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Excitons bound to nitrogen pairs in GaAs

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We have observed radiative recombinations of excitons bound to different nitrogen-pair complexes in GaAs by applying hydrostatic pressure. The samples investigated have relatively high nitrogen concentrations and were grown using a chloride method. By carefully tuning the pressure, we can not only make the NN_i pairs ($1 \leq i \leq 10$) appear successively in the band gap of GaAs and then become the major exciton recombination channel, but also change the binding energy of these levels. A study of thermal quenching of the radiative recombination of excitons bound to a center with different binding energies due to different pressures shows that the quenching mechanism changes from the thermal excitation of the whole exciton when the binding energy is small, to the excitation of the hole when the binding energy of the exciton is greater than that of the hole. A pressure-tuned thermal-state-selection method is developed from the thermal quenching properties. It artificially selects the state to be thermally quenched and is similar to below band-gap excitation or selective excitation spectroscopy. However, it can be applied to a defect the concentration of which is too low for a resonant excitation, as is the case for the GaAs:N samples here. The exciton-phonon coupling strength in GaAs:N is observed to increase slightly with binding energy, and, in agreement with the pressure dependence of NN_i energy levels, indicates an increase in the localization of the nitrogen exciton trap potential. The exciton-phonon coupling factor is observed to be independent of temperature.

I. INTRODUCTION

Because of their physical and technological interest, excitons bound to isoelectronic traps in semiconductors have been studied extensively.[1-7] Among the known cases, excitons bound to nitrogen traps in GaP have attracted the attention of researchers[8-18] and have played a very important role in our everyday life,[4] for instance, in light-emitting diodes. This has led to a persistent search for nitrogen traps in GaAs over recent decades. However, in spite of the dominant role played by nitrogen in GaP and the extensive efforts to observe these states in GaAs, it was not until 1982 that any radiative recombination due to nitrogen was reported in GaAs. Wolford *et al.*[19] studied N-doped GaAs under hydrostatic pressure and identified the excitonic recombination due to isolated nitrogen N_x. More recently, the observation of the rich NN_i complexes of nitrogen in GaAs has also been made possible[20] by (i) epitaxial growth of sufficiently heavily doped GaAs:N and (ii) pressure tuning of the energy-band structure of the GaAs host relative to the excitonic states, allowing each of the different complexes to appear, successively, in the recombination spectra.

In both the well-studied case of GaP:N (Ref. 8) and the newly discovered case of GaAs:N,[20] doping with N gives rise to characteristic radiative recombinations, of excitons bound not only to isolated nitrogen (N_x) but also to pairs of nitrogen atom (NN_i), where $i = 1, 2, \ldots$, in order of increasing pair separation. Up until now, two main models have been proposed for the exciton binding mechanism in nitrogen-doped GaP. One suggests that the exciton is bound as a single entity mainly by the strain introduced by the nitrogen atom.[6,7] The other (the so-called Hopfield-Thomas-Lynch model), however, proposes that the central-cell potential of the isoelectronic trap, N_P, attracts an electron, after which the defect, as a "quasiacceptor," captures a hole.[5] Many experimental results, especially those of deep NN_i centers, seem to favor the latter model.[9,10] In this study, we investigate the exciton binding mechanisms through the study of exciton thermalization. Thermal quenching processes of the luminescence of the exciton bound to these NN_i complexes have thus been studied under different hydrostatic pressures. Nitrogen-doped GaAs provides a unique means of investigating the binding mechanism of excitons bound to this kind of isoelectronic traps, because (i) due to the deep-level-like behavior of nitrogen traps, the binding energy (E_b) of different levels can be tuned by hydrostatically applied pressure[20] and (ii) the state studied can be selected while other higher-energy nitrogen-pair states are still resonant in the conduction band, thus providing a clean background with a low spectral overlap.[20] If a similar study were to be attempted in alloys of varying composition, the separation of defect and alloy phenomena would be complicated. Our results for NN_i centers at different binding energies under different hydrostatic pressures show that their thermal binding energies (E_t) increase with increasing binding energy below about 20 meV, while for greater values of binding energy, E_t remains constant. This means that the luminescence from bound excitons is thermally quenched by the escape of the exciton when $E_b < 20$ meV and by the escape of the hole (with a Coulomb binding energy of about 20 meV) for $E_b > 20$ meV.

From these thermal quenching results, we developed a "pressure-tuned thermal-state-selection" method which is somewhat similar to below band-gap excitation or selective excitation spectroscopy, however, it has its own advantages. It can be applied to a defect with a very low concentration for which a resonant excitation is very difficult, as the GaAs:N samples studied here. This method is believed to be applicable to more general cases for reducing background and resolving peaks in a heavily overlapping spectrum.

