

## Exciton-phonon interaction and energy transfer of nitrogen-bound excitons in GaP

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Heat-pulse and time-resolved-luminescence experiments are performed on bound excitons in dilute GaP:N. A prominent broad luminescent band called the  $V$  band, is shown to arise from both zero-phonon and phonon-assisted recombination of excitons from the lower bound exciton state. A quantitative explanation of the shape of the  $V$  band is given in terms of resonantly enhanced second-order phonon-assisted recombination involving the upper bound exciton state, taking due account of the averaging of the phonon-induced strain over the exciton wave function. From the time-resolved luminescence experiments we derive a time of 300 ns for exciton energy transfer to disturbed sites.

### I. INTRODUCTION

The spectroscopic and dynamical properties of excitons bound to nitrogen substitutionally dissolved in GaP have been extensively studied.<sup>1-13</sup> Nitrogen is an isoelectronic impurity and may bind an electron by virtue of its higher electronegativity relative to that of phosphorus. An exciton is readily formed by trapping of a hole in the Coulomb potential of the bound electron.<sup>2</sup> The bound exciton gives rise to two zero-phonon lines of 0.88-meV separation, and exhibits strong phonon sidebands. The splitting originates from the  $J$ - $J$  coupling between the electron ( $J = \frac{1}{2}$ ) and hole ( $J = \frac{3}{2}$ ) (see Fig. 1). Radiative recombination of the exciton from  $A$ , the upper ( $J = 1$ ) state, is dipole allowed and fast, whereas radiative recombination from  $B$  ( $J = 2$ ) is dipole forbidden and slow. Earlier measurements revealed values for the lifetimes of  $\tau_A = 40$  ns and  $\tau_B = 4$   $\mu$ s.<sup>2</sup> The direct exciton-phonon transition rate from  $A$  to  $B$  is extremely fast and was determined by accumulated photon-echo experiments ( $\tau_{AB} = 25$  ps).<sup>3</sup>

In dilute high-quality samples at low temperatures one observes a luminescence band located directly below the  $B$  line, called the  $V$  band. In spite of extensive investigations, the origin of this band is still not clear. On one hand, thermomodulation experiments by Gal<sup>5</sup> suggested the phonon-assisted nature of the  $V$  band. They explain their signals on the basis of a model that assumed recombination of excitons in the  $B$  state to be resonantly

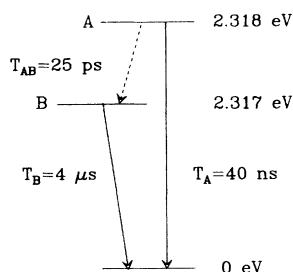


FIG. 1. Level scheme of the nitrogen-bound exciton. Lifetimes and energies of the levels are indicated.

enhanced and phonon assisted.<sup>6</sup> However, this model fails to explain the decline of the  $V$  band at the low-energy side. Later, theoretical calculations of the vibronic-sideband spectrum produced a feature at the position of the  $V$  band.<sup>7</sup> However, the complexity of the calculation prevented a definitive assignment. On the other hand, experiments on GaP:Zn:N showed an undulating structure in the  $V$  band, which is incompatible with phonon sidebands.<sup>8</sup> The presence of real states was subsequently unambiguously demonstrated by Gershoni, Cohen, and Ron.<sup>10</sup> They excited the  $V$  band directly and observed a satellite line in the luminescence spectrum 0.88 meV lower in energy, i.e., equal to the splitting between  $A$  and  $B$ . Consequently they concluded that the  $V$  band originates from real excitons bound to nitrogen but disturbed by distant impurities. However, the fact that the absorption spectrum of GaP:N does *not* reveal significant absorption beyond the  $A$  line forced them to invoke efficient energy transfer between disturbed and undisturbed sites. Direct energy-transfer measurements have been performed on heavily doped GaP:N only<sup>11</sup> and revealed time scales down to 10 ns for pairs of two neighboring nitrogen atoms. Indirect estimates of transfer times in dilute GaP:N have been based on optical dephasing measurements.<sup>3,12</sup> Brocklesby, Harley, and Plaut<sup>12</sup> inferred resonant transfer times of 800 ps for  $B$  from optical hole-burning results. On the other hand Molenkamp and Wiersma<sup>3</sup> showed inelastic energy transfer of  $B$  on time scales as slow as 100 ns. Resonant Raman-scattering studies suggest an extremely rapid energy transfer of  $A$ .<sup>13</sup>

