# Radiative and nonradiative recombination of bound excitons in GaP:N. II. Nonlinear behavior of emission intensity versus excitation power of bound excitons due to exciton transfer

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The luminescence of the free excitons has been observed and its binding energy is thermally measured to be 21±4 meV, for the first time, in GaP:N under normal pressure using high excitation density. The nonlinear behavior of the emission intensity versus excitation power of the bound exciton $NN_1$ has been found. Both results mentioned are thought to be due to the inverse transfer of bound excitons from deeper centers to shallower ones or from bound excitons to free excitons.

## I. INTRODUCTION

In this work, we shall investigate the luminescence spectra of excitons in GaP:N with high excitation density, $10-10^8$ W/cm$^2$, and in the temperature range 65–135 K. Both the emission intensity versus excitation power of bound excitons and the temperature dependence of luminescence of the free exciton will be reported. We paid special attention to the binding energy of free excitons from the thermal-quenching process and the origin of the nonlinearity of emission intensity versus excitation density of the bound excitons and discussed the anomalous behavior of the luminescence as a function of excitation.

## II. FREE EXCITONS AND THEIR BINDING ENERGY

Thomas and Hopfild[1] investigated the spectra of GaP:N, and proposed that the energy level of the free excitons is approximately 11 meV above that of the isolated-nitrogen-trapped exciton. Sturge, Cohen, and Rodgers[2] obtained similar results for the absorption spectra of excitons of GaP:N. So far, the peak of the free exciton in GaP:N has not been seen directly in the photoluminescence spectra under atmospheric pressure. We have just carefully studied this problem and found, for the first time, the zero-phonon line of the free excitons with high excitation density at low temperature and obtained its binding energy by means of the thermoquenching.

The experiment of high excitation density was carried out with a 308-nm line of an Excimer EMG 102 laser which can reach a maximum density of about $10^8$W/cm$^2$.[3] In Figs. 1 and 2, the luminescence spectra of GaP:N for various excitation densities are shown, and the concentrations of nitrogen are, respectively, $5\times10^{17}$ and $7\times10^{18}$ cm$^{-3}$. Here, the excitation density $I_0$ is $2\times10^7$ W/cm$^2$.

In low excitation, the emission spectra include mainly peaks of the isolated nitrogen and its replica of transverse

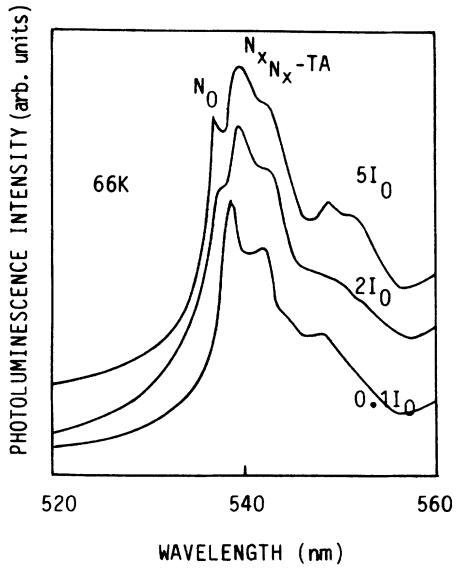


FIG. 1. Photoluminescence spectra of GaP:N for various excitation powers with [N] $\sim7\times10^{18}$ cm$^{-3}$ at 66 K.

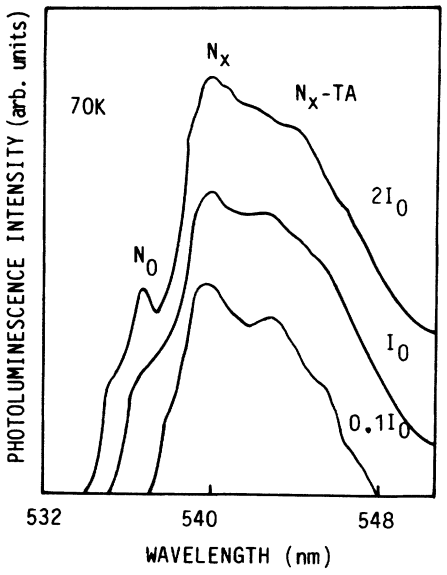


FIG. 2. Photoluminescence spectra of GaP:N for different excitation powers with [N] $\sim5\times10^{17}$ cm$^{-3}$ at 70 K.

 

acoustic (TA) phonon. The isolated-nitrogen-trapped exciton is denoted as $N_x$ and its TA phonon as $N_x$-TA. The peak $N_x$ increases with the excitation density at low temperature. When the excitation density reaches about $10^7$ W/cm$^2$, a new peak denoted $N_0$ occurs at 10.7±0.3 meV above the line $N_x$. From the temperature dependence of $N_0$ in Fig. 3, we get its activation energy, which is 21±4 meV.