Although nitrogen in $GaAs_{1-x}P_x$ alloys seems to give rise to exciton recombination with an exciton-phonon coupling which is highly dependent upon the binding energy of the state,[21] an investigation of the Huang-Rhys factor (S) of NN_1 exciton recombination in GaAs:N under different hydrostatic pressures shows only a slight increase in exciton-phonon coupling with increasing binding energy. This, together with the discussion of a temperature-independent S factor for the NN_3 line at a certain pressure, is illustrated in Sec. III of this study. In the following, a description of the materials investigated and the experimental methods is given in Sec. II. The main results are presented and discussed in Secs. III A–III D. Finally, the results are summarized in Sec. IV. In order to avoid reproducing published results, the reader must consult Ref. 20 to fully grasp the material presented below.

II. MATERIALS AND EXPERIMENTAL METHODS

Our crystals were grown in a halide vapor-phase epitaxy system[22] using different levels of NH_3 inlet pressure as the doping source. The nitrogen concentration obtained varied with the NH_3 flow rate and the deposition temperature, and could be up to 6×10^{17} cm^{-3} as detected by secondary-ion mass spectroscopy and infrared (ir) measurements. As far as we know, no one has ever reached such high concentrations. Thermodynamical calculation[23] shows that the maximum solubility of nitrogen in GaAs should be less than 10^{14} cm^{-3}, and predict nitrogen concentrations of about 10^{19} cm^{-3} in GaP in growth from solution, i.e., close to equilibrium.[4,23] The reason for this large discrepancy in concentration between the theoretical prediction and experimental values in our case of GaAs:N is most probably due to surface kinetic control of growth and, hence, nitrogen impurity incorporation during the chloride growth, allowing a much higher concentration than that predicted by the solubility limit.

For hydrostatic pressure measurements, substrates were removed by lapping to final sample thicknesses of about 30 μm. The samples were then cleaved into about 100×100 μm dies and loaded into a gasketed diamond-anvil cell (DAC) of the Merrill-Bassett type.[24] Argon was used as the pressure-transmitting medium, resulting in hydrostatic pressure conditions. In thermal quenching measurements, different temperatures were obtained by passing cold exchange helium gas through the sample volume. In order to guarantee that the temperature measured is close to the true sample temperature, a carbon resistor was mounted on the DAC close to the sample position, with a good thermal contact. Photoluminescence (PL) was measured in a forward scattering geometry using the focused 5145-Å line of an Ar^+ laser as a source of excitation. Excitation densities were typically 10^2 W/cm^2. The signal was dispersed by a 0.75-m double monochromater and detected in a GaAs photomultiplier and photon-counting equipment. The donor-bound exciton recombination peak of GaAs with a pressure coefficient of 10.73 meV/kbar (Ref. 25) was used for pressure calibration and no corrections were made for the spectral response of the system, which is known to vary only slowly in this wavelength region.

III. RESULTS AND DISCUSSION

A. Nitrogen-pair luminescence

It has been established[20] that excitons bound to nitrogen pairs of different separations in GaAs give rise to efficient radiative recombinations if these nitrogen energy levels are made to appear in the band gap. For an overview of the observed nitrogen-pair luminescence,[20] we show in Fig. 1 how the nitrogen-pair lines appear successively in the PL spectra of GaAs:N under the application of hydrostatic pressure. Special attention should be paid to Figs. 1(d) and 1(f): a comparison of Fig. 1(d) with the lower-energy PL spectrum region of GaP:N (Ref. 16) (see the inset of Fig. 1) allows one to suggest that the new lines are originated from nitrogen pairs; the observation in Fig. 1(f) of a rich spectrum of sharp lines very similar to the higher-energy PL spectrum region of GaP:N in the inset makes it evident that we are observing nitrogen-pair luminescence in GaAs:N.

Some more points are presented below for the observed nitrogen-pair bound exciton luminescence.

(i) A strong luminescence peak (compared with the weak peak about 12 meV on its low-energy side) in Fig. 1(a) of the atmospheric pressure spectrum is labeled NN_1. However, a conclusion drawn by Schwabe *et al.*[26] to their spectra of zero-field and Zeeman splitting of this line was that the center investigated had a C_{3v} point-group symmetry, in contrast to C_{2v} point-group symmetry for the NN_1 oriented in a $<110>$ direction. A comparison of the spectra of zero-field and Zeeman splitting of the NN_1 line in GaP:N (Refs. 8 and 27) with those of this line in GaAs:N (Ref. 26) is shown in Fig. 2. It is obvious that in GaAs:N this peak actually has the same patterns as those of NN_1 in GaP:N, a defect oriented in the $<110>$ direction. This supports our assignment of the defect to the NN_1 state.

