anism contributes negligibly to the observed conduction-electron nonlinearity in Ge.

It is a pleasure to acknowledge the many helpful discussions with R.W. Terhune and the invaluable assistance of R. Crain throughout the experiments.

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Luminescent Properties of Energy-Band-Tail States in GaAs:Si

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Several new properties which are characteristic of energy-band-tail states have been measured by transient photoluminescence in samples of GaAs heavily doped with silicon and partially compensated. Their dependence on temperature, doping and excitation intensity, and geometry has been determined. The primary results are the wide range (~ 100:1) of luminescent rise and decay times within the single emission band found at low temperatures, these times increasing monotonically with decreasing energy. These results are ascribed to the localized nature of band-tail states and to the necessary spatial separation of states in the tails of the valence and conduction bands. These observations also lead to the conclusion that thermalization times of the deeper band tails are very long – exceeding the carrier lifetimes, which reach several microseconds in some cases. Therefore, quasiequilibrium conditions do not develop in any of these experiments.

I. INTRODUCTION

Optical measurements have become very powerful aids to our understanding of both the intrinsic character of solids and the properties of defects within them. The present work is concerned with the nature of the luminescence associated with the presence of high concentrations of charged impurities in semiconductors. For this purpose, it has been found that GaAs: Si provides an interesting system. We regard it, however, as a convenient prototype; most of the conclusions reached here should apply to other cases of heavily doped semiconductors and certain disordered materials.

It is generally accepted that high concentrations of impurities in semiconductors create "tails" in the distribution of allowed states as a function of energy, these band tails extending into the normally forbidden gap.[1-6] The conditions which must be met for this description to be appropriate are (i) low binding energy of the impurities and (ii) impurity concentration high enough so that the spatially varying potentials arising from the charged impurities are sufficiently great to cause the associated energy levels to lose their original discrete character. Furthermore, it is believed that the impurities are usually nearly randomly distributed, so that clusters of various sizes will occur, leading to irregular fluctuations of the electrostatic potential with position. In the case of ordinary shallow donors (i.e., positively charged ions), a cluster forms a region of abnormally low potential in which there may exist states which are neither the original impurity states nor the crystal-band states. Such a state may be localized by the potential well, or only quasilocalized if there is some direction in which the potential barrier drops below the energy level of the state. The situation is thus qualitatively that which has been discussed at length in connection with noncrystalline systems[7]; it appears that the present results should be relevant to such materials.

All our measurements were made on solution-grown wafers of silicon-doped GaAs. Silicon is amphoteric in GaAs and can introduce shallow donors and relatively shallow acceptors, but the site distribution depends on the growth method.[8] The conditions of sample preparation make it highly probable that *all* our samples had a significant degree of compensation. This influences the above considerations in two ways. First, the amount of mobile charge available to screen the ion fields is reduced, thus increasing the magnitude of the potential fluctuations. Second, the presence of both positive and negative ions causes the potential fluctuations to be larger than with a single type of ion.

On the basis of these considerations, we take as a model for our samples that shown in Fig. 1. For all practical purposes, the shallow donor and shallow acceptor states have lost their identity by mixing with the respective conduction- and valence-band states, forming band-tail states. The spatial average of the density of states shown on the right displays these tails. The left side indicates how the potential actually varies with position, creating the "localized" states of the band tails. Also shown schematically are a set of deep acceptor states which are so strongly bound as to retain their identity and merely shift their total energy along with the potential. Previous studies[8,9] in GaAs: Si grown from Ga solution have shown evidence for such a deep acceptor level (~ 0.1 eV) when high Si concentrations are present (> 10^{18} cm^{-3}). These are presumed to arise at some complex, possibly a $\mathrm{Si_{Ga}}$ - $\mathrm{Si_{As}}$ pair.[8,10]

The transitions indicated in Fig. 1 will be discussed in detail below; for the present, only one further aspect of this diagram is emphasized; that is, the conduction-band-tail states are formed at regions of *low* potential and the valence-band-tail states at *high* potentials so *they always are spatially separated* from each other.

Our principal experimental approach to the study of this system has been time dependence of photoluminescence. Related photoconductivity measurements,[11] as well as steady-state photoluminescence,[8] have been reported on the samples of the present study.