The aim of this paper is to present new data that lead to a comprehensive picture of the nature of the  $V$  band. In order to achieve this goal we have performed two types of experiments: (i) Heat-pulse-induced time-resolved luminescence measurements which yield the phonon-assisted contribution to the  $V$  band and the luminescence of the real sites separately, and (ii) picosecond time-resolved luminescence measurements which reveal the transfer of excitons from the  $B$  line to the  $V$  band. We will begin by describing the experimental method (Sec. II), and then present the experimental results (Sec. III). Finally we will discuss our findings (Sec.

IV). The main result of this paper is that the exact shape of the  $V$  band is shown to be connected directly to the finite extent of the exciton wave function and the concomitant effect on the exciton-phonon interaction matrix element involving the  $A$  state.

## II. EXPERIMENT

### A. The sample

Experiments were performed on nominally undoped high-quality liquid-encapsulated-Czochralsky GaP, grown at Philips Research Laboratories. The absorption spectrum (inset of Fig. 2) reveals only intrinsic absorption and a sharp peak from N-bound excitons. The nitrogen concentration is  $(2 \pm 1) \times 10^{16} \text{ cm}^{-3}$ , as determined from the absorption spectrum by the method of Lightowers, North, and Lorimer.<sup>14</sup> The luminescence spectrum (see Fig. 2) is completely governed by nitrogen-bound excitons except for a weak peak at the bottom of the  $V$  band. This peak is only present under band-to-band excitation. It is generally attributed to sulphur and indicates that our sample is slightly  $n$  type. Samples were obtained by cleaving 500- $\mu\text{m}$ -thick [111]-oriented discs of GaP. The [111] surfaces were chemically polished. During all experiments the samples were immersed in pumped liquid helium.

### B. Heat-pulse experiments

Our purpose is to measure the induced changes in the luminescence following injection of a heat pulse. The heater configuration is shown in Fig. 3. Excitons were resonantly excited by means of an actively stabilized single-frequency ring dye laser (Spectra Physics 380D), pumped by a cw argon-ion laser (Coherent Innova 100). The dye laser was operated with Coumarin-6 dye and had a linewidth of 1 MHz, permitting luminescence detection close to the laser line. Heat pulses were generated by

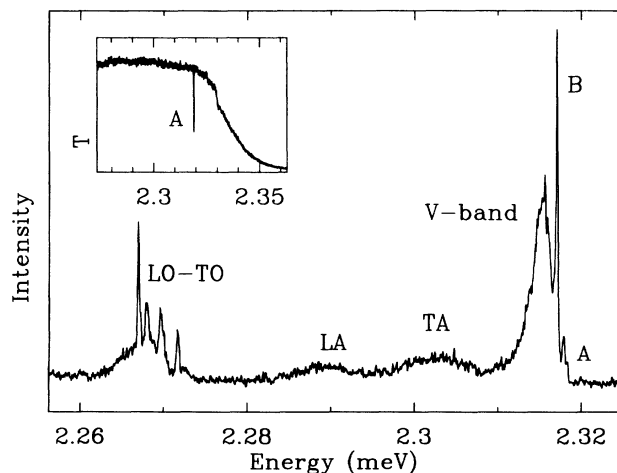


FIG. 2. Luminescence spectrum of GaP:N taken at low temperature, under band-to-band excitation by an argon-ion laser. The inset shows the transmission spectrum.

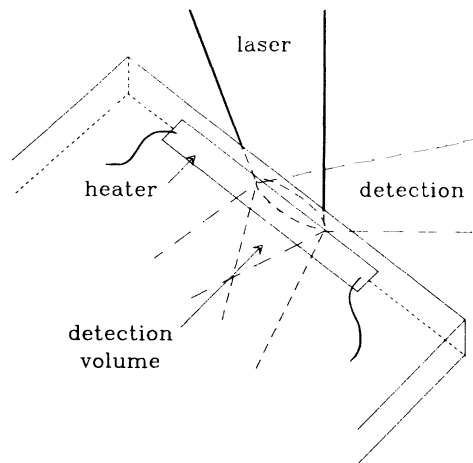


FIG. 3. The configuration of the heater and the detection volume at the GaP:N sample.

