Thermal quenching processes in the low temperature photoluminescence of excitons bound to nitrogen pairs in GaP

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We have measured the photoluminescent efficiency of excitons bound to isolated nitrogen, and to nitrogen pairs of different separations, in GaP. Excitons bound to a particular center were excited selectively with a tunable dye laser, and the temperature dependence of the emission intensity measured between 10 and 100 K. Detailed balance considerations show that the efficiency at 10 K is near 100%. Luminescence from excitons bound by less than 40 meV is found to be thermally quenched by the escape of a free exciton. For excitons bound by 40 meV or more, we find that luminescence is quenched by the escape of the hole. In the case of excitons bound to nearest-neighbor pairs (binding energy 143 meV) the electron remains attached to the pair, forming a charged acceptorlike center with a lifetime long enough for quasiequilibrium to be established with the valence band. This leads to a superlinear dependence of emission intensity on exciting power.

I. INTRODUCTION

The dominant contribution to the photoluminescence of indirect-gap semiconductors at low temperatures comes from the radiative decay of excitons bound to various impurities. In particular GaP, heavily doped with nitrogen and excited with band-gap radiation, shows a series of emission lines from excitons bound not only to isolated nitrogen atoms, but also to nitrogen pairs of different separations.[1] These are labeled NN_i, $i = 1, 2, \ldots$, in order of decreasing binding energy, which is thought also to be in the order of increasing pair separation. The binding energy (relative to the free exciton) decreases from 143 meV for NN_1 to 11 meV for isolated N.

A detailed study[2] of the excited states of excitons bound to NN_i, $i = 1$–10, has shown that for $i \leq 7$ the structure is qualitatively unchanged while the exciton binding energy varies by a factor of 7 through the series. Thus a study of quenching as a function of binding energy alone is possible. For excitons bound to other types of impurity center, the structure is not well understood; nor is there such a wide range of binding energy available.

The deeper bound excitons were found to be well described by the model of Hopfield, Thomas, and Lynch.[3] In this model, one particle (the "primary" particle, in the present case the electron) is taken to be bound in a relatively localized state by the short-range potential of the impurity center. The "secondary" particle (the hole) is then bound by the Coulomb attraction of the "primary" into an acceptorlike state. This model was confirmed by the discovery of acceptorlike excited states of excitons bound to NN_i, $i = 1$–5.[1,2] Similar states, deviating somewhat from their predicted positions, were found for NN_6 and NN_7.

The possible decay modes of excitons bound to isoelectronic traps are as follows: (i) Radiative decay, with or without phonon emission. (ii) Nonradiative decay, while still bound to the center, by multiphonon emission.[4,5] (iii) Nonradiative decay, as in (ii), but by the Auger effect,[6,7] in which the energy of recombination is transferred to a third particle. For an isoelectronic trap, this particle must either be free or attached to another nearby center, since only two particles are bound to the trap. (iv) Tunneling of the whole exciton to another (neutral) impurity center.[8] (Excitons do not appear to bind to charged centers in GaP.) (v) Tunneling of the hole to an ionized acceptor or neutral donor. (vi) Thermal emission of the hole. (vii) Thermal emission of the exciton as a single entity. (viii) Thermal emission of both hole and electron as free particles.

At sufficiently low temperatures, mechanisms (vi)–(viii) are inoperative. So is (iii), since the third particle required for the Auger effect is not normally available.

Mechanisms (iv) and (v) cannot occur in sufficiently pure material. The contribution of (ii) can be found at low temperatures and low concentrations from the absolute quantum efficiency of luminescence. While accurate direct measurements of efficiency are difficult, it can be determined indirectly by a detailed balance comparison of absorption and emission.[9] Such an analysis, for the case of excitons bound to isolated N in GaP, is made in the Appendix. It is shown there that the quantum efficiency is unlikely to be less than 95%, and most probably is 100%. There is evidence that this is also true for excitons bound to nitrogen pairs.[10]

In heavily doped crystals, exciton tunneling [mechanism (iv)] from one type of nitrogen pair to

another is of great importance. Elegant dynamic experiments by Street et al.[8] have led to estimates of some of these tunneling rates. In the work reported here we have used concentrations where this tunneling is not important.

The effects we are primarily concerned with are the thermal effects (vi)–(viii). We have studied them by measuring the relative luminescent efficiency of GaP:N as a function of temperature and nitrogen concentration, when different bound excitons are selectively produced by monochromatic excitation. While there has been extensive work in this area using electron beam or band-gap excitation,[11-13] we will see that at low temperatures (below 100 K) selective excitation is essential to obtain interpretable results. In Sec. II we describe our experimental method. In Sec. III we report our results on excitons bound to isolated N and to NN_i pairs, insofar as they can be described in terms of a power-independent luminescent efficiency. In Sec. IV we describe an unusual superlinear dependence of the NN_1 luminescence on exciting power, which occurs in very concentrated crystals of good quality. The superlinearity can extend over four decades of incident power and is of a type which does not seem to have been reported before. In Sec. V we discuss our results and draw some conclusions.

II. EXPERIMENTAL METHOD

Most of our crystals were grown from the vapor by Frosch.[14] They are needles or small platelets and show little or no donor-acceptor pair luminescence at any temperature. Some crystals were grown by Lynch and were doped with Si as well as N. They had a net donor concentration of about 10^{18} cm^{-3}. Heavily doped epitaxial layers grown by chemical deposition vapor (CVD) were obtained from Plessey of England.

Luminescence was excited selectively with a dye laser tunable from 5200 to 5700 Å, or with an argon laser line between 4569 and 5287 Å. The laser power was attenuated to about 2 mW and slightly defocused to give an incident power density of about 1 W/cm². In the study of the effects of changing power density, described in Sec. IV, the density was varied from about 10 W/cm² to 10 μW/cm² with calibrated neutral density filters. The precise area of illumination is uncertain in these irregularly shaped crystals because of light scattering, so that absolute power densities are only accurate to within a factor of 3.

