

Stochastic transfer of excitations and enhancement of the NN_α -pair luminescence in GaP:N

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We present a stochastic model of exciton transfer in a dilute system and solve the master equations. For GaP:N, this model accounts for the experimental features of the steady-state luminescence spectrum: enhancement of NN_α -pair lines with N concentration, dependence on temperature and on excitation intensity.

There is currently considerable interest in the use of stochastic methods¹ to discuss the transfer of excitations in partially disordered systems. An example is the spectral diffusion in luminescent materials.²⁻⁴ This phenomenon occurs when, owing to the disorder, (i) energies of the luminescent centers are distributed on a continuous or discrete spectrum (inhomogeneous broadening) and (ii) excitations are able to migrate from center to center before recombining. The connection with stochastic methods¹ is obvious: The migration of excitation corresponds to a random walk with a random distribution of hopping probabilities.

This Rapid Communication is aimed to present a stochastic model accounting for the enhancement of the luminescence associated to NN_α pairs in GaP.⁵ A nitrogen impurity in GaP binds an exciton and this bound state may be altered by the presence of nearby nitrogen impurities. Besides the narrow line associated with an isolated nitrogen center (the *A* line), lines at lower energies have been identified in the luminescence spectrum of GaP and attributed to discrete pairs NN_1, NN_2, \dots up to NN_{10} .⁵ Time-resolved experiments⁶ have demonstrated the existence of a transfer mechanism by phonon-assisted hopping which allows the excitation to migrate down to lower-energy pairs. Based on this mechanism, the model quantitatively accounts for the importance of the luminescence coming from the NN_α pairs, even at low N-doping concentration (e.g., $N_t = 3 \times 10^{17} \text{ cm}^{-3}$) and for the N-concentration dependence of this luminescence enhancement. This agrees with a series of new experimental data specifically devised to test the model. Moreover, the model allows us to make quantitative predictions regarding the temperature dependence of the luminescence spectra and its nonlinear dependence on excitation intensity, which are borne out by our experiments.

When studying the migration of an excitation on a lattice,

one is generally interested in the quantity $p_n(t)$, the probability that an excitation created at time zero on the site zero will be at time t on the site n . On a disordered lattice, the calculation of $p_n(t)$ implies performing configuration averages.⁷ The dilute character of the problem in hand allows us to replace configuration averages by averages over the distances of the nearest neighbors. These kinds of averages are most useful in other problems of dilute impurities in semiconductors, namely, magnetic susceptibility⁸ or infrared absorption.⁹ However, in a transfer problem, one needs to consider at least the two nearest neighbors of a given center, the associated probabilities being introduced in the master equation. Another feature of our problem is that the energy distribution and the one of hopping probability are not independent but both depend on the probability distribution of the nearest neighbors.

The probability π_i for a N center to have its first neighbors at a distance $r_\alpha < r_1 < r_\alpha + \delta r_\alpha$ and its second one at $r_\beta < r_2 < r_\beta + \delta r_\beta$ is given,¹⁰ for $r_\beta > r_\alpha$, by

$$\pi_i = (4\pi N_t)^2 \int_{r_\alpha}^{r_\alpha + \delta r_\alpha} dr_1 \int_{r_\beta}^{r_\beta + \delta r_\beta} dr_2 r_1^2 r_2^2 \exp\left(-\frac{4\pi}{3} N_t r_1^3\right),$$

where N_t is the total nitrogen concentration. The concentration N_i of such an i center (corresponding to a triplet $NN_\alpha N_\beta$ configuration) is $N_i = \pi_i N_t$ and we assume its energy to be given by

$$\epsilon_i = \epsilon_0 - \Delta\epsilon(r_\alpha) - \Delta\epsilon(r_\beta), \quad (2)$$

where ϵ_0 is the energy of the isolated center and $\Delta\epsilon(r)$ is taken from the experiment on NN_α pairs.⁵ The concentration n_i of bound excitons at energy ϵ_i , $n_i = N_i f_i$ is the solution of the master equation:

$$\begin{aligned} \frac{dn_i}{dt} = & G_i - \frac{n_i}{\tau_{R,i}} - \sum_{\mu=\alpha,\beta} \gamma n_i N_{T,\mu} \exp\left(-\frac{\epsilon_i - \epsilon_\mu}{k_B T}\right) + \gamma N_i (1 - f_i) \sum_{\mu} n_\mu \\ & - CN_i \sum_{\nu=\alpha,\beta} r_\nu^2 \exp(-2\rho r_\nu) \sum_j f_i (1 - f_j) \exp(\delta_{ij}) J(j, \nu) + C \sum_j N_j \sum_{\nu=\alpha,\beta} r_\nu^2 \exp(-2\rho r_\nu) f_j (1 - f_i) \exp(\delta_{ij}) J(j, \nu). \quad (3) \end{aligned}$$