ohmic heating of a constantan strip with dimensions  $0.2 \times 7 \text{ mm}$  and a thickness of  $0.1 \mu\text{m}$  evaporated on the [111] surface of the crystal. The electrical contacts were made of silver epoxy. Rise and fall times of the electrical pulses were shorter than 10 ns. Dissipation of heat was about  $1 \text{ W/mm}^2$ . Luminescence was collected from the excited zone directly underneath the heater (see Fig. 3). After dispersing the luminescence by a 0.85-m double monochromator (Spex 14018) detection was by a Peltier-cooled photomultiplier tube (RCA 31034) and followed by standard photon-counting electronics and signal averaging by means of a multichannel analyzer (MCA). Time-resolved spectra were obtained by suitable gating of the discriminator.

### C. Time-resolved luminescence

In order to measure energy transfer directly, excitons were resonantly excited by picosecond pulses generated by a synchronously pumped cavity-dumped mode-locked dye laser (Spectra Physics) operated with fluorescein dye. The repetition rate was set to 80 kHz to avoid accumulation of excitons. Part of the laser beam was split off and monitored by a fast photodiode (Antel AR-S2) to serve as a trigger signal, while the remaining light was focused onto the sample. Luminescence was collected at right angles and dispersed in a 1-m double spectrometer (Jobin-Yvon HG.2S). Photons passing the end slit were detected by a fast Peltier-cooled photomultiplier tube (Philips XP2254B). Time resolution better than 300 ps was obtained by time-to-amplitude-conversion techniques. Here, the start and stop pulses were produced by two constant-fraction discriminators (Tennelec TC454), fed by the photomultiplier signal and the delayed photodiode signal, respectively.

## III. RESULTS

In the upper panel of Fig. 4 the luminescence spectrum of the  $V$  band and  $B$  line are shown as recorded at 1.5 K. The lower panel shows the difference between this spectrum and a gated spectrum which was integrated during

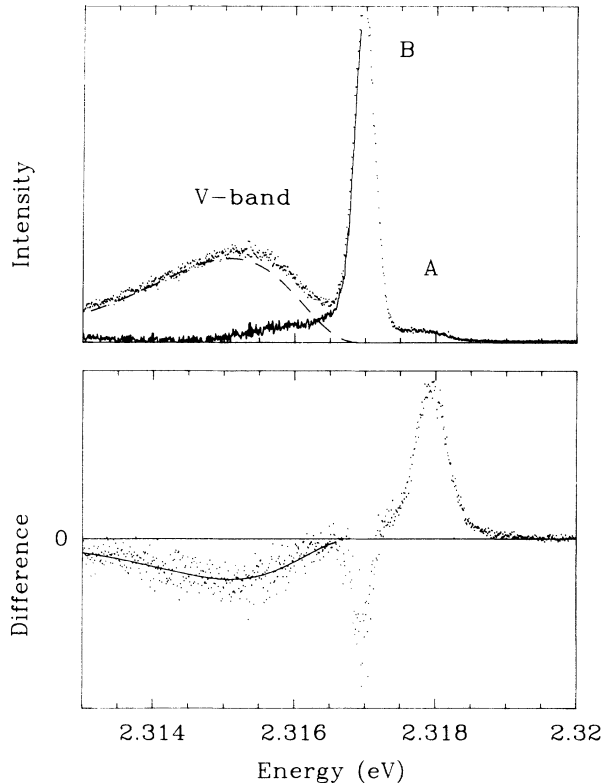


FIG. 4. Luminescence spectrum recorded at 1.5 K (upper panel). The contributions of phonon-assisted (dashed line) and zero-phonon (solid line) recombination are indicated. The lower panel shows the difference between the upper spectrum and a spectrum integrated during a  $2\text{-}\mu\text{s}$  gate after the start of a  $1\text{-}\mu\text{s}$  heat pulse. The solid line is a fit to Eq. (8).