Temperatures between 5 and 100 K were obtained by passing cold helium gas around a copper tube containing the crystal which was mounted on a copper rod and immersed in helium exchange

gas. The temperature was measured with an Au(Fe)–Chromel-P thermocouple attached to the sample mount. The temperature was feedback-stabilized and was stable and reproducible to ±0.1 K; the nominal temperature was checked to be within 0.3 K of the true sample temperature at 77 and 4.2 K.

Typical emission spectra of excitons bound to N and to the NN_1 pair are shown in Fig. 1. Other NN_i pairs give similar spectra. At the temperature shown, emission is predominantly from the $J = 1$ level, which retains its identity even in the pair since the "crystal field" splittings which arise from the axial nature of the pair are less than the exchange splitting of about 1 meV.[15] (See the Appendix for a description of the $J = 1$ and $J = 2$ levels and the A and B lines of the N exciton.)

Our normal procedure was to pump in the no-phonon line and monitor the temperature dependence of the intensity of the phonon sidebands at about 50 meV (see Fig. 1). Sometimes, because of the overlap of spectra from different centers, it was found preferable to monitor a different spec-
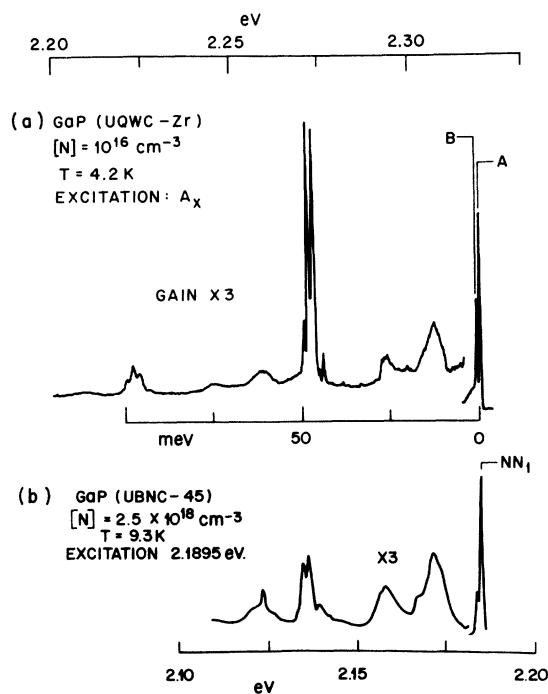

FIG. 1. Parts of the photoluminescent spectra of GaP doped with nitrogen. (a) Emission from excitons bound to N in a dilute crystal: excitation at the free exciton (A_x) line. (b) Emission from excitons bound to NN_1 pairs in a concentrated crystal: excitation in the acoustic sideband of the NN_1 line. In both (a) and (b) the temperature is such that most of the emission is from the $J = 1$ level. Sample numbers correspond to those used in Ref. 2.

tral feature. Errors due to changes in laser output with time were eliminated by use of an analog divider to measure the ratio of emission intensity to laser output.

As the temperature is raised the no-phonon line broadens and the peak absorption decreases. A correction for this was made routinely, based on the well established fact that the integrated absorption is almost independent of temperature up to about 120 K.[16]

At the highest temperature, sensitivity is ultimately limited by the overlap of emission from different centers, and by Raman scattering which is almost independent of temperature. It was possible to reduce interference from the latter by monitoring at the frequency of a zone-boundary phonon, rather than a zone-center one, but this did not eliminate the effect completely since the nitrogen impurity breaks the k-selection rule and makes one-phonon Raman scattering possible throughout the Brillouin zone.

III. RESULTS: LINEAR REGIME

A. Method of presentation

It is shown in the Appendix that the radiative efficiency at low temperatures (about 10 K) of the luminescent centers is essentially 1. The efficiency η as a function of temperature is then given by

$$\eta(T) = I(T)/I(0) = w_R/[w_R + w_{NR}(T)] \ , \qquad (3.1)$$

where $I(T)$ is the integrated emission at temperature T, w_R is the radiative rate (assumed independent of T), and $w_{NR}(T)$ the combined rate of the quenching processes; i.e., all those nonradiative processes which remove excitation from the center under study. Equation (3.1) can be written

$$y(T) = I(0)/I(T) - 1 = w_{NR}(T)/w_R \ . \qquad (3.2)$$

If w_{NR} arises from a single thermally activated process, we should have

$$w_{NR}(T) = w_0 e^{-E_a/kT} \ , \qquad (3.3)$$

where w_0 varies only slowly with T. An Arrhenius plot of $\ln y$ against T^{-1} should give a straight line with slope $-E_a/k$, where E_a is the activation energy, and intercept $\ln y_0 = \ln(w_0/w_R)$. In principle, correction should be made for the temperature dependence of w_0. If $w_0 \propto T^n$, the error in slope is nkT, where T is the average temperature of measurement. Since $|n|$ is unlikely to exceed $\frac{3}{2}$, and in our measurements $E_a/kT > 10$, the error in E_a is at most $\pm 15\%$.

On the other hand, the intercept can be seriously in error, differing by n from the "correct" value of $\ln[w_0(T)/w_R]$. For this reason, and because of

errors of extrapolation, the preexponential factor is only accurate to within an order of magnitude.

In the discussion so far we have assumed that, once an exciton has escaped from a center, it is lost and cannot be recaptured. At sufficiently low concentration this will always be true. However, if the concentration of the center under study is high enough, and the decay of free excitons (due both to radiative and nonradiative recombination and trapping at other centers) slow enough, that there is a high probability that the exciton will be recaptured by a center of the same type before it decays. Equilibrium can then be established between the free and bound excitons. (It is actually only "quasiequilibrium," since excitons do not exist in true equilibrium.) We then have

$$y(T) = (N_x/N_0)e^{-E_a/kT} \ , \qquad (3.4)$$

where N_0 is the number of centers and $N_x = 2(2\pi m_x kT/h^2)^{3/2}$ is the density of states for free excitons (mass m_x). While (3.3) and (3.4) give the same temperature dependence,[17] apart from a possibly different dependence of the preexponential factor y_0, they could in principle be distinguished through the concentration dependence of y_0. Another way to distinguish them, which does not require a change of sample is to compare data obtained with different exciting wavelengths. If equilibrium is established, it can make no difference whether free or bound excitons are created initially. We shall see that a substantial difference is usually found experimentally, showing that in general equilibrium is *not* established.

