq. (28) to be a good approximation to the actual time decay at high temperatures (i.e., where $p_0 \gg N_t$), at low temperature for times longer than τ_{pt} (≈ 10 nsec), and for one or two decades of decrease in l_r . The decay time $\tau_{1/e}$ is determined from Eq. (28) by solving (numerically) for the time at which l_r has decreased to $1/e$ of its $t=0$ value. In general, $\tau_{1/e}$ is not simply related to τ_+ or τ_- , but depends sensitively on the initial conditions. The individual decay times τ_+ and τ_- themselves have especially simple forms at low and high temperature. At low temperature, where $p_0 \approx p_h \approx 0$, we find from Eq. (26) that $\tau_+ \rightarrow \tau_\alpha$ and $\tau_- \rightarrow \tau_\gamma$. Recalling Eqs. (7), (8), and (20), we conclude that τ_+ is the decay time for N_t^x states and τ_- the decay time for N_t^- states. At higher temperatures, we also get simple expressions for τ_+ and τ_- if the hole concentration is sufficient to satisfy the two inequalities

$$\begin{aligned} p_0 + p_h &\gg N_t \tau_{pt} / \tau_\alpha, \\ p_0 + p_h &\gg N_t \tau_{pt} / \tau_\gamma. \end{aligned} \quad (30)$$

In this case, the square root in Eq. (26) can be replaced by the first two terms of its binomial expansion yielding

$$1/\tau_+ \approx p_0 / (f_0 N_t \tau_{pt}), \quad (31)$$

$$1/\tau_- \approx 1/\tau_\gamma + f_0 (1/\tau_\alpha - 1/\tau_\gamma), \quad (32)$$

where $f_0 \approx p_0 / (p_0 + p_h)$ [recall Eq. (17)]. By observing that the rate of thermal emission of holes out of exciton-occupied isoelectronic traps is $e_{pt} \equiv (N_t^x / N_t) (p_h / \tau_{pt})$, we obtain from Eq. (31) (noting that $p_0 \ll p_h$) $e_{pt} = N_t^x / \tau_+$. Thus, under the restrictions of Eq. (30), τ_+

is the lifetime for hole emission out of the electron-occupied traps. In the same temperature range, we can identify τ_- with the total steady-state lifetime τ_t , since thermalization of the deeply trapped particle is negligible so that $\tau_\gamma \approx \tau_\beta$ [cf. Eqs. (15), (20), and (32)]. Since in most cases $\tau_+ \ll \tau_-$, the total luminescence will be dominated by the slower decaying term $\tau_- \approx \tau_t$ and the decay time $\tau_{1/e}$ will be very nearly equal to the total steady-state lifetime τ_t . We emphasize that the identification of $\tau_{1/e}$ with τ_t is only valid when the restrictions of Eq. (30) are satisfied. We showed previously [Eq. (17)] that the first condition in Eq. (30) is equivalent to the assumption that holes bound to the isoelectronic traps are in thermal equilibrium with the valence band. Such equilibrium will not usually exist at low temperature; moreover, for very lightly doped crystals, it may not exist at any temperature. The second condition in Eq. (30) will not be satisfied at the highest temperatures where thermalization of the deeply trapped particle becomes important. In GaP(Zn,O), for example, we find (Sec. IV) that τ_t remains approximately constant above 300°K, while $\tau_{1/e}$ falls off very rapidly.

In summary, we have shown that the time-dependent recombination problem at an isoelectronic impurity can be reasonably approximated in terms of linearized differential equations for N_t^x and N_t^p . The solution of these equations results in an expression for the total luminescence decay [Eq. (28)] in terms of exponential functions. While the exponential solutions, which neglect the $\approx t^{-1}$ pair recombination decay, are admittedly approximations to the actual time dependence, Eq. (28) is nonetheless entirely adequate for calculating the experimentally interesting parameter $\tau_{1/e}$. In Sec. IV we calculate $\tau_{1/e}$ as a function of temperature for the GaP(Zn,O) system, using reasonable values for the initial conditions and lifetime parameters entering in Eqs. (28) and (29). We find good agreement between calculated and experimental values by using as an adjustable parameter the capture cross section σ_{pt} .

IV. TEMPERATURE DEPENDENCE OF DECAY TIME

There are three sources for the temperature dependence of the luminescence decay time $\tau_{1/e}$, namely, the temperature variation of p_0 , τ_{pt} , and τ_{xr} [e.g., see Eq. (26)]. The temperature dependence of p_0 is easily calculated from Fermi-Dirac statistics and a knowledge of the principal acceptor and donor concentrations and energy levels. We will assume that the temperature variations of the Auger recombination terms τ_{xn} and τ_{en} are due solely to variations in p_0 through the expressions

$$1/\tau_{xn} = B p_0, \quad (33)$$

$$1/\tau_{en} = C p_0^2, \quad (34)$$

where B and C are temperature-independent constants evaluated elsewhere.⁶ The temperature dependence of

