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ENERGY TRANSFER AND THERMAL QUENCHING PROCESSES OF BOUND EXCITON LUMINESCENCE IN GaP:N*

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ABSTRACT

In this paper, the temperature dependence of bound exciton luminescence on GaP: N has been studied in the range of 15K—150K using band excitation. The luminescence-kinetic method was used to investigate the energy transfer process among different luminescent centers and the luminesence quenching process related to binding mechanism in the samples with different nitrogen concentrations and different nonradiative recombination conditions. The analyses reveal that nonradiative recombination is a very important factor in the transfer and thermal quenching processes. Because the nonradiative recombination probability increases with increasing temperature, the apparent activation energies of the thermal quenching processes are larger than the activation energies related to the thermalization of luminescent centers, but the more evident the energy transfer is, the larger are the apparent activation energies. For NN_1 and NN_3, detailed analyses have shown that their thermal quenching mechanisms are completely consistent with the HTL model.

I. INTRODUCTION

Since it was proposed by Thomas et al.[1,2] that nitrogen impurities act as isoelectronic traps in GaP, great attention has been paid to the binding mechanism for excitons bound to the traps. There are two models for binding mechanism. One is HTL[3] model in which the electron and the hole are bound separately to form a bound excition; the other is Allen[4,5] model in which the exciton is bound as a whole. At present, theoretical calculations in various works[6-8] do not fit well with the experimental results. In experiments, Cohen and Sturge[9] had observed in excitation spectrum of GaP:N that there exist a series of acceptor-like excited states for NN_i centers, $i\leqslant 7$, with their ionization energies about 40 meV. The ionization energy was considered as the hole binding energy in HTL model, then the hole-ionized state was the electron-obund state (or bare electron state). At low temperature time-resolving spectra of GaP:N, C(Zn, Cd), Sturge et al.[10] have observed the radiative recombinations of bound-exciton state NN_i (i=1, 3, 4, 6) and electrons attached to those nitrogen pairs with holes on neutral acceptors simultaneously. Stunge et al.[11] investigated the thermal quenching mechanism for each A or NN_i center by selected excitation and made it clear that the thermal quenching of luminescene for NN_1, and NN_3 were due to the thermal escape of the hole as

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the thermal activation energies were nearly 40 meV. All these results show that the isoelectronic trap may produce two bound states: the electron bound state and the exciton bound state, for deeper NN_i centers. Zhang Hsinyi et al.[12] indicated that the conclusions drawn in Ref. [11] were on the assumption that the zero-phonon line has the same temperature dependence with its phonon replicas. But using band to band excitation, they observed that the zero-phonon line was absolutely different in temperature relation with relevant LO^r phonon sideband (we will discuss this problem elsewhere[13]. In fact, they both have the same temperature dependence). The thermal activation energies they obtained for each NN_i center were nearly the same as the corresponding exciton binding energies. So they concluded that the thermal quenching of luminescence results from the separation of the exciton from the N-N pair as a whole. In Refs. [11] and [12], the thermal quenching processes were described by a classical formula[14]:

$$I = B/(1 + A \cdot \mathrm{Exp}(-E/kT)). \tag{1}$$

Zhang Weibin et al.[15] pointed out that using above band gap excitation, the exciton transfer from shallower centers to deeper ones would raise the fitting values of the thermal activation energies, if Formula (1) is used to fit experimental data. After considering the transfer effect qualitatively, they reached the same conclusions with Ref. [11].

In this work, the temperature dependence of bound exciton luminescence in GaP :N has been investigated in the range of 15—150 K by using band-to-band excitation. The samples with different nitrogen concentrations and under different nonradiative recombination conditions were studied. The recombination kinetic method has been employed to study the energy transfer processes between different luminescent centers as well as the thermal quenching processes related to the binding mechanism.

II. Experimental Method

Six samples with three nitrogen doping levels, as shown in Table 1, were adopted in this work. The nitrogen concentrations were measured by the optical absorption method[16]. SG-1, SG-2, SG-3 and SG-4 were a set of samples taken from one piece of crystal but treated differently. In order to observe the influence of nonradiative recombination on the energy transfer anl on the thermal quenching processes, nonradiative recombination centers were introduced into those samples intentionally.