B. Excitons bound to isolated nitrogen

The quenching of emission from the "A-LO" line of excitons bound to isolated N is shown in Fig. 2. These data are corrected for changes in the population of the $J = 1$ level with temperature. The full circles show the corrected $y(T)$ for a dilute crystal ($[N] = 1.0 \times 10^{16}$ cm^{-3}), pumped in the A line. These data can be accurately fitted by

$$y = y_0 e^{-E_a/kT} \ , \qquad (3.5)$$

with $E_a = 10.4 \pm 1$ meV and $y_0 = 5 \times 10^4$ sec^{-1}. Since $w_R = 10^7$ sec^{-1}, Eq. (3.3) gives $w_0 = 5 \times 10^{11}$ sec^{-1}. The accurate linearity of the plot over four decades shows that the temperature dependence of the preexponential factor is small; $|n| < 0.7$. The activation energy is in excellent agreement with the binding energy of the exciton to the nitrogen, which is 11 ± 1 meV. The lifetime data[11] are also consistent with this. Thus there is no intermediate state involved in the escape of the exciton.

Different results are obtained if band-gap excitation is used. The open circles in Fig. 2 show the
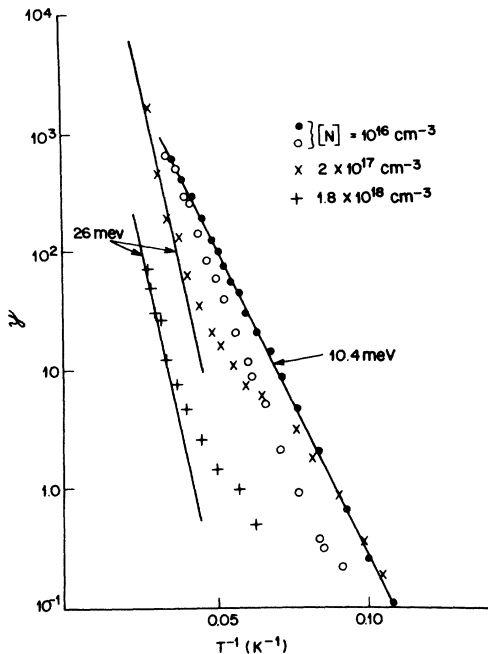
FIG. 2. Arrhenius plot of the thermal quenching of luminescence from excitons bound to isolated N in crystals of different concentrations. The ordinate is y $=I(0)/I(T) - 1$, where $I(T)$ is the integrated emission intensity at temperature T. Filled circles and crosses: A-line excitation (only bound excitons created). Open circles: band-gap excitation (free excitons and free particles created). Concentrations are given on the figure. The lines are Eq. (3.5) with the values of E_a shown.

results obtained on pumping at 5287 Å (2.344 eV) just above the threshold of intrinsic absorption. The discrepancy between the two sets of data is indicative of a temperature-dependent capture efficiency, and illustrates the danger of relying on band-gap excitation data in the study of quenching mechanisms. It also shows, as remarked earlier, that equilibrium between free and bound excitons is not established.

When the nitrogen concentration is higher, the results are quite different, as shown in Fig. 2 (crosses).[18] At low temperatures, the data for N_0 $=2 \times 10^{17}$ cm^{-3} agree with those at lower concentration. However, above 13 K $y(T)$ falls progressively below the Arrhenius line, until another process, with $E_a \sim 26$ meV, takes over above 20 K.[19] The simplest interpretation of these data is that above about 13 K an exciton liberated thermally from an N center has a high probability of being recaptured by another, identical, center before decaying by some other mechanism. Thus equilibrium is partially established between free and bound excitons. If equilibrium were completely

established, Eq. (3.5) would again be obeyed, but y_0 would be small (~ 10) since N_0 is so high. In fact, before equilibrium is established, the exciton begins to thermally dissociate into free particles, a process which requires about[20] 28 meV (relative to the bound exciton) agreeing with the 26 meV observed. The large preexponential factor ($\sim 10^7$) is also consistent with a multiparticle process (see Sec. IV B).

At still higher concentration, 1.8×10^{18}, most of the excitation is transferred to NN pairs, and the A-line emission is weak. It is reasonable to assume that at this concentration transfer from one isolated N to another is rapid, so that the A-line intensity and lifetime will be reduced by a factor $w_R/(w_R + w_t)$, where w_t is the total transfer rate to the pairs. If w_t is independent of T, $y = w_{NR}/(w_R + w_t)$, so it is reduced by the same factor if w_{NR} is independent of concentration. This reduction is observed (see Fig. 2); and, at high temperatures when $w_{NR} \gg w_t(y \gg 1)$, the A-line emission (under conditions of total absorption of the exciting radiation) is roughly independent of concentration, as expected. This shows that the dissociation of the exciton into free particles is a nonequilibrium process, since in equilibrium $w_{NR} \propto N_0^{-1}$ [Eq. (3.4)].

C. Excitons bound to nitrogen pairs

The quenching data for excitons bound to NN pairs in crystals of high concentration ([N]$=2 \times 10^{18}$ cm^{-3}) are shown in Fig. 3.

While the concentration of isolated nitrogen atoms can be deduced from the A-line absorption,[16] there is no such calibration available for the pairs. We made absorption measurements on the NN$_i$ lines ($i = 1, 3$-10) in a crystal containing 2.5×10^{18} N/cm^3. The integrated absorption strengths are consistent (within a factor of 2) with the following assumptions: (a) the integrated cross sections are the same as for the A line, (b) that pairing is random, and (c) the center labeled NN$_i$ is in fact the ith nearest neighbor pair (i.e., the absorption strength scales approximately with the number of equivalent pairs). The pair concentration is about 10^{16} cm^{-3} for the most common species (NN$_7$), and 10^{15} cm^{-3} for the least common (NN$_8$ and NN$_1$).

