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Exciton transfer at low temperature in $Ga_xIn_{1-x}P$:N and $GaAs_{1-x}P_x$:N

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The time-resolved luminescence of excitons bound to isolated nitrogen traps in $Ga_xIn_{1-x}P$ ($x>0.96$) has been investigated under resonant and above-the-band-gap picosecond laser excitation at $T=5$ K. We observe the dynamics of exciton tunneling both between and within the two main bands N_x and A_0 seen in the alloy spectra. The results are a direct proof of the very efficient transfer which occurs for excitons bounds to isolated nitrogen atoms surrounded by four Ga near neighbors (N_x band) to nitrogen atoms with a three-Ga—one-In environment (A_0 band). An analytic model for these transfer mechanisms fits the measured time evolution of the luminescence spectra for $Ga_xIn_{1-x}P$:N. The same model also describes previously published data for $GaAs_{1-x}P_x$:N.

I. INTRODUCTION

The studies of excitons bound to nitrogen isoelectronic traps in $Ga_xIn_{1-x}P$ and $GaAs_{1-x}P_x$ semiconductor alloys are of considerable interest because they reveal both the local disorder due to the alloying state and the spatial and spectral transfer of excitation in such partially disordered systems. In the N-doped GaP binary compound, an isolated nitrogen atom in the column-V substitutional site may bind an exciton, creating a discrete electronic level to which a very narrow line is associated in optical spectra.[1] In the substitutional alloys, excitons are still localized at the nitrogen atoms. However, they now sample the differing local configurations which exist around the nitrogen atoms.[2,3] This gives rise to different electronic states with varying energies. Thus, luminescence spectra in the alloys consist of either a single structureless broad band[2,4] or several bands,[3] depending on the relative importance of the energy difference between these states caused by the different local configurations.

In $GaAs_{1-x}P_x$:N the principal energy variation of excitons bound to isolated nitrogen (N_x) is due to the 13 As-P possible configurations which may occur statistically within the shell of the 12 second-nearest neighbors of the N atoms. The energy difference between each of these levels is of the order 1—2 meV, with each of them being broadened by more distant As-P configurations.[2] As a consequence of these many possible local configurations surrounding an N site, the combined exciton level widens to form the single broad band seen in luminescence and excitation spectra.[2,4] The energy shift of this band observed at $T=2$ K between the two types of spectra has been attributed to a transfer of excitons from high energy N_x sites to lower energy N_x sites.[2] With time-resolved luminescence measurements, the emission spectrum was observed to gradually shift towards lower energy with time.[5] Thus the cw emission comes principally from N_x sites of low energy within the density of states for N impurities. This observed energy relaxation inside a broad band was a direct proof of the spatial and spectral diffusion of the N_x excitons, i.e., of N-bound exciton migration from one isolated nitrogen to another. Even though the diffusion is an energy relaxation process, the N_x emission line shape in cw luminescence spectra does not correspond to thermal equilibrium (in that case at $T=2$ K it would fall sharply on the high-energy side). This feature was explained by a model developed by Kash[6] who was able to give a quantitative prediction of the N_x cw emission line shape in agreement with experiments.

The study of $Ga_xIn_{1-x}P$:N has not been so advanced. The problem of the nitrogen isoelectronic center in this alloy looks somewhat different from $GaAs_{1-x}P_x$:N. For $Ga_xIn_{1-x}P$ alloys, the local disorder around nitrogen atoms occupying column-V substitutional sites occurs not on the twelve second-nearest-neighbor sites as in $GaAs_{1-x}P_x$, but instead on the four neighbors immediately bonded to the N defect. Experimentally, one observes additional bands in the luminescence spectra of $Ga_xIn_{1-x}P$:N alloys[3,7–9] compared to the single one seen in $GaAs_{1-x}P_x$:N. A systematic study of GaP-rich $Ga_xIn_{1-x}P$:N samples at $T=4.2$ K shows clearly that two nitrogen exciton bands characterize the high-energy part of the luminescence spectra of these alloys.[3,7] By investigating these features for $Ga_xIn_{1-x}P$:N with different nitrogen concentrations and at various temperatures, together with the study of cw excitation spectra, one of us has proposed[3] that the high-energy band (N_x) was due to N surrounded by four Ga atoms as first neighbors and the lower one (originally named[7] A_0) to N surrounded by three Ga and one In with an important exciton transfer rate between both. The energy difference between the energy maxima of these two bands is 12 meV for $x=0.99$. The other configurations (two-Ga—two-In, etc.) are very low in concentration for Ga-rich materials and not easily observed.[3] By developing a theory based on a cluster embedded in an effective alloy medium, it has been possible recently to account for this value of the energy difference between the two alloy-split levels.[10]