According to Refs. 1 and 2, it is well known that the energy level of the free exciton is approximately 11 meV above that of the isolated-nitrogen-trapped exciton, and its binding energy is estimated to be about 17–22 meV.[4] Our results about energy position and binding energy of $N_0$ are in agreement with Ref. 4 within the experimental error. Thus, we believe that the new line $N_0$ appearing in the spectra originates in the radiative recombination of the free exciton.

When GaP:N is excited by light of above-band-gap energy, free excitons are first created, then trapped by nitrogen impurities, and become the bound excitons.[5] By virtue of temperature and tunneling effect, they may transfer from one center to the other, and in the same center there exists the exchange between the substrates $A$ and $B$ ($J=1,2$).[6] In short, the excitons may go to the ground state in the way of radiative or nonradiative transition. If the excitation density is not strong enough, free excitons are, to a great extent, trapped rapidly to turn into bound excitons. In this case, the luminescence of free excitons is too weak to be observed. The excitation density is so high that the deeper-centers-trapped excitons have been saturated and their interaction is strengthened. In view of this, the exciton transfer from the deeper centers to the shallower ones and/or from bound excitons to free excitons will be enhanced (see paper III in this series and Ref. 6). This kind of inverse transfer of the excitons increases with the excitation power.[6] Therefore, we may conclude that the inverse transfer of excitons caused by high excitation is a reason that we are able to observe the free-exciton luminescence. Since GaP is an indirect-band-gap material, the free-exciton emission must be phonon assisted.

## III. NONLINEAR BEHAVIOR OF EMISSION INTENSITY VERSUS EXCITATION POWER OF BOUND EXCITONS

The luminescence spectra of excitons in GaP:N have been well investigated.[1–8] With the increasing temperature and excitation density of experiment, both the zero-phonon lines and phonon sidebands of excitons are gradually broadened, and sometimes it is very difficult to identify these overlapped bands in spectra. So, other lines are put out of account except for excitons bound to isolated nitrogen ($N_x$) and to $NN_1$. We focus our attention on the relationship of luminescence intensity of $N_x$ and $NN_1$.

Figure 4 shows the relations of photoluminescence intensity ($I_{em}$) and excitation density ($I_{ex}$) of $N_x$ and $NN_1$. GaP:N is excited by an $Ar^+$ laser (with light chopper) of power 10–$10^4$ W/cm$^2$ that is changed by a set of neutral filters. For the excitation density of below $10^3$ W/cm$^2$, the intensity of luminescence of $NN_1$ appears gradually saturated and at about $10^3$ W/cm$^2$ reaches a maximum. For excitation of above $10^3$ W/cm$^2$, that of $NN_1$ decreases obviously with the excitation. On the other hand, in Fig. 4 the luminescence intensity of $N_x$ is proportional to the excitation in the whole excitation range, and the relation of the intensity versus excitation is linear, but for $NN_1$ this slope is less than 0.5 below $10^3$ W/cm$^2$.

Sturge and his colleagues[2] studied the excitation density dependence of the luminescence intensity of the bound excitons in GaP:N with a dye laser in the excitation range between $10^{-4}$ and 1 W/cm$^2$. Reaching approximately 1 W/cm$^2$ the luminescence intensity of $NN_1$ appears out of

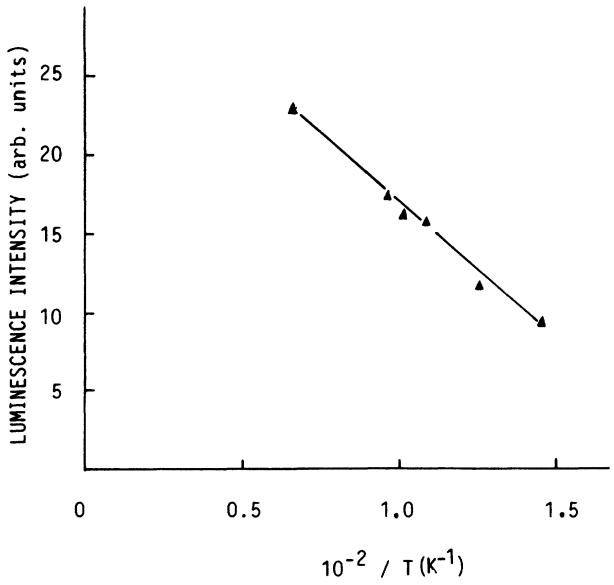


FIG. 3. Temperature dependence of intensity of free excitons: $E_a \sim 21\pm4$ meV.