Except for NN$_1$, essentially similar quenching data are obtained for [N]$=2 \times 10^{17}$ cm^{-3}, where the pair concentrations are 100 times smaller. At this low concentration exciton transfer processes from one type of pair to another are negligible, and once an exciton or other particle has escaped from a pair, it is most unlikely to be recaptured by another.

The data on NN$_7$, NN$_9$, and NN$_{10}$ were obtained by pumping into the A line at a concentration of
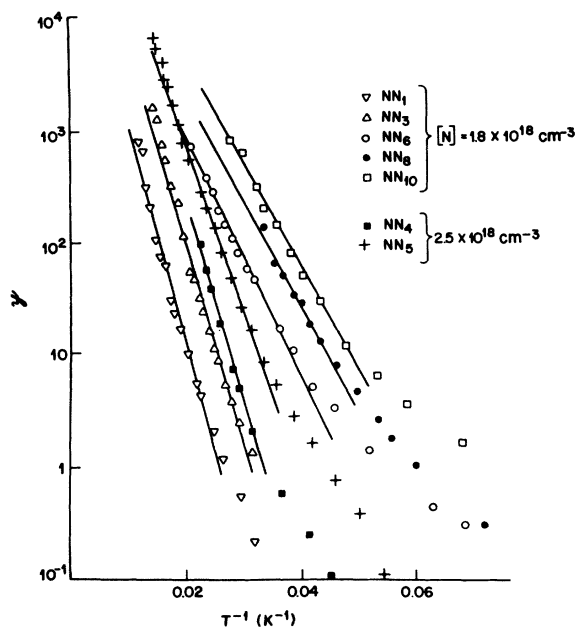
FIG. 3. Thermal quenching of luminescence of ex-
citons bound to NN_i pairs in concentrated crystals.
The ordinate is the same as in Fig. 2. The data points
for NN_7 and NN_9 are almost indistinguishable from those
for NN_8 and NN_{10}, respectively, and are omitted for
clarity. The lines are Eq. (3.5) with the parameters
given in Table I.

2×10^{18} cm^{-3}, where A-line excitation is rapidly
transferred to shallow pairs even at 10 K. As re-
marked earlier, such data are slightly suspect be-
cause of the possibility of a temperature-dependent
transfer efficiency. However, in the case of NN_8,
we find no difference between the quenching data
obtained by exciting in the A line or in the NN_8 no-
phonon line, and it is reasonable to assume that

this is true for all the shallower pairs. It is, how-
ever, untrue for the deeper pairs such as NN_3 and
NN_1, whose intensities first *increase* with temper-
ature when excitation is in the A line.

Data on NN_2 are omitted from Fig. 3; they can-
not be obtained with any precision because of
strong interference from the nearby NN_1 line, to
which energy is transferred even at the lower con-
centration.

Many of the curves in Fig. 3 show a region of low
activation energy, about 7 meV, at low tempera-
tures. The preexponential factor for this varies
markedly from sample to sample, and even from
point to point in a single sample. It is presumably
an impurity effect and will be neglected.

At the highest temperatures the data for the
deeper traps show a steep rise corresponding to a
large apparent activation energy ($\sim$100 meV) and
an exceptionally large preexponential factor (w_0
$\sim 10^{16}$ in the case of NN_1, for instance). This large
w_0 shows that more than one particle is involved in
the process. One multiparticle process which
could in principle give the observed behavior is
Auger recombination with the aid of thermally ex-
cited free carriers.[6] The observed activation en-
ergy would then be the binding energy of these
carriers. The fact that the process occurs even in
our best samples, which have donor and acceptor
concentrations at the 10^{15}-cm^{-3} level, makes this
explanation implausible. A more likely explanation
is offered in Sec. IV B.

In between these two limits there is a region of
two or three decades in $y(T)$ where the curve is
characterized by a single activation energy E_a.
The values of E_a and y_0 obtained by fitting this
part of each curve are given in Table I. Also
shown are data obtained at other concentrations.
In this table we compare the observed E_a's with

TABLE I. Thermal quenching processes for bound excitons.[a]

Center	[N] (cm^{-3}) E_f	E_I	1×10^{16} E_a	$\log_{10} y_0$	2×10^{17} E_a	$\log_{10} y_0$	1.8×10^{18} E_a	$\log_{10} y_0$	2.5×10^{18} E_a	$\log_{10} y_0$
N	11		10.4	4.6	26		27			
NN_{10}	17						18	5.4		
NN_9	18						18	5.4		
NN_8	19				23	5.7	19	5.2		
NN_7	22	34?					20	4.6		
NN_6	25	34?			23	5.0	22	5.0		
NN_5	31	37			33	5.8			32	6.0
NN_4	39	38			40	6.0			36	6.0
NN_3	64	40			38	5.7	35	5.4	38	5.8
NN_2	138	41								
NN_1	143	40			37	5.8	38	5.0	37	4.5 [b]

[a] All energies in meV.
[b] At low pump power (see Sec. IV).

the two energies characteristic of the deeper bound excitons: E_f the binding energy of the exciton to the center relative to the free exciton at 2.328 eV, and E_h, the binding energy of the hole alone, which was determined spectroscopically in Ref. 2.

The range over which E_a can be fitted is too narrow for it to be possible to determine if the preexponential factor is temperature dependent. (It is not possible to fit the whole curve with a single activation energy, for any reasonable temperature dependence of y_0.) Consequently, as discussed in Sec. III A, E_a is only accurate to ±15%, and the absolute value of y_0 only to within an order of magnitude. Since the temperature dependence of y_0 is unlikely to vary greatly from one pair to another, *relative* values of y_0 should be accurate within a factor of 2. Bearing this in mind, one sees from Table I that the E_a's fall into two distinct classes. For weakly bound excitons (NN_6 and above) $E_a = E_f$ within experimental error. There is no sign of a higher activation energy corresponding to E_h, i.e., to thermal emission of the hole. Thus, as for isolated N, quenching arises from the escape of the exciton as a single entity. The preexponential factor y_0 is about 10^5 for all these centers, corresponding to $w_0 \sim 10^{12}$ sec^{-1}.