τ_{pt} is governed by the thermal velocity $v \approx (3kT/m^*)^{1/2}$ and by the cross section σ_{pt} , which we take to have the form

$$\sigma_{pt} = C_{pt} T^{-m}, \quad (35)$$

where C_{pt} is a constant. We will use C_{pt} and m as fitting parameters in calculating $\tau_{1/e}$. Finally, the intrinsic lifetime of the exciton τ_{xr} may also be temperature-dependent due to the existence of two angular momentum states for the bound exciton.^{2,13} If τ_A is the lifetime of the higher-lying $J=1$ state and τ_B the lifetime of the $J=2$ state, then at low temperatures the exciton lifetime becomes¹⁴

$$\tau_{xr} = \tau_B (1 + g e^{-\Delta E/kT}) / (1 + \gamma g e^{-\Delta E/kT}), \quad (36)$$

where ΔE is the energy difference between the two levels, g is the ratio of degeneracies of the A -to- B levels, and $\gamma = \tau_B/\tau_A$. When the two angular momentum states are mixed, τ_{xr} is a temperature-independent average of the lifetimes for the two states, and the temperature dependence of the decay time is determined only by p_0 and τ_{pt} .

The decay time $\tau_{1/e}$ of the red luminescence in Zn,O-doped GaP has been measured as a function of temperature by CHD.⁵ In this system, considerable mixing of the two angular momentum states of excitons bound to Zn-O complexes apparently occurs.⁵ Consequently, τ_{xr} is approximately constant. Moreover, the electrical properties of GaP(Zn,O) are known well enough that the temperature dependence of p_0 can be determined with some degree of accuracy. Therefore, in this section, we fit the $\tau_{1/e}$ data of CHD to the theoretical expression [see Eq. (28)] using m and C_{pt} [Eq. (35)] as fitting parameters. As we shall show, the low-temperature behavior of $\tau_{1/e}$ is controlled by σ_{pt} while the high-temperature behavior is dominated by the Auger processes and thermalization of the deeply trapped electron.

To calculate $\tau_{1/e}$ from Eq. (28), we must make an assumption about the initial values $N_i^x(0)$ and $N_i^-(0)$. If we assume that steady-state equilibrium prevails prior to the decay, the initial conditions are determined by the occupancy factor f_0 through the relations $N_i^x(0) = f_0 N_i^e(0)$ and $N_i^-(0) = (1 - f_0) N_i^e(0)$. If the N_i^e states are generated at a constant rate G , then the steady-state kinetics require (illustratively)

$$N_i^e(0) = G\tau_i, \quad (37)$$

where τ_i depends on f_0 through Eq. (15). At high temperatures, f_0 is independent of G , since p can be replaced by p_0 in Eq. (16). However, at low temperatures where $p_0 \rightarrow 0$, we must solve for p in terms of G and use this value in Eq. (16). In the realistic case where compensating donors are present, Eq. (21) is no longer adequate for expressing the condition of charge

neutrality. Without compensation, all acceptor levels are neutral at low temperatures and the only effective hole-trapping centers are the N_i^- states. In this idealized limit, Eq. (21) applies, i.e., the photogenerated holes are immediately trapped onto N_i^- states, thereby forming exciton states with the result that $f_0 \approx 1$. In the presence of compensation, some ionized acceptor levels exist and compete with the charged N_i^- states for the capture of photogenerated holes with the result that $f_0 < 1$. A low-temperature expression for f_0 using a more general statement of charge neutrality than Eq. (21) is derived in the Appendix. The result is

$$f_0 = \left[1 - \frac{D}{G} \left(\frac{1}{\tau_\alpha} - \frac{1}{\tau_\beta} \right) \right]^{-1} \left\{ 1 + \frac{D}{2G\tau_\beta} - \left[\frac{1}{4} \left(\frac{D}{G\tau_\beta} + 2 \right)^2 + \frac{D}{G} \left(\frac{1}{\tau_\alpha} - \frac{1}{\tau_\beta} \right) - 1 \right]^{1/2} \right\}, \quad (38)$$

where

$$D \equiv (p_h + N_i(\tau_{pt}/\tau_\alpha)(N_D/N_A)(\tau_{er}/\tau_{pA})).$$

Here N_A is the acceptor concentration, N_D is the compensating donor concentration, and τ_{pA} is the lifetime for capture of holes into the ionized acceptor levels [defined analogously to τ_{pt} in Eq. (3)]. In the limit $D/G \rightarrow 0$, Eq. (38) yields $f_0 \rightarrow 1$. This limit corresponds either to high excitation densities or to low compensation ratios. In the limit $D/G \rightarrow \infty$ corresponding to low excitation densities, a binomial expansion of the square root in Eq. (38) yields

$$f_0 \approx G\tau_\beta/D. \quad (39)$$

Thus, we expect in steady state and at low temperatures that pair luminescence will be dominant under low excitation for which $f_0 \ll 1$, while the excitonic emission will predominate for high excitation where $f_0 \approx 1$. These conclusions agree with the findings of CHD who observed for GaP(Cd,O) that low pumping intensity favored pair recombination, while high pumping intensity favored excitonic emission.