In this expression, G_i accounts for the optical generation of excitons at energy ϵ_i . For N-bound excitons, there is no other decay channel than the radiative recombination one¹¹ specified by $\tau_{R,i}$. $\tau_{R,i}$ depends on ϵ_i as $\tau_{R,i} = C_R(\epsilon_i - \epsilon_\Gamma)^{-2}$, ϵ_Γ being the energy of the Γ minimum of the conduction band and C_R taken from the direct experiment.¹² In (3) the third term accounts for the thermally activated transfer of an exciton from a bound level at ϵ_i to the free-exciton band at ϵ_x or to the electron-hole band at ϵ_f . $N_{T,\mu} = 2(2\pi m_\mu^* k_B T/h^2)^{3/2}$ is the free-exciton ($\mu = x$) or the electron-hole-pair ($\mu = f$) density of states. In absence of transfer between N centers, this third term is responsible for the quenching of the luminescence.¹¹ The fourth term in (3) is the reverse of the third one and accounts for the generation of exciton at ϵ_i either from the free-exciton or from the electron-hole band (γ is a constant). The fifth term in (3) specifies the exciton transfer from an i triplet to a j one. $W_{ij} = Cr_{ij}^2 \exp(-2\rho r_{ij}) \exp\delta_{ij}$, corresponds to the phonon-assisted hopping mechanism.¹³ Owing to the detailed balance requirement,¹⁴ $\delta_{ij} = (\epsilon_i - \epsilon_j)/k_B T$ for $\epsilon_i < \epsilon_j$ and $\delta_{ij} = 0$ otherwise. The function $J(j, \nu)$ is nonvanishing only if the center j is the first ($\nu = \alpha$) or the second ($\nu = \beta$) neighbor of i ; $\sum_j J(j, \nu) = 1$.

Finally, the last term in (3) accounts for the reverse transfer from j to i . One may also take into account, in an average way, transfers from or to more distant neighbors. Should one define for r_α a set of discrete values (for the pairs NN_1 to NN_{10}) plus a set of average values for the more distant pairs and the same set of average values for r_β , then, through (1) and (2), π_i and ϵ_i are specified (we have neglected configurations like NN_1N_1). The luminescence of a discrete pair line NN_α will be obtained by adding contributions of all the triplets $NN_\alpha N_\beta$ which have their first neighbor at the distance r_α . The system of equations (3) is supplemented by two equations which give the evolution of populations in the free-exciton band and in the electron-hole one.

We have not introduced any other deep traps¹⁵ which may play a role. For the sake of simplicity, we have neglected the $J=1, J=2$ splitting and restricted our discussion to the temperature range where the luminescence is dominated by the $J=1$ line. We have also neglected the phonon replica. The master equations are solved for the steady-state regime ($dn_i/dt = 0$). At low excitation, they are linearized by putting $1 - f_i = 1$. This allows one to calculate the quantities $n_i/\tau_{R,i}$ which are proportional to the luminescence intensity.

Most of our samples were epitaxially grown by liquid-phase epitaxy using an ammonia-hydrogen mixture above the melt to achieve the nitrogen doping. It is important to have a precise determination of the N-doping level in the epilayer: this is obtained by performing on each sample low-temperature-optical absorption measurements from which the N concentration can be deduced.¹⁶ In most of the experiments to be reported, luminescence was excited above the band gap. However, we have also studied the luminescence under excitation on the A line, with a tunable dye laser. As regards the T and N dependence of the luminescence, we did not observe any significant differences between both types of excitations; this observation is borne out by calculations. In addition, excitation spectra, detected on, e.g., the NN_1 line, were also recorded. The temperature was varied between 1.8 and 80 K and the power was changed from 0.1 to 20 mW (corresponding to a power density of about 1 W/cm²).

Typical luminescence spectra were observed with no evidence of emission originating from other impurities: (i) at low-N concentration ($\approx 10^{16}$ cm⁻³) the luminescence spectra are dominated by the A line and (ii) for concentration larger than 10^{18} cm⁻³ spectra are completely due to the NN_α lines. As pointed out in Ref. 6, the change in the statistics of NN_α pairs cannot explain this quenching of the A -line luminescence for $N_i > 10^{18}$ cm⁻³. This is confirmed by the absorption and luminescence excitation spectra which, at these concentrations, are still dominated by the A line.