Table 1

Sample Conditions

Sample	G_1-Y	HG-1	SG-1	SG-2	SG-3	SG-4
(N) (cm^{-3})	1.0×1.0^{19}	2.0×10^{18}	2.4×10^{18}	2.4×10^{18}	2.4×10^{18}	2.4×10^{18}
Treating	—	—	—	$\phi=10^{12}/cm^2$ a)	$\phi=10^{14}/cm^2$ a)	surface abraded

a) Irradiated by electrons with energy of 1 MeV and dosage of ϕ.

The 4880Å line of an Ar^+ laser with a power 4 mW was used as excitation source. The luminescence from the sample was dispersed by a GDM-1000 grating double monochrometor and detected by a cooled C31034 photomultiplier and a PAR124A lock-in am-

plifier, then recorded. The samples were set in the sample cell of CSA-202E refrigerator with an accuracy of ± 0.5 K for both temperature control and indication. Spectral response calibration had been done for all the results given in this paper.

III. Experimental Results

In low temperature photoluminescence spectra we can observe all the NN_i ($i=1,2, \ldots 10$) lines and the A line. The splitting of doublet A and B is measured to be 0.87 meV. Fig. 1 is a photoluminescence spectrum from sample HG-1 at 17 K. We have calculated the integrated intensities for each line at different temperatures for the six samples; the results are shown in Figs. 2—6. With increasing temperature, the luminescence from shallower centers ($i \geqslant 5$) quenches quickly, but the luminescence from NN_4, NN_3 and NN_1 increases first, then begins to quench orderly after reaching a maximum respectively. Luminescence of non-treatment samples, gets to the maximum below 30 K for NN_4 and below 50 K for NN_3 in most cases, but it gets to the maximum between 50 K —80 K for NN_1, varying from sample to sample. For NN_1 and NN_3, the maximum of luminescence can reach a value two or three times that at low temperatures, indicating that the exciton transfer due to the thermalization is quite evident. For the electron-irradiated samples, the increasing amplitude of luminescence drops obviously with increasing irradiation dosage, and the maximum-temperature reduces at the same time, indicating that the transfer effect got weakened. For the surface-abraded sample, we can hardly observe the increase in the luminescence intensity. In this case, the trans-

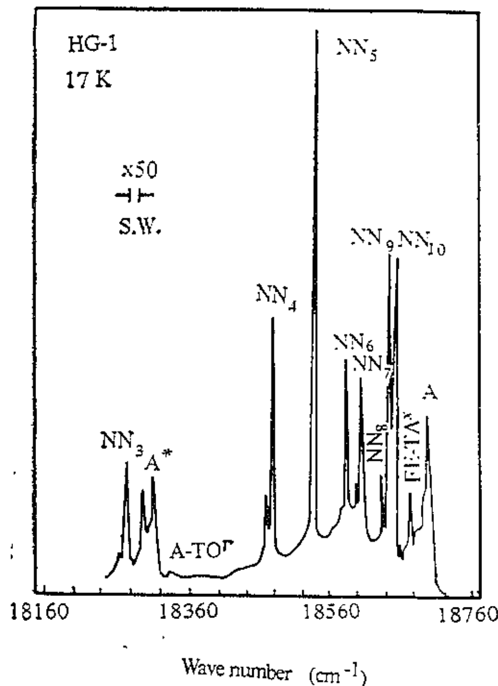

Fig. 1. Low temperature photoluminescence in GaP:N.

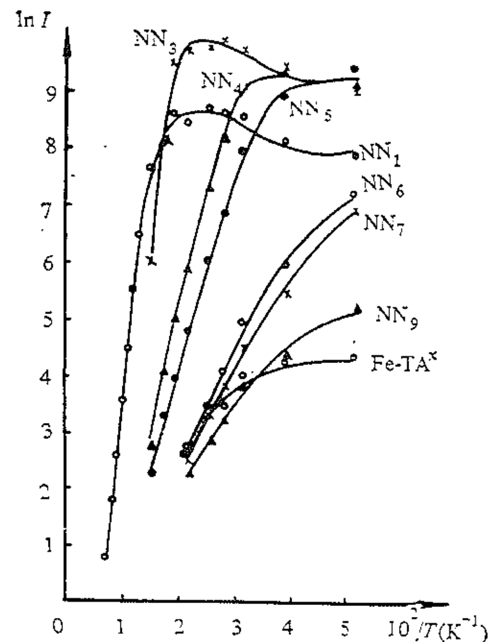

Fig. 2. The experimental results and the fitting curves of sample G_1-Y.