In the first part of this paper we provide and discuss experimental data on GaP-rich $Ga_xIn_{1-x}P$:N. In particular, we present time-resolved luminescence spectra with a time resolution of 250 psec which allows us to see, for the first time, the dynamics of excitons tunneling both between (interband) and within (intraband) the two bands N_x and A_0. This investigation confirms the interpretation proposed in Ref. 3 and gives a direct proof of the very efficient tunneling which occurs at low temperature for excitons bound to isolated nitrogen surrounded by four Ga atoms to nitrogen centers with a three-Ga—one-In local environment.

The second part of the paper gives a quantitative interpretation of these direct transfer processes observed both in $GaAs_{1-x}P_x$ and $Ga_xIn_{1-x}P$ at low temperature. This approach is based on the analytic theory developed by Kash,[6] which assumes that an exciton tunnels to sites of lower energy until a "local energy minimum" site is reached. This site is a minimum in energy for the bound exciton states within a sphere of radius R_0, R_0 corresponding to a characteristic tunneling distance which grows logarithmically with time. In both $GaAs_{1-x}P_x$:N (intraband tunneling) and $Ga_xIn_{1-x}P$:N (intraband plus interband tunneling) we are able to fit the measured time evolution of the luminescence to the theory.

II. EXPERIMENTAL METHODS

The $Ga_xIn_{1-x}P$:N samples were grown by liquid-phase epitaxy on GaP substrates under an ammonia-hydrogen mixture to achieve the nitrogen doping.[11] The homogeneity of the composition was checked from measurements in many points of the surface and along a beveled edge (layer thickness $\simeq 20\ \mu m$) by electron microprobe analysis (Cameca MS 46). By performing low-temperature optical-absorption measurements, we were able to determine the nitrogen-doping level.[12]

The time-resolved luminescence measurements were performed with a mode-locked Ar^+ laser operating at 4880 Å synchronously pumping a cavity-dumped dye laser. The energy and the duration of the dye-laser pulses using Coumarin-6 dye were, respectively, 3 nJ and 20 psec. The pulse-repetition rate was a convenient submultiple of the 70 MHz Ar^+ pulse train, usually 700 kHz. Samples were mounted in a gas-exchange liquid-He Dewar and held at $T=5$ K. Luminescence was collected in backscattering geometry by a Spex 1401 double monochromator and focused onto a Varian Associates VPM154A1 photomultiplier. The luminescence kinetics at a particular photon energy were measured with a time-correlated single photon counting system described in previous work.[5] Time resolution was 250 psec full width at half maximum.

III. RESULTS

Figure 1 presents $Ga_xIn_{1-x}P$:N luminescence spectra recorded with excitation energy above the band gap, both cw [Fig. 1(a), solid curve] and time resolved [Fig. 1(b)]. The cw excitation spectrum [Fig. 1(a), dashed curve] is detected at the LO-phonon replica of A_0. The big difference observed between the cw luminescence and the excitation spectra in Fig. 1(a) may be understood from the time-resolved luminescence spectra (TRL) of Fig. 1(b). The TRL at very short times (< 1 nsec) resemble the excitation spectrum. As time increases after the pulse, the TRL become progressively more like the cw luminescence spectrum. More precisely, three main features occur in the TRL spectra as the time increases. (i) The ratio between the two peaks A_0 and N_x is completely inverted (the ratio A_0/N_x steadily increases from 0.5 at 200 psec to more than 100 at 80 nsec). (ii) There is an energy shift of $\simeq 3$ meV to lower energy for the higher band (N_x), with most of this dynamic shift occurring within the first nanosecond. (iii) There is also a corresponding shift of $\simeq 3$ meV within the lower band (A_0), but over a longer time scale than for the N_x band.