At low N_i , most of the configurations are such that $\epsilon_j \approx \epsilon_0$ and $Cr_{ij}^2 \exp(-2\rho r_{ij})\tau_{R,0} < 1$. At higher concentration, though the probability of configuration with $\epsilon_j < \epsilon_0$ stays low, the transfer term becomes important, $Cr_{ij}^2 \exp(-2\rho r_{ij})\tau_{R,0} > 1$, i.e., the majority of excitons created at energy ϵ_0 transfer and recombine at lower energies. At low temperature, when upward energy transfers are negligible, one may estimate as a function of N_i , from equation (3) the ratio $R_i = n_0\tau_{R,0}/(\sum_i n_i\tau_{R,i})$ where n_0 is the exciton concentration at the A line energy. R_i varies rapidly between 0 and 1 for $3 \times 10^{16} < N_i < 10^{18}$ cm⁻³ (Fig. 1). This experimental variation is well accounted for by using in solving (3) $\rho = 32 \text{ \AA}$ and $C = 3 \times 10^{23} \text{ sec}^{-1} \text{ cm}^{-2}$, we note that this value of ρ is close to the one given in Ref. 6 but that Cr_{ij}^2 is lower than ω_0 in Ref. 6. This steady-state result is a strong evidence for the importance of the transfer mechanism in GaP:N.

From Eqs. (1) and (2) we have also calculated the absorption spectrum, proportional to $N_i/\tau_{R,i}$ and accounted, in agreement with experiment, for the differences between absorption and luminescence spectra in the concentration range $3 \times 10^{17} < N_i < 3 \times 10^{18}$ cm⁻³.

Let us now turn to the temperature dependence of, respectively, the A line and the NN_α -pair lines; some of them are displayed on Fig. 2(a). Noticeably, in the temperature range $5 < T < 40$ K, intensities of all the NN_α -pair lines exhibit some variations with T , like an increase rather than a monotonic decrease.^{17,18} These interdependent variations come about from the presence of two mechanisms in the transfer processes. On the one hand, for $\epsilon_i > \epsilon_j$, the transfer $i \rightarrow j$ is partially balanced by the transfer $j \rightarrow i$, as T increases, so the downward energy shift is less important. On the other hand, higher-energy lines are quenched [see the third term in (3)], while the lower-energy lines are not,

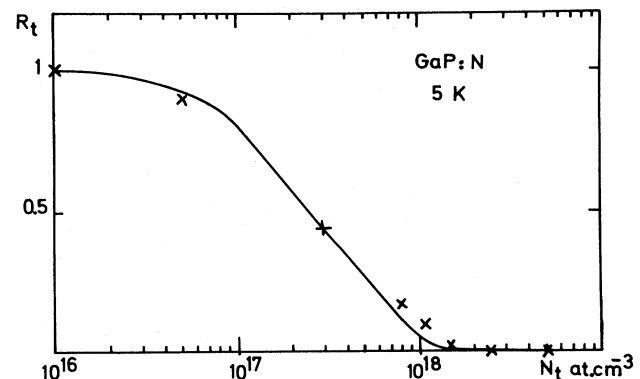


FIG. 1. (x) Experimental transfer ratio R_i corresponding to the luminescence intensity of the A line compared to that of all the excitonic lines due to nitrogen (—) calculated transfer ratio.

