Radiative and nonradiative recombination of bound excitons in GaP:N. I. Temperature behavior of zero-phonon line and phonon sidebands of bound excitons

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The temperature behavior of zero-phonon lines and phonon sidebands of bound excitons is carefully studied. In the very-low-temperature range, the internal transition between exciton A and B causes a decrease in the luminescence intensity of zero-phonon lines with decreasing temperature. In different temperature ranges, the different activation energies indicate that the thermal quenching of bound excitons consists of three mechanisms: the ionization of the free exciton, the escape of the hole, and the debinding of the whole bound exciton. We also develop a model for the components of phonon sidebands to explain the fact that the thermal quenching of the phonon sidebands does not have the same temperature behavior as the corresponding zero-phonon lines.

I. INTRODUCTION

The absorption and emission due to excitons bound to the isoelectronic impurity nitrogen (N) and/or nitrogen-nitrogen pairs (NN_i, $i=1,2,3,\ldots$) in GaP:N have been studied since the 1960s by many authors.[1-6] As the concentration of nitrogen is high enough (typically up to 10^{19} cm^{-3}), the photoluminescence of GaP:N is mainly due to the radiative recombination of excitons bound to a nitrogen atom on the phosphorus site with another nitrogen atom on the nearest phosphorus shell, NN_2 then has a nitrogen on the next-nearest phosphorus shell, and so on.

The temperature dependence of the photoluminescence in GaP has been studied by different methods. Sturge, Cohen, and Rodgers[2] measured the photoluminescence efficiency, as a function of temperature, of excitons bound to N and various N-N pairs. Excitons bound to a particular center were excited selectively with a tunable dye laser, and their procedure was to pump in the no-phonon line and monitor the temperature dependence of the intensity of the phonon sideband. Therefore, the phonon sidebands were considered to have the same temperature dependence as the no-phonon bands in their work. They pointed out that below 100 K, the photoluminescence from excitons bound by less than 40 meV was found to be thermally quenched by the escape of an exciton as a whole and that from excitons with a binding energy of 40 meV or more was quenched by the thermal excitation of a free hole.

Chang (Zhang), Hirlimann, Kanehisa, and Balkanski[4] measured the integrated intensity of no-phonon lines and phonon sidebands in GaP:N by using the above-band-gap excitation and found experimentally, for the first time, that the temperature behavior of the phonon sidebands was quite different from that of no-phonon lines, and the ratio of intensity between them could be strongly dependent on temperature. They came to two main conclusions. First, the thermal ionization of the exciton from the impurities gave the most important contribution to the quenching of no-phonon lines when the temperature was high enough. The fact that the activation energies were very close to the corresponding binding energies of excitons supported this idea. Secondly, the quenching of various phonon sidebands was specific to the exciton-phonon coupling regardless of the excitons with different binding energies, considering that all the phonon sidebands had almost the same activation energy.

In our opinion, if the temperature behavior of no-phonon emission bands and phonon sidebands is different, the temperature dependence of the phonon sidebands should not be considered as that of corresponding no-phonon lines. On the other hand, if the quasiequilibrium is not established between bound excitons, free excitons, and free particles, the above-band-gap excitation method should not be used, as pointed out by Sturge *et al.* In addition, there are several questions left to be answered, such as the mechanism of thermal quenching of bound excitons, the migration or tunneling of bound excitons between different NN pairs, the origin and character of phonon sidebands, etc. Hence, it is necessary to study the temperature behavior and the character of zero- and one-phonon bands more carefully in both experiment and theory.

First of all, the different temperature behavior between no-phonon lines and phonon sidebands has not yet received much attention. It was just this result that made us consider that the phonon sideband consists of two components, multiphonon process in direct transition and phonon-assisted momentum-conserving indirect recombination (called the two-component model).[7] For the former, the thermal quenching usually influences the zero- and one-phonon bands in the same manner. Then,

in the latter case, it is not unreasonable to consider that zero- and one-phonon bands should not depend on the temperature in the same manner. Consequently, the zero-phonon line and the corresponding phonon sidebands show different temperature behavior.