(ii) All the NN_1 pair energy levels exhibit deep-level-like pressure dependence.[20] They do not follow any particular conduction-band minimum under the application of hydrostatic pressure; this is true even when the levels are resonant in the conduction band, making it possible to push them into the band gap and change their binding energies by applying hydrostatic pressure. Their pressure coefficients range from 3.5 meV/kbar to 5 meV/kbar (Fig. 2 in Ref. 20). When the state appears close to the band edge, it is about 5 meV/kbar, decreasing continuously to 3.5 meV/kbar as the state leaves the band edge and becomes further displaced from the Γ conduction-

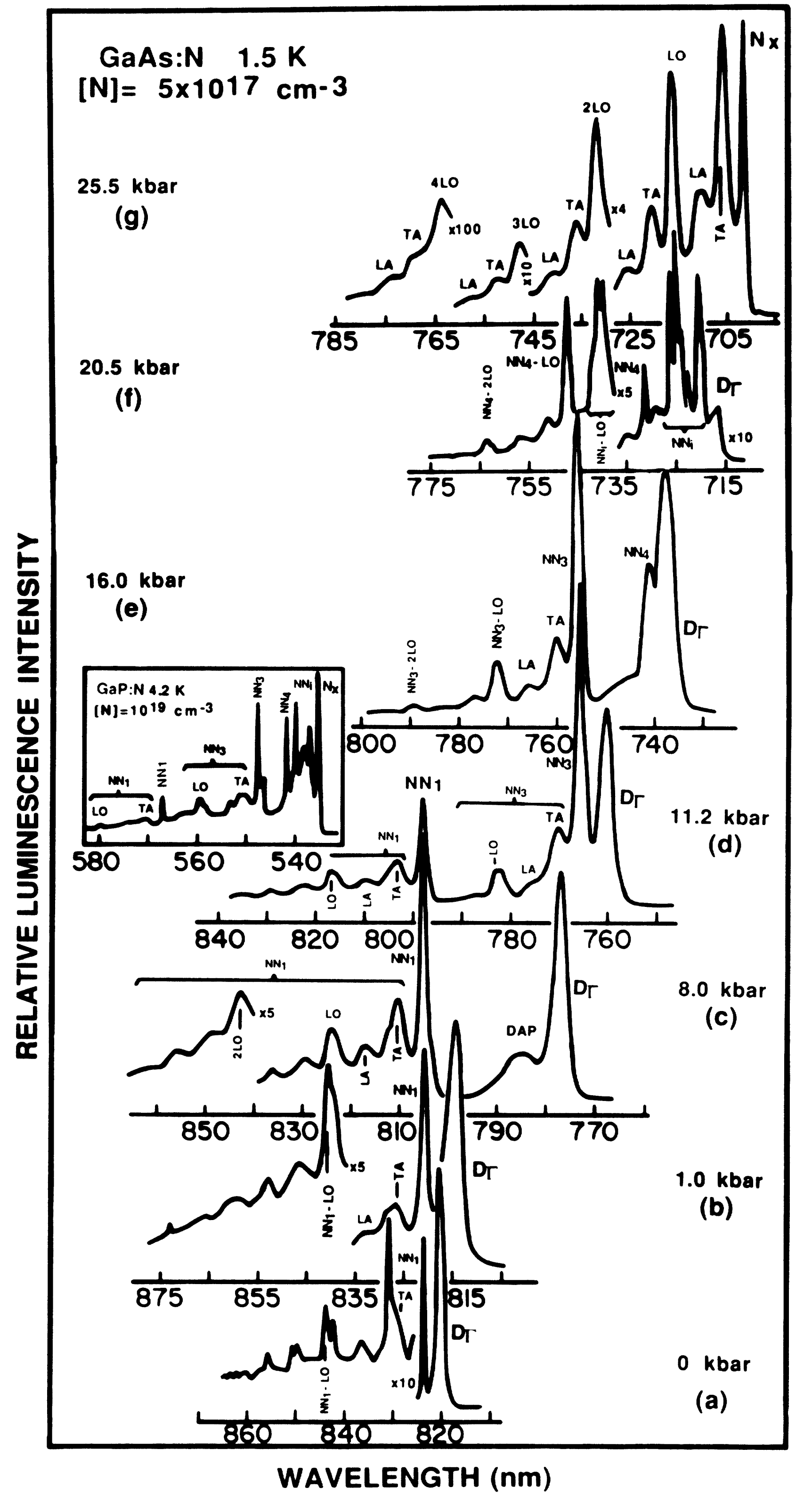

FIG. 1. Photoluminescence spectra of nitrogen-doped GaAs at different pressures. For clarity, the NN_i peaks are aligned in consecutive spectra. The spectra consist of zero-phonon transitions, together with replicas of these lines resulting from coupling to momentum-conserving TA (transverse acoustic) and LA (longitudinal acoustic) phonons and configuration coordinate coupling to LO (longitudinal optical) phonons. In the inset, the atmospheric pressure spectrum of nitrogen-doped GaP in Ref. 16 is shown.

