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Optical dephasing and excitation transfer of an impurity-bound exciton in a semiconductor: Photon-echo experiments on GaP:N

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We report low-temperature results of accumulated and two-pulse picosecond photon-echo experiments on the optical transition of the nitrogen-bound exciton in GaP:N. The observed temperature dependence of the dephasing of the so-called A line at 534.95 nm can be explained in terms of (stimulated) phonon processes involving the lower B state and, at higher temperatures, the free-exciton band. The low-temperature-echo decay time of 25.5 ± 0.5 ps is shown to be determined by the lifetime of a A state. Analysis of the factors governing the intensity of the accumulated photon echo as a function of temperature leads to the conclusion that in the B state temperature-independent excitation transfer occurs. The rate constant of this phenomenon, which we ascribe to excitation tunneling, is 10^7 s^{-1}.

I. INTRODUCTION

Impurity-bound excitons in semiconductors have been the subject of extensive research efforts in the last two decades.[1] One of the most studied systems, for both experimental (high oscillator strength and in a convenient wavelength region) and theoretical reasons (a wide variety of interesting phenomena), is the nitrogen-bound exciton in GaP:N.

Nitrogen, although isoelectronic with phosphorus, has a higher electronegativity, and can therefore bind an electron when substitutionally dissolved in the GaP lattice.[2] Consequently, the electron's Coulomb field binds a hole, thereby generating a bound Wannier exciton with a radius of some 30 Å. Since the electron wave function is a linear combination of $S_{1/2}$ conduction-band states near the X point in the Brillouin zone, and the hole is associated with the $P_{3/2}$-type top of the valence band (at the Γ point), an exchange interaction between the two particles produces new electronic states, a triplet and a quintuplet. The upper $J=1$ triplet, which historically is named the A state, can directly be excited from the $J=0$ ground state, leading to an absorption line at 534.95 nm (2.3172 eV).[3] Direct absorption from the ground state to the $J=2$, or B state, is dipole forbidden. The B state can only be observed in luminescence at very low temperatures, when the Boltzmann factor heavily favors the B-line emission after rapid relaxation of the A-state population. From these measurements one can conclude that the B state is 7.1 cm^{-1} (0.90 meV) lower in energy than the A state.[4] Moreover, from such experiments it is evident that J $(=L+S)$ is a good quantum number, and that crystal-field-induced splittings of the multiplets are negligible. This pictures changes, however, when the crystal is subjected to strain, or placed in a magnetic field. Detailed studies have been made of these stress-induced[5] and Zeeman[4] splittings, and excellent agreement between theory and experiment was obtained. It thus seems that the static spectroscopy of GaP:N is well understood.

Because of the commercial interest in GaP:N as a LED material, also various luminescence quenching studies have been performed on the system. Cuthbert and Thomas have shown[6] that the luminescence lifetime of the nitrogen-bound exciton can be described by assuming thermal equilibrium between the A and B states. A much more detailed picture of luminescence quenching in GaP:N under better controlled excitation conditions was given by Sturge *et al.*[7] However, it is not possible to determine from such measurements the relaxation rate from A to B.

There is also little information available on the occurrence and nature of the line-broadening processes that take place at low temperatures, where the optical transition is still inhomogeneously broadened. Hu *et al.*[8] reported preliminary results of a photon-echo experiment on the A line of GaP:N. Recently, Harley and Macfarlane[9] used saturation hole burning to study the optical dynamics of a B line corresponding to an exciton bound to a N-N dimer in a heavily doped GaP:N sample. In this so-called[2] N-N$_1$—dimer system a small crystal-field-induced splitting of A and B lines exists.[2] Harley and Macfarlane proposed that the temperature-induced dephasing they observed for holes burnt in the energetically lowest line of the resulting B multiplet was due to nonadiabatic phonon-scattering processes to other nearby members of the multiplet. However, due to the limited temperature range in which the experiments were performed, it was not possible to assign the proposed dephasing mechanism with certainty.

