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Auger coefficient of GaP(Zn,O). I. Evaluation from the luminescence decay

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Measurements have been made of the luminescence time decay and Hall effect in epilayers of GaP(Zn,O). Both measurements were made on the same samples, as a function of temperature from 77 to 300°K. From the results we have been able to more accurately evaluate the Auger (nonradiative) coefficient at the nearest-neighbor (Zn, O) center. It was necessary to include the effect of screening on the energy levels in order to fit the data. After this correction, the Auger coefficient still depends on (i) the Hall factor, and (ii) the screening dependence of the transition probabilities. For a Hall factor of unity and for screening-independent transition probabilities, one obtains an Auger coefficient of $(2 \pm 0.5) \times 10^{-11}$ cm^3/sec. The possible effect of screening on the transition probabilities was also considered, but it was not possible to tell from the data whether this correction is required.

I. INTRODUCTION

It is well known that the luminescence efficiency in semiconductor phosphors is degraded by (nonradiative) Auger processes.[1] The strong red luminescence of GaP(Zn, O) is associated with an exciton bound to a substitutional Zn and O nearest-neighbor pair.[2] Centers of this type are also favorable for Auger transitions.[1] It is the aim of the present paper to evaluate the magnitude of the Auger effect at the (Zn, O) center more accurately than has been done previously. To achieve this, we have measured the luminescence time decay and the Hall effect as a function of temperature from 77 °K to room temperature on a series of samples with doping ranging from N_A of 0.5×10^{18} to 2×10^{18} cm^{-3} (the range of interest for efficient light emitting diodes).

In the present paper, we consider only the Auger and radiative transitions at the (Zn, O) center, shown in Fig. 1. To ensure that these are the only transitions of importance, we restrict the evaluation to low temperatures ($T \lesssim 250$ °K), such that thermal release of the exciton electron to the conduction band ("thermalization") is negligible. A further discussion of this point, as well as of other "minor" transitions, is given in the Appendix. Based on the transitions of Fig. 1, the Auger coefficient can be determined if the hole concentration and the occupancy of the exciton hole levels is known (Sec. II). The present analysis differs from prior[3-6] determinations of the Auger effect as regards both these factors: (i) Prior[3-6] determinations did not have Hall measurements of hole concentrations at the low temperatures where thermalization can be neglected. (ii) Corrections to the occupancy factor resulting from a sample and temperature dependence of the hole energy level were previously treated only empirically.[3,4] It has since been shown[7] that level energies are reduced by screening, and improved estimates of the magnitude of the energy reduction are thus available (Sec. II B). We show in this paper that the change in the hole energy *must* indeed be included in order to explain the data, and that screening gives a proper account of the magnitude, sample, and temperature dependence.

Two further complications in the analysis are also included in the present treatment: (i) The hole concentration is uncertain to within the Hall factor (the ratio of Hall to drift mobility), which is usually close to unity but can vary from this by factors of about 2. This quantity is not accurately known for our samples (nor for p-GaP in general); we therefore use several plausible values (Sec. II D) and compare the results.
(ii) Screening may modify not only the energy levels but also the transition probabilities. This is analyzed (Sec. II C) by use of the screened hydrogenic equation. In Sec. IV we compare results with and without inclusion of this effect.

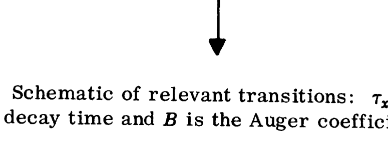

FIG. 1. Schematic of relevant transitions: τ_{xr} is the radiative decay time and B is the Auger coefficient.

The theory for the evaluation of the Auger effect is given in Sec. II, the experimental results in Sec. III, and the analysis of the data in Sec. IV. The results are discussed in Sec. V.

II. REVIEW OF THEORY

A. Kinetic equations and parameters

The transitions at the (Zn, O) center treated in the present analysis are limited to the two shown in Fig. 1. Other transitions customarily[3,4] considered at this center— specifically, the electron thermalization, pair decay, and Auger processes involving two free holes— are neglected here. The justification for neglect of these processes is given in the Appendix.

Following the kinetic treatments of earlier[3,4] works, the basic equation for the decay of the system of Fig. 1 is

$$\tau^{-1}=f(\tau_{xr}^{-1}+Bp)\,, \tag{1}$$

where

$$f=[1+(N_v/D_h p)e^{-E_h/kT}]^{-1}\,. \tag{2}$$

In Eqs. (1) and (2), τ is the observed decay constant, τ_{xr} is the radiative decay constant of the exciton, f is the fraction of exciton hole levels which are filled (the occupancy factor), B is the Auger coefficient at the Zn-O center, p is the free-hole concentration, N_v is the valence-band density of states, E_h and D_h are the energy and the degeneracy factor of the exciton hole level, respectively, k is Boltzmann's constant, and T is the temperature.