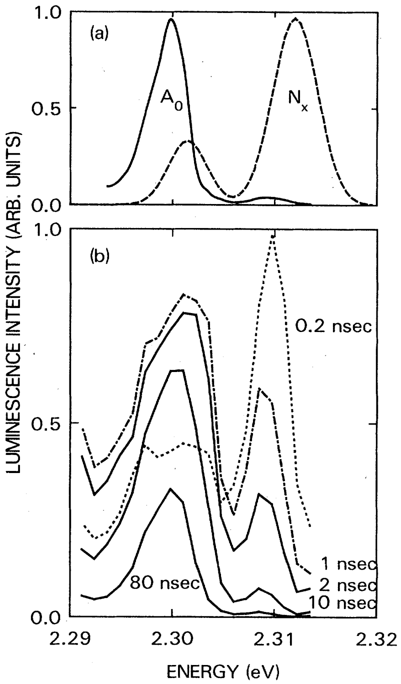

FIG. 1. Luminescence and excitation spectra of $Ga_xIn_{1-x}P$:N, $x=0.99$, $[N]=10^{18}\ cm^{-3}$, $T=5$ K. (a) cw luminescence spectrum (solid curve) under above-band-gap pumping and cw excitation spectrum (dashed curve) observed at the LO-phonon replica of the A_0 band. (b) time-resolved luminescence spectra under above-band-gap pumping.

All these observations reflect a large energy relaxation within and between both the N_x and A_0 bands. To observe this process more directly we have measured TRL spectra for an excitation energy resonant with the maximum of the N_x band seen in the excitation spectra. These data are plotted in Figs. 2 and 3. Figure 2 shows representative kinetic curves of the luminescence intensity at two energies within each of the two bands. The delay found here between the maxima of the two pair of curves corresponds to the time necessary for most of the excitons to diffuse from the N_x-like (i.e., four Ga nearest neigh-

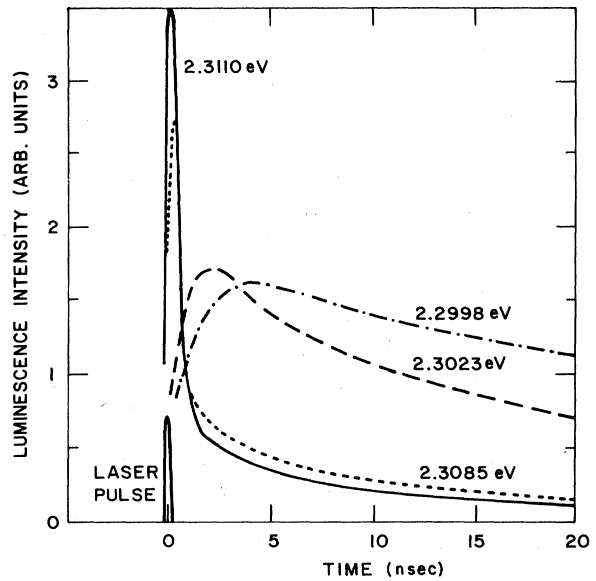

FIG. 2. Kinetic of luminescence of $Ga_xIn_{1-x}P$:N for $x=0.99$, [N]$=10^{18}$ cm^{-3}, and $T=5$ K. Laser excitation was resonant in the N_x band at 2.3120 eV. The solid and dotted curves correspond to two energies within the N_x band, the dashed and dotted-dashed curves to two energies within the A_0 band.

bors) to the A_0-like centers (three Ga and one In nearest neighbors). From a large family of such decay curves we deduce the TRL spectra shown in Fig. 3 for these resonant excitation conditions. Again, as in Fig. 1(b) for above-gap excitation, the A_0-to-N_x intensity ratio varies very rapidly with the time and the energy shift within the N_x band is faster than that found with A_0.

The same set of experiments were performed for samples with different indium and nitrogen concentration. For $Ga_xIn_{1-x}P$:N with higher indium amount ($x \leq 0.96$), the N_x band appears only as a shoulder on the A_0 one.[9] Thus, the TRL are not as clear as the one for $x > 0.96$: They show an energy shift of the broad A_0 main band to low-energy side as time increases after the laser pulse. The effect of different nitrogen concentration was investigated for a $Ga_{0.99}In_{0.01}P$:N sample with [N]$=3\times10^{17}$ cm^{-3}. We obtained data very similar to that presented in Figs. 1—3, except we do not reach an A_0-to-N_x intensity ratio as high as the one observed for [N]$=10^{18}$ cm^{-3}.