This situation is quite in contrast to the one in the field of organic mixed crystals. Recent experiments on such systems have shown[10] that very detailed information on excitation-phonon coupling can be extracted from optical-coherence experiments such as photon echo.[10(b)]

We have developed[10,11] a versatile method for photon-echo experiments on a picosecond timescale: the accumulated photon-echo technique. This technique uses directly the 100-MHz train of low-power optical pulses produced by a synchronously pumped dye laser, rather than the strongly amplified pulses usually employed in photon-echo studies. The main prerequisite for application of the method is a bottleneck in the optical-pumping cycle of the transition of interest.

The *B* state of GaP:N has a lifetime in the μs region and is very effectively populated (virtually 100% quantum yield) after excitation into the *A* line.[6] Thus, the *B* state appears to be a very effective bottleneck. We therefore decided to use the accumulated photon echo for a study of the temperature-dependent optical dephasing of the *A* line in GaP:N. Recently, a preliminary report of this study was given.[12] In this paper we give a full account of the photon-echo work. We show that the relaxation rate from the *A* to the *B* state is much faster than previously reported.[8] On the basis of the experimental data, we arrive at a dephasing model where nonadiabatic modulation of the excitation,[13] due to phonon-scattering processes both to the *B* state and, at higher temperatures, to the free-exciton band, causes the broadening of the *A* line. Furthermore, from an analysis of the echo intensity as a function of temperature, combined with luminescence-quenching data, we conclude that fast (10^7 s^{-1}) excitation tunneling occurs in the *B* state of the nitrogen-bound exciton.

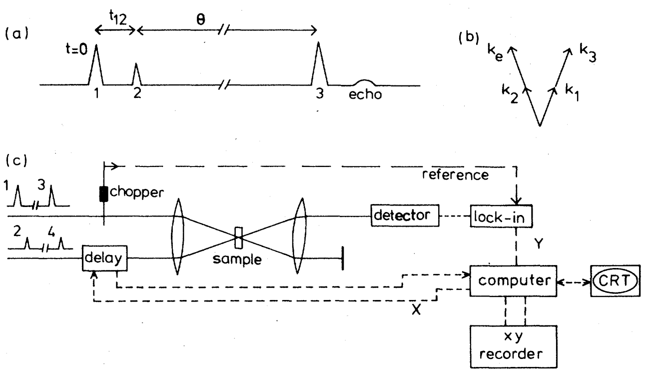

FIG. 1. Schematical setup for the generation and detection of accumulated photon echoes. (a) Excitation pulse cycle; t_{12} is the variable delay time between the excitation pulses and Θ the fixed cycle time. (b) Phase-matching diagram of excitation pulses and echo. (c) Setup for detection of intensity modulations on the probe beam (2 and 4) from modulation of the pump beam (1 and 3). An Apple II computer steps the delay t_{12} between the excitation pulses and also digitizes the incoming signals from the lock-in amplifier.

II. EXPERIMENTAL

The samples of GaP:N used in our experiments were grown by either liquid-phase epitaxy (LPE) or liquid-encapsulated Czochralski (LEC) techniques. They were supplied to us by Dr. H. Veenvliet and Dr. A. T. Vink of Philips Research Laboratories, Eindhoven, The Netherlands. The nitrogen dopant concentration in the crystals used for the data reported in this paper ranged from 0.4—4×10^{16} atom cm^{-3}, as determined by the method of Lightowlers *et al.*[3] All crystals had carefully polished surfaces. Both $\langle 111 \rangle$- and $\langle 100 \rangle$-cut samples were used. For comparison with previous reports on echo relaxation in GaP:N,[8] we also performed experiments on crystals supplied by Dr. S. Chu of AT&T Bell Laboratories, Holmdel, New Jersey, and by Dr. R. Romestain of the University of Grenoble. In all experiments we used a temperature-variable cryostat (Oxford Instruments).