Equation (1) is the fundamental decay equation of the present paper: the decay rate depends on the occupancy of the hole level f, times the inverse sum of the decay rates of the radiative (τ_{xr}) and Auger $(Bp)^{-1}$ processes at a filled center. The occupancy factor is taken as the thermal equilibrium value [Eq. (2)], which is appropriate for the present experimental conditions (the hole thermalization is fast compared to the other transitions— see, for example, Ref. 3).

It follows from Eqs. (1) and (2) that five parameters (τ_{xr}, p, E_h, N_v, and D_h) are required for evaluation of the Auger coefficient. Of these five, the valence-band density of states (N_v) and the degeneracy (D_h) are reasonably well known. The former is given by

$$N_v=2.245\times10^{15}T^{3/2}\,, \tag{3}$$

using an effective mass of $m^*/m=0.6$. This value of m^* was derived from the cyclotron resonance results of Schwerdtfeger[8] and of Bradley *et al.*[9] Following Cuthbert *et al.*,[10] the expression for D_h is

$$D_h=2(1+e^{-116/T})\,. \tag{4}$$

The remaining parameters are less well known. The activation energy E_h depends on screening[7] and is thus a function of temperature. Its evaluation is discussed in Sec. II B. The exciton decay τ_{xr} has been obtained by Jayson and Bachrach[11] at low doping, where screening can be neglected. If screening affects the transition probabilities, values of τ_{xr} become more problematical. This is discussed in Sec. II C. Finally, the hole concentration p, as already mentioned (Sec. I), is determined only to within the Hall factor. This is covered in Sec. II D.

B. Activation energy (E_h)

Evaluation of the occupancy factor given in Eq. (2) requires the activation energy E_h. The reduction of E_h by screening has been discussed in Ref. 7. In the "intermediate"[7] doping range, the energy depends on the inverse screening length q as,

$$E_h/E_h^0=1.00-1.81(q/\beta_0)+0.81(q/\beta_0)^2\,, \tag{5}$$

where E_h^0 is the energy and β_0 is the inverse Bohr radius at infinite dilution. For E_h^0 we use the same value as deduced in a previous paper,[12] namely 27 meV, and for β_0 we use $1/\beta_0=18$ Å, which is slightly lower (10%) than the earlier[13] value. The screening length is obtained here, for $T\gtrsim150$ °K, from the relation

$$q^2=\frac{4\pi e^2}{\kappa k}\left[\frac{p}{T}+\frac{N_D+p}{T}\left(1-\frac{N_D+p}{N_A}\right)\right]\,, \tag{6}$$

where e is the electron charge, κ is the dielectric constant, and N_D and N_A are the donor and acceptor concentrations. Equation (6) is basically an earlier[7] expression, modified to include a Brooks-Herring[14] term in the screening. The restriction in temperature follows since Eq. (6) predicts $q\to\infty$ as $T\to0$. This is due to a breakdown of the approximations leading to Eq. (6). Stern[15] has carried out an alternate treatment of screening at $T=0$, using a spread in the energies of the impurity levels. This approach gives a finite q at $T=0$:

$$q=(8\pi^2N_D)^{1/3}C\,, \tag{7}$$

which we shall use for $T\lesssim100$ °K. Here, C is the inverse to the correction factor given by Stern[15] (Fig. 1) for the screening length as a function of compensation; for the present samples, with compensation ratios of 0.20 to 0.25, the corresponding value of C is $\simeq0.62$ to 0.59. Since the hole concentration in our samples is negligible for $T\lesssim100$ °K, we do not expect much variation in the screening length between 0 and 100 °K.

The calculated values of the activation energies for layers 120 and 124 are given in Table I. In the calculation we used $N_A = 5\times 10^{17}$ cm^{-3}, $N_D/N_A = 0.25$ for layer 120, and $N_A = 2\times 10^{18}$ cm^{-3}, $N_D/N_A = 0.25$ for layer 124. The concentrations and compensation ratios were obtained from analysis of the Hall data (for unity Hall factor).