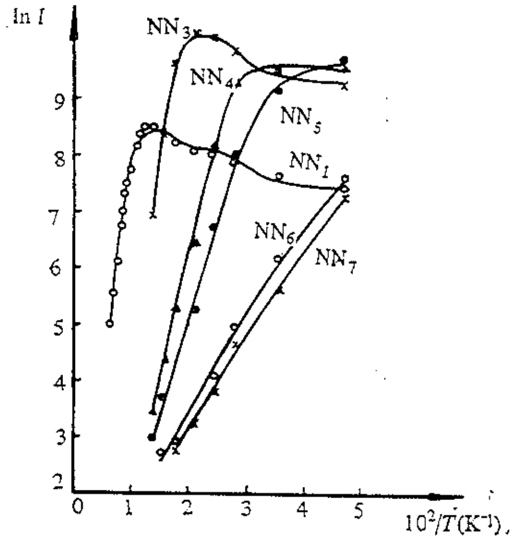

Fig. 3. The experimental results and the fitting curves of sample SG-1.

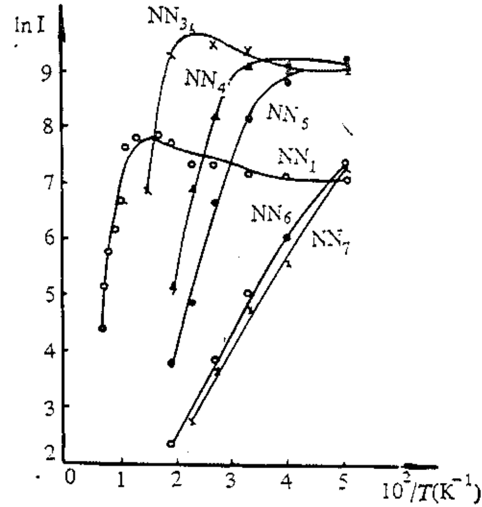

Fig. 4. The experimental results and the fitting curves of sample SG-2.

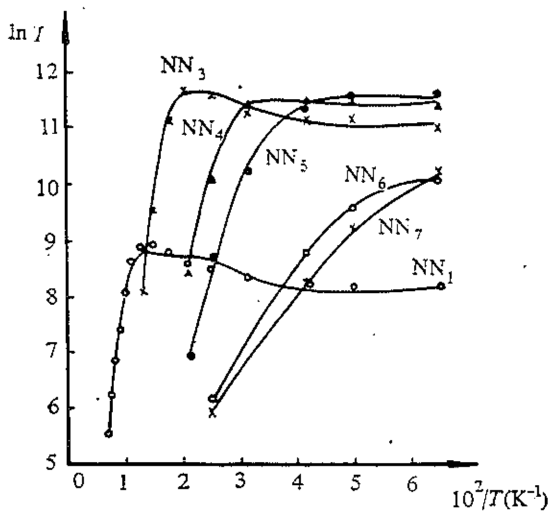

Fig. 5. The experimental results and the fitting curves of sample SG-3.

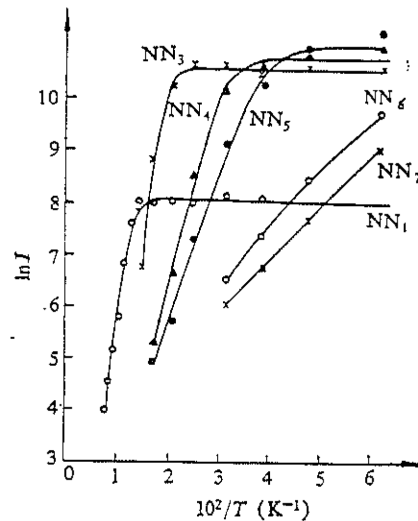

Fig. 6. The experimental results and the fitting curves of sample SG-4.

fer effect is very weak while the surface recombination is very strong.