We have studied the luminescence properties of GaP:N in a much larger temperature range, up to 165 K, and with much higher excitation power, up to 10^8 W/cm^2, and paid more careful consideration to the kinetic analysis, the origin, and the character of phonon sidebands. We shall report our new experimental results and theoretical calculations about these in a series of papers, labeled papers I, II, III, and IV.

Based on the fact that in a different temperature range the activation energy for the thermal quenching of zero-phonon lines has different values, we conclude that bound excitons are quenched by three kinds of mechanisms: the ionization of free exciton, the escape of hole, or the escape of the whole bound exciton, as discussed in the present paper (hereafter, paper I). We point out, in paper II, that the observation of free excitons and the nonlinear relationship of emission intensity versus excitation power are considered to be due to the inverse transfer of bound excitons from deeper N-N pairs to shallower ones. The proof of the existence of the inverse transfer is given in paper III. We believe that such a kind of inverse transfer is a phonon-assisted back-tunneling of bound excitons. We have also compared the kinetic processes both under selective excitation and above-band-gap excitation. Paper III shows that the temperature behavior of the luminescence of excitons is the same for both excitation conditions. The special attention is paid to the origin and the line shape of phonon sidebands. In paper IV, based on our two-components model for the formation of phonon sidebands mentioned above, we calculate the LO-phonon sideband of excitons bound to NN and explain its double-peak structure and abnormal temperature behavior observed in previous experiments (see paper I). Also, we inquire further the physics mechanism of back-tunneling of bound excitons (see paper III) which influences the kinetic processes of bound excitons and is related to the two-component model about the formation of phonon sidebands.

II. EXPERIMENTAL

The experimental method for measuring the temperature dependence of zero-phonon lines in relatively low temperatures (shown in Fig. 1) is described in Ref. 4. In a much larger temperature range, up to 165 K, we have carefully studied the thermal behavior of photoluminescence of excitons in GaP:N where the nitrogen concentration ranges from 5×10^{17} to 7×10^{18} cm^{-3}. GaP:N is placed in the Cryogenic refrigeration system in which the temperature is available to regulate continuously within the range 10–300 K. The excitation source is the 488-nm line of an Ar laser and the spectrum is recorded and processed by a microprocessor.

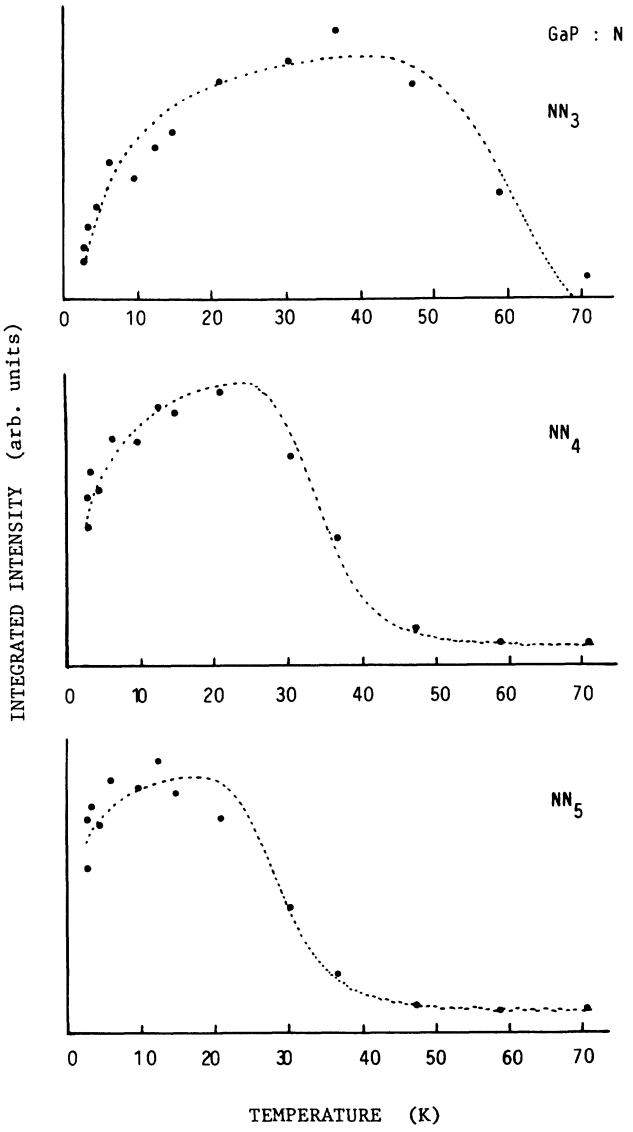

FIG. 1. Temperature dependence of intensity of luminescence due to NN_3, NN_4, and NN_5 in GaP:N.