$2\ \mu\text{s}$  after the start of a  $1\text{-}\mu\text{s}$  heat pulse. It is observed that the intensities of the  $B$  line and  $V$  band decrease, whereas the intensity of the  $A$  line increases. The crucial point of this experiment is that in the  $V$  band the difference luminescence spectrum exclusively consists of the phonon-assisted contribution. The reason is that the total zero-phonon luminescence in the  $V$  band, i.e., of  $B$

and  $A$  levels of disturbed sites, remains constant for stationary pumping for reasons of detailed balance. This means that the feeding rate must balance the recombination rate, i.e., the combined decay from the  $A$  and  $B$  levels. Both are to a good approximation independent of the presence of the heat pulse. A striking observation is the vanishing background in the dip between the  $B$  line and  $V$  band, indicating that in this energy region there is a strongly reduced phonon-assisted recombination.

Next we turn to results obtained from the time-resolved luminescence experiments. In Fig. 5 the rise and fall of the luminescence is shown of the  $B$  line (left) and  $V$  band (right) following excitation in the  $A$  line. The instrumental response of the detection system to the laser pulse is indicated. To establish the rise time of the luminescence, we assumed an exponential rise of the signal followed by a linear decay. This trial function was convoluted with the known instrumental response of the system and subsequently fitted to the data. This process was repeated with different values for the parameters until an optimum fit was obtained. We find that the rise time virtually coincides with the time resolution of our setup, and we can only establish an upper limit of about 100 ps for the rise time both for the  $B$  line and the  $V$  band. In Fig. 6 the decay of the luminescence is shown for three different detection frequencies: in the  $B$  line, between the  $B$  line and the  $V$  band, and at the low-energy side of the  $V$  band. Excitation of all traces was in the  $A$  line. The decay is not single exponential. The decay time at long-time scales is about  $2.5\ \mu\text{s}$ , whereas the initial decay time is about 300 ns. We note that the decay profile is remarkably constant throughout the entire  $B$  line and  $V$  band.

## IV. DISCUSSION

### A. Heat-pulse results

The results presented in Sec. III allow us to separate straightforwardly the otherwise interlaced contributions of phonon-assisted and direct recombination in the  $V$ -band luminescence. We contend that the shape of the  $V$

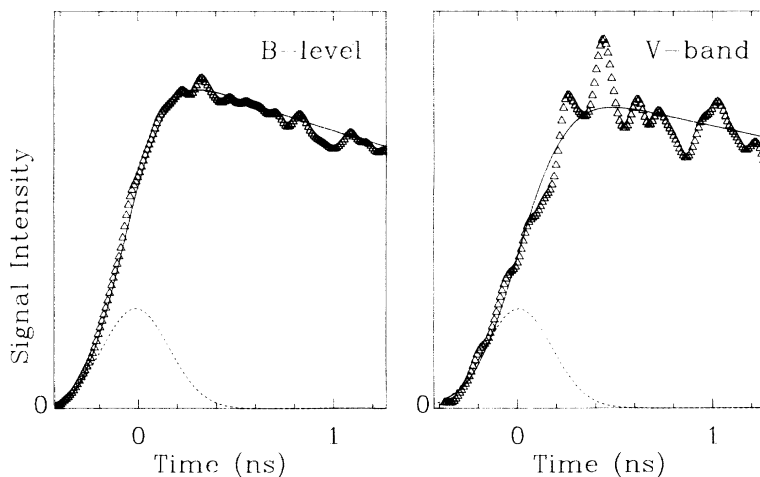


FIG. 5. Time-resolved luminescence traces from the  $B$  line (left) and  $V$  band (right) upon excitation in the  $A$  line. The instrumental response is indicated (dashed line). The solid line is a fit to the data (see text).