For the remainder of this section, we assume that, over the whole temperature range $0 < T < 440^\circ\text{K}$, the traps are saturated by the steady-state value of G prior to the decay, i.e., $N_i^e(0) = N_i$.¹⁵ This restriction corresponds to the high-excitation limit $G \rightarrow \infty$ for which $f_0 = 1$ at low temperature. In the Appendix, Eq. (21) is shown to be valid when $p_A/\tau_{pA} \gg N_i/\tau_{er}$, where p_A is the free hole density when the Fermi level ϕ coincides with the acceptor energy level [c.f. Eq. (9)]. We estimate that this inequality is satisfied above 60°K for GaP(Zn,O) when $N_A \approx 10^{18} \text{ cm}^{-3}$; i.e., above this temperature the initial values $N_i^x(0)$ and $N_i^-(0)$ are independent of compensation effects. The analysis is greatly simplified if we neglect compensation effects below 60°K as well and use Eq. (21) to relate

¹³ J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters **17**, 312 (1968).

¹⁴ J. D. Cuthbert and D. G. Thomas, Phys. Rev. **154**, 763 (1967).

¹⁵ This is a good assumption under the conditions for which the data of Ref. 5 were taken [J. D. Cuthbert (private communication)].

p and f_0 . Using $N_t^- = (1 - f_0)N_t$ in Eq. (21) and substituting for p in Eq. (16), we obtain the following useful approximation for the full temperature range:

$$f_0 = [1 + \tau_{pt}/2\tau_\alpha + (p_0 + p_h)/2N_t] - \{[1 + \tau_{pt}/2\tau_\alpha + (p_0 + p_h)/2N_t]^2 - (1 + p_0/N_t)\}^{1/2}. \quad (40)$$

At low temperatures where $\tau_{pt} \ll \tau_\alpha$, we find from Eq. (40) $f_0 \approx 1$ in agreement with the high-excitation limit of the more general low-temperature expression in Eq. (38). In obtaining a fit to the measured $\tau_{1/e}$ decay time, we choose to use Eq. (40) rather than Eq. (38) to calculate f_0 over the full temperature range. This has the advantage of eliminating the unknown lifetime τ_{pA} [and, hence, two adjustable parameters cf. Eq. (35)] at the expense of achieving an exact fit below 60°K. Consequently, our fit below 60°K is only qualitative. However, we emphasize that our use of Eq. (40) retains all important physical processes operative at all temperatures.

With the above restrictions on the initial conditions, we now show that our model predicts the measured temperature dependence of $\tau_{1/e}$ in GaP(Zn,O) using *two* adjustable parameters, viz., the values of m and C_{pt} entering in the expression for σ_{pt} in Eq. (35). Before comparing the calculated and measured values of $\tau_{1/e}$, we review the selection of parameters used in the calculation. To determine p_0 , we take $N_A = 10^{18} \text{ cm}^{-3}$ and $N_D = 10^{17} \text{ cm}^{-3}$, which are appropriate to the sample investigated by CHD. For the zinc-acceptor ionization energy E_A , we use an empirical relation⁶ derived from Hall measurements¹⁶

$$E_A = E_{A0} - 3 \times 10^{-8} N_A^{1/3}, \quad (41)$$

where E_{A0} is the dilute ionization energy¹⁷ ($E_{A0} = 0.064 \text{ eV}$), with the energies in eV and N_A in cm^{-3} . We also choose⁴ $E_h = 0.036 \text{ eV}$ for use in Eq. (9). For the non-radiative Auger lifetimes, we use Eqs. (33) and (34), which implicitly assume that the Auger processes are negligible at low temperature. We choose the relative values of the Auger lifetimes to agree with a first-principles calculation,⁶ i.e., $B/C = 10^{19} \text{ cm}^{-3}$. The value of B (or C) is then constrained by the measured value of the Zn-O radiative efficiency b_r in crystals with doping levels in the range $N_A \approx 10^{18} \text{ cm}^{-3}$. The relationship between b_r , B , and B/C is given elsewhere.^{6,7} Using a measured value⁷ of $b_r \approx 0.1$, we have calculated $B \approx 10^{-10} \text{ cm}^3/\text{sec}$ for $B/C = 10^{19} \text{ cm}^{-3}$. Also, on the basis of the measurements reported elsewhere,⁷ we choose $N_t = 10^{16} \text{ cm}^{-3}$. This then leaves undetermined only the radiative lifetimes τ_{er} and τ_{xr} . We relate τ_{er} to τ_{xr} through the relation

$$1/\tau_{er} = f_A K / \tau_{xr}, \quad (42)$$

¹⁶ H. C. Casey, F. Ermanis, and K. B. Wolfstirn, J. Appl. Phys. **40**, 2945 (1969).

¹⁷ P. J. Dean, C. J. Frosch, and C. H. Henry, J. Appl. Phys. **39**, 5631 (1968).

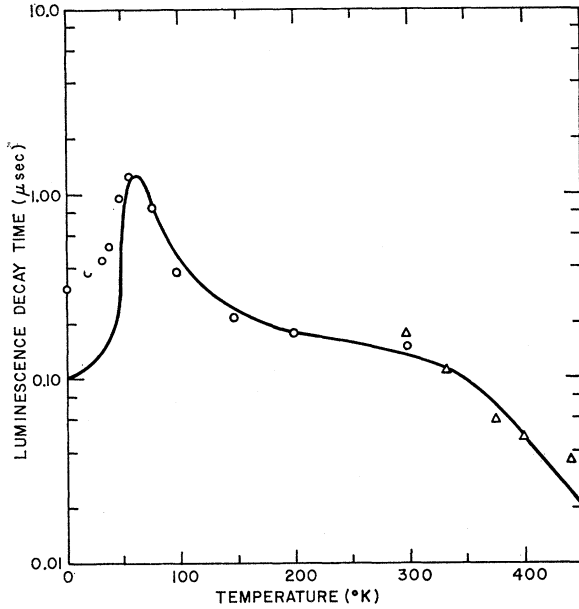


FIG. 2. Comparison of temperature dependence of measured and calculated luminescence decay time $\tau_{1/e}$ for GaP(Zn,O). The model parameters used in calculating the solid curve are given in Table I. Open circles are experimental points of CHD (Ref. 5). Open triangles are obtained from Ref. 23.