II. EXPERIMENTAL PROCEDURES

A. Samples

To investigate the above model, samples that are both highly doped and highly compensated are desired. Silicon-doped GaAs grown from Ga solution was chosen for the measurements for the following reasons: (i) The solubility of Si in GaAs is high enough (~ 1%) to permit high doping levels without precipitation of the impurities. (ii) The donor states produced by Si substituting for Ga are very shallow (~ 5 meV). (iii) Si on As sites creates relatively shallow (~30-meV) acceptors. Thus *n*- and *p*-type and highly compensated material can be used. The measurements reported here were made on materials whose characteristics are shown in Table I.[12]

Some samples heavily doped with Zn and Te were also examined. However, in these the luminescence was much weaker, and the response times

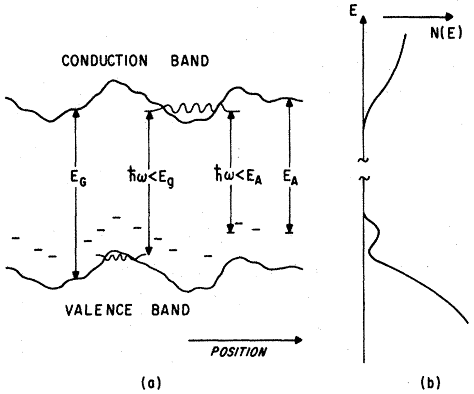

FIG. 1. (a) Schematic representation of the variation of the electrostatic potential within the crystal due to the charged impurities. The singularities at the ions have been omitted. In the approximation used, the valence- and conduction-band-state energies follow the potential fluctuations, as do the deep localized acceptor-state energies. Wave functions for electrons localized at potential fluctuation extrema are indicated. E_G is the gap energy in pure material and E_A the acceptor-conduction-band energy. Transitions connecting valence- and conduction-band-tail states and conduction-band-tail and deep acceptor levels are also shown. (b) The energy dependence of the density of states resulting from this model.

TABLE I. Properties of GaAs:Si samples studied.

Sample	Majority carrier type	Free carrier density (cm^{-3})	Total impurity density (cm^{-3})
CM79-As	n	1.6×10^{18}	5.2×10^{18}
CM79-Ga	n	5.6×10^{15}	$>10^{18}$
S-4	p	$6\ \times10^{16}$	$\sim10^{18}$

were unresolvable with our apparatus. The strengths of the fluctuating potentials in the Zn-Te material are expected to be much weaker than in the Si-doped samples, as the solubility of Te in GaAs is much lower than that of Si, and precipitates form when too high ($>3\times10^{18}$-cm^{-3}) Te concentrations are used.[13]

Photoluminescence at 77 °K was observed with both etched[14] and unetched material. The spectra and transient behavior were identical; the only observed difference was in the luminescence intensity, where etched samples gave a somewhat stronger signal. Therefore, the samples were generally etched at the start of each set of runs.

B. Equipment

A schematic diagram of the basic experimental setup is shown in Fig. 2. The photoluminescence was excited using injection lasers, mounted either in close proximity to the sample within a common Dewar, or in an auxiliary Dewar, in which case the laser beam was focused onto the sample with a suitable large-aperture lens. Injection laser pumping was chosen to provide very short turn-on and turn-off times, so that the transient photoluminescent response would not be distorted by the excitation pulse shape. Injection lasers present difficulties, however; it is hard to obtain a long flat-topped pulse at high drive levels (heating often leads to a decrease in output at the end of the pulse), and there are usually frequency-shift effects during the pulse, again due to laser heating. Throughout the experiments reported herein, we have striven to eliminate or minimize these effects; we believe that our conclusions have not been influenced by any residual effects which could not be suppressed completely.

The pump lasers were generally grown by liquid-phase epitaxy on highly doped GaAs substrates.[15] Because we experienced difficulties with laser substrate luminescence after the drive pulse, we used lasers from which the substrate had been removed. The (Al_xGa_{1-x})AS lasers, with output centered at 1.6 eV, had observable output in a "tail" extending into the spectral range of interest. This was weak compared to the sample fluorescence over most of the range; however, it may have distorted intensities somewhat at 1.4 eV and above.

At 77 °K, measurements were made with both sample and excitation laser immersed in liquid nitrogen. For temperatures above 77 °K, the samples were mounted in a vacuum on a copper cold finger with high thermal conductivity paste. The temperature of the finger was monitored with a copper-constantan thermocouple. Below 77 °K, a variable-temperature Dewar was used in which the sample was mounted on a copper block in (atmospheric-pressure) helium gas. The temperature at the position of the sample was measured with a germanium resistance thermometer.

In measuring the transient photoluminescent response, the laser current pulse was carefully adjusted to be long enough that a steady-state luminescent condition was attained by the end of the pulse. Pulse lengths and pulse-top flatness were monitored after each change by tuning the spectrometer to the laser wavelength. This also permitted the response time of the system to be repeatedly checked: The system response so determined was usually about 10 nsec, and never was more than 15 nsec. As all measured response times were larger than this, the reported data are not biased by system response times.