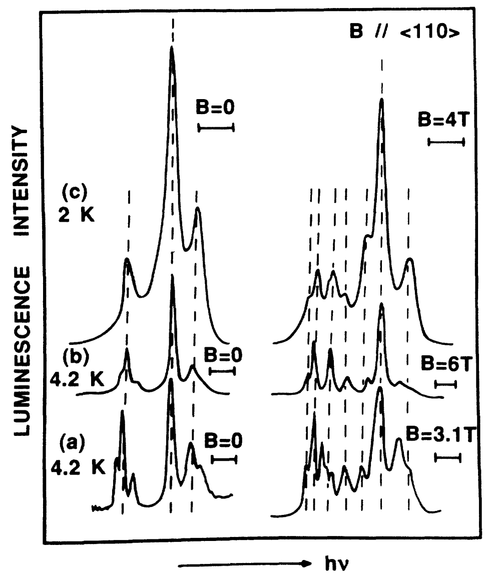

FIG. 2. Comparison of the zero-field and Zeeman-splitting observed for the NN_1 line in GaP:N and GaAs:N observed at atmospheric pressure. Curves (*a*) and (*b*) are for the NN_1 line in GaP:N in Refs. 8 and 27, respectively. Curve (*c*) is for the 1.508 eV line in GaAs:N in Ref. 26. The bars below the values of the magnetic field are energy separations of 0.5 meV corresponding to each of the patterns.

band minimum. This behavior is in qualitative agreement with theoretical results for the energy-level shifts with alloying or pressure for this type of isoelectronic defect with very localized potentials.[28] However, the pressure coefficient of a perfect deep level should be independent of the changes of the conduction-band minima. Due to the deviation in the behavior of a real nitrogen defect from a perfect deep level there is a decrease in the pressure coefficient with increasing pressure for each level and this is explained as follows. When, in reality, such a defect is close to the Γ conduction-band minimum, although it is still an exciton trap with a short-range large-momentum transfer potential, with its behavior affected by the Bloch states of the conduction band throughout the Brillouin zone, its pressure dependence may reflect a preference for the Γ conduction-band minimum in **k** space even though the Brillouin-zone center contains only about 1% of the conduction-band density of state. Since the Γ conduction-band minimum moves with pressure at a higher rate (10.73 meV/kbar) than those of L and X minima (5.5 meV/kbar and -1.34 meV/kbar, respectively[25]), the defect would then show a higher pressure coefficient when it is close to the Γ conduction minimum. As the state becomes deeper, however, the electron wave function near point Γ plays a less important role and the pressure dependence of the defect manifests itself as a mixture of that of the host band structure from all **k** space, thus slowing down the rate at which the energy level shifts with pressure.

(iii) PL excitation measurements were carried out for the nitrogen-pair luminescence. This was intended for the investigation of the acceptorlike excited states[9] of a hole in the Coulomb field of an electron tightly bound to the nitrogen-pair defect, especially for the case where the binding energy of a nitrogen-pair level is over 20 meV. As will be presented in Sec. III B, 20 meV exciton binding energy is the onset of the acceptorlike binding of a hole in an exciton bound to NN_i pair defects in GaAs. However, the measurements were not quite successful due to the extremely weak signal resulting from too low nitrogen-pair concentration in the sample for a resonant excitation.

B. Thermal quenching mechanisms

The thermal quenching process offers a good method of investigating the dissociation channel of excitons bound to nitrogen traps, thus serving as a probe of the exciton binding mechanism. It has therefore been intensively studied in N-doped GaP and Ga(As,P) alloys. Sturge *et al.*[10] measured the photoluminescence efficiency as a function of temperature and drew the conclusion that the quenching mechanism for each N or NN_i center in GaP at low temperature was the thermal excitation of either a free exciton or a free hole, whichever had the lowest binding energy. This agrees with their luminescence excitation results[9] which they observed the hole excited states for deep NN_i pair centers in GaP:N. However, Zhang *et al.*[13] achieved an almost linear relationship between activation energy and binding energy for different NN_i no-phonon lines, and concluded that the escape of free excitons from NN_i centers made the most important contribution to the quenching. The different results of these two groups were analyzed[14] due to the energy transfer from shallow to deep NN_i centers in the high N concentration sample (3×10^{19} cm^{-3}), resulting in larger activation energies observed in the latter group. In our GaAs:N samples, however, this difficulty is efficiently overcome not simply because the nitrogen concentration is much lower (5×10^{17} cm^{-3}), but we can make shallow NN_i states resonant in the conduction band while investigating the deep NN_i state, completely eliminating energy transfer between nitrogen defects. We believe the effect of donors on the thermal quenching of NN_i pairs is negligible due to the low concentration of donors in the samples studied.[22]

From the luminescence efficiency point of view, the temperature dependence of the integrated intensity of the bound exciton luminescence can be expressed by[10,29]

$$I(T)/I(0)=W_R/[W_R+W_{\mathrm{NR}}(T)]\ , \tag{1}$$

where $I(T)$ is the luminescence intensity at temperature T and $I(0)$ is the luminescence intensity in the temperature limit $T\rightarrow0$ K. W_R and W_{NR} are the radiative rate and nonradiative quenching rate, respectively. As described above, two main quenching channels for excitons bound to NN_i pair centers are possible:

$$(\mathrm{NN}^0+X)\rightarrow\mathrm{NN}^0+X\ (\text{with rate}W_{\mathrm{NR1}})\ , \tag{2a}$$

$$(\mathrm{NN}^0+X)\rightarrow\mathrm{NN}^-+h\ (\text{with rate}W_{\mathrm{NR2}})\ . \tag{2b}$$

These processes [(2a) and (2b)] represent the thermal emission of a free exciton and of a free hole, respectively.