where f_A is the fraction of acceptors filled with holes and K is a constant. Equation (42) was derived by CHD with $K \approx 0.01$. We also choose $\tau_{xr} = 0.1 \text{ } \mu\text{sec}$, which is the best estimate of CHD.⁵

In fitting the measured temperature dependence of $\tau_{1/e}$, we recall that $\tau_{1/e}$ is essentially independent of compensation above 60°K, but is likely to be sample-dependent below this temperature. Accordingly, we choose $m = 1$ and $C_{pt} = 3.6 \times 10^{-16} \text{ cm}^{-2} \text{ } ^\circ\text{K}$ [see Eq. (35)] in order to obtain good agreement with the data of CHD in the range $60 \leq T \leq 300^\circ\text{K}$. The resulting fit is shown in Fig. 2. In Table I,^{17a} we list separately the values of all the parameters entering into the fit of $\tau_{1/e}$. Not surprisingly, below 60°K, only qualitative agreement is achieved because of the approximate validity of Eq. (40). In the limit $T \rightarrow 0$, we showed previously (Sec. III) $\tau_+ \rightarrow \tau_\alpha$ and $\tau_- \rightarrow \tau_\gamma$. Inserting these values in Eqs. (28) and (29) yields

$$l_r \approx [N_t^x(0)/\tau_{xr}]e^{-t/\tau_{xr}} + [N_t^-(0)/\tau_{er}]e^{-t/\tau_{er}}, \quad (43)$$

where we have made use of Eqs. (7) and (8), and taken $1/\tau_{xn} = 1/\tau_{en} = 0$ and $n_t = 0$. Thus, the low-temperature limit of $\tau_{1/e}$ is an average of τ_{xr} and τ_{er} with weighting factors determined by the initial conditions. The

^{17a} Note added in proof. In a forthcoming paper (Ref. 7) several of the parameters given in Table I which enter into the calculation of the temperature dependence of $\tau_{1/e}$ have been re-evaluated. In particular, based on the measured concentration and temperature dependence of the luminescence quantum efficiency and time decay we find that $E_t = 0.230 \text{ eV}$, $B = 5 \times 10^{-11} \text{ cm}^3/\text{sec}$, and $C = 2.5 \times 10^{-30} \text{ cm}^6/\text{sec}$. These values are in substantial agreement with those given in Table I. They do not result in serious modification of the calculated $\tau_{1/e}$ versus T curves shown in Fig. 2.

TABLE I. Parameters used in the calculation of the red-luminescence decay time $\tau_{1/e}$ for GaP(Zn,O).

Zn-O electron-trap level	$E_t = 0.300$ eV
Exciton-hole ionization energy	$E_h = 0.036$ eV
Zn-acceptor ionization energy	$E_A = 0.064 - 3 \times 10^{-8} N_A^{1/3}$ eV
Exciton radiative lifetime	$\tau_{xr} = 0.100$ μ sec
Bare-electron radiative (pair) lifetime	$\tau_{er} = 10/f_A$ μ sec
Zn-O electron-trap capture lifetime	$\tau_{nt} = 0.030$ μ sec
Zn-O hole-trap capture cross section	$\sigma_{pt} = 3.6 \times 10^{-16} T^{-1}$ cm ²
Auger B coefficient [Eq. (33)]	$B = 10^{-10}$ cm ³ sec
Auger C coefficient [Eq. (34)]	$C = 10^{-29}$ cm ⁶ /sec
Zn concentration	$N_A = 10^{18}$ cm ⁻³
Compensation ratio	$N_D/N_A = 0.1$
Zn-O complex concentration	$N_t = 10^{16}$ cm ⁻³

crystal used by CHD in obtaining the data of Fig. 2 was purposely chosen to emphasize the pair luminescence and, hence, to maximize the value of $N_t^-(0)$.¹⁸ For a sample with low compensation, $N_t^-(0) = 0$ under high-excitation conditions, and we expect an improved fit over the whole temperature range.