III. RESULTS AND DISCUSSION

A. *A-B* transition temperature behavior of zero-phonon lines

It is well known that the isolated nitrogen or nitrogen-nitrogen pairs bound exciton in GaP has two substates ($J=1,2$) from which the radiative emission is labeled *A* and *B* lines, respectively. The exciton recombination from the substate *A* ($\Delta J=1$) is allowed and that from *B* ($\Delta J=2$) is normally forbidden, but, in reality, is partially allowed due to the asymmetry of the luminescence centers. As a result, the zero-phonon line consists of lines *A* and *B*. In a previous work, the contribution of transition from *A* and *B* to the total intensity of the zero-phonon line was studied.[8] It was found that in GaP:N the integrated emission intensity of N-N pairs bound excitons passed through a maximum in the temperature range 5–40 K, as shown in Fig. 1, which is re-

printed after Ref. 4. By studying the temperature dependence of the ratio of the intensity of B and A lines (cf. Fig. 2 in Ref. 4), we believe that a thermal quasiequilibrium between the substates A and B was established in the temperature range $T<40$ K. At lower temperatures, the exciton trapped at the substate B (exciton B) had a relatively greater contribution to the intensity of zero-phonon lines, and the redistribution of the population of exciton A and B should cause the intensity ratio of lines A and B, and also the total intensity of A and B lines, to change with temperature. We know that the lifetime of exciton B is much longer than that of exciton A. It is likely that the excitation energy of bound excitons can be transferred to other centers when it is in the substrate B due to its longer lifetime. Therefore, the efficiency of luminescence due to exciton B is lower than that of exciton A. That is why as the temperature is low enough, the intensity of the zero-phonon line is decreased with the decrease in temperature. The kinetic analysis was carried out in another previous work.[9] Figure 2 shows the kinetic model for proposed radiative and nonradiative processes. The meaning of notations in the figure are given as follows: N, concentration of nitrogen; n_0, density of free excitons; n_A and n_B, population of bound excitons trapped at substate A or B; G, generation probability of free excitons; p_A and p_B, probability of capture of free excitons on substate A or B; p'_A and p'_B, probability of escape of bound excitons from substate A or B into free excitons; T_{AB} and T_{BA}, probability of nonradiative transition from A to B or from B to A, respectively; W_{RA} and W_{RB}, probability of radiative transition $\Delta J=1$ (A) or $\Delta J=2$ (B); W_{INA} and W_{INB}, rate of nonradiative energy transfer from substate A or B to other centers; W_{TNA} and W_{TNB}, probability of thermal quenching of exciton A or B, respectively:

$$W_{TNA}=W_0 e^{-E_{aA}/kT},$$

$$W_{TNB}=W_0 e^{-E_{aB}/kT},$$

where E_{aA} and E_{aB} are the activation energy of thermal quenching for exciton A or B, W_0 is constant, called a frequency factor, W_R, probability of radiative recombination of free excitons; W_N, probability of nonradiative recombination of free excitons,

$$W_N=W_0 e^{-E_{a0}/kT},$$

where E_{a0} is the activation energy of thermal quenching for free excitons and W_0 is a constant which is supposed to be equal to the frequency factor of exciton A or B; ΔE_J, energy difference between substates A and B.