Taken together, all these dynamic results suggest that excitons bound to differing N centers in $Ga_xIn_{1-x}P$ efficiently transfer from site to site by spatial and spectral diffusion. This exciton migration (spatial diffusion) with energy dissipation (spectral diffusion) occurs on the same time scale as the one observed by Collet *et al.*[5] in $GaAs_{1-x}P_x$:N and could again be attributed to tunneling processes assisted by acoustic phonons. These transfer mechanisms, which depend on both the energy and the distance between N sites, have been used successfully to describe the GaP:N luminescence and excitation spectra.[13,14] In the current example of $Ga_xIn_{1-x}P$:N, the different exciton transfer processes that we observe at low temperature are indicated schematically in Fig. 4. (Thermally assisted transfer has been seen in these materials at higher temperature and will be reported in another publication.[15])

From our experimental results we know that the N_x intraband tunneling processes occur mainly into the first nanosecond after excitation, while the A_0 intraband and $N_x \rightarrow A_0$ interband tunneling take place over of 50 nsec after the pulse. The fact that the observed A_0 intraband tunneling rate is much slower than that within the N_x band is a natural consequence of the smaller density of states of the A_0 centers, as reflected in the excitation spectrum, Fig. 1(a). In this connection we should note, however, that the ratio of A_0-to-N_x sites as measured in the

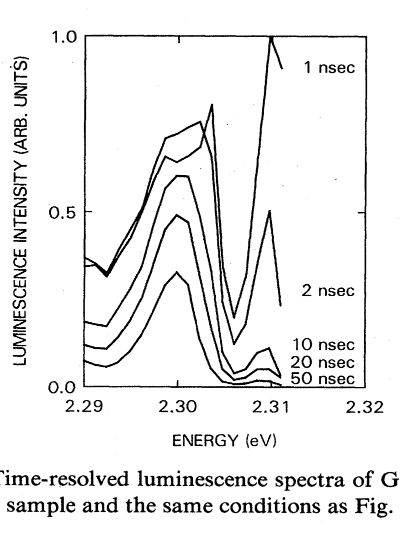

FIG. 3. Time-resolved luminescence spectra of $Ga_xIn_{1-x}P$:N for the same sample and the same conditions as Fig. 2.

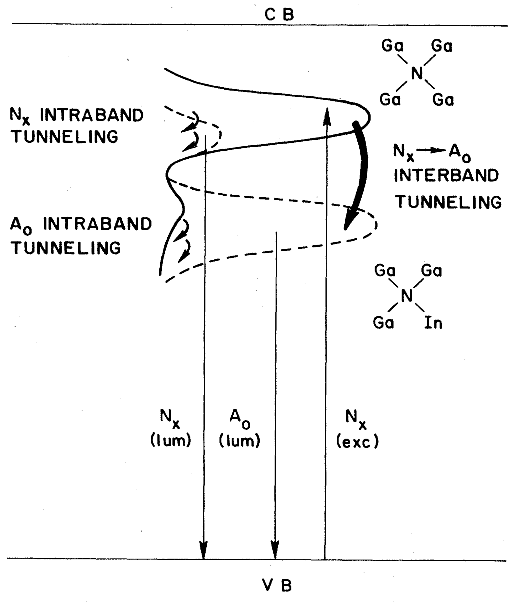

FIG. 4. Schematic of the model proposed to explain the nitrogen-bound exciton transfer processes seen at low temperature in $Ga_xIn_{1-x}P$:N alloys.

excitation spectrum is larger than expected from a purely random distribution of N atoms in the Ga-In matrix. This suggests that local segregation occurs for the N impurities, i.e., the N atoms prefer sites with an In atom as a nearest neighbor. Such a segregation effect gives a probability of NIn_1 pairs (notation analog to that of the NN_i pairs[1]) higher than its value in randomly disordered alloys. We suggest that atomic size considerations between Ga, In, P, and N atoms could explain this segregation. N atoms are smaller than the P atoms they replace, and In atoms are bigger than Ga atoms, therefore the NIn_1 pair association could minimize the strains in the alloy lattice.