V. DISCUSSION OF RESULTS

Using our model, we now consider the physical basis for the main features of the $\tau_{1/e}$ -versus- T curve, i.e., the increase in $\tau_{1/e}$ from 0 to 60°K, the maximum near 70°K, the decrease in $\tau_{1/e}$ beyond 70°K, and the inflection point near 300°K. In Fig. 3, we plot the individual decay times τ_+ and τ_- along with f_0 as a function of temperature. As noted previously, at low temperatures the individual decay times saturate to values given by $\tau_+ = \tau_{xr}$ and $\tau_- = \tau_{er}$. Based on our assumptions concerning the low-temperature initial conditions, we have $f_0 \approx 1$, and the luminescence decay is dominated by the excitonic component. We showed earlier that τ_+ is associated with the decay of the N_t^x states, while τ_- is related to the decay of the N_t^- states. As the temperature is increased, both decay times are perturbed by the thermalization of holes bound to exciton-occupied Zn-O sites. The longer decay time τ_- is shortened because Zn-O sites originally occupied by bare electrons (N_t^- states) can capture holes thermalized from sites originally occupied by excitons (N_t^x states), and decay with the shorter excitonic lifetime. Thus, a decay route for the N_t^- states is created in addition to the pair decay mode (lifetime τ_{er}). This mixing of excitonic and pair-decay paths can be seen in Eq. (15), which is the high-temperature limit of τ_- under the restrictions of Eq. (30).

The faster decay time τ_+ is also shortened by the hole-thermalization process. This can be understood by recalling that, at elevated temperatures, τ_+ is the lifetime governing the thermal emission of bound holes from Zn-O centers. Consequently, it decreases as more thermal energy becomes available as shown in Fig. 3.

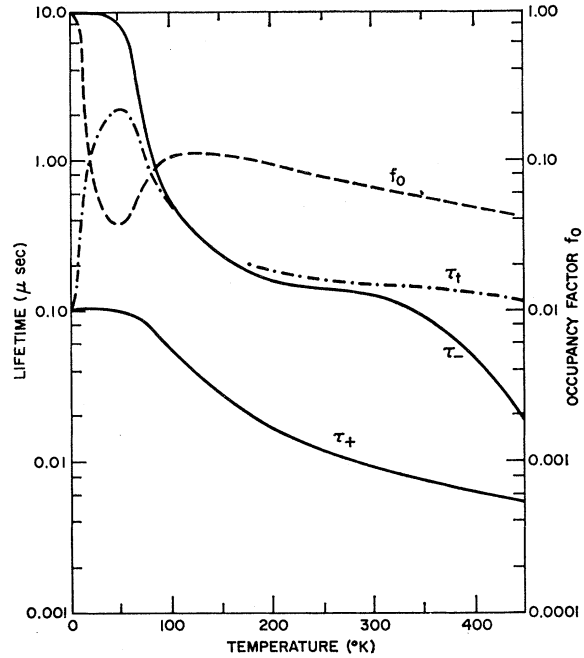


FIG. 3. Temperature dependence of lifetimes τ_+ , τ_- , and τ_t together with exciton occupancy factor f_0 for the model parameters in Table I.

The shortness of τ_+ results in a very rapid decay of the first term in the expression for the red emission in Eq. (28). The bound excitons do not decay this rapidly, however, since the thermalization process is matched by an equally fast recapture of holes onto the Zn-O sites. In this sense, τ_+ can be thought of as a readjustment time¹⁹ during which the initial distribution of holes is changed into a quasithermal-equilibrium distribution before the longer decay (time constant τ_-) begins. At lower temperatures, the capture dominates over the thermalization process and the quasithermal equilibrium is no longer maintained. In this situation, the readjustment time becomes comparable with the intrinsic exciton lifetime and τ_+ approaches τ_{xr} .

Even though the individual decay times τ_+ and τ_- decrease with increasing temperature, the measured decay time $\tau_{1/e}$ increases at first as a result of the temperature dependence of f_0 shown in Fig. 3. As the temperature is raised, f_0 decreases very rapidly due to the increased thermalization of the bound holes on Zn-O sites. Therefore, in the saturated steady-state conditions assumed to prevail prior to the decay, the fraction $N_t^-(0)/N_t^x(0)$ increases with temperature. The increased initial bare-electron concentration favors the slower-decaying component, since a larger fraction of the total decay can take place via the long-lived pair transition. As a result, the total red decay becomes longer as pair transitions become progressively more important. This increase in $\tau_{1/e}$ continues until about

¹⁸ J. D. Cuthbert (private communication).

¹⁹ D. J. Sandiford, Phys. Rev. **105**, 524 (1957).

70°K, above which $\tau_{1/e} \approx \tau_-$. Since τ_- continues to decrease with temperature beyond this point, the result is to produce a maximum in the plot of $\tau_{1/e}$ versus T near 70°K.

The temperature dependence of $\tau_{1/e}$ in the range $10 \leq T \leq 60^\circ\text{K}$ is very sensitive to the magnitude of the capture coefficient C_{pt} . From Fig. 4, it is seen that increasing C_{pt} while holding the other parameters constant can eventually cause $\tau_{1/e}$ to decrease with increasing temperature. The added strength of the capture cross section causes f_0 to decrease less rapidly with temperature, thus, favoring the occupation of N_c^x states prior to the decay. In this case, $\tau_{1/e}$ tends to follow the temperature variation of τ_+ rather than increasing toward τ_- as happens with smaller values of C_{pt} . This decrease in $\tau_{1/e}$ does not go on indefinitely, since f_0 eventually decreases to a point where the pair transitions become important. When this happens, $\tau_{1/e}$ again increases and a minimum is produced in the curve (see Fig. 4). Beyond the temperature at which the minimum occurs, the variation in $\tau_{1/e}$ proceeds as described above. For this case, the maximum in $\tau_{1/e}$, for which $\tau_{1/e} \approx \tau_-$, now appears at a higher temperature than before. It should be noted that these considerations tacitly assume a temperature-independent τ_{xr} . We point out that an initial decrease in $\tau_{1/e}$ with increasing temperature is also predicted by Eq. (36).