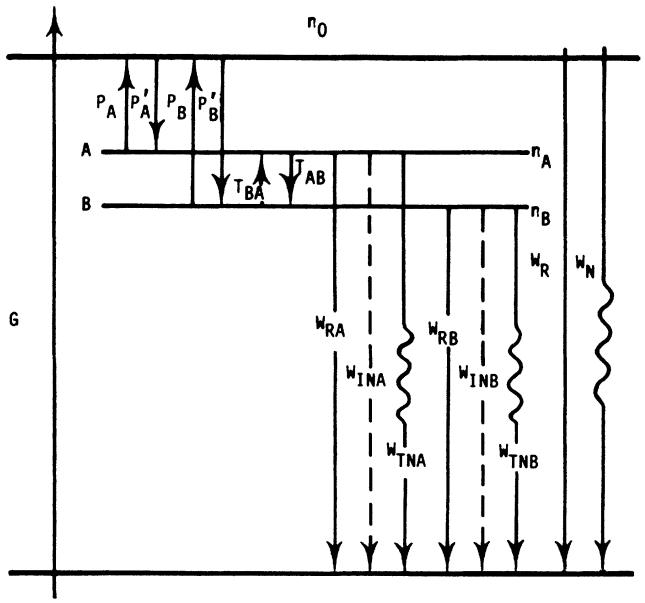

FIG. 2. Kinetic model for proposed radiative and nonradiative processes.

The rate equations were written as follows:

$$\frac{dn_0}{dt}=G-n_0(P_A+P_B)\left[1-\frac{n_A+n_B}{N}\right]+n_A P'_A+n_B P'_B-n_0(W_R+W_N),$$

$$\frac{dn_A}{dt}=n_0 P_A\left[1-\frac{n_A+n_B}{N}\right]-n_A P'_A-n_A(W_{RA}+W_{TNA}+W_{INA})+n_B T_{BA}-n_A T_{AB},$$

(1)

$$\frac{dn_B}{dt}=n_0 P_B\left[1-\frac{n_A+n_B}{N}\right]-n_B P'_B-n_B(W_{RB}+W_{TNB}+W_{INB})-n_B T_{BA}+n_A T_{AB}.$$

We supposed that the quasiequilibrium of the substates A and B was established. On solving the rate equation (1), we derived the following formula, which described very well the temperature dependence of the zero-phonon line of bound excitons:

$$I(T)=\frac{B}{1+Ce^{-E_{a0}/kT}}\left[\frac{3e^{-\Delta E_J/kT}+5\alpha}{3e^{-\Delta E_J/kT}(1+\beta+Ae^{-E_a/kT})+5(\alpha+\beta+Ae^{-E_a/kT})}\right], \quad (2)$$

where E_{a0} and E_a were the activation energies of thermal quenching for free or bound excitons, respectively, the ratio of radiative recombination probability of exciton B to that of exciton A was $\alpha=W_{RB}/W_{RA}$, and the ratio of the probability of nonradiative energy transfer of excitons A or B to that of radiative recombination of exciton A was

$$\beta=W_{INA}/W_{RA}\approx W_{INB}/W_{RA}.$$

A, B, and C were parameters and C was nitrogen concentration dependent. The calculated I versus T curves with Eq. (2) are also given in Fig. 1. The values of α and β have the order of magnitude of 0.01 and 0.1, respectively. These values imply that in the low-temperature range ($T < 40$ K) the decrease of luminescence efficiency is due to the nonradiative energy transfer from bound exciton B to other centers, or say, due to the long lifetime of the exciton B as mentioned above.