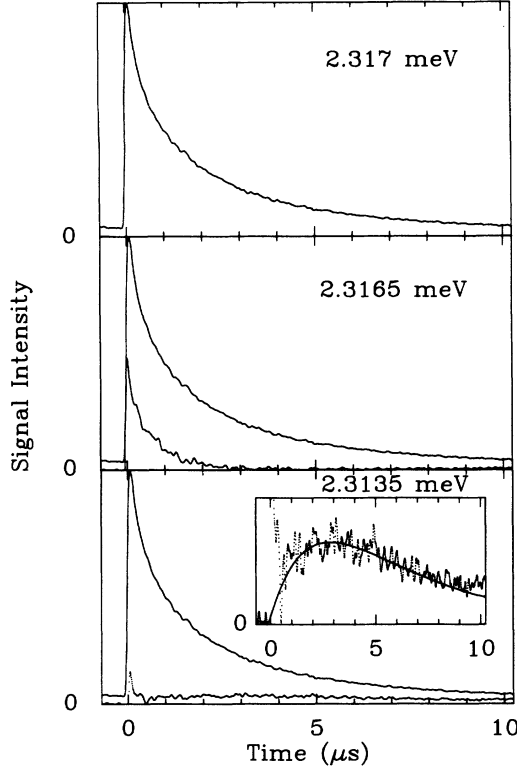


FIG. 6. Decay of the luminescence in the  $B$  line (top), in the dip between the  $B$  line and  $V$  band (middle) and at the low-energy side of the  $V$  band (bottom). In the two lower panels the contribution of disturbed excitons is also indicated. In the inset this contribution is blown up, and a fit to Eq. (11) is shown.

band is largely dominated by phonon-assisted recombination, although there is some direct recombination of excitons residing in the  $V$  band. This becomes apparent from the difference spectrum in Fig. 4, which is the phonon-assisted contribution to the  $V$  band. The shape is indeed nearly identical to the  $V$  band. For the theoretical determination of the shape, we will calculate the Stokes vibronic sideband transition rate versus frequency in second-order perturbation theory. It is crucial to take into account two effects that play a role in the shape of the acoustic-phonon sidebands in GaP:N, i.e., (i) the admixing of the  $A$  level and (ii) a form factor in the strain matrix element expressing the finite dimension of the bound exciton. The fit of the resulting expression to the data yields in a direct way a value for the Bohr radius of the exciton. Finally, we determined the relative weight of zero-phonon and phonon-assisted recombination of  $B$ .

(i) Admixing of  $A$ . The proximity of the  $A$  level greatly enhances phonon-assisted recombination of excitons from  $B$  for two reasons. First, the phonon coupling that mixes  $A$  and  $B$  is very strong and, second, the radiative lifetime is short. The dipole-allowed character of the radiative recombination from  $A$  can make, as we will show, the second-order recombination process integrated over the frequency even faster than the dipole-forbidden zero-phonon  $B$  transition.

(ii) The form factor. For GaP:N it is crucial to correct

the strain induced by a phonon for the finite spatial extent of the exciton wave function,<sup>15</sup> as indicated by uniaxial stress experiments.<sup>16</sup> Here one observes an isotropic strain-induced splitting between  $A$  and  $B$ , which is indistinguishable from the one expected for free excitons. The idea is that the hole wave function governs the relative strain-induced shifts of  $A$  and  $B$ . Since the electron is pinned down to the nitrogen, and the hole is weakly bound to it to form an exciton, the diagonal strain matrix elements for exciton-phonon coupling are averaged over a sphere of roughly the Bohr radius. We now assume that the *off-diagonal* matrix elements are also governed by the valence-band wave functions. We approximate the position-dependent part of the strain exerted by a phonon by averaging  $e^{i\mathbf{k}\cdot\mathbf{r}}$  over a spherically symmetric wave function  $|\Psi(\mathbf{r})|^2 \propto e^{-2|\mathbf{r}|/a}$ , with  $a$  the effective Bohr radius of the exciton. Consequently the net strain experienced by the exciton is reduced for high  $\mathbf{k}$  vectors and leads to a form factor

$$\begin{aligned} f(\mathbf{k}) &= \int_V \Psi^* e^{i\mathbf{k}\cdot\mathbf{r}} \Psi d\mathbf{r} \\ &= \frac{1}{\pi a^3} \int_V e^{i\mathbf{k}\cdot\mathbf{r}} e^{-2|\mathbf{r}|/a} d\mathbf{r} \\ &= \frac{1}{[1+(ak/2)^2]^2}. \end{aligned} \quad (1)$$

As expected, if  $ak \gg 1$  the strain is completely averaged out over the volume of the exciton, and the exciton-phonon coupling vanishes. On the other hand, for a local impurity  $f(\mathbf{k})=1$ .