IV. THEORETICAL APPROACH

In this section we quantitatively consider the problem of excitons hopping between different localized states of differing energy. In the case of the nitrogen-doped III-V alloys, these localized states are the N centers surrounded by different local configurations of As-P or Ga-In. We start with the usual form for the hopping rate[16,17]

$$\nu_{ij}=\nu_0\exp-\left[\frac{2R_{ij}}{a_0}\right]\times\begin{cases}\exp(E_i-E_j)/kT & \text{if } E_i<E_j\ ,\\ 1\ \text{if } E_i>E_j\ ,\end{cases}$$

where ν_{ij} is the hopping rate between a site occupied by an N-bound exciton at an energy E_i and an unoccupied site j at an energy E_j. Here, R_{ij} is the distance between the sites i and j, a_0 is the effective exciton radius and ν_0 is a constant corresponding to the attempt-to-hop frequency. At low temperatures we can assume that the hopping towards the sites of higher energy ($E_i<E_j$) is negligible (this hopping-up process is thermally activated[14,15]). This leads to a transfer rate

$$\nu_{ij}(R_{ij})=\nu_0\exp\left[\frac{-2R_{ij}}{a_0}\right] \tag{1}$$

corresponding to a mechanism in which excitons may only hop to sites of lower energy (the term "tunneling" is usually used for this process).

Following the procedure developed by one of us,[6] the inverse tunneling rate ν_{ij}^{-1} may be regarded as a typical time t for a tunneling event between N traps separated by R_{ij}. This leads to the concept of a characteristic tunneling radius R_0 which varies with time according to the expression.