A schematic of the setup used to generate the accumulated photon echo is shown in Fig. 1. A train of twin psec dye-laser excitation pulses, at the full 100-MHz repetition rate of the mode-locked Ar^+-ion laser, is focused onto a 100-μm-diam spot of the sample. Total incident power is about 1 mW. The exciting-pulse pair creates a "frequency grating"[12,14] in the absorption line. This is built up (accumulated) in the ground state by virtue of the *B* state, which slowly relaxes on the timescale of the repetition time (10 ns) of the laser. From this accumulated grating in the ground state, which contains all phase information of the optical transition, one of the twin-excitation pulses, acting as a third pulse, scatters an echo. In the phase-matching scheme employed in Fig. 1, the echo-polarization interferes constructively with a fourth excitation pulse, enabling heterodyne detection of the echo. In this mode, the echo decay measures $T_2/2$.[14] A more detailed discussion of accumulated-photon-echo generation and detection is given in Ref. 11.

We also performed regular two-pulse picosecond photon-echo measurements on GaP:N. For this purpose, the dye-laser pulses were amplified by use of a yttrium-aluminum-garnet (YAG) laser at a repetition rate of 10 Hz. This resulted in excitation pulses with an energy of about 10 μJ. The photon echo was time-resolved through frequency up-conversion with a pulse from a second dye laser at a different frequency.[15] In general, these experiments were performed as described in Ref. 15.

Luminescence-lifetime-quenching data were obtained using a nitrogen-pumped dye laser with a pulse width of 5 ns as excitation source. The luminescence was detected by an EMI 9816 QB photomultiplier tube and displayed on a Tektronix digitizer. Absorption spectra were taken using a filament lamp as a light source, and a Spex 1402 double monochromator as dispersing medium. For line-broadening measurements the relevant portion of the lamp spectrum was filtered out with a predisperser to avoid heating of the sample.

III. RESULTS AND DISCUSSION

A. Spectroscopy

The absorption spectrum at 1.5 K of a typical sample used in the echo experiments is shown in Fig. 2. The nitrogen concentration in this sample, with a crystal thickness of 0.475 mm, is about 1.4×10^{16} cm^{-3}. Apart from the nitrogen-bound-exciton absorption at 534.95 nm, another impurity line ("*C* line"[16]), due to an exciton bound to a sulfur neutral donor, is also observed. The feature denoted $A_{x'}$ 10.3 meV to the blue of the absorption of the

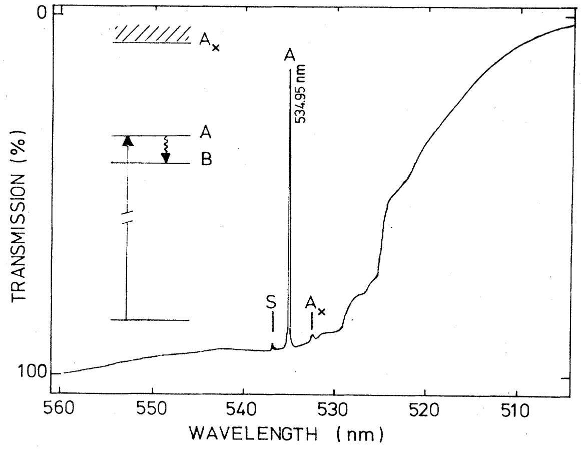

FIG. 2. Level scheme and optical-absorption spectrum at 1.5 K of the nitrogen-bound exciton in GaP. The N concentration is 1.4×10^{16} cm^{-3}. The origin of the lettered lines is discussed in the text.

nitrogen-bound exciton, marks the onset of the GaP free-exciton band continuum. Its existence has been explained[17] in terms of interference between the exciton continuum and electron-hole continuum (E_0 denotes the ground level of either continuum). Finally, it is evident that there is no trace of the B line in absorption. From emission spectra we inferred the position of the B line to be 0.90 meV lower in energy as compared to the A line, consistent with existing literature.[4] We further note that excitation of the A line did not result in any emission at the wavelength of the sulfur-bound exciton. This implies the absence of communication between the different traps. Linear spectroscopy thus leads to a Jablonski diagram for the nitrogen-bound exciton, which is depicted in the inset of Fig. 2. Note that we have not included the excited exciton states in this picture. Cohen and Sturge[18] have argued that the 2s-like state of the A exciton should be 40 meV higher in energy, i.e., well into the free-exciton continuum. Hence, we did not include any internal exciton excitation in the discussion of the dephasing which follows below.