In the transient measurements, the luminescent signal was often so weak that no light pulse could be discerned on the sampling oscilloscope. To enhance the signal-to-noise ratio, a PAR Waveform Eductor was driven from the vertical output of the

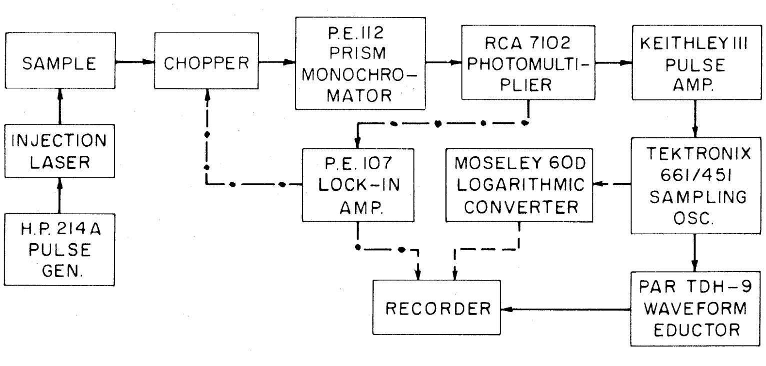

FIG. 2. Block diagram of apparatus. Three sets of connections used in the experiments are shown: solid line, connections for measuring transient response times; dashed line, connections for obtaining time-resolved spectra; dot-dashed line, connections for obtaining steady-state spectra.

sampling oscilloscope. This permitted signal integration with time constants up to 100 sec in 100 channels across one sweep of the oscilloscope. The Eductor output was then recorded on an *X-Y* chart recorder.

C. Measurements

Three types of measurements, indicated schematically in Fig. 2 by the three possible signal paths, were made: (i) transient response, both rise and decay, to pulsed photoexcitation; (ii) "time-resolved" spectra taken during and at specific delay times after an excitation pulse; (iii) "steady-state" spectra, taken with a long excitation pulse and conventional lock-in techniques. Since the signal levels varied over more than an order of magnitude across the spectrum, a logarithmic converter was used when taking the time-resolved and steady-state spectra. Only when the steady-state spectra were being taken was the beam chopper shown in Fig. 2 used.

III. RESULTS

A. Steady-State Spectra

The steady-state photoluminescence of the three GaAs: Si samples shown in Table I has been reported in the literature[8] at temperatures between 77 and 300 °K. Kressel *et al.* interpret these data in terms of three transitions. At 77 °K, the dominant transition in all these materials is from conduction-band-tail states to deep (~100-meV) acceptor states introduced by the silicon. This transition gives rise to a broad luminescence band centered about 100 meV below the "band gap." Kressel *et al.* also report additional transitions. One is interpreted as band-tail-to-band-tail recombination and is only seen at temperatures above ~100 °K. This grows in strength relative to the main transition as the temperature increases. Another, seen only in the *p*-type sample (*S*-4), is interpreted as a transition from conduction-band-tail states to a very deep acceptor level about 220 meV above the valence band. These results are to be contrasted with those of Hill[16] which show luminescence bands in uncompensated *melt*-grown GaAs to peak near the band gap regardless of doping level. Hill also observed peaks about 100 meV below the band gap in Si- and Ge-doped samples. It should be noted that in all our samples (heavily Si-doped compensated solution-grown GaAs) there is no luminescence at energies near the band gap, and all that is seen at 77 °K is a single broad luminescence band about 90 meV wide, centered at about 1.38 eV, 130 meV below the gap energy E_G, as illustrated in Fig. 3.

The steady-state spectra we have taken on the samples are in basic agreement with those reported by Kressel *et al.* However, we have observed a slight dependence upon excitation intensity that has not previously been reported: As the intensity of the exciting radiation is increased, the energy of maximum luminescence remains essentially unchanged, but there is a reduction in the relative amount of low-energy fluorescence and an increase in the high-energy fluorescence. This is also shown in Fig. 3.

B. Response Times

1. *Nature of the Response*

When a sample was illuminated by a "rectangular" pulse of laser light, the luminescence built up rapidly at first and then flattened off to a steady-state value, if the pulse were sufficiently long. (Care was taken to always use pulses of adequate length.) After the pulse, the fluorescence decayed roughly exponentially. However, a careful examination of many rise and decay curves showed that, in general, neither the rise nor the decay was truly exponential. A power law of the form $I \propto t^{-n}$ also did not accurately represent the data, where I is the luminous intensity at a given wavelength, *t* is the time after the pulse, and *n* is a constant. In fact, occasionally "*S*-shaped responses" were observed, with a (quite short) "latency period," either at the beginning or at the end of the luminescent pulse.