$$R_0(t)=\frac{a_0}{2}\ln(\nu_0 t)\ . \tag{2}$$

Statistically, then, an exciton trapped on a nitrogen site i

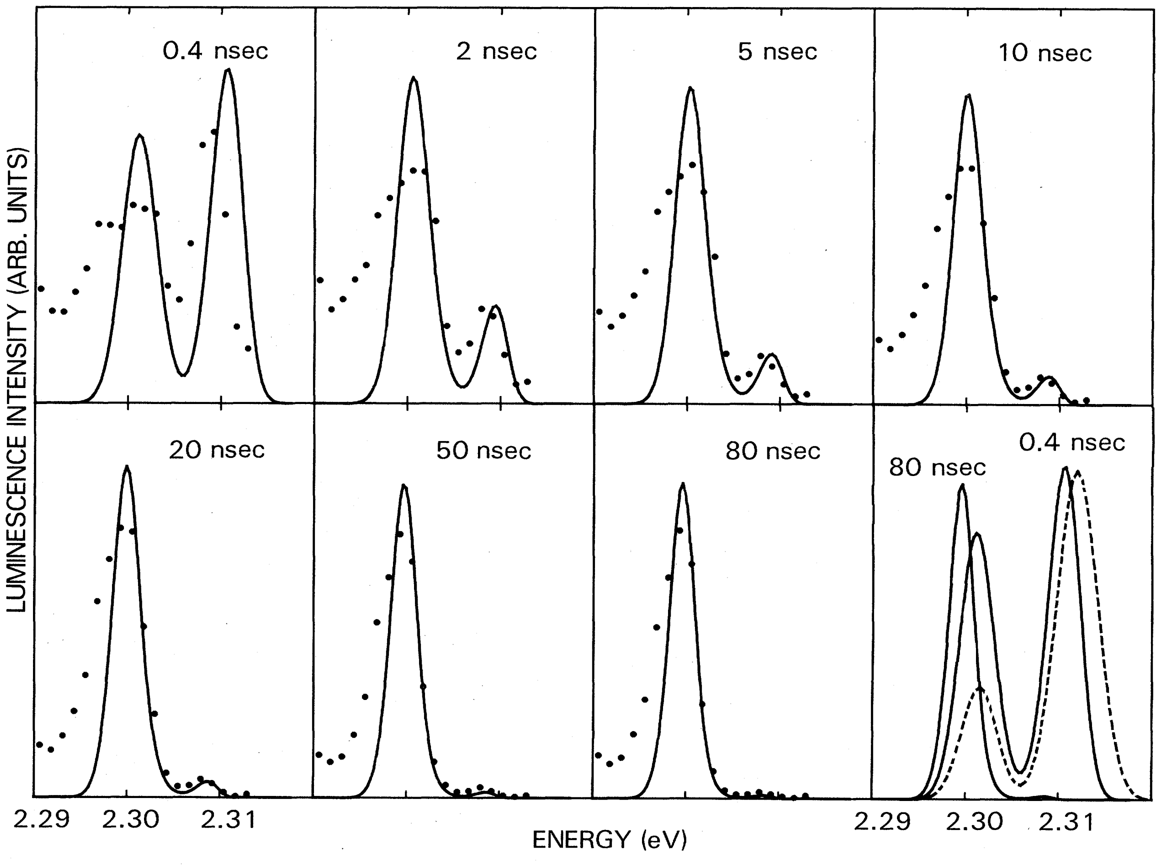

FIG. 5. Comparison of the experimental time-resolved luminescence data (filled circles) with the analytic theory, Eq. (3) (solid curves) for $\mathrm{GaAs}_{1-x}\mathrm{P}_x$:N. Data are for $x=0.96$, $[\mathrm{N}]=10^{18}\ \mathrm{cm}^{-3}$, and $T=5$ K, under above-band-gap excitation. To make the spectral shift more apparent, the 0.4 and 80 nsec theory curves are repeated in the final frame, along with the initial Gaussian used for the density of states $n_0(E)$ (dashed line).

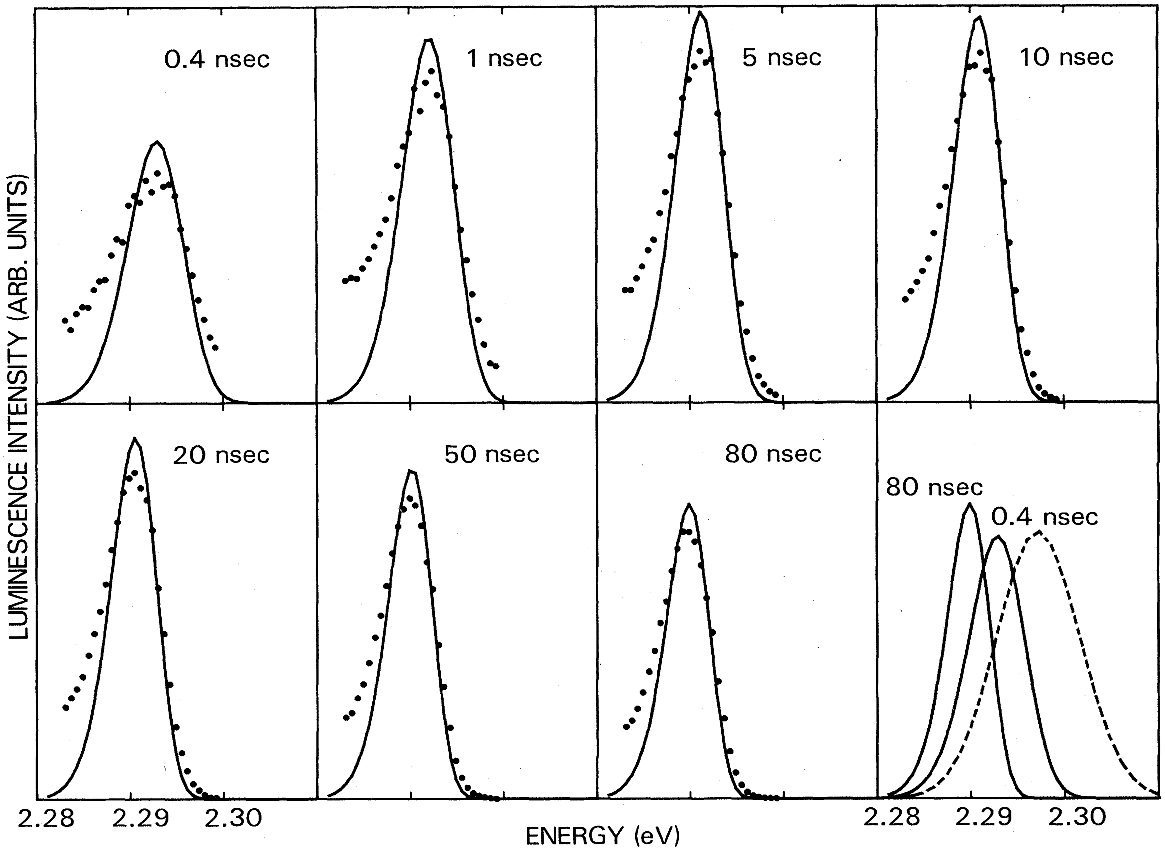

FIG. 6. Same as Fig. 5 but for the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$:N data reported in Fig. 1(b).