$W_{\mathrm{NR}1}$ and $W_{\mathrm{NR}2}$ are quenching rates for the corresponding processes. Then,

$$\frac{I(T)}{I(0)}=\frac{W_R}{W_R+W_{\mathrm{NR}1}(T)+W_{NR2}(T)}$$
$$=\frac{1}{1+W_{\mathrm{NR}1}(T)/W_R+W_{\mathrm{NR}2}(T)/W_R}$$
$$=\frac{1}{1+C_1\exp(-E_{a1}/kT)+C_2\exp(-E_{a2}/kT)}\ . \tag{3}$$

We therefore obtain

$$I(0)/I(T)-1=C_1\exp(-E_{a1}/kT)+C_2\exp(-E_{a2}/kT)\ , \tag{4}$$

where E_{a1} and E_{a2} are the activation energies of thermal quenching processes (2a) and (2b), respectively. C_1 and C_2 are assumed to have much weaker temperature dependences than those of the exponential factors, and are assumed to be constant.

Several examples of a plot of $\ln A=\ln[I(0)/I(T)-1]$ as a function of $100/T$ are shown in Fig. 3. In the plots, $I(0)$ is taken from the almost temperature-independent luminescence intensity near 0 K (for instance 5 K). It can be seen in Fig. 3 that all the curves have a linear region where the luminescence intensity decreases by about 2–3 orders of magnitude. However, from Eq. (4) we know that $\ln A$ versus $100/T$ would not be linear. The measured linear region must be dominated by one of the nonradiative processes in Eq. (4). The corresponding activation energy obtained by fitting this region with a single activation energy represents the dominating nonradiative channel. Thermal quenching under different pressures, and hence different binding energies, has been investigated. The activation energies measured are plotted as a function of binding energy, relative to that of the free exciton in Fig. 4. In the figure, we assume that with the variation of pressure, the donor-bound exciton line follows the conduction-band minimum, and its energetic distance, $E_{DX}=h\nu_{\mathrm{FE}}-h\nu_D\approx 3$ meV relative to the free exciton,[30] remains constant. The binding energy of a NN_i center relative to the free exciton would then be

$$E_b=\Delta E+E_{DX}\ , \tag{5}$$

where ΔE is the separation in energy between a NN_i line and the donor-bound exciton line under a certain hydrostatic pressure.

Figure 4 shows quite clearly that, for the states investigated, the thermal binding energy (E_t) is nearly equal to the exciton binding energy (E_b) and increases linearly with E_b for $E_b<20$ meV, however, E_t remains approximately constant for $E_b>20$ meV. 20 meV is therefore believed to be the hole binding energy in the bound exciton [Eq. (2b)] which remains constant even though the exciton binding energy increases greatly. It is thus concluded that the luminescence of NN_i centers (at least for NN_1 and NN_3) in GaAs:N is quenched by the thermal emission of the whole exciton when the binding energy is

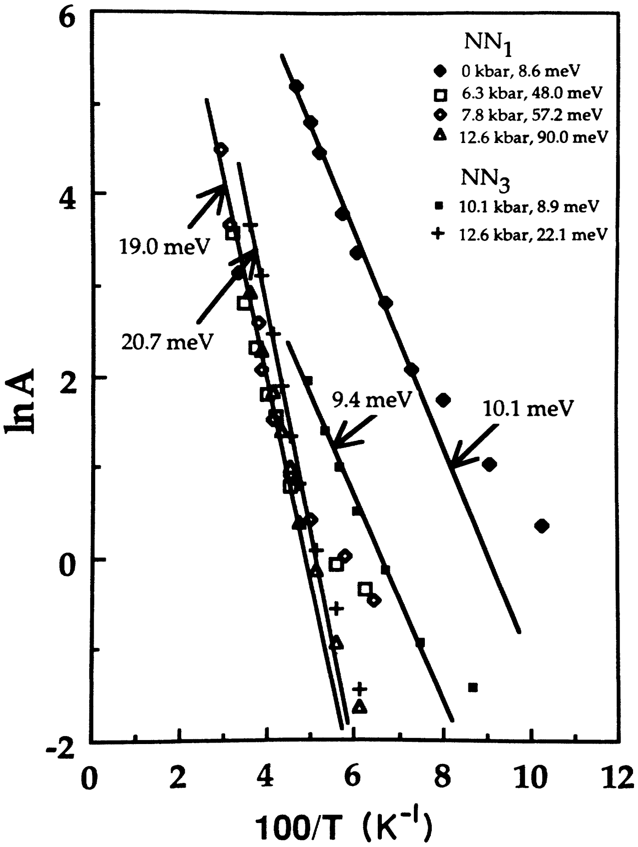

FIG. 3. Thermal quenching data in a plot of $\ln A=\ln[I(0)/I(T)-1]$ vs $100/T$ for the different NN_i pair lines under several different hydrostatic pressures. The thermal-activation energies are obtained by fitting the linear portion of the plot. Also listed in the upper right corner are the binding energies of the states relative to free excitons and the hydrostatic pressure applied.