An illustration of a typical luminescent decay is given in Fig. 4. It is seen here that while the curve shows a slower-than-exponential tail, the early part of the decay can be approximated by a simple exponential. Because of the complexity of the lumin-

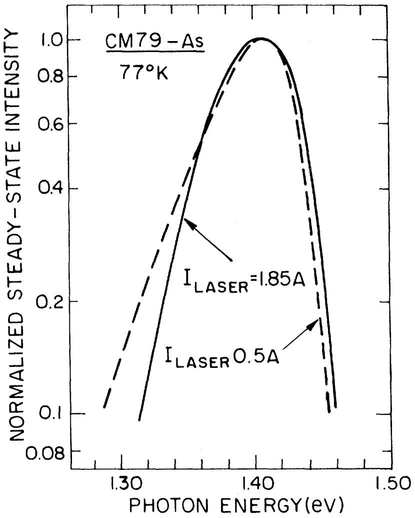

FIG. 3. Steady-state fluorescent spectra taken at two excitation levels. Both curves have been normalized to unity peak intensity. At this temperature E_G = 1.51 eV.

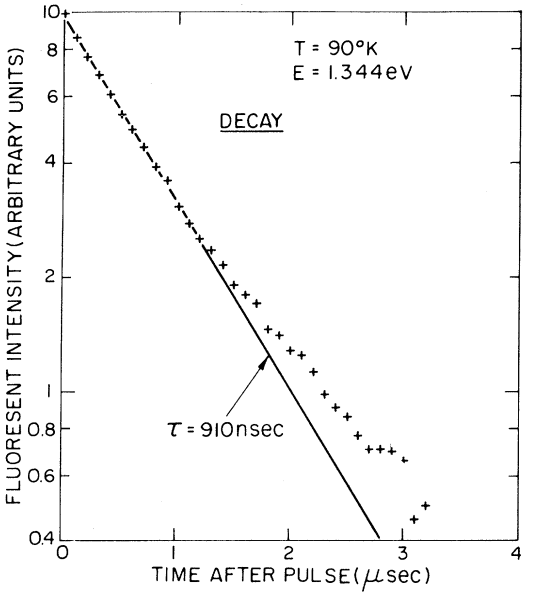

FIG. 4. Typical fluorescent decay curve showing an initial quasiexponential decay, followed by a slowing of the decay rate. Similar curves are obtained for the fluorescent buildup during the excitation pulse.

escent system, as discussed in detail below, no theoretical explanation of the details of the pulse shape seems feasible. To permit a semiquantitative discussion of our data, we therefore fit a "best" exponential to the early portion of both rise and decays (neglecting any latency period that may appear), and arbitrarily *define* the luminescence response times as the associated (exponential) time constants.

2. *Spectral Dependence of Response Times*

The luminescence shows a strong dependence of response time on photon energy across the luminescence band.[17] This is shown in Fig. 5 for the 77 °K behavior of the closely compensated CM79-Ga sample. It is seen that the high-energy side of the band has very short rise and decay times, approaching those of the instrumental response. However, as the photon energy decreases, between 1.45 and 1.35 eV, the response times lengthen over two orders of magnitude, becoming over a microsecond at the lower energies. The behaviors of the *n*- and *p*-type samples were qualitatively the same, although the *n*-type sample (CM79-As) exhibited somewhat shorter response times at low photon energies (~ 200 nsec for rise and ~ 350 nsec for decay) than did the highly compensated and *p*-type samples.

A significant feature of these curves is that the rise and decay response times are roughly equivalent in all cases. We note further that although the rise times are shorter at the lower energies, they become somewhat longer than the decay times at high energies.

3. *Time-Resolved Spectra*

While in principle the same information is contained in the transient response data, it is instructive to consider spectra taken at fixed times after an excitation pulse. An example is shown in Fig. 6; note the logarithmic intensity scale. The uppermost curve was taken 200 nsec before the end of the pulse, and shows the "steady-state" response. After the pulse, the very rapid fluorescent decay at high energies is clearly seen, as is the relatively slow decay at lower energies, resulting in large shifts of the luminescence peak to progressively lower energies as the decay proceeds.

4. *Dependence on Excitation Intensity*

Within the available range and accuracy of our measurements, there was *no* dependence of response times, *either rise or decay*, upon the intensity of the exciting radiation.

5. *Temperature Dependence*

There is a marked dependence of response times upon temperature, as shown in Fig. 7. Note that here the energy scale has been referred to the (temperature-dependent) band-gap energy E_G. Below 77 °K, the dependence is weak, with slight increases in response times occurring as the sample is cooled to liquid-helium temperatures. However,

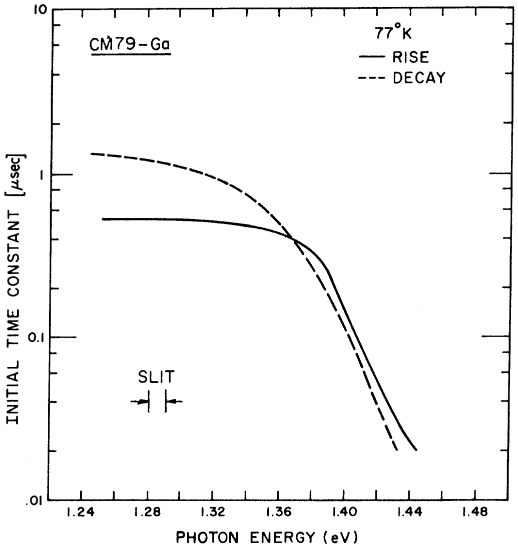

FIG. 5. Energy dependence of the rise and decay response times for a highly doped highly compensated GaAs:Si sample. Similar curves were obtained for both *n*- and *p*-type compensated samples.