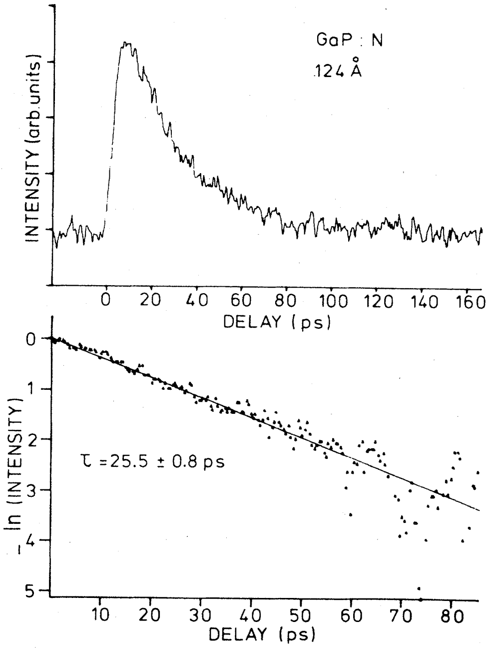

FIG. 3. Traces of the accumulated photon echo of the A line in GaP:N at 1.5 K, on linear and logarithmic scales.

B. Low-temperature photon echo

The result of a low-temperature (1.5 K) accumulated-photon-echo experiment is depicted in Fig. 3. As is evident from the log plot in the lower half of the figure, the observed decay is neatly exponential with a decay constant of 25.5 ps. This decay time was observed in all the samples studied. It was independent of the concentration of sulfur impurities, which varied from $<10^{15}$ to 10^{17} atoms cm^{-3}, and also remained at the same value in samples with high optical densities, even in those with about 99% absorption at the A line. This latter fact clearly illustrates the remarkable insensitivity of the accumulated echo to optical-density effects,[19] which, in contrast, severely distort the regular two-pulse photon-echo decay.[20] It can be shown[14] that the heterodyne-detected accumulated photon echo decays exponentially with a time constant equal to $T_2/2$, where the dephasing time T_2 obeys the well-known relation[21]

$$\frac{1}{T_2}=\frac{1}{2T_1}+\frac{1}{T_2^*} . \tag{1}$$

This relation implies that in the absence of pure dephasing (T_2^*) processes, T_2 equals $2T_1$, where T_1 is the population relaxation time. From temperature-dependent studies (*vide infra*) we established that the temperature-induced shortening of the decay vanishes asymptotically at low temperature, leading, in *all* samples studied, to a (25.5±0.5)-ps decay constant below about 5 K. We infer from this fact that this low-temperature echo-decay time is identical to the lifetime of the exciton A state.

This short echo-decay time surprised us originally, since Hu *et al.*[8] recently presented preliminary two-pulse photon-echo data indicating a (200—300)-ps lifetime for the A state. It can be envisioned[22] that near-resonant spectral diffusion on the timescale of the bottleneck lifetime could cause an apparently faster decay of the accumulated echo as compared with the "normal" two-pulse echo (i.e., with amplified pulses). We therefore decided to perform also such a two-pulse photon-echo experiment on GaP:N.

In samples with up to 50% absorption, we again found[23] a 25-ps echo-decay time. For samples with higher optical density the echo decay became nonexponential. This can be explained in terms of optical-density effects.[20] In the tail of these distorted echo-decay traces, where optical-density effects become less important, the decay time again approached 25 ps. Thus, spectral diffusion can be excluded from affecting the accumulated-echo-decay time. This does not mean that excitation transfer and spectral diffusion do not occur in the GaP:N system, as will be discussed in Sec. III D.

Another possible explanation for the discrepancy between our results and those of Ref. 8 would be variations in the quality of the samples used. Therefore, we repeated our experiments with crystals used by Hu *et al.* Once again, we found the same short lifetime in all crystals suitable for echo experiments. We notice here that the crystals used in "photon-echo" experiments of Hu *et al.* had very high (>2) optical densities. Given this observation, and the fact that in the experiment of Hu *et al.* the echo was not time-gated, we suggest that their results must be explained in terms of observation of pulse-breakup effects rather than photon echoes. A later publication[24] on pulse propagation in GaP:N by the same workers indeed reports that such pulse-breakup effects can easily be observed in this system.