IV. Kinetic Analyses and Calculations on Bound Exciton Luminescence

Using band-to-band excitation, the free carriers produced by the excitation may interact with various radiative and nonradiative recombination centers. As the temperature relations for the capture and thermalization processes are quite different for each center, the distribution of the excitation energy among these centers will vary with temperature. Thus, in studying the thermal quenching process of certain center, we should

consider the influence of the variations of other centers. Therefore, for any one center, the expression of its luminescence intensity must include the related factors of other centers, Formula (1) is too simple for general case. In this work, we shall consider the case where there are more than one kind of luminescent center. The adopted kinetics model is shown in Fig. 7.

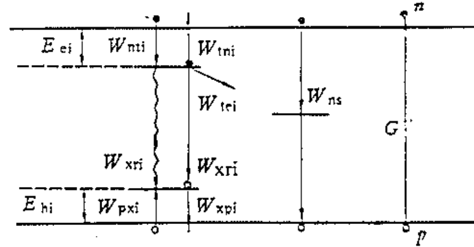

Fig. 7. Kinetics model for boundexciton luminescence in GaP;N.

W_{nti}, NN_i center electron capture probability; W_{tni}, NN_i center bare electron thermalization probability; W_{tei}, NN_i center bare electron escape probability (bare electron can either tunnel to a neutral acceptor or to a deep ionized donor[11] or directly make a radiative recombination with a acceptor hole[10]); W_{pxi} NN_i center bare-electron state hole capture probability; W_{xri}, NN_i center bound-exciton state hole thermalization probability; W_{xri}, NN_i center bound exciton radiative recombination probability; W_{xni}, NN_i center bound exciton nonradiative recombination probability (including multiphonon emission and Auger effect, at lower temperatures, the two processes are very less important[11]); W_{ns}, deep centers electron capture probability; G, free electron-hole pair generation rate.

At low-level band-to-band excitation, the kinetic equations under steady-state are given by

$$dn/dt = G - n \sum_i W_{nti} - nW_{ns} + \sum_i N_{ti}^- W_{tni} = 0,$$

$$dN_{ti}^c/dt = nW_{nti} - N_{ti}^-(W_{tei} + W_{tni}) - N_{ti}^x W_{xri} = 0,$$

$$dN_{ti}^x/dt = N_{ti}^- W_{pxi} - N_{ti}^x(W_{xpi} + W_{xri}) = 0.$$

In the above equations, $N_{ti}^c = N_{ti}^- + N_{ti}^x$ represents the total concentration corresponding to NN_i centers occupied by electron, N_{ti}^- is the bare-electron state concentration of NN_i centers, N_{ti}^x is the bound exciton state concentration of NN_i centers. Here we have neglected the contributions from the thermal equilibrium carriers since the carriers excited optically are much more than that excited thermally at lower temperatures. From above equations, we have

$$N_{ti}^x = \frac{p_i \left[G + \sum_{j \neq i} (W_{xrj} + W_{xpj}) \frac{W_{tnj}}{W_{pxj}} N_{tj}^x \right]}{W_{xri} + \frac{W_{tei} + (1 - p_i)W_{tn}}{W_{pxi}} (W_{xri} + W_{xpi})}, \tag{2}$$

where $p_i = W_{nti}/(\sum_i W_{nti} + W_{ns})$ represents the relative electron capture probability for NN_i center. Writing the thermalization probability in the form of activation

energy:

$$W_{\text{tni}} = W^0_{\text{tni}} e^{-E_{\text{ci}}/kT}, \quad W_{\text{xpi}} = W^0_{\text{xpi}} e^{-E_{\text{hi}}/kT}$$

and introducing $A_i = W^0_{\text{xpi}}/W_{\text{xri}}$, $C_i = W_{\text{tci}}/W_{\text{pxi}}$, $D_i = W^0_{\text{tni}}/W_{\text{pxi}}$, we obtain the expression for the luminescence intensity

$$I_i = N^x_{\text{ti}} W_{\text{xri}} = \frac{p_i \left[G + \sum_{j \neq i} (1 + A_j e^{-E_{\text{hj}}/kT}) D_j e^{-E_{\text{cj}}/kT} I_j \right]}{1 + [C_i + (1 - p_i) D_i e^{-E_{ci}/kT}](1 + A_i e^{-E_{\text{hj}}/kT})}. \tag{3}$$