above 77 °K, there is a marked decrease of the low-energy response times, the times dropping by over an order of magnitude as the sample is heated to about 200 °K. Throughout all the temperature range, only the low-energy fluorescence was affected, the high-energy response times remaining essentially temperature independent. Note also that the rise times remain approximately equal to the decay times at all temperatures.

6. *Dependence on Energy of Exciting Radiation*

No dependence of the response times upon excitation energy was observed. Three different kinds of injection lasers were used in our studies. We first used a Ga(As_xP_{1-x}) laser with an energy of 1.9 eV, well above the band gap of $E_G = 1.51$ eV at 77 °K. As some trouble was experienced with luminescence of the GaAs substrate on which the laser was grown, we switched to (Al_xGa_{1-x})As lasers at 1.6 eV. The substrates on which these lasers were grown were carefully lapped off before laser fabrication. Finally, we used some GaAs lasers whose output energy could be tuned thermally over the range 1.41–1.44 eV to study the effects of penetrating excitation radiation *within* the luminescent band itself. (Unfortunately, we could not lower the minimum available excitation energy in this way sufficiently to examine fluorescence at energies above that of the exciting radiation.)

7. *Dependence on Excitation Geometry*

Only a small area of the sample was normally excited, and most measurements were made with 1.6-eV radiation that is absorbed in about a micron from the surface. Moreover, the spectrometer "sees" a slit-shaped area that includes some unilluminated portions of the sample. Thus, the possibility existed that some, if not all, of our observed response times were associated with spatial carrier diffusion phenomena.[18] To eliminate this possibility, two sets of experiments were performed. The first has been mentioned above, and consisted of exciting with *penetrating* radiation from a thermally tuned GaAs laser. Here the sample, only ~0.014 cm in thickness, was excited throughout the bulk, over depths long compared to diffusion lengths. No changes in response times were observed with this penetrating excitation radiation.

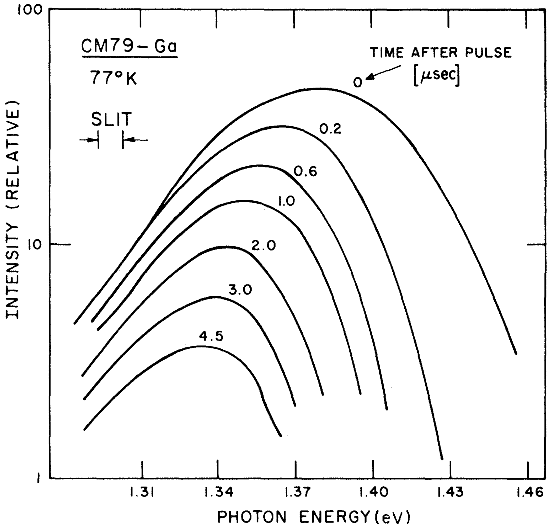

FIG. 6. Time-resolved spectra, showing the spectral shape of the fluorescence in the steady state (near the end of a long excitation pulse) and at various times after the end of the pulse.

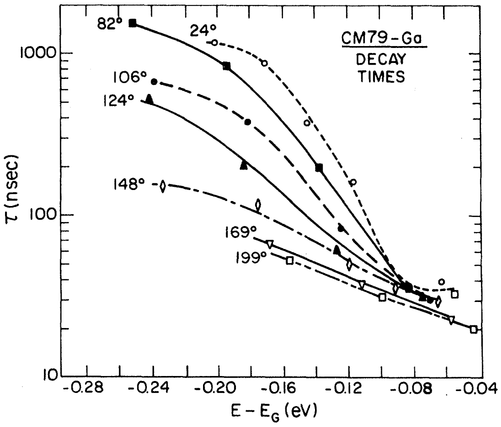

FIG. 7. Temperature dependence of the decay times for a highly doped highly compensated GaAs:Si sample. The temperature dependence of the rise times is very similar. Note that the zero of the energy scale is taken at the (temperature-dependent) band gap of pure material.

In the second set of experiments, the spacing of the excitation laser from the sample was varied from 0.04 to 0.18 cm, while the laser intensity was varied to keep the peak excitation intensity at the sample constant. Thus the relative sizes of the sample area excited and "looked at" by the spectrometer were changed. Again, no effect on the response times were observed. Thus, geometrical effects do not seem to play a significant role in the observations.