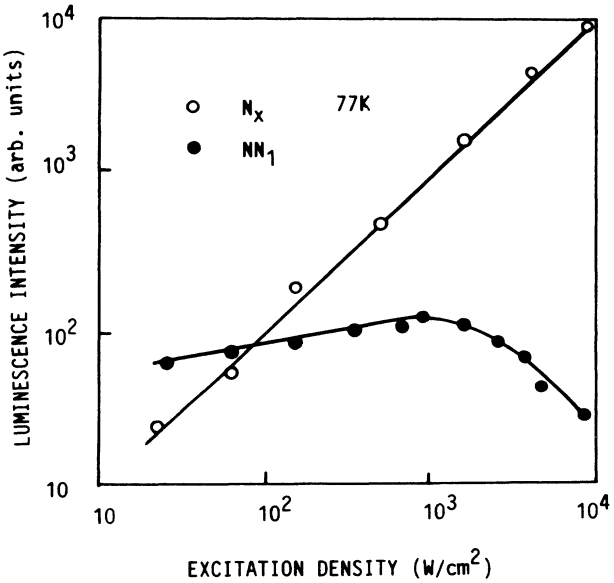


FIG. 4. Relationship of luminescence intensity vs excitation power.

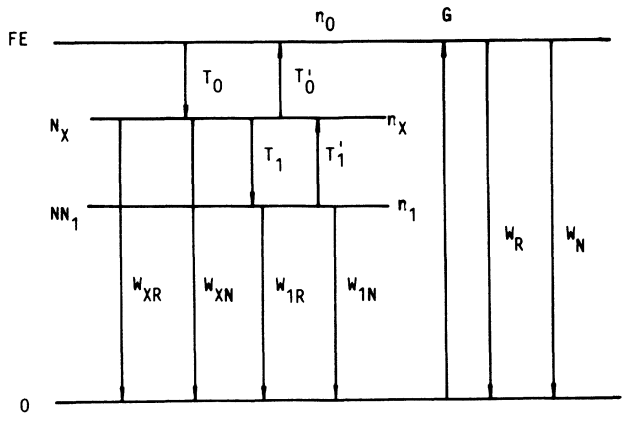


FIG. 5. Kinetic model for high excitation density.

linearity, and it was thought that this might have been due to the exciton saturation of the impurities with the increasing of excitation. Wolf[9] pointed out that in GaP:N the high excitation would make the exciton produce the interaction and simultaneously cause the Auger effect; these resulted in the nonlinear relation.

It should be pointed out that the Auger effect plays a much less important role in our work, because the concentration of nitrogen doped in GaP and the excitation used are not high enough. We suppose that this nonlinearity of emission intensity versus excitation power may result from the energy transfer among excitons bound to N-N pairs. We have taken into account two energy transfer processes: the exciton transfer of thermal ionization, i.e., the thermal ionized excitons being recaptured by other centers, and the tunneling transfer of exciton including the positive and inverse processes, the positive from shallower centers to deeper ones or from free excitons to bound excitons, and the inverse or the back transfer in the reverse direction.

Figure 5 shows the diagram of energy levels which is used as a model of luminescence dynamics. Here the splitting of the substates $A$ and $B$ of each exciton is neglected. We do not consider the thermal ionization of the deepest center $NN_1$. The notations in Fig. 5 are explained as follows: FE, $N_x$, and $NN_1$, energy level of free excitons and excitons bound to isolated nitrogen and to $NN_1$ centers, respectively; $n_0$, $n_x$, and $n_1$, density of FE, $N_x$, and $NN_1$, respectively; $T_0$ and $T_0'$, probability of transition from FE to $N_x$ and in reverse from $N_x$ to FE; $T_1$ and $T_1'$, probability of $N_x$ to $NN_1$ and $NN_1$ to $N_x$; $W_{1R}$ and $W_{1N}$, probability of the radiative and nonradiative transition of $NN_1$; $W_{XR}$ and $W_{XN}$, probability of the radiative and nonradiative transition of $N_x$; $W_R$ and $W_N$, probability of the radiative and nonradiative transition of FE; $G$, rate of generation of FE.

We can obtain the following rate equations:

$$\frac{dn_0}{dt}=G-n_0(W_R+W_N+T_0)+n_xT_0' ,$$

$$\frac{dn_x}{dt}=n_0T_0+n_1T_1'-n_x(W_{XR}+W_{XN}+T_1+T_0') ,$$

$$\frac{dn_1}{dt}=n_xT_1-n_1(W_{1R}+W_{1N}+T_1') .$$

Under the condition of stable state,

$$\begin{aligned} &G+n_XT_0'=n_0(W_R+W_N+T_0) ,\\ &n_0T_0+n_1T_1'=n_x(W_{XR}+W_{XN}+T_1+T_0') ,\\ &n_XT_1=n_1(W_{1R}+W_{1N}+T_1') . \end{aligned} \tag{1}$$