B. Exciton transfer of multicenters and thermal quenching of zero-phonon line

As discussed above, when GaP:N is excited with the method of the above-energy-gap excitation, first, free electrons and free holes are simultaneously created in the conduction band and in the valence band, respectively. Due to the interaction between electron and hole, the complexes of electron-hole pairs, or free excitons, are formed. Free excitons, in the first place, may give contribution to the luminescence by way of radiative recombination (see paper II), and in the second place may be deexcited into the ground state by way of nonradiative transition. On the other hand, free excitons can be captured by impurities, such as nitrogen or nitrogen-nitrogen pairs, and then become bound excitons, i.e., nitrogen or nitrogen-nitrogen pair trapped excitons. Under the condition of low temperature and certain excitation power, there exists the A-B transition and their mutual exchange in the inner part of each center, which produces a nonnegligible influence on the exciton luminescence as discussed in Sec. I. In the meantime, the exciton tunneling plays an important role in the exciton transfer from the shallower centers to the deeper ones. It should be pointed out that because temperature must affect, on a large scale, the redistribution of population of excitons, for instance, bound excitons escape thermally from the impurity center and move around as free excitons that may be recaptured to be bound excitons trapped by the other centers. Hence, the exciton population has been changed due to the thermal ionization of excitons. From this point, the luminescence character of excitons must be associated with temperature.[10] As temperature increases, the thermal transfer and tunneling transfer of excitons have a greater effect on the luminescence. In a higher temperature range, besides the A-B transition of excitons in the same center, the exciton tunneling and thermal ionization transfer among many centers should also be specifically taken into account. In short, bound excitons have two ways to go; the first is the radiative recombination giving out luminescence, and the second is the nonradiative transition through which the energy of a bound exciton can be conveyed, including tunneling and thermal ionization transfer. Because of spectrum overlapping at higher temperature, we only choose NN_1 trapped excitons as an object to study. We are sure that a lower temperature, the thermal quenching of bound excitons may result from the A-B transfer of bound excitons and/or the ionization of free excitons with less binding energies. The latter is equal to reducing the number of generating excitons. In mid-temperature range, the escape of the hole from the bound exciton whose binding energy is larger than 40 meV is dominant in the luminenscence quenching, and the bare electron is left at ion site to recapture another hole forming a bound exciton or to annihilate, accompanied with the thermal ionization of the free exciton and the whole bound exciton. Around higher temperature, apart from the thermal-quenching processes as mentioned above, the thermal ionization of bound exciton as a whole is mainly devoted to the thermal quenching. This idea will be supported by the experiment and dynamic calculation. The experimental results are shown in Fig. 3.

To derive conveniently dynamic equations, we do not consider the A-B transition of excitons. Depending on the analysis given above, our dynamic model can be drawn as shown in Fig. 4, whose notations are defined as follows (some of them are listed in Sec. I): W_{iR} and W_{iN}, probability of radiative and nonradiative transition of NN_i trapped excitons; W_{ij}, transfer probability from NN_i to NN_j ($i > j$); N_i, concentration of NN_i centers.

The dynamic rate equations are written as

$$\frac{dn_0}{dt} = G - n_0 \sum_j P_j \left[1 - \frac{n_j}{N_j}\right] + \sum_j n_j P_j' - n_0 (W_R + W_N) , \tag{3}$$

$$\frac{dn_i}{dt} = n_0 \left[1 - \frac{n_i}{N_i}\right] P_i - n_i P_i' - n_i (W_{iR} + W_{iN}) + \sum_{j\,(>i)} n_j W_{ji} \left[1 - \frac{n_i}{N_i}\right] - \sum_{i\,(<j)} n_i W_{ij} \left[1 - \frac{n_j}{N_j}\right] .$$

Then, the emission intensity can be derived and simplified to be[11]

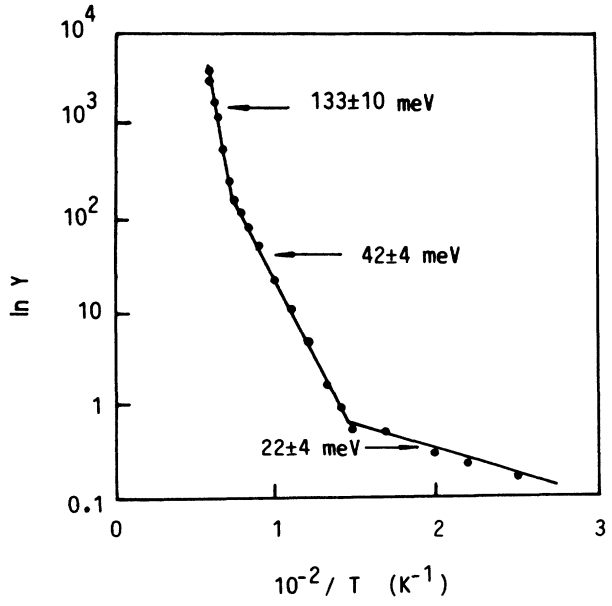

FIG. 3. Temperature dependence of Y [$Y = B/I(T) - 1$]. The values labeled on the figure represent the activation energies measured from the slope.