For the more strongly bound NN_3 and NN_1 excitons, the activation energy is close to E_h, the binding energy of the hole alone. Thus the quenching mechanism in this case is thermal loss of the hole, the electron remaining bound to the center. If the system is not to saturate, this electron must ultimately escape, either thermally or by tunneling to a neutral acceptor or to a deep ionized donor; this point will be discussed in Sec. IV.

As remarked earlier, the preexponential factor of the high-energy process observed at the higher temperatures is too large to be consistent with thermal emission of an exciton, which would have a similar activation energy. However, this rapid multiparticle process may well obscure the exciton contribution.

The value of y_0 is somewhat larger for the hole emission process. Since emission is the inverse process to capture, and the capture cross section of a charged center is usually larger than that of a neutral one, this is to be expected.

The intermediate cases of NN_4 and NN_5 are ambiguous. For NN_4, E_f is close to E_h and the observed value of E_a would be consistent with either; the large value of y_0 is closer to that observed for hole emission than for exciton emission. For NN_5, the large value of y_0 suggests hole emission, but the value of E_a, and the absence of any higher energy process, suggests exciton emission. Probably both are present.

IV. NONLINEAR EFFECTS IN NN₁ LUMINESCENCE

A. Results

In the case of crystals heavily doped with nitrogen ($[N] \geq 2.5 \times 10^{18}$) but otherwise pure, we find a nonlinear dependence of NN_1 emission intensity on pump power.[20,21] This nonlinearity is illustrated in Fig. 4, which is a log-log plot of the emission intensity against pump power at several temperatures. The crystal here is a needle with concentration 2.5×10^{18} cm^{-3}, and excitation is into an NN_1 phonon sideband. At low temperatures the plot is linear, the luminescent efficiency being near 100% at all powers: but as the temperature is raised the efficiency drops off much more rapidly at low powers than at high. Over the entire nonlinear range (four orders of magnitude in laser power G at 70 K) a single exponent is found, 1.55 ± 0.05. The fact that this is greater than 1 shows that the nonlinearity is not just a heating or saturation effect. The wide range of G over which the superlinearity is observed distinguishes it from the well-known effects observed, for example, in CdS.[22]

Similar results were obtained with a CVD epitaxial layer containing 2×10^{19} N per cm^3. No nonlinearity was found at lower concentrations than 2.5×10^{18}. Except for a very slight nonlinearity in

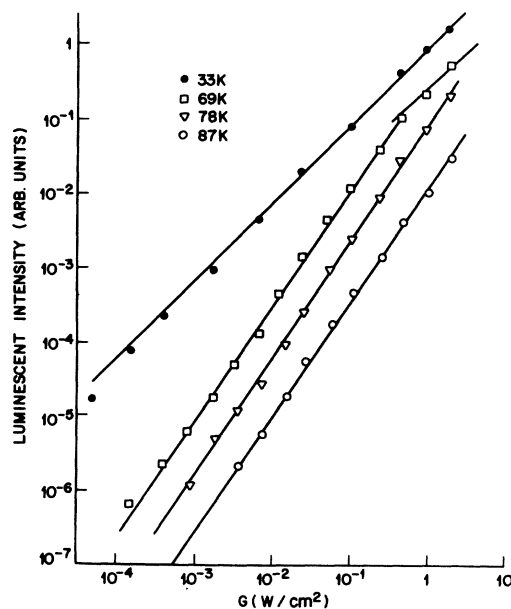FIG. 4. Power dependence of the luminescent intensity of excitons bound to NN_1 pairs in a concentrated crystal ($[N] = 2.5 \times 10^{18}$ cm^{-3}). Excitation was in the (NN_1 +local mode) peak at 2.241 eV (see Fig. 1 of Ref. 2) where the absorption coefficient is about 0.1 cm^{-1}. The lines have a slope of either 1.0 or 1.55.

the NN_3 emission at the highest concentrations, no nonlinearity was found for other bound excitons.

If the excitation is applied in short intense pulses, the luminescent efficiency drops off as the pulse separation is increased. This demonstrates the existence of a nonzero integration time; however, the drop off is not so fast as would be expected if the integration time were infinite, in which case the mean power (rather than the peak power) would be the determining factor in the efficiency.[23]

In the nonlinear region the luminescent efficiency of the bulk crystals (but not the CVD layers) was found to be very sensitive to background infrared illumination. Figure 5 shows the reduction in emission intensity as a function of incident power [$I(0)$ in the ordinate refers to the intensity at zero background]. The slope of this curve is found to be inversely proportional to pump power. This fact and the dynamic effects discussed below show that this, too, is not a heating effect.

The excitation spectrum of this background quenching effect was found crudely with the aid of a wedge interference filter. The spectrum has a threshold at 0.85 ± 0.05 eV and levels off around 1.3 eV. This is in close agreement with the photoionization spectrum of neutral oxygen donors,[5,24] and strongly suggests that the quenching process involves electrons liberated from these donors.[25]