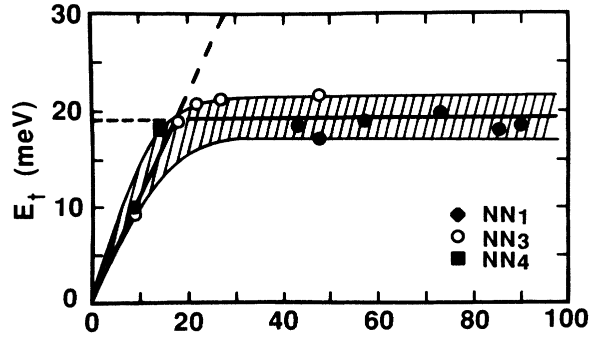

FIG. 4. Thermal binding energy (E_t) as a function of binding energy (E_b) relative to the free exciton for NN_i defects under different hydrostatic pressures. In the region where E_t increases with E_b, the escape of the whole exciton dominates the thermal quenching processes, while in the region where E_t remains constant with increasing E_b, the escape of the free hole dominates. The crossover point is at about $E_b=20$ meV, which is believed to be the binding energy of the hole.

less than 20 meV (the hole binding energy in the bound exciton), in agreement with the binding mechanism proposed by Allen,[6,7] for nitrogen centers in GaP:N. The thermal quenching channel switches to the thermal emission of the free hole in the bound exciton when the binding energy is increased by pressure to a value larger than that of the hole, corresponding to the binding mechanism proposed by Hopfield *et al.*[5]

It should be indicated here that in Fig. 4, according to Eq. (4), we should have observed two activation energies corresponding to Eqs. (2a) and (2b), one dominating the lower temperature region and the other the higher. But if we assume that $E_{a2} > E_{a1}$, and the temperature is low, the second term on the right-hand side of Eq. (4) can be neglected. This accounts for the single activated process we observed in Fig. 3, as the temperature is not high enough (the reason we did not go to higher temperature is that the signal becomes very weak) for the second activated process with higher activation energy to be observed. In the crossing region in Fig. 4, however, scattering of data prevents us from obtaining reliable separate values of the two activation energies when both parallel quenching channels are operational.

C. Pressure-tuned thermal-state selection

Since the binding energy of NN_i pair levels is tunable by pressure and their thermal binding energy (E_t) discussed in Sec. III B increases with their binding energy before E_t reaches a value of about 20 meV, we are now going to describe a method which is somewhat like below band-gap excitation or selective excitation spectroscopy. The application of this method to our GaAs:N samples sheds light on a confusing feature of the NN_i pair luminescence, which is very difficult when a selective excitation is used since the NN_i pair concentration in our sample is very low. It therefore shows a potential for more general applications of the method in other similar cases.

It can be seen from the spectra in Fig. 1 that the luminescence intensity of a NN_i pair line dominates the spectrum soon after it appears in the band gap. When a more shallow state is pressed out of the conduction band, the deeper one seems to give up its luminescence to the more shallow one. For instance, the clear and quite strong luminescence of NN_i ($5 \le i \le 10$) in Fig. 1(f) cannot be seen at all when N_x appears [Fig. 1(g)]. This is quite confusing because why should a state, when it becomes deeper and hence may even have a higher capture probability, disappear in the spectrum.

Notice the increase in absolute luminescence intensities from the NN_i pair lines which become progressively stronger for more distant pairs. We assume that all the pair luminescences have approximately the same decay time and believe that this effect results from the increasing concentration of more distant pairs. Due to the spectrum overlapping, the weak close pair luminescence is covered by the strong distant pair luminescence. If this is true, a selective excitation with a photon energy lying between that of the deep and shallow lines would, in principle, be able to reduce the background and recover the close pair luminescence in the spectrum. However, such a selective excitation luminescence spectrum is sometimes difficult to obtain due to the lack of suitable laser, and/or the too low concentration of the defect for a resonant excitation. In fact, we have performed selective excitation spectroscopy for our samples under hydrostatic pressure using a Ti:sapphire laser pumped by an Ar^+ laser. But no satisfying result was obtained due to the extremely low signal level resulting from the low concentration of NN_i pairs. It is, therefore, of importance that we have been able to bring the deep pair luminescence back to the spectrum by a pressure-tuned thermal-state-selection method described below.