C. Radiative decay time (τ_{xr})

Jayson and Bachrach[11] have shown that the exciton radiative decay time τ^0_{xr} at low doping and low temperatures (i.e., no screening) is well represented by

$$\tau^0_{xr} = \frac{4\times 10^{-7}(1+0.6e^{-31.4/T})}{1+6.86e^{-31.4/T}}\ \text{(sec)}\,. \tag{8}$$

However, it has been suggested[3,4] that τ_{xr} can increase with decreasing level activation energy. The specific dependence suggested was[3,4]

$$\tau_{xr} = \tau^0_{xr}(E^0_h/E_h)^{l/2}\,, \tag{9}$$

$$E_h \approx E^0_h - 10^{-8}p^{1/3}\,, \tag{10}$$

where $l = 3$ was used by Jayson *et al.*[3] and $l = 5$ by Dishman, DiDomenico, and Caruso.[4] Relation (9) is a consequence of two assumptions: (i) $\tau_{xr} \sim \beta^{-l}$, where β is the inverse Bohr radius; (ii) $\beta \sim (E_h)^{1/2}$, which has been used as a modified effective mass approximation. Relation (10) is empirical.

Subsequent to the publication of Refs. 3 and 4, it has been shown that the reduction in the level energies is due to screening.[7] It thus seems reasonable that changes in the parameter β are also caused by screening. Since the screened hydrogenic equation has been solved for β by Lam and Varshni,[16] we can use their results in gauging the effect of screening on the radiative decay. Retaining the results $\tau_{xr} \sim \beta^{-l}$, and taking $l = 3$,

$$\tau_{xr}/\tau^0_{xr} = (\beta_0/\beta)^3 \equiv S^3\,, \tag{11}$$

where S can be obtained as a function of E^0_h/E_h from Lam and Varshni,[16] and E_h can be derived by fitting to the decay data, as discussed in Sec. IV. We note that the variation of β as given in Ref. 16 is much slower in the range of interest than would be predicted from the relation $\beta \sim (E_h)^{1/2}$ of Refs. 3 and 4; for example, $\beta/\beta_0 \approx 0.9$ at $E_h/E^0_h = 0.5$, whereas the relation $\beta \sim (E_h)^{1/2}$ would give $\beta/\beta_0 = 0.71$.

In the analysis of the data in Sec. IV, we have used Eqs. (8) and (11) in combination, as well as Eq. (8) alone (i.e., no dependence of τ_{xr} on screening), and then compared the results.

TABLE I. Theoretical exciton activation energies (meV).

T (°K)	Layer 120	Layer 124
100	17.0	12.2
150	14.3	5.5
200	13.4	4.7
250	13.0	4.3
300	13.2	4.6

D. Hole concentration

The hole concentration p is assumed equal to the "dark" hole concentration (i.e., that in the absence of optical excitation), since we employ low-density optical excitation ($\Delta p \ll p$). The dark concentration is obtained from Hall measurements by the well-known[17] relation

$$p = r/Re\,. \tag{12}$$

Here r is the Hall factor (the ratio of Hall to drift mobility) and R is the (measured) Hall coefficient.

The value of the Hall factor r is close to unity[17] and is, therefore, customarily taken as $r = 1$. Although this procedure is often used for convenience, as long as the exact value is unknown, other values $0.5 \lesssim r \lesssim 2$ cannot be ruled out.[17] In the present paper, we analyze the case $r = 1$ (and independent of temperature) but also consider two additional cases: $r = 0.7$ at all temperatures, and $r = 1$ at $T \lesssim 100$ °K and decreasing linearly[18] with temperature to $r = 0.7$ at 300 °K. These particular two additional cases for r have been chosen because it has been shown, from neutron activation analysis[19] and use of radioactive Zn,[20] that at room temperature and above $r/eR \lesssim N_{\text{Zn}}$ (note that this however assumes Zn as the only acceptor). This leads to the requirement $r < 1$, with estimates[19,20] of $r = 0.6 - 0.7$. Such low values of r, although unusual, can arise from energy-band warping.[17,21] This suggests the choice $r = 0.7$, independent of temperature. The reason for the choice of r varying with temperature is as follows: The dominant room-temperature carrier scattering in GaP is believed to be acoustic and nonpolar optical lattice scattering.[22] For a spherical band, these mechanisms give[17] $r \approx 1$ to 1.2. (For a single warped band, the overall r is a product of the warping reduction and the scattering mechanism.[17]) At lower temperatures, ionized impurity scattering becomes dominant.[19] For this case (and a spherical band), one obtains[17] $r \approx 1.98$. Thus, r could easily decrease with increasing temperature. This suggests use of $r = 1$ at 100 °K and below, with r decreasing to 0.7 at 300 °K.