C. Photoluminescent Efficiency

No measurement was made of the absolute luminescent efficiency. However the temperature dependence of the relative efficiency was determined and is shown in Fig. 8. This represents a plot of the total steady-state luminescent power, integrated over the entire luminescent band, versus sample temperature. To make these measure-

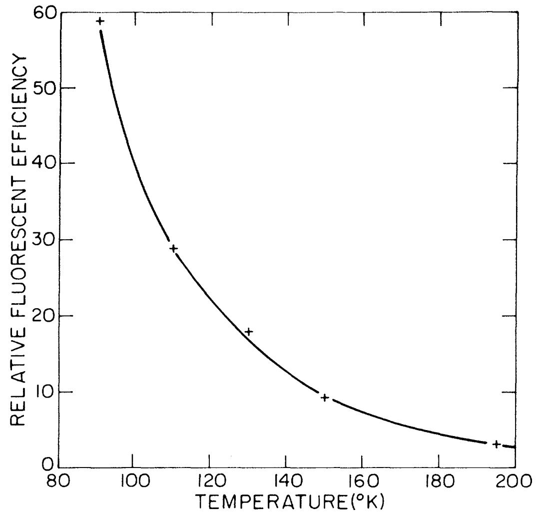

FIG. 8. The relative fluorescent efficiency of the entire luminescent band (integrated over the spectrum) as a function of temperature.

ments, the sample was mounted on a variable-temperature cold figure in the same Dewar as the excitation laser, which was mounted nearby on a cold finger nominally kept at 77 °K. However, because of radiative coupling, the laser cold finger increased slightly in temperature as the sample was heated. This did not significantly alter the laser wavelength, but its intensity did fall off by about $\frac{1}{3}$ (at the highest sample temperature). A correction for this effect has been made assuming a *linear* dependence of sample fluorescence on laser intensity; the (peak) luminescent intensity increased slightly sublinearly with excitation intensity.

IV. DISCUSSION

Of the foregoing results, the major ones are the spectral dependence of both the rise time and decay time within the single emission band and the temperature dependence of those response times. This discussion offers an interpretation of these effects in terms of the model of Fig. 1, which appears consistent with the other results. We have been unable to find any alternate interpretation with this consistency.

A. Spectral Dependence of the Decay Times

The sharp drop in decay times with increasing photon energy shown in Fig. 5 follows directly from the diagram on the left-hand side of Fig. 1, and its prediction was the original motivation for the present work. It is a direct consequence of the two salient features of band-tail states: (i) quasi-localization and (ii) spatial separation of the conduction- and valence-band-tail states. A low-energy transition ($\hbar\omega < E_G$) necessarily involves initial and final states whose wave functions overlap only in classically forbidden regions in which they are strongly damped. Furthermore, the lower the energy of the transition, the greater must be the spatial separation of the initial and final states, hence, the greater is the damping.[19] Thus the matrix element for the transition gets (roughly) exponentially smaller at lower emission energies, thus increasing the lifetime. This is the central feature of our interpretation.

Several further remarks should be made concerning the model. First, these same considerations apply irrespective of whether the final state is a valence-band-tail state or a discrete deep acceptor state as indicated by the unperturbed transition energy E_A of Fig. 1. This follows from the fact that both are localized and both have smaller energy differences from the initial state (i.e., $\hbar\omega < E_A$) when they are far separated from it. Therefore, the presence of the deep levels is not essential to the model although it may be that its existence in our GaAs: Si samples caused a shift of the range of response times into a measurable regime. [This conjecture is based on two factors: (i) The luminescent decay times of samples doped with impurities other than Si were too fast to measure. (ii) It has been observed qualitatively that deeper levels in GaAs are associated with longer luminescent response times.[20]]

The essential similarity of the decays from n-type, p-type, and closely compensated samples also follows from the model since the same types of states are present in all three. The somewhat shorter response times of the n-type sample may be a consequence of screening of the potentials by the large number of free electrons.

It is clear that there is a very close similarity between our interpretation of these luminescent decays and the corresponding features of donor-acceptor pair recombination.[21] The differences are that in our case we have continuous distributions of energy levels and of spatial separations of initial and final states. The analysis of the kinetics of recombination involving low-energy transitions is, therefore, analogous as long as the initial-final-state overlap integrals are dominated by exponentially damped wave functions. In the discrete case it is known[22] that the transition probability as a function of the initial-final-state distance r has the form

$$W(r) = W_m e^{-r/R} , \qquad (1)$$

where W_m is a constant and R is a measure of the attenuation factor governing the overlap of wave functions. Our model invokes the statistical dependence of the emission photon energy on this distance; lower energy corresponds to greater mean distance and, by Eq. (1), an exponentially reduced transition probability.