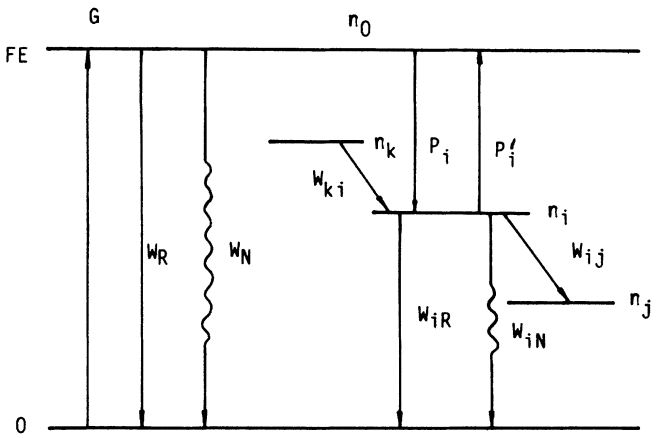

FIG. 4. Dynamic model for GaP:N considering the exciton transfer among multicenters.

$$I_{\mathrm{NN}_i}=\left[B+\sum_{j(>i)} I_{\mathrm{NN}_j}P_j(T)\right]\Big/(1+Ae^{-E_a^i/kT}), \quad (4)$$

where E_a^i is the activation energy of thermal quenching of NN_i trapped excitons, both A and B are a constant, and $P_j(T)$ represents the transfer rate of NN_j. $\sum_{j(>i)} I_{\mathrm{NN}_j}P_j(T)$ is so small that it can be put out of consideration when the temperature is high enough. Thus, the emission intensity is

$$I_{\mathrm{NN}_i}=B/(1+Ae^{-E_a^i/kT}). \quad (5)$$

For the several processes of thermal quenching, Eq. (4) becomes a common expression:

$$\frac{1}{I_{\mathrm{NN}_i}}\left[B+\sum_{j(>i)} I_{\mathrm{NN}_j}P_j(T)\right]-1=\sum_q A_q e^{-E_{aq}^i/kT}. \quad (6)$$

Much attention has been paid to the thermal quenching of luminescence of NN_1. We used formula (6) to fit the thermal-quenching curve and found that the fit values of the possible activation energies are very close to that measured directly from the temperature dependence of luminescence of NN_1 in Fig. 3. It is evident that the thermal-quenching curve in Fig. 3 consists of three processes corresponding, respectively, to the lower middle, and higher temperature range. We notice that both fit and experimental activation energy approach, within experimental error, the binding energy 21±4 meV (Ref. 11) for the free exciton, 40 meV (Ref. 2) for the hole, and 143 meV for the NN bound exciton. Therefore, we believe that in a different temperature range the mechanism of the thermal quenching is quite different, at least consisting of three parts, the thermal ionization of the free exciton into the free electron and hole, the escape of the hole away from the bound exciton, or the debinding of the bound exciton as a whole into the free exciton.

C. Thermal quenching of phonon sidebands dependence on the exciton phonon coupling

In Ref. 4, Chang *et al.* pointed out that all the phonon sidebands in GaP:N have the same activation energy and the quenching of them is thus specific to the exciton-phonon coupling regardless of the excitons with different binding energies. This is the first observation of the different behavior between the no-phonon bands and the associated phonon sidebands. Unfortunately, not enough attention has been paid to this experimental finding. We think it is necessary to represent one most important result of Ref. 4 in this paper, that is, the temperature dependence of integrated intensity of zero-phonon bands NN_i and one-phonon sidebands NN_i^*, as shown in Figs. 5 and 6. The different temperature behavior between zero- and one-phonon bands is obvious. After the data published in Ref. 4, we have measured the thermal-quenching activation energy of one-phonon sidebands for various samples with different nitrogen concentration and obtained their values from 50 to 60 meV. These values are gathered in Table I.

We suppose that this character of phonon sidebands comes from the two-component formation of phonon sidebands (see paper IV). As we shall discuss in paper IV, the phonon sideband consists of the multiphonon process in direct transition and phonon-assisted momentum-conserving indirect recombination of bound excitons. For the former, the theory of Huang and Rhys tells us that the ratio of the probability of radiative transition of zero- and one-phonon bands can be characterized by a parameter almost independent of temperature.[12] Therefore, in this case, the zero- and one-phonon bands should show the same temperature behavior. But for the latter, we can image the thermal quenching of phonon sidebands to be the inverse process of phonon-assisted momentum-conserving indirect transition. As a result, the thermal quenching of phonon sidebands depends strongly on the exciton-phonon coupling and has no relation to the binding energy of the bound exciton. The activation energy of 50–60 meV is very close to the phonon (LO or nitrogen local mode) energy. This fact supports our suggestion mentioned above.