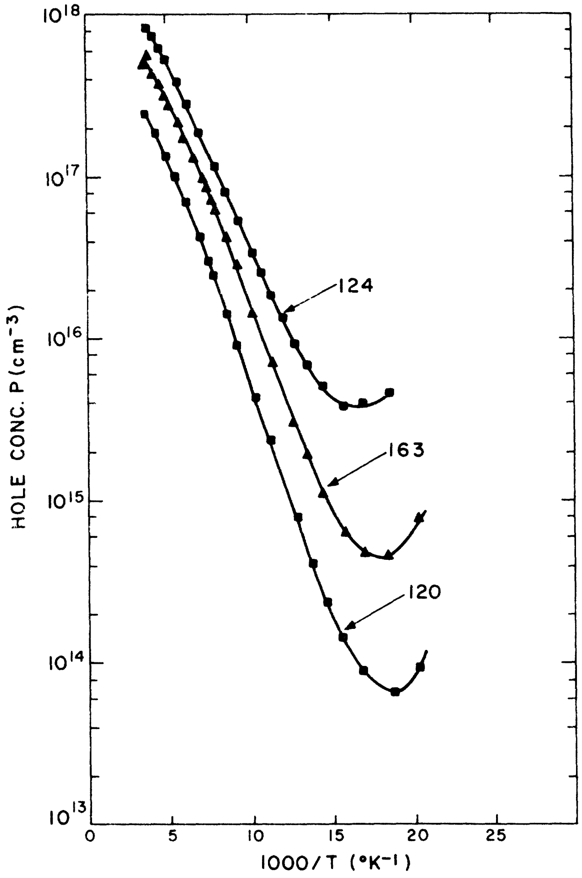

FIG. 2. Measured hole concentrations vs reciprocal temperature, assuming a Hall factor of unity. The doping concentrations derived from these data are $N_A \approx 0.5 \times 10^{18}$, 1.2×10^{18}, 2×10^{18} cm^{-3}, and $N_D/N_A \approx 0.25$, 0.2, and 0.25 for layer 120, 163, and 124, respectively. The solid lines are drawn to give a best fit.

III. EXPERIMENTAL

Luminescence time decay and Hall effect were measured as a function of temperature on p-type (Zn, O) doped layers. Three samples were selected for detailed study, and both measurements were taken on each of these three layers. Growth of the material was at ~1040 °C by liquid-phase epitaxy, utilizing a dipping apparatus.[23] The selected layers were 20–60 μm thick, and the room-temperature hole concentration varied from 2×10^{17} cm^{-3} to 9×10^{17} cm^{-3} (which is the doping region of main interest[3,23] for high-efficiency red GaP light-emitting diodes). We next describe the measurements in more detail.

A. Hall measurements

For measurement of the Hall coefficient R, samples were first fabricated into a rectangular slab with six protruding arms for proper contact geometry.[17] Fabrication was accomplished with a YAlG:Nd Q-switched laser scriber (Quantronix Model 900), which cut the appropriate sample shape as outlined by a metallic reflecting mask; the depth of the cut was set to go through the p layer, i.e., at about 100 μm. The resulting Hall specimen size was approximately 1×5.5 mm^2, with four side arms 0.5 mm wide. Ohmic contacts were attached to the ends of each sample and to the side arms.

Hall effect and resistivity over the temperature range of 40–300 °K were measured in a variable temperature liquid-He Dewar. Figure 2 shows the resultant values of hole concentration (for $r = 1$) versus reciprocal temperature, and Fig. 3 those of Hall mobility versus temperature. The accuracy of the experimental points is estimated to be $\lesssim 20\%$, based on the usual problems with Hall measurements (Ettingshausen effect, misalignment problems, layer thickness, etc.).

B. Decay-time measurements

The photoluminescent decay times were measured by a method previously described by one of the authors.[24] Multimode 5145-Å radiation from an argon-ion laser was used as the excitation source. The collimated beam was electro-optically modulated into a 10-kHz sequence of rec-

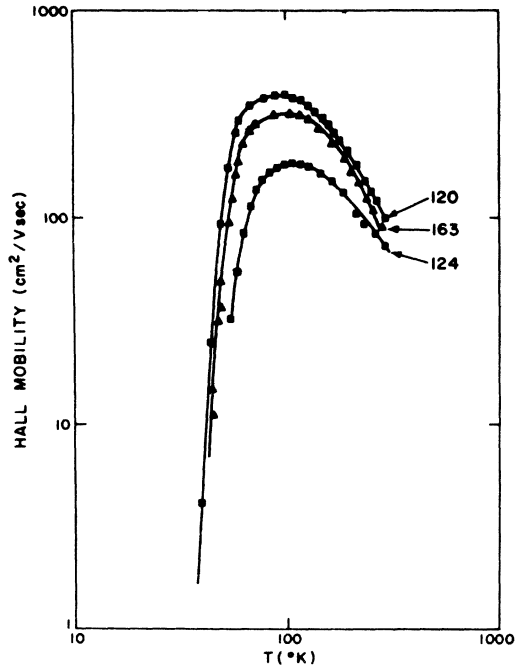

FIG. 3. Measured mobility vs temperature. The solid lines are drawn to give a best fit.