This analogy to pair recombination suggests that the time dependence be analyzed for possible t^{-1} behavior which characterizes some pair decay. As mentioned in Sec. III B1, however, we were unable to fit the data in this way. The continuum nature of the band-tail system may be responsible for this difference from the case of discrete donor-acceptor pairs.

All of the foregoing arguments to explain the energy dependence of the radiative lifetime can be applied to other types of recombination processes as well. If, for example, decay occurs with phonon assistance, the attenuation of the electron and hole wave functions would also reduce greatly the net transition probability even though the matrix element contains a very different interaction operator. By the same arguments, a general nonradiative transition should be similarly affected. This point will appear again in the discussion of the temperature dependence.

In addition to the analogy with pair recombination, the present results and interpretation have relevance to at least two other previously reported observations. First is the stepwise excitation of luminescence in GaAs samples of just the type used here.[23] That result was ascribed to deep band-tail states which must have had relatively long lifetimes. Second is the demonstration that the optical absorption edge in such materials is associated with the electrical state of charge of impurities present.[24] Here, too, the penetration of the wave functions into classically forbidden regions was invoked to explain the exponential shape of the absorption edge.

B. Spectral Dependence of the Rise Times

In contrast to the spectral variation of the decay, the observed wide range of luminescent *rise* times was unexpected and has led to rather surprising conclusions. We had expected that a degenerate quasiequilibrium condition would develop in a time much shorter than our observation times. If this were so, however, all the lowest electronic states would be filled "instantly" and would, therefore, begin to radiate immediately. The results for the rise times shown in Fig. 5 show that this is far from the case. On the contrary, the lowest-energy states have the slowest luminescent rise times. Furthermore, the closeness of the rise and decay times at all photon energies is striking.

Thus, none of the states involved in the luminescence saturate under the conditions of these experiments, even during the very long times (~ 5 μsec) required for establishing some of the steady-state conditions. This nonsaturation of the low-energy states is equivalent to nonquasiequilibrium of the system because an equilibrium distribution of our photoexcited carriers should be highly degenerate, as we now show. A typical excitation pulse of ~0.1 W (optical) is absorbed in a region ~10^{-4} cm thick by ~ 5×10^{-4}-cm^2 area, thus generating ~10^{25} carriers/cm^3 sec. The resulting steady-state population density for carriers having a lifetime of 100 nsec (the measured value near the emission peak) is then ~ 10^{18} cm^{-3}. This concentration of electrons in a GaAs conduction band is known to be degenerate even at room temperature.

This conclusion that quasiequilibrium does not prevail is supported by several other observations. First, the decay of a degenerate equilibrium gas of carriers should progressively drop the quasi-Fermi level, leaving the lowest states full until all the higher ones are empty. This would cause a delay in the onset of the decay of low-energy emission while the lowest states are full. Such a delay has not been observed under any of our experimental conditions. Furthermore, the rise and decay times are independent of excitation intensity. This requires that the states are never saturated, as they would be in a degenerate quasiequilibrium situation. The studies on various excitation geometries described in Sec. III B7 also support the present interpretation.

It should be added that the present observations are incompatible with a nondegenerate quasiequilibrium as well. In that case, all of the excited carriers would have to decay at a single common rate regardless of their energy level.

For these reasons, we do not believe that quasiequilibrium conditions existed at any time during our measurements. The deeper band-tail states do not thermalize readily – an effect that is less surprising when one considers the localization and spatial separation of different states at approximately the same energy. Thus, the thermalization time for deep tail states must be longer than the carrier lifetimes, which we have observed to be as long as several microseconds. Indeed, quasiequilibrium conditions do not develop even in the steady state with continuous excitation. Such a condition has been suggested previously on the basis of indirect evidence,[25] but appears not to have been demonstrated directly. Also, these results provide new information on the processes which may have contributed to the stepwise excitation of luminescence referred to earlier[23]: The first excitation step places electrons in tail states having a much longer lifetime than previously expected, and the electrons excited out of such states do not readily trickle back down to them, but decay from some intermediate levels. (There, the low-energy excitation directly into the tail states appears to have saturated them.)

C. Relation of Rise and Decay Times

With the foregoing explanations of the rise and decay times, we can now also explain their close similarities and the fact that rise times are nearly the same in *n*-type, *p*-type, and closely compensated materials, just as the decays are. The close equality of the rise and decay times is a direct consequence of the nonsaturation of the luminescent states: Consider the kinetics of a single class of states which are optically excited. If this set of nonsaturating states has a mean lifetime τ, the differential equation for the occupation number n is well known to be

$$\frac{dn}{dt}=g-\frac{n}{\tau}, \qquad (2)$$

where g is the generation (optical excitation) rate. It is well known that the solution of such an equation has both rise- and decay-time constants equal to τ because the rise curve simply reflects how the decay reduces n below the linear generation number. Thus, the nonsaturation uncovered in the rise-time studies results in simplifying the relation between rise and decay.