For NN_i centers with $i \geqslant 3$, the electron-binding energies are always smaller ($E_{\text{ci}} \leqslant 41$ meV[9]). The electron and the hole may be thermalized simultaneously at high temperature. For deep center NN_1, the electron-binding energy is so large ($E_{\text{c1}} = 120$meV[9]) that the electron thermalization process need not be considered if temperature is not too high. We can take $C_i \ll 1$, that is, the bare-electron state is much likely to capture a hole to form a bound exciton than to escape to the other centers[18]. Further we consider the deep center electron capture probability W_{ns} is dependent on temperature. In practice, W_{ns} includes the contributions from various nonradiative recombination centers. Let W'_{ns} denote the temperature-independent factors, the temperature-dependent factors may be equivalent to an exponental form[19], $W^0_{\text{ns}} e^{-E_0/kT}$, then

$$p_i = p_{i0}/(1 + A_0 e^{-E_0/kT}), \quad p_{i0} = W_{\text{nti}}/(\sum_i W_{\text{nti}} + W'_{\text{ns}}), \quad A_0 = W^0_{\text{ns}}/(\sum_i W_{\text{nti}} + W'_{\text{ns}}).$$

According to the meaning of relative capture probability, one can take $p_i \ll 1$. Let $B_{i0} = p_{i0} G$, $B'_{i0} = p_{i0}$. Finally the luminescence intensity can be expressed as follows:

$$I_i = \left(B_{i0} + B'_{i0} \sum_{j \neq i} F_j I_j \right) \Big/ [(1 + A_0 e^{-E_0/kT})(1 + F_i)], \tag{4}$$

where

$$F_i = \begin{cases} D_i e^{-E_{ci}/kT}(1 + A_i e^{-E_{hi}/kT}), & i \geqslant 3 \\ C_1 A_1 e^{-E_{hi}/kT}. & i = 1 \end{cases}$$

Each term in Expresson (4) possesses an explicit physical interpretation: B_{i0} is the luminescence intensity of NN_i center at low temperatures (more exactly, B_{i0} is the steady-state intensity for two substates A and B when thermalization process has not yet occurrent); B'_{i0} was known as the transfer factor, in fact it is the value of the relative electron capture probability of NN_i center at low temperature. This parameter is closely related to the nonradiative recombination conditions. $B'_{i0} \sum_{j \neq i} F_j I_j$ represents the contributions to the NN_i intensity by exciton thermalization from the other centers, that is the transfer amount; F_i is the thermal quenching law of the NN_i center itself; $A_0 e^{-E_0/kT}$ reflects how the variations of nonradivative recombination probability with temperature influence each of the NN_i centers. Formula (4) reflects the competition among different radiative and nonradiative centers. It describes how the distribution of exciting energy among the centers changes with temperature. It can be seen from (4) that the thermalization of any one center will influence all the other centers at the same time.

We have used Expression (4) to fit the experimental data. For NN_i center with $i \geqslant 3, F_i$ in (4) is not a monoexponential form. To reduce difficulty in fitting calculation, we have written F_i as a monoexponential form equivalently: $F_i = H_i e^{-E_i/kT}$ $(i \geqslant 3)$. For NN_4 and NN_5, the obtained activation energies were nearly 40 meV and 30 meV respectively, being in agreement with the results given by Sturge et al.[11]. For NN_3, the obtained activation energies were 70 meV—80 meV, close to the total binding energy of electron and hole with 81 meV. For NN_1 center, we took E_{h1}=40 meV in fitting calculations, so we can fit out the A_0 and E_0 conveniently. The fitting values for the concerned parameters are partially listed in Table 2. Figs. 2—6 show the comparisons between the fitting curves and experimental results with a quite good agreement. Most of the relative errors are less than 10%. If the variation of nonradiative recombination probability with temperature is neglected, for NN_1, the observed thermal activation energies were about 45 meV when the fitting was undertaken below 70 K; when the fitting points were up to 150 K, the observed thermal activation energies were 70 meV—90 meV. Such results imply that the thermal quenching process of NN_1 center is not a monoexponential process. At lower temperatures, it may be considered as the hole thermalization. At higher temperatures, the greater activation energies are mainly caused by the variations of nonradiative recombination probability with temperature since the electron-binding energy is several times of the hole-binding energy so the electron thermalization hardly happens in the concerned temperature range ($T<150$ K). In addition, we have made some more letailed calculations for NN_3 center in samples G_1-Y and SG-1. With F_i taken in the form given originally in Expression (4), the obtained values for parameters belonging to NN_3 center are listed in Table 3. All the obtained results are reasonable. See an example of G_1-Y, the fitting value of $A_3 \sim 10^4$ since $W_{xr} \sim 10^7$ s^{-1}[20], thus $W^0_{xp3} \sim 10^{11}$s^{-1}, which is a reasonable value (if therma-