tangular pulses of 30-mW peak intensity and 10% duty cycle with an extinction ratio of greater than 10/1. The rise-fall times of these pulses were found to be approximately 50 nsec. The output signal from the photomultiplier was fed into a field-effect-transistor probe, and was then preamplified and fed both to an oscilloscope and to a boxcar integrator (Brookdeal 145A) and recorded.

The decay data were taken at 15 °K intervals between 77 and 300 °K. For this measurement, the sample was mounted on a Cu block fitted with a heating coil, a Cu-Constantan thermocouple, and a cold finger. This assembly was placed in a glass Dewar and backheated against liquid N_2 to vary the temperature. The data were taken on the central section of the Hall samples, in the low-level excitation regime (power density $< 0.1 \mathrm{mW/cm^2}$). The reported decay times were $1/e$ values extrapolated from the initial exponential slope. (This procedure reduces the influence of pair decay—see Appendix). The values of decay time τ obtained in this way are plotted in Fig. 4 as a function of temperature.

IV. ANALYSIS OF DATA

As discussed in Sec. II A, the primary parameters required in the evaluation of the Auger coefficient (B) from the measured decay constant (τ) are the hole concentration (p), the radiative exciton decay constant (τ_{xr}), and the activation energy (E_h).

We first consider the case of $r = 1$, independent of temperature (Sec. II D), and screening independent transition probabilities [Sec. IIC, i.e., τ_{xr} is given by Eq. (8)]. As to E_h, *approximate* values are known from screening theory (Table I). However, in unfavorable cases, a 1-meV change in E_h gives appreciable variation (~factors of 2) in B, so we bypassed this problem by first setting values of B. Several such values were selected, and B was assumed independent of temperature—as expected from theory.[25] Then "experimental" values of E_h at various temperatures $T \lesssim 250$ °K (negligible thermalization) were calculated from Eqs. (1) and (2), and compared with the theoretical values of Table I. Those values of B which resulted in good agreement between the two sets ("experimental" and theoretical) of E_h values were considered satisfactory. In gauging the agreement, some attention was (obviously) given to the magnitude of the E_h values. However, absolute theoretical values, especially for low E_h, are only approximate.[26] More emphasis was therefore given to *relative* variation in E_h. For example, (i) E_h decreases with temperature from 100 to 200 °K; (ii) it is approximately constant below 100 °K and from 200 to 300 °K; and (iii) for consistency, E_h cannot vary with temperature for one layer if it does not vary for the other. As discussed (Sec. I), the main emphasis in this fitting is in the 77–250 °K range, where thermalization is negligible. However, some use was also made of data for $T > 250$ °K: Values of τ were here calculated via Eqs. (1) and (2) using the same E_h values as obtained at 250 °K. For a value of B to be acceptable, the resultant "calculated" τ values then had to be higher (*slower*) than the observed decay. This requirement follows since thermalization, which is neglected for the "calculated" τ values, can lead only to a faster decay. With use of these considerations, good agreement can be obtained only for a relatively narrow range of B, with acceptable values varying by (30–40)%.

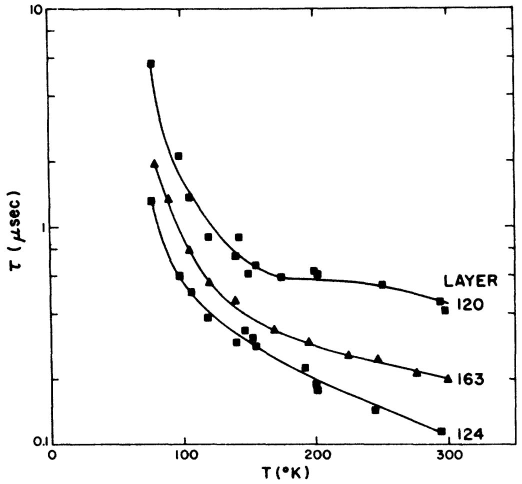

FIG. 4. Measured luminescence decay vs temperature. The values are the $1/e$ decay times as obtained from extrapolating the initial slope of the decay (see Appendix). The solid lines are drawn to give a best fit.