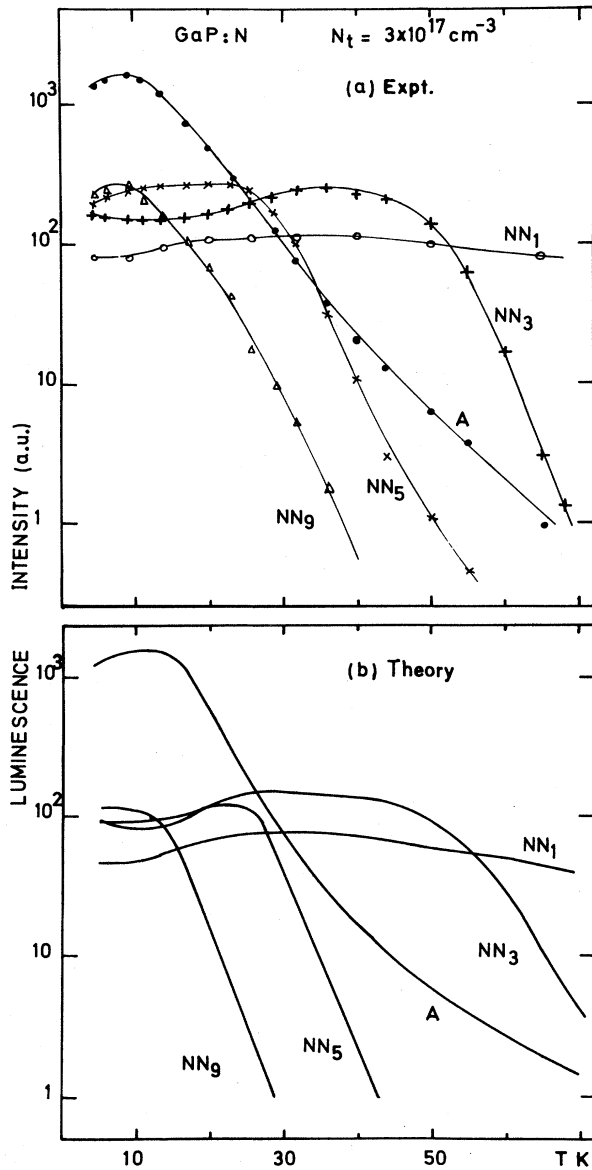


FIG. 2. Temperature dependence of the luminescence intensity of some excitonic lines due to nitrogen.

and, owing to the fourth term in (3), the free-exciton band and the electron-hole band redistribute excitons within the lower-energy configurations thus enhancing their luminescence. The full calculation (lower curve in Fig. 2) accounts for the features of the experiment: namely, (i) the A line is quenched for $T > 15$ K, (ii) the NN₁-line intensity does not change much in the whole temperature range, and (iii) intermediate-energy pairs are quenched at temperatures which scale with their binding energies. We have used a unique constant γ ; i.e., we have neglected any dependence of the capture cross section on the nature of either the initial or the final state. Finally, the system of equations (3) being nonlinear, one expects that, under strong excitation, transfer towards low-energy pairs for which $(1 - f_i) < 1$ will be less efficient, i.e., that the intensity of the corresponding lines will tend to saturate while the A line will increase

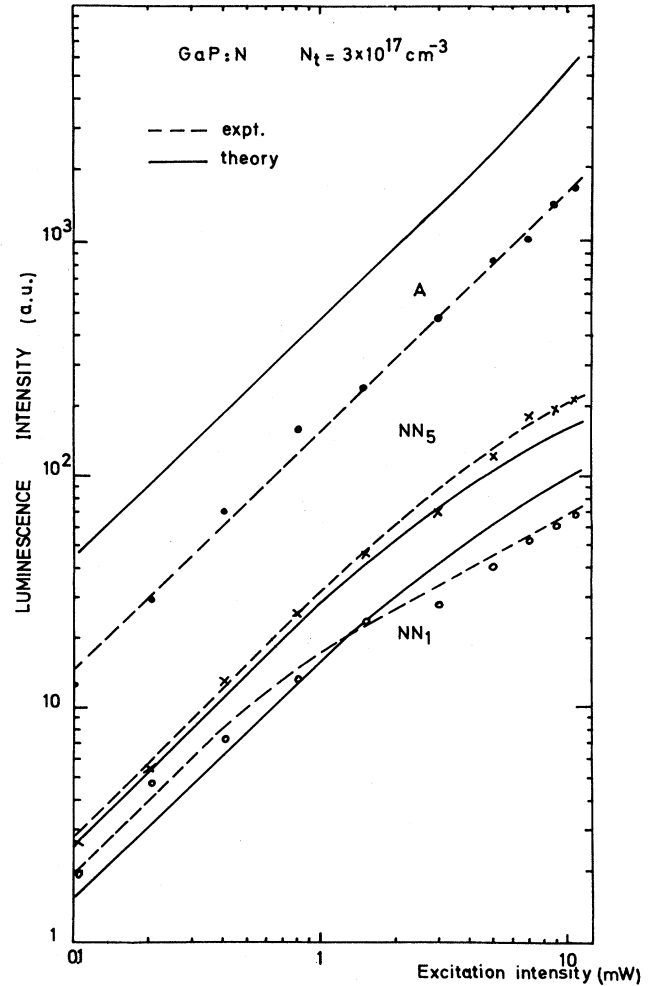


FIG. 3. Excitation intensity dependence of the luminescence intensity of A, NN₅, and NN₁ excitonic lines at 5 K.

linearly with the excitation intensity (or faster than linearly). This specific effect is experimentally observed (Fig. 3), in fair agreement with the calculation.

To summarize, we have presented a stochastic model of exciton transfer which, for the first time, accounts quantitatively for the giant enhancement of the lower-energy lines in the GaP:N luminescence spectrum, i.e., for the delocalization of N-bound exciton on the timescale $\tau_{R,0}$. As transfer probabilities depend on both energy and distance (variable range hopping), the model accounts for the temperature dependence of transfer efficiencies. Finally, the model would allow one to deal with other experimental aspects of the spectral diffusion (e.g., time dependence) or with other partially random systems (e.g., GaAs_{1-x}P_x:N).

Note added in proof. We are pleased to mention related work on exciton transfer which was published when this work was in proof [J. A. Kash, Phys. Rev. B **29**, 7069 (1984)].

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