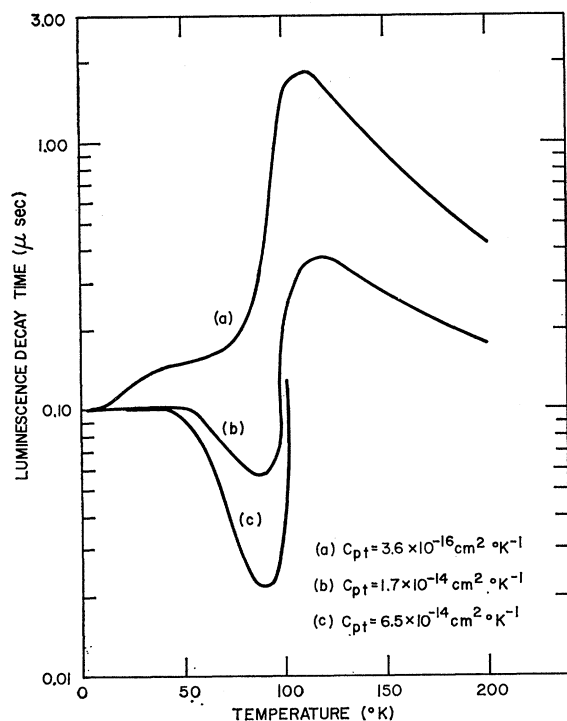


FIG. 4. Effect of varying the hole-capture coefficient C_{pt} [see Eq. (35)] on the temperature dependence of the luminescence decay time $\tau_{1/e}$. The model parameters are identical to those in Table I except that a higher value of E_A was used, i.e., $E_A = 0.064$ eV more appropriate to GaP(Cd,O).

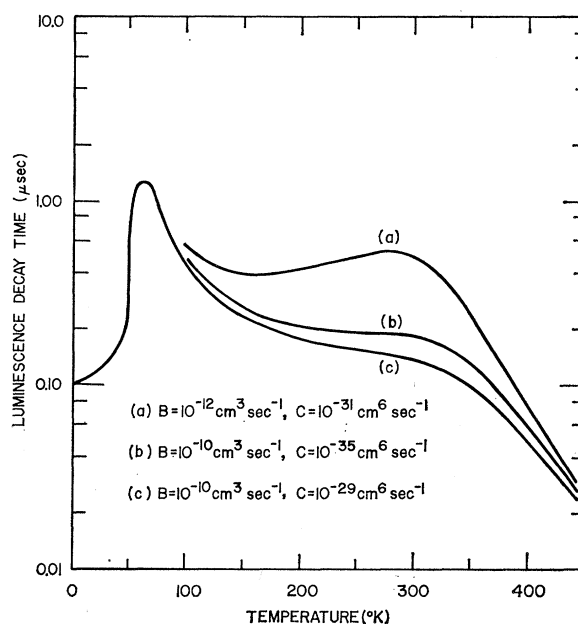


FIG. 5. Effect of varying the Auger B and C coefficients [see Eqs. (33) and (34)] on the temperature dependence of the luminescence decay time $\tau_{1/e}$. The model parameters are identical to those in Table I.

Thus, two explanations are possible for the observed temperature dependence of $\tau_{1/e}$ in the cadmium-oxygen system of GaP—one involves thermalization between the two angular-momentum states of the bound exciton [Eq. (36)], and the other involves thermalization of the hole in the bound exciton (Fig. 4).

The fitting parameters used in calculating $\tau_{1/e}$ for Fig. 2 yield a capture cross section of the form

$$\sigma_{pt} = 3.6 \times 10^{-16} T^{-1} \text{ cm}^2. \quad (44)$$

The magnitude of the cross section over the range $1 \leq T \leq 300^\circ\text{K}$ varies from 10^{-16} cm^2 to 10^{-18} cm^2 , which is appropriate for an attractive Coulombic center. The temperature variation is less rapid than observed for most attractive centers,²⁰ but this may not be surprising since the Zn-O complex is not a simple point defect. It is important to note that the magnitude of σ_{pt} is not sufficient to satisfy the inequalities of Eq. (30). As a result, τ_t which is about 10% larger than $\tau_{1/e}$ over the range $70 \leq T \leq 300^\circ\text{K}$, is not the actual luminescence decay time. On this basis, we expect an even larger disparity between τ_t and $\tau_{1/e}$ for crystals whose net acceptor concentration is lower than 10^{18} cm^{-3} .