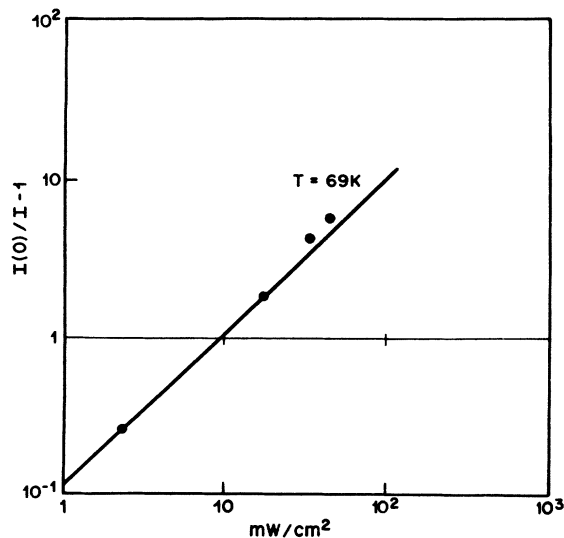If the background illumination is cut off, the NN_1 emission takes time to recover its unquenched value, and the rate of recovery is proportional to the pump power. The recovery is not exponential, and we have arbitrarily defined a recovery time $\tau_{1/2}$ as the time taken for the emission to reach half its unquenched value. This is plotted against inverse pump power in Fig. 6 for a typical temperature. The plot is linear up to recovery times of more than 10 sec. The infrared quenching effect, in which the production of free electrons reduces the fluorescent efficiency, shows that the filling of hole traps is playing an important role. These traps can be emptied if enough electrons are created; the number needed is proportional to the rate at which traps are filled and therefore to the laser power, as observed. Note that if the oxygen donor were itself the hole trap, the quenching effect of a given infrared intensity would be *independent* of laser power. The data obtained with pulse excitation shows that there is a range of trap lifetimes, extending from milliseconds to tens of seconds. The traps are most probably acceptors, whose lifetime when filled depends on the distance to the nearest neutral donor.

If the infrared background intensity is increased sufficiently, no further decrease in NN_1 emission is observed; presumably all the hole traps are then emptied. Thus the temperature dependence of the luminescent efficiency can be studied under two extreme conditions; traps empty and traps full. An Arrhenius plot of $y = I(0)/I(T) - 1$ under these two conditions is shown in Fig. 7. The open
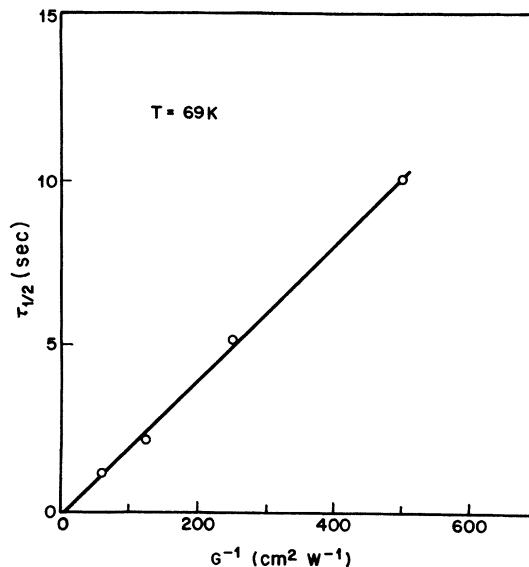

FIG. 5. Effect of broad-band infrared illumination, peaked around 1 μm, on the NN_1 luminescence. Excitation intensity about 2 W/cm^2. $I(0)$ is the intensity at the same temperature in the absence of background illumination.

FIG. 6. Recovery time to half intensity $\tau_{1/2}$ after switching off background illumination, plotted against inverse exciting power G^{-1}.
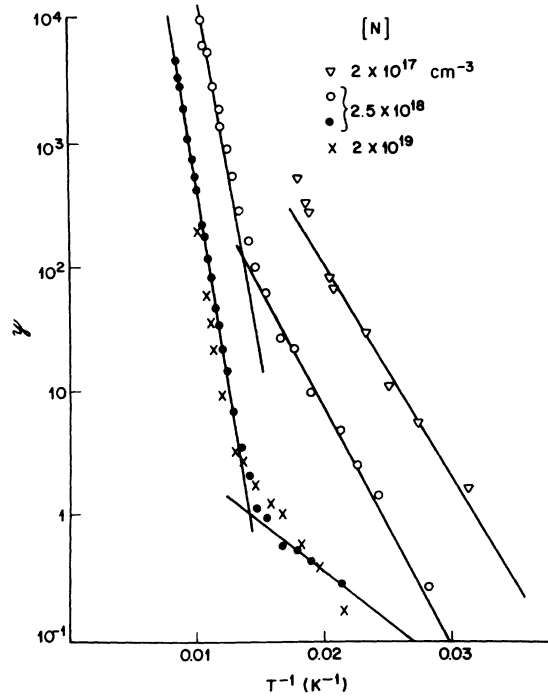
FIG. 7. Thermal quenching of NN_1 luminescence in crystals of three different nitrogen concentrations. The open circles and triangles are data obtained with hole traps empty, the filled circles and crosses with them filled. The lines are Eq. (3.5) with the parameters in the text.

circles are data obtained on the sample of Figs. 4 and 5 under low excitation (0.3 W/cm²) and strong infrared background illumination. The filled circles are data on the same sample under high excitation (5 W/cm²) and no background. The absorption coefficient of the excitation wavelength is about 0.1 cm⁻¹. Essentially similar results (crosses) are obtained on the CVD material ([N] = 2×10¹⁹ cm⁻³) under similar high excitation conditions. Also shown for comparison are the NN_1 data for [N] = 2×10¹⁷ cm⁻³.

The results with the hole traps emptied show the same activation energy at moderate temperatures as those reported in the previous section for NN_1 emission; 38 meV, corresponding to thermal emission of the hole. At high temperatures a much higher energy process (E_a~ 115 meV) takes over, with a very large preexponential factor (y_0~ 10¹⁰). This is unphysically large for a single particle process, and cannot be attributed to exciton emission. Its origin will be discussed later.

The results with the hole traps saturated are quite different. The 38-meV activation energy is no longer present. A weak effect at low tempera-

tures, with E_a~ 20 meV and y_0~ 10, gives way at about 70 K to a very strong quenching process with E_a = 125 meV and y_0~ 10⁹.