Take a typical case in the pressure region of Figs. 1(f) and 1(g) as an example. From the discussion in Sec. III B we know the luminescence of a shallow (in the meaning that it has just been pushed into the band gap) nitrogen level quenches at a lower temperature than that of a deeper one. Therefore, if the pressure is tuned carefully to a critical value where the N_x has just been pushed into the band gap, it dominates the spectrum with its strong phonon replicas, while all the other NN_i lines and their phonon replicas cannot be observed [see Fig. 5(a)]. The N_x line cannot be observed either in this spectrum because of a strong band gap and self-absorption. In such a situation, N_x has a very small binding energy and starts

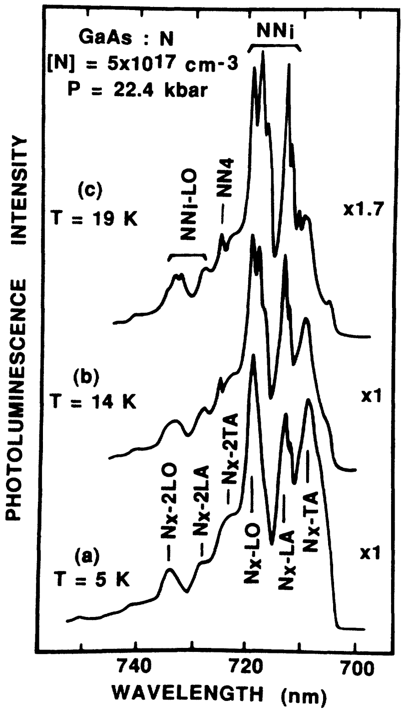

FIG. 5. Spectra at different temperatures under a pressure of 22.4 kbar, illustrating the application of the pressure-tuned thermal-state-selection method. It shows that the NN_i lines dominate the spectrum at higher temperatures when the strong N_x-related luminescence at lower temperatures quenches in intensity. This is similar to band-gap selective excitation. However, such a resonant excitation is too weak to be observable for the GaAs sample investigated.

to quench at a very low temperature. In Fig. 5(b), at 14 K, we start to see the traces of NN_i pair lines as the N_x phonon replicas become weaker. At 19 K, however, the spectrum [Fig. 5(c)] is dominated again by the sharp NN_i pair lines due to the thermalization of N_x excitons. Obviously, the above pressure-tuned thermal-state selection recovers the unobserved NN_i pair luminescence by quenching the strong N_x luminescence background. This confirms our suggestion that the disappearance of close pair lines in a spectrum is due to their low concentrations. We believe such a pressure-tuned thermal-state-selection method will be applicable to more general cases.

If the temperature is further increased, however, we cannot make the NN_4 luminescence in Fig. 5(c) dominate the spectrum. This, in agreement with the conclusions drawn in Sec. III B, is because the NN_4 luminescence quenches at almost the same temperature as those of shallow NN_i ($i>4$) pairs since all their binding energies are larger than 20 meV. Their thermal binding energies are therefore determined by the thermal excitation energies of the holes which are about 20 meV and almost independent of the exciton binding energies.

D. Exciton-phonon coupling

Similar to GaP:N, in GaAs:N all the NN_i lines have pronounced phonon replicas. According to the linear phonon coupling theory [31] at low temperatures the integrated nth-phonon coupling intensity would be

$$I_n = e^{-S}(S_n/n!) , \tag{6}$$

where S, known as the Huang-Rhys factor, is a temperature-independent parameter characterizing the lattice relaxation. From Eq. (6), it is easily seen that $S = I_1/I_0$, the ratio of the integrated intensity of the first phonon replica to that of the zero-phonon line. In GaP:N, a strong temperature-dependent S factor has been found[13] for almost all NN_i pair lines. This, however, was later found[15] to be due to the overlapping of the spectra and energy transfer, which were not considered in Ref. 13. When taking these factors into account, a temperature-independent S factor was found.

In GaAs:N, the pressure applied can be used to select a typical state for investigation of its exciton-phonon coupling. For example, in the pressure range 10–15 kbar, the spectra observed appear somewhat like that in Fig. 1(d). There NN_3 has just appeared in the band gap and all the shallow NN_i are resonant in the conduction band. It seems that in the energy region from NN_1 to NN_3 all the observed peaks are the phonon replicas of the NN_3 line. The S factors observed for some of the phonon replicas at different pressures are shown in Fig. 6. It is seen that the S factors for the LO phonons are independent of temperature, while for the TA phonon, at 11.8 kbar, there is a significant increase in the S factor with temperature. However, when the pressure increases to 14.6 kbar, the S factor for the same TA-phonon replica becomes temperature independent. This puzzling behavior can be explained by the overlapping at 11.8 kbar of the NN_3-TA peak with the donor-acceptor (or band to acceptor) peak which quenches at a temperature higher than that of NN_3, resulting in an apparent increase in intensity at the peak position of NN_3-TA, and hence the S factor. At 14.6 kbar, there is no overlapping of the donor-acceptor peak which has moved to the higher-energy side of the NN_3 line with a pressure coefficient of 10.73 meV/kbar. Therefore, the S factor is observed to be temperature independent. This illustrates the important role played by spectral overlap.