Over the range $60 \leq T \leq 300^\circ\text{K}$, $\tau_{1/e}$ is dominated by the two Auger mechanisms defined by Eqs. (33) and (34). Although τ_{en} is in general much longer than τ_{xn} , its inclusion is essential in fitting the high-temperature data for $\tau_{1/e}$. If τ_{en} were neglected completely, a mini-

²⁰ V. T. Bonch-Bruевич and E. G. Landsberg, Phys. Status Solidi 29, 9 (1968) (see Tables 1-4 and accompanying references).

imum would be produced in the $\tau_{1/e}$ curve at $T \approx 250^\circ\text{K}$ resulting from the onset of saturation of the hole concentration (see Fig. 5). The $1/p_0^2$ dependence of τ_{en} [see Eq. (34)] emphasizes even the slow variations of hole concentration and causes $\tau_{1/e}$ to continue to decrease as temperature increases. Likewise, if both Auger terms were weakened relative to τ_{ar} , the high-temperature fit is substantially destroyed (see Fig. 5). Consequently, we conclude that the two Auger mechanisms are the main limitations on the quantum efficiency of the red luminescence in GaP(Zn,O) at room temperature.²¹ For crystals with $N_A - N_D \approx 10^{18} \text{ cm}^{-3}$, the maximum efficiency is estimated to lie in the range 5–10%.²²

Above 300°K , the temperature dependence of $\tau_{1/e}$ is controlled by thermalization of the deeply trapped (0.3 eV) electron.^{17a} In this temperature range, the term $n_t/N_t\tau_{nt}$ dominates the expression for $1/\tau_\gamma$ in Eq. (20), and, for sufficiently high temperatures, the second inequality in Eq. (30) is violated. Consequently, $\tau_{1/e}$ decreases rapidly above 300°K while the total lifetime τ_t remains approximately constant. In Fig. 2, we show recent decay-time data²³ above room temperature for a crystal of GaP(Zn,O) with doping similar to that examined by CHD. The calculated curve is in reasonable agreement with the measured points for $T > 300^\circ\text{K}$ using a value $\tau_{nt} = 0.03 \mu\text{sec}$. This value for τ_{nt} corresponds to $\sigma_{nt} \approx 10^{-16} \text{ cm}^2$, in agreement with previous determinations.³

VI. SUMMARY AND CONCLUSIONS

We have presented a model describing the kinetics of electron and hole (exciton) recombination at isoelectronic impurities. To adequately describe the transient behavior of the recombination, it is necessary to consider three separate states of the isoelectronic impurity (empty, electron-occupied, and exciton-occupied), rather than two (empty, and electron-occupied), as in the standard SRH formulation. Under certain reasonable restrictions, the time decay of the occupation factors can be determined in terms of exponential functions. These solutions permit one to compute the temperature dependence of the decay time $\tau_{1/e}$ of the observed luminescent processes. Applying the model calculations to the red luminescence in GaP(Zn,O), we have achieved a good fit to the measured temperature dependence of $\tau_{1/e}$ using only two adjustable parameters (see Fig. 2).

It is of interest to compare the qualitative features

of Figs. 2 and 4 with the measured values of $\tau_{1/e}$ for luminescence associated with isoelectronic traps in ZnTe:O¹⁴ and CdS:Te.²⁴ All show maxima in $\tau_{1/e}$ at intermediate temperatures ($80 \leq T \leq 400^\circ\text{K}$). It was suggested in Ref. 14 that the increase in $\tau_{1/e}$ with increasing temperature on the low-temperature side of the maximum results from thermalization of the weakly bound particle from the trap. This suggestion is supported by the model calculations of Sec. IV. The temperature at which the maximum occurs depends sensitively on the strength of the pair transition through the parameter K . If no pair transitions take place, then $K=0$ and we have $\tau_- \rightarrow \infty$ as $T \rightarrow 0$. As a result, the τ_- curve in Fig. 3 is displaced upward and the maximum is shifted to higher temperatures. This is to be compared with the experimental maxima for ZnTe:O and CdS:Te occurring near room temperature. The rapid decrease in $\tau_{1/e}$ on the high-temperature side of the maxima occurring for both cases is very similar to the rapid falloff observed in GaP(Zn,O) for $T > 300^\circ\text{K}$ and, thus, is attributed to thermalization of the deeply trapped particle.^{14,22} The Auger mechanisms [Eqs. (33) and (34)] do not seem as important for recombination at these isoelectronic impurities as in the case of GaP(Zn,O).

Decay-time data are also available for two other isoelectronic impurities in GaP, i.e., GaP:N and GaP:Bi.¹⁴ In each case, both electron and hole are trapped at shallow levels at the isoelectronic center. Thus, above 10°K in GaP:N and 25°K in GaP:Bi, the decay time is controlled by thermalization of the more deeply trapped particle and the $\tau_{1/e}$ curves show the rapid falloff characteristic of this process. The low-temperature data for these crystals are reasonably fit by Eq. (36)¹⁴ which expresses thermalization between the two angular momentum states of the bound exciton.

Finally, we note that recombination at isoelectronic impurities can be treated using SRH kinetics only under the conditions of steady-state equilibrium and for sufficiently low temperature that thermalization of the deeply trapped particle is negligible. In this case, the occupation factors N_t^- and N_t^x can be combined simply using Eqs. (10) and (11). In a separate paper,⁷ we treat the steady-state recombination problem in p -type GaP(Zn,O), including the effects of trapping at oxygen donors and other residual impurities. On this basis, we are able to determine the concentrations of Zn-O complexes and oxygen donors using optical measurements alone.

ACKNOWLEDGMENTS

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²¹ Evidence for Auger recombination involving a single free carrier in GaP(Zn,O) and GaP(Cd,O) has been presented previously by B. Welber, T. N. Morgan, and J. E. Scardefield, *Bull. Am. Phys. Soc.* **12**, 383 (1967); B. Welber, and T. N. Morgan, *Phys. Rev.* **170**, 769 (1968).