Table 2

Fitting Values for Some Parameters

Center / Parameter / Sample	NN_1				NN_3				NN_4				Nonradiative	
	B_{10}	B'_{10}	C_1A_1	$E_{h1}^{a)}$	B_{30}	B'_{30}	H_3	E_3	B_{40}	B'_{40}	H_4	E_4	A_0	E_0
G_1-Y	2910	0.114	2.61×10^3	40	10000	0.402	2.26×10^7	76.7	10100	0.564	5.60×10^5	37.9	2.72×10^3	58.8
HG-1	2930	0.0592	4.20×10^3	40	9850	0.506	1.80×10^7	75.9	11700	0.597	3.20×10^5	36.3	6.22×10^4	76.8
SG-1	1650	0.0519	14.9	40	10600	0.417	8.86×10^6	78.7	13100	0.475	3.41×10^5	38.7	2.39×10^3	74.3
SG-2	1120	0.0353	16.0	40	8130	0.370	1.12×10^6	65.8	8970	0.425	3.06×10^5	37.0	3.50×10^3	74.0
SG-3	3270	0.0125	3.92	40	61800	0.257	1.27×10^6	70.2	92700	0.193	2.83×10^5	38.8	3.81×10^3	74.1
SG-4	3090	0.00269	16.0	40	38300	0.00511	1.38×10^7	73.9	48100	—	2.75×10^5	35.1	1.04×10^4	64.0

a) E_{h1} = 40meV is taken in fitting calculation. E_3, E_4, E_0 are in unit meV.

lization probability is written as $W^0 e^{-E/kT}$, $W^0 \sim 10^{12} s^{-1}$ typically[21]). If we think $A_1 \sim A_3$, then $C_1 \sim 10^{-1}$, which is consistent with the above assumption $C_i \ll 1$. If we also think $D_1 \sim D_3$, then at $T = 150\,K$, $D_1 e^{-E_{e1}/kT} \sim 10^{-2}$, indicating that the electron bound to NN_1 center is scarcely thermalized up to 150 K.

The results of NN_1 and NN_3 from fitting calculations show that the bound-exciton thermalization of NN_3 is owing to the simultaneous thermalization of hole and the electron, but the thermalization of NN_1 is the hole thermalization. Both their thermal quenching processes are affected by the nonradivaive recombinations.

Table 3

Fitting Parameter Values for NN_3 Center

Sample \ Parameter	B_{30}	B'_{30}	A_3	D_3	E_{e3}(meV)
G_1-Y	10000	0.414	4.61×10^4	6.50×10^2	38.7
SG-1	10600	0.422	2.40×10^4	5.98×10^2	41.8

Note. $E_{b3} = 40$ meV in fitting calculation.

V. Discussions

It can be seen fro mexperimental results that the temperature at which the luminescene of NN_3 begins to quench thermally is not very different from sample to sample, but it is quite different for NN_1. This can be explained as follows. For NN_3, the luminescence quenching caused by the hole thermalization is realized by means of the simultaneous, thermalization of electron; but for NN_1 by the escape of electron, i.e. it is determined by C_1 which has some thing to do with the impurity conditions in the samples. Form Table 2, we can estimate the difference for C_1 between two samples G_1-Y and SG-1 to be approximately in two orders. C_1 of sample SG-1 is very small ($C_1 \sim 10^{-3}$), so the electron-escaping probability of the bare electron state is very small. Maybe the hole thermalization has taken place earlier, but which does not lead to an obvious quenching in NN_1 luminescence until 80 K. Kash et al.[18] also observed a similar phenomenon in the investigations on temperature depedence of Ga(As, P):N luminescence decay time. For sample G_1-Y, C_1 is comparatively greater ($C_1 \sim 10^{-1}$) in region 50 K—70 K, the hole thermalization leads to quite obvious quenching in NN_1 lumiiescence.