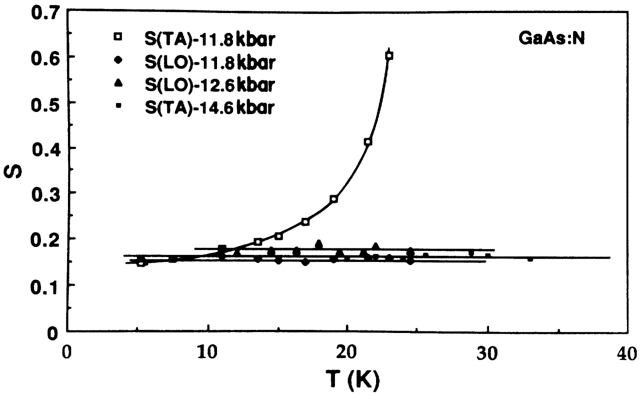

FIG. 6. Temperature dependence of the Huang-Rhys factor, S, for some lines at various pressures, illustrating its temperature-independent property. The explanation of the increase in S_{TA} with temperature at 11.8 kbar can be found in the text.

It has previously been reported that S factors for isolated nitrogen-bound exciton luminescence in $GaAs_{1-x}P_x$ alloys change significantly with composition, x, and hence the binding energy of the N_x center.[21] Our data for S factors of LO phonon replicas of the NN_1 line under different hydrostatic pressures are plotted as a function of the binding energy in Fig. 7. The data are be-

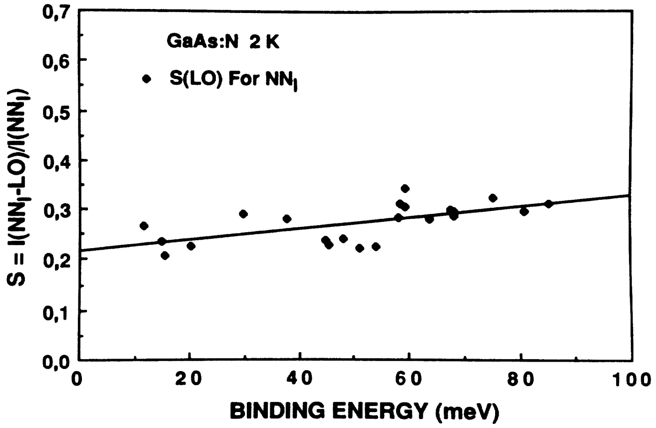

FIG. 7. Huang-Rhys factor S for the NN_1 line as a function of the binding energy of the state. It increases slightly with binding energy and indicates an increase in the localization of the state, in agreement with the decrease in the pressure coefficient for different NN_i energy levels at a higher pressure (Fig. 2 in Ref. 20).

lieved to be quite reliable, since we have measured the relatively clean case of NN_1 luminescence of GaAs:N under hydrostatic pressure. The S factor is observed, however, to increase very slowly with binding energy. This indicates anyway a small increase in the localization of the defect. As a matter of fact, such a slow increase in exciton-phonon coupling with binding energy is in excellent agreement with the small decrease in the pressure coefficient of a NN_i energy level at higher pressure hence higher binding energy discussed in Sec. I, and is also attributed to the deviation of the behavior of the nitrogen defect from a perfect deep level. The localization of a perfect deep level with a short-range, large-momentum transfer potential should be insensitive to a change in the conduction-band structure, and should manifest itself through a constant exciton-phonon coupling strength. There is a qualitative agreement between our data and the behavior of N_x in alloys, but the slope of dS/dE_b in our pressure experiment is a factor of 3 smaller than that in the alloy experiment.[21]

IV. SUMMARY

We have reported the observation of luminescence of excitons bound to nitrogen pairs of different separations as well as to isolated nitrogen atoms in GaAs using pressure tuning of these states relative to the GaAs band edges. All the nitrogen defects exhibit a deep-level-like behavior under hydrostatic pressure. We can thus push them successively into the band gap and change the binding energies of different NN_i defects through the application of hydrostatic pressure. By investigating the thermal quenching processes of NN_i luminescence under different hydrostatic pressure, we concluded that the thermal quenching mechanism for NN_i luminescence is changed from thermal excitation of the free exciton to the free hole as their binding energies were increased from lower than to higher than the hole binding energies. Hydrostatic pressure is used as a tool for tuning the binding energy of the defects. We have thus been able to bridge the two models for exciton binding; in one case the binding of the exciton as an entity, in the other case the strong non-Coulomb attraction for the electron followed by the binding of the hole to the long-range Coulomb potential in a quasiacceptor fashion.

A pressure-tuned thermal-state-selection method is developed from the thermal quenching results. By carefully tuning the pressure, one can artificially set the binding energy of a state, and therefore choose the state one wants to quench. Thus, it is of importance for resolving overlapping spectra. In some aspects, it is similar to below band-gap or selective excitation spectroscopy. However, it has its own advantage in that it can be used even for defects of very low concentration when a resonant excitation is not applicable, as for the nitrogen pairs in the GaAs:N samples investigated here.

The Huang-Rhys exciton-phonon coupling factors S were observed to be independent of the temperature, and are in agreement with the linear phonon coupling theory. A slow increase in the S factor for the NN_1 level with binding energy was observed, corresponding to the small decrease in pressure coefficient from 5 meV/kbar to 3.5 meV/kbar for almost all the NN_i energy levels when their binding energy is larger at higher hydrostatic pressure, which indicates that the localization of the deep-level-like nitrogen defects increases slightly as their energy levels move further away from a particular conduction-band minimum.

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