TABLE I. The thermal activation energies of one-phonon sidebands.

Sample (nitrogen concentration)	Activation energy of one-phonon sidebands (meV)	
	NN_1^*	NN_3^*
7×10^{18} cm^{-3}	57±4	59±4
5×10^{17} cm^{-3}	55±5	57±5

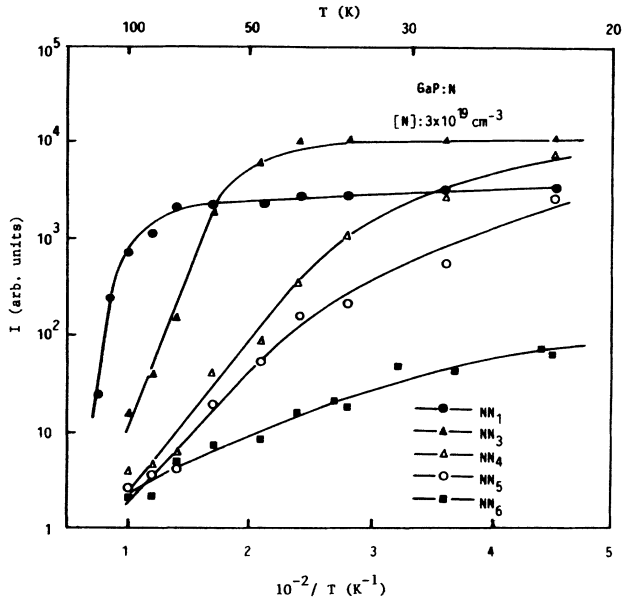

FIG. 5. Dependence between integrated intensity and $1/T$ for no-phonon lines.

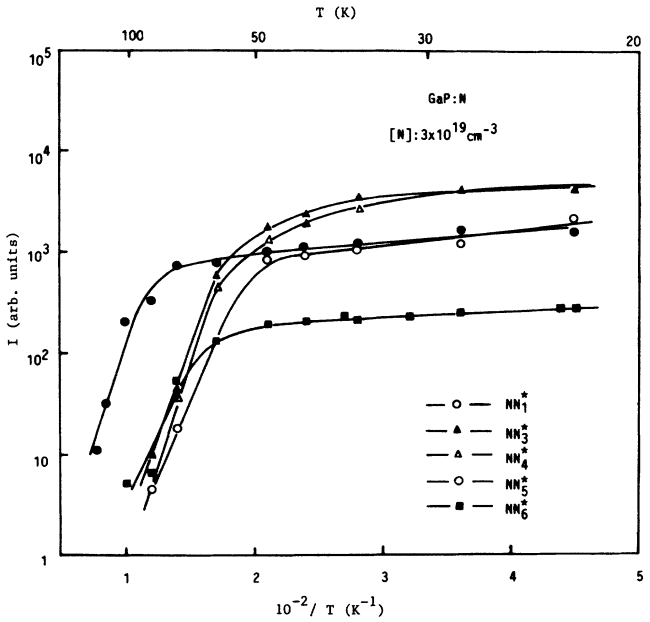

FIG. 6. Dependence between integrated intensity and $1/T$ for phonon sidebands.

IV. CONCLUSION

In the low-temperature range ($T < 40$ K) the decrease of the luminescence efficiency is due to the nonradiative energy transfer from bound exciton B to other centers.

According to the fact that the activation energy for the thermal quenching of zero-phonon lines has different values in different temperature ranges, we conclude that in the thermal quenching of bound excitons there are three kinds of mechanisms: the ionization of free exciton, the escape of the hole, or the debinding of the whole bound exciton. From the result that thermal quenching of phonon sidebands depends strongly on the exciton-phonon coupling regardless of the binding energy of bound excitons, we suppose that such a behavior comes from the two-component formation of phonon sidebands, i.e., multiphonon process in direct transition and phonon-assisted momentum-conserving indirect recombination. The latter is attributed to the different temperature behavior between phonon sidebands and zero-phonon lines.

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