It has been shown in Table 2 that with enhancing nonradiative recombination, the transfer factor B'_{10} decreases. For surface-abraded sample SG-4, B'_{10} are almost equal to zero. After removing the transfer item $B'_{i0} \sum_{j \neq i} F_j I_j$ in Expression (4), we get

$$I'_i = B_{i0}/[(1 + A_0 e^{-E_0/kT})(1 + F_i)]. \qquad (5)$$

I'_i describes the temperature relation of luminescence intensity in the non-transfer case. Results for sample SG-4 nearly belong to this case. The curves in Fig. 8 are drawn according to Expressions (4) and (5). One can see clearly in Fig. 8 that two curves by

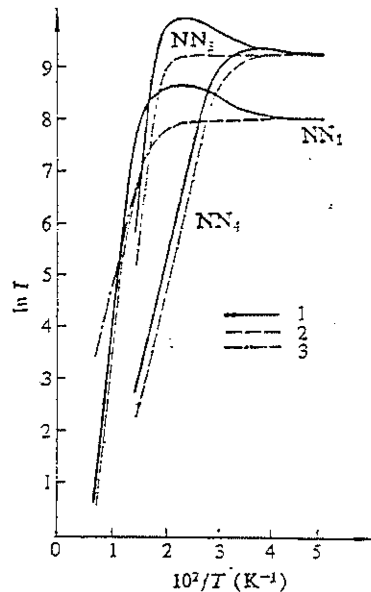

Fig. 8. Influence of energy transfer and nonradiative recombination in sample G_1-Y.
1, with transfer; 2,non-transfer; 3, hole thermalization.

Expressions (4) and (5) are coming nearer and nearer towards each other with increasing temperature. This is because that nonradiative recombination probability increases with increasing temperature, as a result the energies released thermally from shallower centers transfer more rapidly to the nonradiative recombination centers, and then the transfer amount is reduced. Just because the nonradiative recombination probability varies with temperature, if we fit the experimental results by Formula (1), the observed apparent activation energy will be increased with the enhanced. transfer effect. The fitting results for NN_1 are given in Table 4. The results for SG-1—SG-4 confirm the deduction made above. Otherwise, it can be seen from Expression (5), using band-to-band excitation, even the influence of transfer effect has been eliminated, bacuse of the variation of nonradiative recombination probability with temperature, it is still improper to describe the luminescence quenching process simply by Formula (1). Also, in Fig. 8, we have drawn the curve for NN_1 in which the influence of nonradiative recombination term have been deducted.

Table 4

Fitting Results for NN_1 by Using $I = B/(+Ae^{-E/kT})$

Parameter \ Sample	SG-1	SG-2	SG-3	SG-4	G_1-Y	HG-1
A	4710	2780	8170	4810	3790	3940
B	2.59×10^4	2.29×10^4	1.55×10^4	2.79×10^4	6.71×10^5	2.43×10^6
E(meV)	86.2	80.6	78.8	66.4	95.6	78.7

VI Conclusions

Three conclusions can be drawn from this work.

(1) In GaP:N, the distribution of the external excitation energy among various radiative and nonradiative centers will change with temperature. Macroscopically, it exhibits that the excitions transfer from shallower center to deeper center or to nonradiative recombination centers with increasing temperature.

(2) Nonradiative recombimation plays an important part in the energy transfer and luminescence thermal quenching processes. Since the nonradiative probability increases with increasing temperature, the thermal quenching for each luminescent center is not merely caused by the thermalization of the center itself. The influence of nonradiative recombination quickens the thermal quenching process, and increases the apparent activation energy. The more evident is the energy transfer, the larger is the apparent activation energy observed.

(3) For center NN_1 and NN_3, their luminescence quenching processes are completely consistent with that expected by HTL model. For the other centers we have not yet reached any concrete conclusions.

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