In Sec. IV A we showed that the decay times on *n*-type, *p*-type, and compensated samples should be about equal. Now it follows that the rise times should also be essentially the same in all samples.

D. Temperature Dependence

There are two distinguishable aspects of the observed temperature dependences, one familiar and one new. First, we recognize in Fig. 8 the general result that the integrated luminescent efficiency declines rapidly as the temperature increases above ~ 80°K. (We have not extended this measurement to lower temperatures, but there are reasons to expect a much weaker temperature dependence there.) As with the other observations of this behavior, we ascribe this to some (unspecified) nonradiative transition having an increasing probability at higher temperatures. The detailed nature of this nonradiative effect has not, to our knowledge, been established. From its temperature dependence, we see that it is phonon dominated, not of the Auger type. There is some evidence that surface effects may be responsible for reduced efficiency at higher temperatures.[26]

The new feature of the temperature dependence is that it has a spectral variation as shown in Fig. 7 for the response times. That is, raising the temperature above ~80 °K causes a marked decrease in the (longer) response times at low energies, but has a progressively smaller effect on the (shorter) times at higher energies. There is, in fact, virtually no temperature dependence to the response times near the highest energy (1.43 eV) we can measure. An empirical analysis of the central portion of Fig. 7 indicates that for temperatures between 80 and 160 °K, the data can be approximately described by an Urbach rulelike formula:

$$\tau=\tau_0 \exp[a(1.43-\hbar\omega)/kT], \qquad (3)$$

where $\tau_0 \simeq 25$ nsec, $a \simeq 0.2$, and $\hbar\omega$ and kT are in electron volts. It is interesting to note that, as with Urbach's rule for absorption, the temperature dependence disappears below ~ 80 °K.

The temperature dependence of the response-time spectrum has an important effect on one aspect of the interpretation of the present data. This is because there should be no temperature dependence for a simple radiative transition between states which overlap in the energy gap as displayed in Fig. 1. Therefore, the variation with temperature of the response time at fixed energy requires the participation of some other process, e.g., phonon assistance. This is consistent with the foregoing discussion of the efficiency and, as discussed in Sec. IV A, the localization and separation of the initial and final states will lead to a spectral variation of response times regardless of the detailed nature of the recombination mechanism.

One process which may explain these results is that at higher temperatures electrons are thermally excited from deeper to shallower states of the tail. From there they can recombine more rapidly either radiatively or by nonradiative recombination centers to which they can move more easily because of the reduced localization of excited states. The latter is more likely here because we could find no evidence of enhanced emission at higher energies as the temperature was raised.

It should be remarked in this connection that the response time measured by luminescence is not just that of the radiative component, but rather the total excitation lifetime, which is given by

$$\tau_{\text{tot}}^{-1}=\tau_{\text{rad}}^{-1}+\tau_{n-r}^{-1}, \qquad (4)$$

where we have lumped in τ_{n-r} all recombination processes other than the observed radiative one. The emitted radiation is just a convenient tool by which we can determine τ_{tot}.

V. SUMMARY AND CONCLUSIONS

The technique of time-dependent photoluminescence has provided new information on properties of energy-band-tail states. By the choice of GaAs:Si prepared by solution growth we have been able to observe the independence of these properties on doping type (i. e., n type, p type, or nearly compensated). The central feature of the results is the range of luminescent rise- and decay-time constants for different wavelengths within the single luminescence band. Together with the other observations, these results lead to the following interpretation: The spectral dependence of the decay times arises from the localization and spatial separation of valence- and conduction-band-tail states in a continuum analog to discrete donor-acceptor pair recombination. The corresponding range of the rise times shows that states deep in the band tails do not saturate under any intensity of optical excitation and, therefore, quasiequilibrium is not attained, even in the steady state. Thus, the thermalization times for deep tail states is longer than the recombination time. The temperature dependence of the results requires the participation of phonons in nonradiative recombination, at least for temperatures above ~ 80 °K and for energies below 1.43 eV. At lower temperatures or at 1.43 eV, the absence of temperature dependence could indicate either a dominance of the radiative process or a change to temperature independence of the nonradiative process. The available evidence does not provide a basis for making this distinction. We can, however, compare the $\tau \simeq 25$ nsec we observed with various previous estimates of radiative recombination time of ~ 1 nsec for presumably band-to-band transition in GaAs.[27-29]

[As this paper was being prepared for publication, we learned of somewhat similar measurements at 1.8 °K on a sample compensated to about the same extent as our CM79Ga (but with different doping) by Leite, Shah, DiGiovanni, and Whelan. In spite of several differences in method, their primary results and conclusions agree with those presented here.]

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