B. Origins of the nonlinearity

The dynamic effects clearly show that the saturation of long-lived traps is involved. A qualitative energy-level scheme is shown in Fig. 8. Because the electron binding energy (120 meV) to NN_1 is much greater than that of the hole (40 meV) there is a wide range of temperature in which the hole can be thermally ionized while the electron cannot. The center behaves just like an acceptor in this region, although the *number* of "acceptors" depends, of course, on the excitation level. Since excitation is selectively into NN_1, excited NN_1 centers are the only source of free carriers at low temperatures.

Even in a crystal of high purity there are always many ionized acceptors which are sufficiently far from other impurities that a hole, once captured, will remain trapped indefinitely unless thermally ionized or annihilated by a free electron. When these acceptors are neutralized by holes which have escaped from excited NN_1 centers, the hole lifetime becomes long enough for quasiequilibrium to be established between the NN_1 "acceptors" and the valence band. The hole lifetime will then be limited with "killer centers," i.e., nonsaturable recombination centers such as those associated with dislocations.[26]
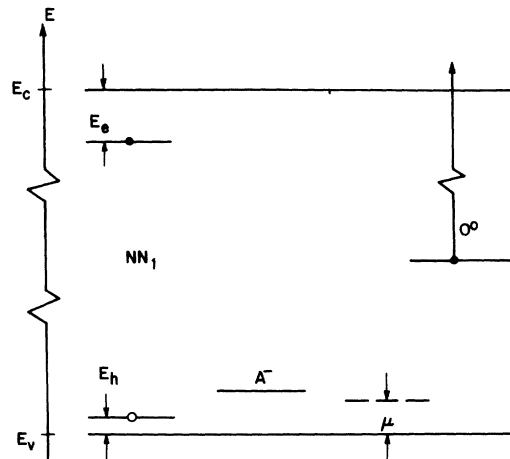

FIG. 8. Energy-level scheme for the model of Sec. IV B. "NN_1" refers to the NN_1 bound exciton; "A^-" is an ionized acceptor which acts as a hole trap; "O^0" is the neutral oxygen donor (not present in the CVD material), which can be ionized by near-infrared light; μ is the separation of the quasi-Fermi level from the valence band. Not shown are the "killer centers" which limit the hole lifetime when the traps are filled.

A quasi-Fermi level for holes μ can be defined, in terms of which the fractional occupation of the NN_1 acceptors is

$$f = [1 + e^{-\beta(E_h - \mu)}]^{-1} \ , \tag{4.1}$$

where $\beta = (kT)^{-1}$ and E_h is the binding energy of the hole. Conservation of electrons and holes separately give for the generation rate g

$$g = n[w_e(1 - f) + w_R f] = w_h p + w_R f n \ . \tag{4.2}$$

Here n is the total number density of NN_1 centers with electrons or excitons attached; p the density of free holes; g the pumping rate (i.e., the rate of generation of bound excitons per cm^{-3}); w_R the radiative decay rate; w_h the inverse hole lifetime; and w_e the rate of escape of electrons from those excited NN_1 centers which have lost their hole. The mechanism of this escape at low temperatures is obscure since (as we shall see) w_e must be quite large: presumably the electron tunnels to a recombination center. At the high temperatures w_e will increase rapidly through thermal emission.

Ordinary semiconductor statistics give

$$p = N_v e^{-\beta\mu} \ , \tag{4.3}$$

where $N_v = 2(2\pi m_h kT/h^2)^{3/2}$, the valence band density of states.

The intensity of emission in photons per second per unit volume is $I(T) = w_R nf$; at $T = 0, I(0) = g$. Solving Eqs. (4.1)–(4.3) for $y = I(0)/I(T) - 1$, we find

$$y^2/(1 + y) = (w_e w_h N_v/w_R g)e^{-\beta E_h} \ . \tag{4.4}$$

For small y (low T) this becomes

$$y = (w_e w_h N_v/w_R g)^{1/2}e^{-\beta E_h/2} \ , \tag{4.5}$$

while for large y (high T)

$$y = (w_e w_h N_v/w_R g)e^{-\beta E_h} \ . \tag{4.6}$$

Since in the latter case $I(T) = g/y$, we see that a quadratic dependence of I on g is predicted. The physical interpretation of Eq. (4.6) is that $I(T)$ is proportional to the product np, which for small f equals $g^2/w_e w_h$. In fact we observe a somewhat weaker dependence on g. Because there is a range of more or less saturable traps, w_h should decrease with p and hence with g. However, w_e presumably increases with p, since it is sensitive to the presence of neutral acceptors.

At low temperatures w_e and w_h are determined by tunneling and should not be strongly temperature dependent. As the temperature is raised thermal emission of the electron becomes possible (note that thermal emission of the hole from the traps does not affect w_h because of the quasi-equilibrium in the valence band). Then we have $w_e = w_{e0}e^{-\beta E_e}$ and

$$y = (w_{e0}w_h N_v/w_R g)e^{-\beta(E_e + E_h)} \tag{4.7}$$

This should give an activation energy of 160 meV, if the electron is excited to the conduction band. The observed activation energy of about 125 meV suggests that this is not necessary. It appears that the NN_1 exciton has an excited state 85 meV above the "ground" state[2]; this is thought to be an excited state of the electron. Exciton (and, consequently, electron) transfer away from NN_1 is rapid in this state, and it is not unreasonable that E_e in (4.7) should be 85 meV, giving $E_a = E_e + E_h = 125$ meV, as observed. However, the numerical coincidence must not be taken too seriously.

The very large preexponential factor in this region ($y_0 \sim 10^9$ for $g \sim 10^{18}$ cm^{-3} sec^{-1}) is also understandable. Substituting $N_v \sim 10^{18}$ cm^{-3}, $w_R = 10^7$ sec^{-1}, $w_h \sim 10^5$ sec^{-1}, and $y_0 = 10^9$ in (4.7), we find $w_{e0} \sim 10^{11}$ sec^{-1}, a reasonable value.

The data taken at high pump power ($g \sim 10^{18}$ cm^{-3} sec^{-1}) show no region with $E_a = E_h$, since the region where (4.5) holds, with $E_a = \frac{1}{2}E_h$, runs directly into that of (4.7). The preexponential factor in the former region is about 10, whence [from Eq. (4.5)] $w_e \sim 10^5$ sec^{-1}. This is the limiting value at low temperatures, and is determined by tunneling.