Figure 5 shows the fit between the experimental results (lines) and values calculated via Eqs. (1) and (2) (points) for $B = 2 \times 10^{-11}$ cm^3/sec, and values of E_h as given in the figure. The fit is good for all three layers at all temperatures up to 250 °K; and for 275 and 300 °K, the calculated τ points are higher than the measured decay, as required (see previous paragraph). Figure 6 shows the corresponding results for $B = 3 \times 10^{-11}$ cm^3/sec. The fit for layer 124 is poor for $E_h = 4$ meV and worsens for higher values of E_h (the results for $E_h = 8$ meV indicate the sensitivity to variation of E_h). Values of E_h lower than 4 meV appear unreasonable (Table I). Next, the results for $B = 1 \times 10^{-11}$ cm^3/cm are shown in Fig. 7. Now, layer 124 can be fitted with a constant value $E_h = 12$

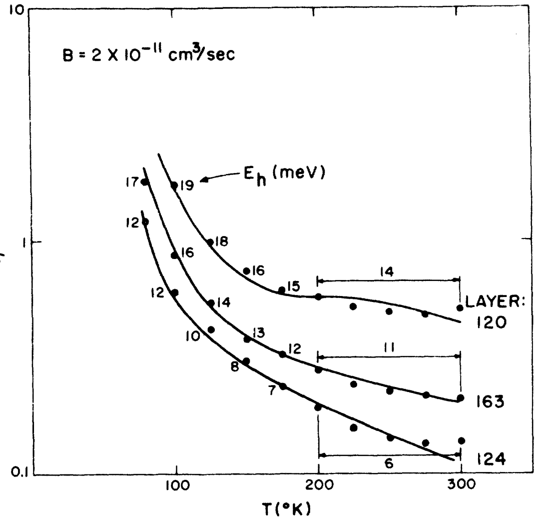

FIG. 5. Luminescence decay vs temperature. The solid curves are experimental. The points are calculated from Eqs. (1) and (2), using the measured values for p (with $r = 1$), level activation energies (E_h) as shown in the figure, and for an Auger coefficient (B) of 2×10^{-11} cm^3/sec.

meV; however, in view of screening, some decrease of E_h with temperature can be expected. In fact, layer 120 requires such a decrease; for a good fit, $E_h = 19$ meV at low temperature and 16 meV at higher temperature. We thus feel that the overall fit is best for $B = 2 \times 10^{-11}$ cm^3/sec, and estimate $B = (2 \pm 0.5) \times 10^{-11}$ cm^3/sec for the present case.

A similar analysis was carried out, still with τ_{xr} as given by Eq. (8), for $r = 0.7$ and independent of temperature, and for r varying (linearly) from $r = 1.0$ at 100 °K to $r = 0.7$ at 300 °K (Sec. II D). The results are summarized in Table II.

The last case considered was that of $r = 1$, but with the transition probabilities dependent on screening in accordance with Eq. (11). For consistency, one must here assume that B shows a similar dependence, except that the transition probability for B is proportional to the fifth power of radius[27]

$$B/B_0 = (\beta/\beta_0)^5 = S^{-5}; \tag{13}$$

here S is obtained as described in connection with Eq. (11), and B_0 is the Auger coefficient with no screening. The results are again given in Table II.

V. DISCUSSION AND CONCLUSION

The extensive data of the present study have permitted a more detailed comparison between experiment and theory than has previously been possible. In particular, the effect of a variation in Hall factor and of screening dependent transition probabilities could be examined.

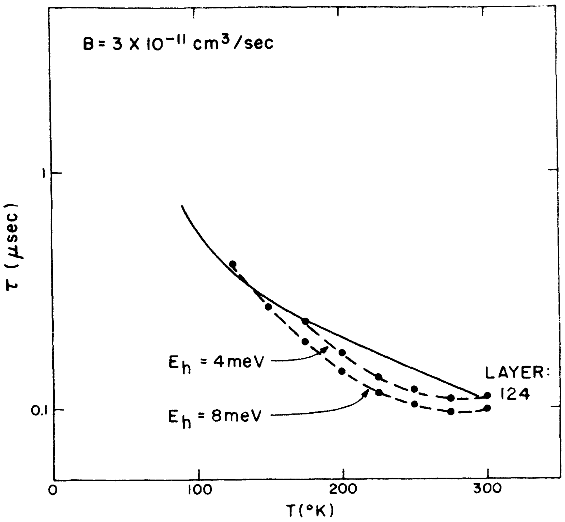

FIG. 6. Same as Fig. 5, but for $B = 3 \times 10^{-11}$ cm^3/sec. The dashed lines are drawn through the points.