In second-order perturbation theory the transition rate for resonantly enhanced Stokes recombination of excitons from  $B$  induced by a phonon of wave vector  $\mathbf{k}$  reads<sup>17</sup>

$$\begin{aligned} W_{\mathbf{k}} &= \sum_{\mathbf{q}} \frac{2\pi}{\hbar^2} \frac{|\langle G|\mathcal{H}_0|A \rangle|^2 |\langle A|\mathcal{H}_{\text{ep}}|B \rangle|^2}{(\hbar\omega_{\mathbf{k}} + \hbar\omega_0)^2} \\ &\quad \times \delta(\omega_{\mathbf{k}} + \omega_{\mathbf{q}} - \omega_B). \end{aligned} \quad (2)$$

Here  $\mathbf{q}$  is the photon wave vector,  $\mathcal{H}_{\text{ep}}$  and  $\mathcal{H}_0$  are the Hamiltonians to describe the deformation-potential exciton-phonon and exciton-photon coupling, respectively.  $G$  is the ground state including the phonon and photon excitation of wave vectors  $\mathbf{k}$  and  $\mathbf{q}$ , and  $A$  is the virtual intermediate state of the exciton, including the phonon with wave vector  $\mathbf{k}$ . The usual energy denominator  $(\hbar\omega_{\mathbf{k}} + \hbar\omega_0)^2$  takes into account the energy difference between the virtual state and the  $B$  state. The angular frequencies  $\omega_B$  and  $\omega_0$  correspond to energy splittings between  $B$  and  $G$ , and  $A$  and  $B$ , respectively, and  $\omega_{\mathbf{k}}$  and  $\omega_{\mathbf{q}}$  are the phonon and photon angular frequencies. The summation is over all outgoing  $\mathbf{q}$ . The radiative recombination rate  $T_A^{-1}$  of  $A$  reads, according to Fermi's golden rule,

$$\frac{1}{T_A} = \sum_{\mathbf{q}} \frac{2\pi}{\hbar^2} |\langle G|\mathcal{H}_0|A \rangle|^2 \delta(\omega_{\mathbf{q}} - \omega_A). \quad (3)$$

Since  $T_A^{-1} \propto \omega_A^3$  and using  $\omega_A^3 \approx (\omega_A - \omega_{\mathbf{q}} - \omega_0)^3$ , we may substitute Eq. (3) into Eq. (2) and arrive at

$$W_{\mathbf{k}} = \frac{|\langle A | \mathcal{H}_{\text{ep}} | B \rangle|^2}{(\hbar\omega_{\mathbf{k}} + \hbar\omega_0)^2} \frac{1}{T_A}. \quad (4)$$

$\mathcal{H}_{\text{ep}}$  is expanded to first order in powers of the strain. The matrix element is subsequently decoupled into two parts: one originates from the strain operator  $\varepsilon$ , and the other from the crystalline electric potential  $V^{(1)}$ ,<sup>17</sup>

$$|\langle A | \mathcal{H}_{\text{ep}} | B \rangle|^2 \approx |\langle p_{\mathbf{k}} + 1 | \varepsilon | p_{\mathbf{k}} \rangle|^2 |\langle A | V^{(1)} | B \rangle|^2. \quad (5)$$

Here  $|p_{\mathbf{k}}\rangle$  is the phonon state vector with occupation  $p_{\mathbf{k}}$  and wave vector  $\mathbf{k}$ , and  $\varepsilon$  is the strain operator. Taking into account the form factor  $f(k)$  we find, for the strain matrix element squared,

$$\begin{aligned} |\langle p_{\mathbf{k}} + 1 | \varepsilon | p_{\mathbf{k}} \rangle|^2 &= |\mathbf{k}|^2 \frac{\hbar(p_{\mathbf{k}} + 1)}{2\omega\rho V} f^2(k) \\ &= \frac{\hbar\omega_{\mathbf{k}}(p_{\mathbf{k}} + 1)}{2\rho Vv^2} \frac{1}{[1 + (a|\mathbf{k}|/2)^2]^4}. \end{aligned} \quad (6)$$

Here  $\rho$  is the density of the crystal, and  $v$  is the sound velocity of transverse phonons, and  $V$  is the volume of the crystal. The crystal-field matrix element part also follows straightforwardly from Fermi's golden rule, and, including the form factor of Eq. (1), reads

$$|\langle A | V^{(1)} | B \rangle|^2 = \frac{[1 + (a\omega_0/v)^2]^4 v^5 \rho h}{2T_{AB}\omega_0^3}. \quad (7)$$