In our experiment there exists $G \gg n_XT_0'$, therefore,

$$G=n_0(W_R+W_N+T_0) . \tag{2}$$

Equations (1) and (2) are joined together to be solved, giving

$$n_1=G/(A'+B'T_1')$$

or the luminescence intensity of $NN_1$ ($I_1$):

$$I_1=n_1W_{1R}=W_{1R}G/(A'+B'T_1') . \tag{3}$$

Here,

$$\begin{aligned} A'&=AW_{1R}\\ &=\frac{1}{T_0T_1}(W_{1R}+W_{1N})(W_R+W_N+T_0)\\ &\quad\times(W_{XR}+W_{XN}+T_0'+T_1) ,\\ B'&=BW_{1R}\\ &=\frac{1}{T_0T_1}(W_R+W_N+T_0)(W_{XR}+W_{XN}+T_0') . \end{aligned}$$

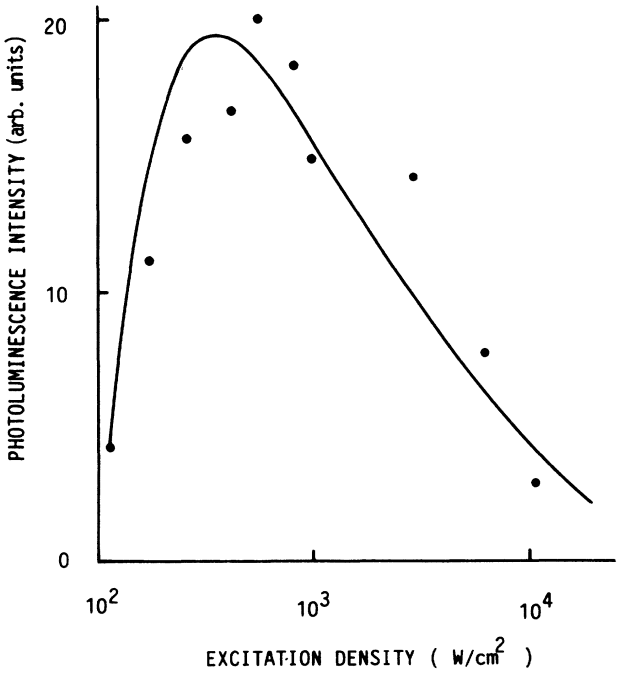


FIG. 6. Dependence between luminescence intensity vs excitation power: circles show the experimental values, and solid line is the fitted curve.

In our other experiment,[6,10] we knew that the inverse transfer of bound excitons increases with the excitation; from this point the item $T_1'$ concerned with the inverse transfer may be supposed to be $G^q$, where parameter $q$ will be determined by the experiment. Thus, we have

$$I_1 = G/(A + BG^q) . \quad (4)$$

Here, $A$, $B$, and $q$ are parameters which will be determined.

Figure 6 shows a typical fitting curve of $NN_1$. The fitting curve is drawn by means of Eq. (4) and the parameters are, respectively,

$$A = 1.0 \pm 0.2 ,$$

$$B = (1.1 \pm 0.1) \times 10^{-6} ,$$

$$q = 2.00 \pm 0.03 ,$$

therefore Eq. (4) is given by

$$I_1 = G/(1 + 1.1 \times 10^{-6} G^2) .$$

Now we discuss whether or not the values of parameters $A$ and $B$ are reasonable:

$$\frac{1}{B} \approx \frac{A}{B} = (W_{1R} + W_{1N})[1 + T_1/(W_{XR} + W_{XN} + T_0')] .$$

As we know, both $W_{1R} + W_{1N}$ and $W_{XR} + W_{XN}$ are $10^6 - 10^7$ sec$^{-1}$ from our experiment. The tunneling of excitons, $T_1$ and $T_0'$, can be described as

$$T(r) = T^0 \exp(-2r/a) \text{ (Refs. 11 and 12)}$$

exciton radius $a \sim 32$ Å, the separation between nitrogens may be taken as 65 Å when the concentration of nitrogen is about $7 \times 10^{18}$ cm$^{-3}$, and $T^0$ is given by $10^{11} - 10^{13}$.[10] Thus

$$1/B \sim (W_{1R} + W_{1N}) \sim 10^6 - 10^7 .$$

or

$$B \sim 10^{-7} - 10^{-6} .$$

This is in good agreement with the fitting value of $B \sim 1.1 \times 10^{-6}$, which is basically reasonable.

## IV. CONCLUSION

It is thought that both luminescence of free excitons and nonlinearity of $NN_1$ result from the inverse transfer of excitons under high excitation. The binding energy of free excitons is thought to be about 21 meV.

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