will tunnel to a nearby N-site j of lower energy at the time t when the sphere of radius $R_0(t)$, centered on site i, just encompasses the site j. A site having no lower energy sites within R_0 may be called a local-energy-minimum site. Under pulsed excitation, the time evolution of the distribution of these local-energy-minimum sites describes the time evolution of the N-bound exciton population, i.e., the time-resolved luminescence spectra. If $n_0(E)$ is the density of exciton traps (normalized to unity) and if each site has, on the average, m neighboring N sites within R_0, then the distribution of local-energy-minimum sites is given by

$$n_m(E)=n_0(E)P_m(E)$$
$$=n_0(E)\left[\int_E^{\infty} n_0(E')dE'\right]^m , \tag{3}$$

where $P_m(E)$ is the probability that a site of energy E is a local-energy minimum; this is the same as the probability that all other m sites are each of energy greater than E. From the definition of m and Eq. (2), the relation between m and R_0 is

$$m=\tfrac{4}{3}\pi R_0^3[\mathrm{N}] , \tag{4}$$

where [N] is the concentration of nitrogen centers ($[\mathrm{N}]\simeq 10^{18}$ cm^{-3} for the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ and $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ samples reported here). We deduce the density of states $n_0(E)$ from our measured excitation spectra by fitting them to a single Gaussian for $\mathrm{GaAs}_{1-x}\mathrm{P}_x$:N (Fig. 5) and to a pair of Gaussians for $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$:N (Fig. 6).

The quantity $n_m(E)$ may be derived directly from the time-resolved luminescence data. Because *a priori* values of a_0 and ν_0 are unknown, each TRL spectrum must be fit with Eq. (3), allowing m and the overall amplitude to vary as needed. The values of m thus obtained are compared to those given by Eq. (4). By choosing $a_0=22$ Å and $\nu_0=1.3\times 10^{13}$ sec^{-1} for $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ data, and $a_0=26$ Å and $\nu_0=1.5\times 10^{12}$ sec^{-1} for the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ data, self-consistent determination of m versus t may be deduced. Equation (3), using the final values of $m(t)$ computed from Eq. (4), fit the time-resolved luminescence data at all times. These values of a_0 and ν_0 obtained for $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ and $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ alloys both agree with earlier estimates found for exciton tunneling in GaP:N.[13,14]

Figures 5 and 6 compare the calculated spectra with the experimental data. Together, these results show that our model accounts for all of the main features of the time-resolved luminescence spectra.

(i) The energy shift with time of the maximum energy of the N-exciton emission band in $\mathrm{GaAs}_{1-x}\mathrm{P}_x$.

(ii) The narrowing of this emission band in $\mathrm{GaAs}_{1-x}\mathrm{P}_x$:N with time.

(iii) The strong variation of the ratio between N_x and A_0 in $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$:N which results from the $\mathrm{N}_x\rightarrow A_0$ interband tunneling.

(iv) The energy shift of each of these N_x and A_0 bands in $Ga_xIn_{1-x}P$ as a consequence of intraband tunneling.

V. CONCLUSION

In this paper we have reported time-resolved luminescence spectra in GaP-rich $Ga_xIn_{1-x}P$:N and have observed the dynamics of excitons tunneling both between (interband) and within (intraband) the two bands N_x and A_0 occurring in these alloys. These results explain the strong difference observed at low temperature between the excitation and luminescence spectra: The excitons bound to isolated nitrogen impurities surrounded by four Ga atoms (N_x band) efficiently transfer by spatial and spectral diffusion, to states of lower energy derived from nitrogen centers surrounded by a three-Ga—one-In environment (A_0 band). At $T=5$ K, the dominant transfer processes are essentially the migration of excitons down to states of lower energy as opposed to thermally activated hopping. We have reported here the first observation of such a transfer between two distinct exciton bands which arise from the random-disorder alloy splitting. Using an analytic model for these transfer mechanisms measured time evolution of the luminescence spectra were well described in both $Ga_xIn_{1-x}P$ and $GaAs_{1-x}P_x$ alloys doped with nitrogen.

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