Substituting Eqs. (6) and (7) into Eq. (4) and multiplying by the Debye density of phonon states in the crystal volume, we obtain an analytical expression for the phonon-induced Stokes transition rate per unit of angular frequency:

$$W(\omega_{\mathbf{k}}) = \frac{[1 + (a\omega_0/v)^2]^4 \omega_{\mathbf{k}}^3 (1 + p_{\mathbf{k}})}{[1 + (a\omega_{\mathbf{k}}/v)^2]^4 2T_A T_{AB} \omega_0^3 (\omega_{\mathbf{k}} + \omega_0)^2}. \quad (8)$$

We have fitted Eq. (8) to track the  $V$ -band difference spectrum of Fig. 4. In the fit a proportionality constant and the effective exciton Bohr radius are the only free parameters. A remarkably good fit is obtained, and we find directly a value for the Bohr radius,  $a = 19 \pm 2$  Å. To our knowledge only a few experimental data are known for the Bohr radius of the N-bound exciton in GaP. Wiesner, Street, and Wolf<sup>11</sup> quote a value of about 40 Å based on their experiments and the exciton-tunneling model. Our determination of the Bohr radius is based on the form factor of the scattering of phonons. The prefactor of Eq. (8) contains information on the product  $T_{AB} T_A$  and is discussed below.

We can now make a reliable estimate of the relative contribution of phonon-assisted and direct recombinations. To extract the contribution of *direct* recombination, we follow a straightforward procedure. We divide the  $V$ -band spectrum at low temperatures (Fig. 4, upper panel) by the phonon contribution (Fig. 4, lower panel), subtract the energy-independent contribution, and finally multiply again by the phonon contribution. Now we are left with a luminescence contribution from *direct* recombination only. The result is shown in the upper panel of Fig. 4. The luminescence from excitons residing in the  $V$

band turns out to constitute only a small fraction of the total luminescence (0–20%) and rapidly decreases toward the bottom of the  $V$  band. We conclude that the shape of the  $V$  band is dominated by phonon-assisted recombination.

## B. Time-resolved luminescence results

The conclusions from Sec. IV A lead to a straightforward interpretation of time-resolved luminescence data. The rapid rise ( $< 100$  ps) of the luminescence at short-time scales (Fig. 5) does *not* result from fast energy transfer to disturbed sites in the  $V$  band, but is a one-site effect and governed by phonon-assisted recombination of excitons residing in  $B$ . As a result, the rise time is limited by the  $A \rightarrow B$  spontaneous decay time of 25 ps, which is shorter than our instruments can resolve. The nonexponential decay of the luminescence (Fig. 6) is interpreted in the same spirit. Since mainly phonon-assisted decay of the  $B$  line is observed over the entire  $V$  band, we conclude that the *slow* decay at longer time scales reflects the intrinsic lifetime of isolated  $B$  excitons, and the *fast* component the energy transfer from  $B$  excitons to the  $V$  band. The energy transfer apparently takes place in 300 ns. This explanation is corroborated by the nonexponential character of the signal at short-time scales. This indeed is expected for nonresonant energy transfer, since a wide range of time constants is involved in the tunneling process for reasons of the variation of the spatial separation between sites and the energy mismatch of the initial and final states. The fact that roughly two components can be resolved suggests that two distinct classes of  $B$  excitons exist in our dilute sample: one that is able to transfer and another that is isolated from the  $V$  band. The observed energy-transfer times are consistent with the results of Molenkamp and Wiersma<sup>3</sup> in dilute GaP:N, and the findings of Wiesner, Street, and Wolf<sup>11</sup> for energy transfer between pair lines in heavily doped samples. Both results were obtained from direct observation of transfer processes. On the other hand, the processes are much slower than the rate extracted from homogeneous linewidth measurements reported by Gershoni *et al.*<sup>9</sup> and Brocklesby, Harley, and Plaut.<sup>12</sup> We stress here that the latter are sensitive to *all* processes causing dephasing, i.e., both *elastic* and *inelastic* energy-transfer processes. We therefore conclude that these results point to (near-) resonant energy transfer or, alternatively, to dephasing caused by one-site processes, rather than phonon-assisted transfer to the  $V$  band. The absence of fast transfer to the  $V$  band is further consistent with the fact that no saturation effects whatsoever are observed. Fast energy transfer would inevitably lead to such a saturation at the pump powers used in the present experiments.