²² Similar estimates have been made by P. J. Dean [unpublished results based on J. C. Tsang, P. J. Dean, and P. T. Landsberg, *Phys. Rev.* **173**, 814 (1968)].

²³ R. N. Bhargava (private communication); and (to be published).

²⁴ J. D. Cuthbert and D. G. Thomas, *J. Appl. Phys.* **39**, 1573 (1968).

for helpful comments and the high-temperature data in Fig. 2. Useful comments by J. S. Jayson are also acknowledged.

APPENDIX: GENERAL EXPRESSION FOR f_0 AT LOW TEMPERATURES

At low temperature, the occupancy of the major acceptor levels can change substantially from the thermal equilibrium value under the influence of an external excitation. This effect modifies the calculation of f_0 given in the text, where a simple relation [Eq. (21)] was used to express charge neutrality. We now derive f_0 using the more general expression of charge neutrality in a p -type crystal:

$$p + N_D = N_A^- + N_t^-, \quad (\text{A1})$$

where N_A^- is the concentration of ionized acceptors. We assume that the steady-state external excitation generates N_t^e states at a rate G . Neglecting thermalization of the electron-occupied states, recombination at the isoelectronic center is governed by

$$G = [N_t^- / (1 - f_0)] / \tau_t, \quad (\text{A2})$$

where we have used Eq. (11) to express N_t^e in terms of N_t^- . Recombination at acceptor levels is determined by hole capture and thermalization, and by pair recombination with N_t^- states of the isoelectronic traps, i.e.,

$$(N_A^- / N_A)(p / \tau_{pA}) = (1 - N_A^- / N_A)(p_A / \tau_{pA}) + N_t^- / \tau_{er}. \quad (\text{A3})$$

The quantities τ_{pA} and p_A are defined by

$$\tau_{pA} = (v\sigma_{pA}N_A)^{-1}, \quad (\text{A4})$$

$$p_A = (N_V/\beta_A)e^{-E_A/kT}, \quad (\text{A5})$$

in analogy to Eqs. (3) and (9), respectively.

Eliminating N_A^- between Eqs. (A1) and (A3), we obtain a quadratic expression for p :

$$p^2 + p(p_A + N_D - N_t^-) + p_A(N_D - N_t^- - N_A) - N_A N_t^- \tau_{pA} / \tau_{er} = 0. \quad (\text{A6})$$

At low temperature, p_A vanishes exponentially and,

neglecting terms of this order, we obtain

$$p = -\frac{1}{2}(N_D - N_t^-) + \frac{1}{2}[(N_D - N_t^-)^2 + 4N_A N_t^- (\tau_{pA} / \tau_{er})]^{1/2}. \quad (\text{A7})$$

Since we expect the capture lifetime τ_{pA} to become short at low temperature, we make a binomial expansion of the second term in Eq. (A7), which yields

$$p \approx N_A N_t^- \tau_{pA} / (N_D - N_t^-) \tau_{er}. \quad (\text{A8})$$

Such an expansion may not be valid when N_t is comparable to N_A . As applied to the Zn-O complex in GaP, however, N_t is always much smaller than both N_A and N_D , and we can neglect N_t^- in the denominator of Eq. (A8). Equations (A2), (A8), and (15) can be used to eliminate p , N_t^- , and τ_t in the general expression for f_0 in Eq. (16). When this is done, we obtain

$$f_0^2 [(D/G)(1/\tau_\alpha - 1/\tau_\beta) - 1] + f_0 [D/(G\tau_\beta) - 1] - 1 = 0, \quad (\text{A9})$$

where

$$D \equiv (N_D / N_A)(\tau_{er} / \tau_{pA}) [p_h + (N_t \tau_{pt}) / \tau_\alpha]. \quad (\text{A10})$$

The solution is

$$f_0 = [1 - (D/G)(1/\tau_\alpha - 1/\tau_\beta)]^{-1} \times \left\{ 1 + \frac{D}{2G\tau_\beta} - \left[\frac{1}{4} \left(\frac{D}{G\tau_\beta} + 2 \right)^2 + \frac{D}{G} \left(\frac{1}{\tau_\alpha} - \frac{1}{\tau_\beta} \right) - 1 \right]^{1/2} \right\}. \quad (\text{A11})$$

We also wish to show under what conditions Eq. (21) is valid. From Eq. (A3), we have

$$N_A^- = N_A \tau_{pA} (p_A / \tau_{pA} + N_t^- / \tau_{er}) (p + p_A)^{-1}. \quad (\text{A12})$$

For $p_A / \tau_{pA} \gg N_t^- / \tau_{er}$, Eq. (A12) yields

$$N_A^- = (1 + p/p_A)^{-1} N_A = (1 - f_A) N_A, \quad (\text{A13})$$

where f_A is the fraction of neutral acceptors [see Eq. (42)]. Since charge neutrality applied at thermal equilibrium requires $p_0 = (1 - f_A) N_A - N_D$, Eq. (A1) becomes

$$p = p_0 + N_t^-, \quad (\text{A14})$$

in agreement with Eq. (21).