The analysis has led to one clear-cut conclusion: The values of τ in the low-temperature region 77–125 °K can only be satisfactorily explained by our inclusion of the screening reduction of the activation energy E_h. The decay in this region is much slower than would be predicted if the infinite dilution energy ($E_h^0 = 27$ meV) were used in Eq. (2); for this E_h^0 value, the decay cannot be fitted even with $B = 0$. Moreover, other decay paths could only speed the decay, not slow it. In principle, a slow

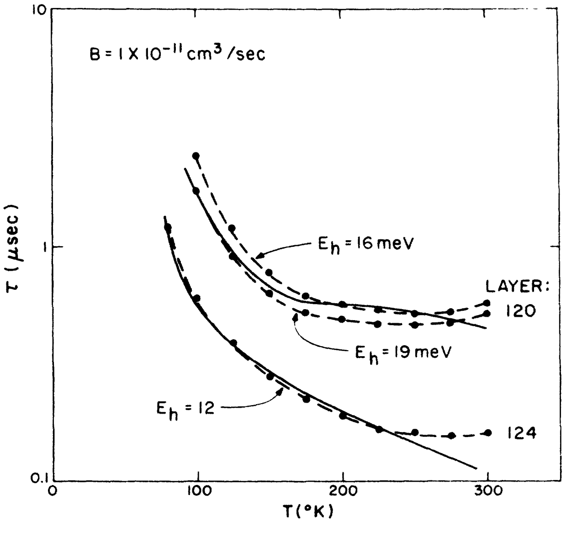

FIG. 7. Same as Fig. 6, but for $B = 1 \times 10^{-11}$ cm^3/sec.

TABLE II. Values of the Auger coefficient.

Case	Hall factor ($r = \mu_H/\mu_D$)	Transition probabilities	Auger coefficient B_0 (10^{-11} cm^3/sec)
1	$r=1$, independent of temp.	Independent of screening	2 ± 0.5
2	$r=0.7$, independent of temp.	Independent of screening	3.5 ± 1
3	$r=1$ at 100 °K, $r=0.7$ at 300 °K varying linearly in between	Independent of screening	3 ± 0.7
4	$r=1$, independent of temp.	Dependent on screening	6 ± 2

emptying of shallow donors can give a slow decay,[11,28] but for GaP this process is expected[11,28] to take place only at temperatures below ≈ 80 °K. In addition, the good agreement between the E_h values obtained from fitting the data and as calculated theoretically (Table I) is very gratifying; this is especially true at low temperature, where B has a very minor effect on E_h as obtained from τ. And the theoretical screening values were obtained [via Eq. (5)] with the same E_h^0 and almost the same β_0 values as used in Ref. 12 to fit the decay of different samples in a different decay range (data of Ref. 11). Thus, the data are obviously consistent with standard decay theory, but only *provided* the effect of screening on the exciton energy E_h is properly taken into account.

Another satisfying aspect of the analysis are the qualitative features. As is logical, for lower Hall factors, and thus lower hole concentrations, one requires a higher value of the Auger coefficient. Similarly, if one assumes that the transition probabilities are reduced by screening, a higher value of B is again required for an acceptable fit.

As for the quantitative results, summarized in Table II, we feel the uncertainty in E_h is not too serious for evaluation of the Auger coefficient (B); for any one model, the value of B is uncertain to only ≈ (30–40)%, which is not unreasonable under the circumstances. Similarly, a 30% change in r leads to about a 70% change in B, which is still in an acceptable range. However, the problem of a possible influence of screening on the transition probabilities leads to greater uncertainties. It could not be established from the decay data whether this behavior is indeed taking place. Since this effect changes B by about a factor of 3, B has only been determined to within an order of magnitude, i.e., the range of values is $B \approx (1.5\text{–}4.5) \times 10^{-11}$ cm^3/sec if the transition probabilities are independent of screening, $B \approx (4.0\text{–}13.5) \times 10^{-11}$ cm^3/sec otherwise. A comparison of these values with those obtained from the temperature dependence of the efficiency as well as with earlier[3-6] values is given in a companion paper.[29]

ACKNOWLEDGMENT

The authors are indebted to Dr. S. K. Kurtz for his encouragement in this work.

APPENDIX

It has been customary in earlier[3,4] kinetic treatments of GaP(Zn,O) to include more decay paths than have been used here. A summary of such additional paths is shown in Fig. 8.