From a comparison between the phonon-assisted recombination rate at one particular phonon frequency [cf. Eq. (2)] and the direct recombination rate from  $B$ , we can estimate  $T_A/T_B$ . By inserting the experimental value  $I_B/I_V = 0.3$ , we arrive at  $T_A/T_B = 10^{-2}$ , in excellent agreement with the value of  $9 \times 10^{-3}$  reported by Cuthbert and Thomas.<sup>2</sup>

To conclude our discussion we extract the contribution of the time-resolved luminescence emitted by the disturbed sites in the  $V$  band. To accomplish this we take the ratio of the luminescence emanating from  $V$  and that from  $B$ . In this ratio the phonon-assisted decay of the signal gives rise to a large time-independent contribution. By subtracting this contribution and multiplying the remnant by the time trace of the  $B$  line luminescence, we end up with the time-resolved luminescence originating from disturbed excitons. The result is shown in Fig. 6. Indeed only a small contribution is found: on the order of 20% in the dip between  $V$  and  $B$ , and a few percent at low energies. This result is consistent with the values found in our heat-pulse experiments (cf. Fig. 4). In the dip between  $V$  and  $B$ , there is still significant direct feeding of excitons. The decay time of excitons in this spectral region is measured to be  $\sim 700$  ns, which we again attribute to energy transfer because the decay is strongly nonexponential.

We can obtain quantitative values for the transfer time from *undisturbed* into *disturbed* nitrogen sites by deriving an analytical expression for the feeding and decay of bound excitons in the  $V$  band. The approach is based on simple rate equations describing  $B \rightarrow V$  transfer with an effective time  $T_t$  and spontaneous radiative recombination of excitons residing in the  $V$  band ( $T_V$ ). Back transfer is neglected, consistent with the absence of saturation. The rate equations then reduce to

$$\frac{dN_B}{dt} = -\frac{N_B}{T_t} \quad (9)$$

and

$$\frac{dN_V}{dt} = \frac{\alpha N_B}{T_t} - \frac{N_V}{T_V}. \quad (10)$$

Here  $\alpha$  expresses the fact that only a fraction of the exciton transferring from  $B$  ends up inside the detection window in the  $V$  band. Straightforward integration of Eq. (9), substitution of the solution in Eq. (10), and subsequently solving Eq. (10) yields

$$N_V(t) = \frac{\alpha N_{B_0} T_t}{T_V - T_T} (e^{-(t/T_t)} - e^{-(t/T_V)}). \quad (11)$$

Here,  $N_{B_0}$  is the population of  $B$  at  $t=0$ . The fit of this

expression to the data is shown in the inset of Fig. 6, with  $T_t=2 \mu\text{s}$  and  $T_V=4 \mu\text{s}$ . Evidently the lifetime of excitons in the  $V$  band is comparable to the lifetime of excitons residing in  $B$ , at least in our sample. The transfer time at this particular detection energy is longer than the average transfer time of 300 ns for  $B$  discussed above. This suggests that relatively long distances between the disturbed and undisturbed sites are present. As a consequence, the transfer times should depend on the detection energy.

## V. CONCLUSION

We have shown that the  $V$  band in high-quality dilute GaP:N consists of both zero-phonon and phonon-assisted contributions. Its shape is largely dominated by phonon-assisted recombination of excitons residing in the  $B$  state. The direct recombination of excitons bound at disturbed sites carries only  $\sim 10\%$  of the total luminescence. Of course, the relative contributions of the two components will be dependent on sample quality. We have demonstrated that the averaging of the phonon-induced strain over the exciton Bohr radius and the coupling to the  $A$  state is of crucial importance for a correct description of the exciton-phonon interaction of N-bound excitons. From the shape of the  $V$  band an effective exciton Bohr radius of about  $19 \text{ \AA}$  is found. Finally we assessed that energy transfer between the  $V$  band and  $B$  line is governed by a distribution of time scales, consistent with a range of spatial separations and energy mismatches between transferring states. The average transfer time is about 300 ns. In another paper we will take advantage of the present findings and demonstrate the application of GaP:N as an extremely sensitive and fast phonon detector.<sup>18</sup>

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