When w_h and w_e get too large, the number of NN_1 "acceptors" is too small for holes to be recaptured before they recombine. Quasiequilibrium is then no longer established, and the conditions for superlinearity disappear. This is presumably the case in material of low purity; and also for NN_3, where E_e is no greater than E_h, so that w_e is already large at temperatures where thermal ionization of the hole is taking place.

V. CONCLUSIONS

From this work we can draw the following conclusions concerning the quenching of luminescence in GaP:N.

Below 100 K, quasiequilibrium is not usually established between bound excitons, free excitons, and free particles. Consequently, band-gap excitation cannot be used to obtain reliable quenching data. Selective excitation of the center of interest is essential.

The quenching mechanism for each N or NN_i center at low temperatures is loss by thermal excitation of either a free exciton or a free hole, whichever has the lowest binding energy.

At high concentrations quasiequilibrium can be established between excitons bound to NN_1 centers and free holes, once the hole traps in the crystal are saturated. This leads to superlinear photoluminescence over a factor of up to 10^4 in pump power. The question of what happens to the elec-

tron, left attached to NN_1 when the hole has es-
caped, is still outstanding.

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APPENDIX: DETAILED BALANCE FOR THE N EXCITON

It is well known that the 1S "ground" level of the
exciton bound to isolated nitrogen is split by ex-
change into a $J = 1$ and $J = 2$ level, the latter lying
0.8 meV below the former. In an unstrained crys-
tal only the $J = 1$ no-phonon transition is allowed
(the "A line"); however, at low temperatures
"B line" emission is observed from the $J = 2$ level
because of various symmetry-breaking processes.
The integrated absorption cross section $\int \sigma \, d\nu$ of
the A line has been measured very accurately by
Lightowlers et al.[16] The Einstein relation then
gives the spontaneous no-phonon emission rate[27]

$$w_{NP} = 8\pi n^2 \nu^2 \frac{g_l}{g_u} \int \sigma \, d\nu \ . \tag{A1}$$

Here ν is the wave number in cm^{-1}, g_l/g_u the de-
generacy ratio between lower and upper states,
and n the refractive index. The total radiative
rate is given by

$$w_A = e^S w_{NP} \ , \tag{A2}$$

where e^{-S} is the Debye-Waller factor, i.e., the
ratio of no-phonon emission to total emission, in-
cluding phonon-assisted transitions. S is called
the Huang-Rhys parameter, and in the case of
linear electron-phonon coupling represents the
mean number of phonons emitted in the optical
transition.

The Debye-Waller factor can be found experi-
mentally by measuring the integrated emission at
a temperature where it is predominantly from the
$J = 1$ level; i.e., above about 5 K. Care must be
taken to avoid self-absorption of the A line; fail-
ure to do this in the past has led to widely differ-
ent estimates of e^{-S}. We reduced this effect to a
minimum by using a low nitrogen concentration
($10^{16} \, cm^{-3}$), and by exciting with the shortest-

wavelength laser line available (4579 Å). The re-
sidual effect, which was only a few percent, was
corrected for by varying the exciting wavelength,
and hence the penetration depth, and extrapolating
to zero penetration. We find $e^{-S} = 0.33 \pm 0.02$, or
$S = 1.11 \pm 0.06$.

Reference 16 gives

$$\int \sigma \, d\nu = 9.5 \times 10^{-15} \ cm \ ,$$

and if we take $n = 3.4$,[28] $\nu = 1.87 \times 10^4 \ cm^{-1}$, g_u/g_l
$= 3$, we find for the $J = 1$ level

$$w_A = (29.8 \pm 1.5) \times 10^6 \ sec^{-1} \ . \tag{A3}$$

We have measured the radiative decay rate of the
$J = 2$ level in an unstrained crystal, in which it is
entirely due to phonon-assisted emission, and
found it to be $w_B = (1.6 \pm 0.2) \times 10^5 \ sec^{-1}$. This
makes a negligible contribution to the total w_R at
high temperature, which is given by $w_R = \frac{1}{8}(3 w_A + 5 w_B)$.

The fluorescent lifetime measurements of Cuth-
bert and Thomas[11] give $w_A = (26 \pm 2) \times 10^6 \ sec^{-1}$.
The probability of there being any appreciable
nonradiative contribution is thus less than 15%.
In view of the fact that multiphonon nonradiative
decay would involve the emission of some 40 pho-
nons, this is perhaps not surprising. In the case
of the doubly occupied oxygen donor, where multi-
phonon relaxation is known to be important,[5] the
coupling to the phonons is much stronger (i.e., S
is larger), and the number of phonons to be emit-
ted is less.

No precise calculation is possible for the exci-
tons bound to NN pairs since the concentration of
pairs is not independently measurable. However,
the fact that neither the $J = 1$ lifetimes[10] nor the
$J = 2$ lifetimes[15] differ appreciably from those for
the N exciton[11] indicates that nonradiative decay
is negligible in these cases too.

If multiphonon nonradiative decay is small at
0 K, it will remain so as the temperature is
raised until the Debye temperature is approached.
By this time other nonradiative processes are
dominant.

This detailed balance analysis has shown that
the radiative efficiency of the luminescing bound
excitons is essentially 100% at low temperature
and low concentration. It does not rule out the
possibility that some fraction of the bound excitons
does not luminesce at all, but decays entirely
nonradiatively.

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[18] These data must be interpreted with caution since even at the lower concentration shown ($[N] = 2 \times 10^{17}$ cm^{-3}) the absorption at the peak of the A line is so strong that nonradiative surface recombination can be an important factor. The fact that the curves for $[N] = 2 \times 10^{17}$ and $[N] = 1.8 \times 10^{18}$ differ only by a constant factor suggests that the effect of surface recombination, which, if present at all, will be more important at the higher concentration, is independent of temperature in the range studied.

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