The path denoted by τ_{er} is the pair recombination between an exciton center missing a hole and an isolated Zn center. Inclusion of this effect modifies Eq. (1) as follows:

$$\frac{1}{\tau} = f\left(\frac{1}{\tau_{xr}} + Bp\right) + \frac{(1-f)f_A}{\tau_{er}}, \qquad \text{(A1)}$$

where f_A is the fraction of Zn acceptors with holes (non-ionized acceptors). To evaluate the effect of this contribution, we use data of Jayson and Bachrach[11] to evaluate τ_{er}. At low temperatures (≲ 25 °K) and low-excitation intensity, the measured decay is primarily due to pairs. Moreover,

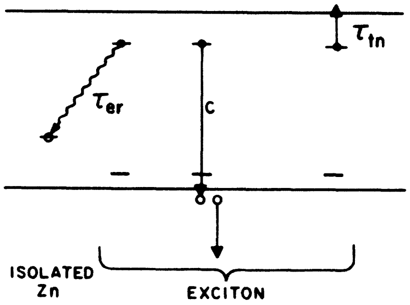

FIG. 8. Schematic of transitions in GaP(Zn, O) which have frequently been considered (Refs. 3 and 4), but are neglected here. The τ_{er} path is pair recombination of an exciton electron with a hole on an isolated zinc, and C represents Auger recombination with two free holes. The τ_{tn} process is the thermalization of the exciton electron.

we use their *initial* decay. This procedure is convenient, since the initial pair decay is exponential, as can be seen by solving the decay equations of Thomas *et al.*[30] in the limit $t \to 0$. As a check, we considered layer 124 in the range 200–250 °K (i.e., for temperatures below appreciable thermalization); this layer provides the highest p values and thus the greatest sensitivity to the Auger effect. For this case, $f \ll 1$ and $f_A \approx 0.5$, and the pair contribution leads to a decay of about 1.5 μsec. The observed decay is $\lesssim 0.2$ μsec, and is thus appreciably faster; this, in itself, shows that the role of pair decay is expected to be minor. As a further check, we calculated the Auger coefficient by a fit to the data (for $r=1$, $\tau_{xr}=\tau^0_{xr}$) by use of Eq. (A1). This gives B values (depending slightly on E_h) about 30% lower than the corresponding values without the pair decay. The importance of this contribution is thus reasonably less than that of the variation in r (~70%), and considerably less than the question of whether or not screening affects the transition probabilities (~300%); in view of these considerations it was neglected. However, since any nonexponential contribution is expected to be pair decay, and thus gives "spurious" lengthening of the decay, our data (Fig. 4) is presented as extrapolated initial slopes (and not the *measured* $1/e$ point).

The path denoted by C is Auger recombination between an electron on the exciton center and two free holes. Equation (1) is modified as follows:

$$1/\tau = f(1/\tau_{xr} + Bp) + Cp^2 . \qquad \text{(A2)}$$

We again compare the magnitude of the additional term Cp^2 with that of the original Equation (1). Prior[3,4] estimates of C give $C \approx 2.5 \times 10^{-30}$ cm^6/sec. The C term will be most important at high hole concentrations, and we therefore consider layer 124 at 250 °K, where $p = 7.5 \times 10^{17}$ cm^{-3}, $f \approx 0.25$. Consequently, $Cp^2 \approx 1.4 \times 10^6$ sec^{-1}, whereas $fBp \approx 4 \times 10^6$ sec^{-1}. Thus, the C term is $\lesssim 40\%$ of the B term, which is again less than given by uncertainties in r and in the screening dependence of the transition probabilities. Moreover, C will be less important at the lower temperatures and for the other layers. It was also checked (for $r=1$, $\tau_{xr}=\tau^0_{xr}$) whether use of larger values of C, *without* the B term, could fit the data, but it could not. For $C = 5 \times 10^{-30}$ cm^6/sec, layer 124 could be fitted without energy reductions of the exciton hole energy (E_h), but layer 120 required the "usual" reduction (~4 meV). For larger values of C, use of a constant E_h from 250 to 300 °K (as expected from theory) forced the calculated high temperature τ's below the experimental values.

The path denoted by τ_{tn} is the thermalization process: an exciton electron is released into the conduction band, and can then either be recaptured by an exciton center, or alternately, recombine via a different center (the "shunt" path). Jayson *et al.*[31] determined τ_{tn} near room temperature from data on crystals doped only with zinc (no oxygen doping—the main decay is now the τ_{tn} path); using a slight extrapolation on their[31] Fig. 8, one obtains $\tau_{tn} \approx 3$ μsec at 250 °K. This is at least five times slower than the observed decay times of our samples at this temperature, and this path can thus reasonably be neglected at 250 °K and below [excitation out of the level decreases approximately as $\exp(E_t/kT)$, where E_t is the depth of the level].

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