We therefore accept the 25.5-ps decay time as reflecting the population relaxation of the A state. Such a short lifetime seems, at first sight, remarkable in view of the fact that a direct, pure phonon-relaxation process between A and B states is forbidden as it involves a change in electronic angular momentum. The relaxation mechanism therefore must involve lattice-orbit coupling. As the relevant matrix elements are known from stress experiments,[5] a rough estimate of the relaxation rate is possible. Such a calculation, as performed very recently by Romestain[25] in response to Ref. 12, yields a 7-ps lifetime for the A state. This means that the decay time found in the present experiment is consistent with the known effect of strain on the A line.

Finally, in the next subsection we will show that, from the temperature-induced dephasing of the A line, we again conclude a value of 25.5 ps for the A-level lifetime at low temperatures.

C. Temperature-induced optical dephasing

Upon raising the temperature the decay time of the echo shortens, since phonon-induced phase-destroying events start to take place in the crystal. In Fig. 4 the homogeneous linewidth [$(\pi c T_2)^{-1}$ in cm^{-1}] of the A line, inferred from the echo data, is given by the solid squares.

At still higher temperatures (above about 20 K) the echo transient becomes both too short (in time) and too feeble (in intensity; cf. Sec. III D) to be measurable. Fortunately, in the same temperature region the absorption line becomes predominantly homogeneously broadened, thus allowing us to obtain the homogeneous width from a line-shape analysis. The results of these experiments are the open circles in Fig. 4, which are in good agreement with those reported in Ref. 3.

Many mechanisms have been proposed to explain the dephasing of optical-absorption lines in solids. The oldest, and perhaps the best known, is the McCumber-Sturge theory,[26] which applies to transitions connecting isolated electronic levels. This theory assumes adiabatic modulation of the transition frequency through scattering to virtual band-phonon states. More recently, however, Cohen-Tannoudji pointed out[27] that in the case of additional vibronic levels, close in energy to the states of interest, nonadibatic scattering involving these levels will contribute dominantly to the dephasing. De Bree and Wiersma[13] later applied Cohen-Tannoudji's quantum-mechanical version of optical Redfield theory to solids. Their proposal was that for organic mixed crystals librational excitations of the guest molecule serve as the "doorway" states to which the nonadiabatic phonon scattering takes place. In the meantime this assertion has been verified for a number of model systems.[10]

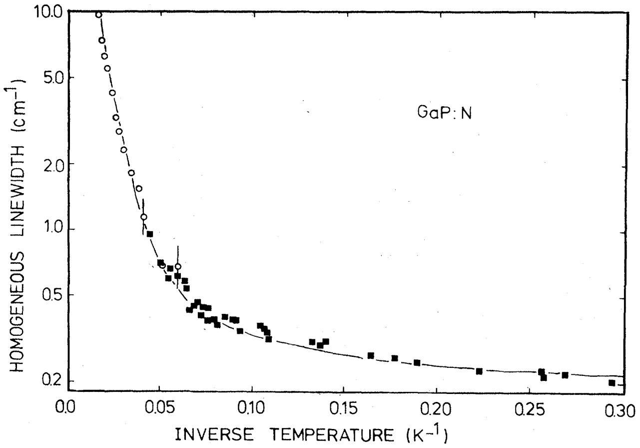

FIG. 4. Homogeneous linewidth (in cm^{-1}) versus inverse temperature of the A line in GaP:N. The solid squares were obtained from accumulated-photon-echo experiments. Open circles were deduced from the absorption line shape by deconvoluting the low-temperature inhomogeneous linewidth. The solid line is a fit assuming nonadiabatic phonon scattering as the dominant dephasing agent.

As the B and A_x levels in GaP:N lie close to the A state, it is necessary to calculate the contribution of dephasing processes involving nonadiabatic scattering to these levels. An expression for this contribution can readily be given, on the basis of the theory of de Bree and Wiersma.[13] The solid line in Fig. 4 assumes that only nonadiabatic processes determine the dephasing of the A line. The fit obeys the following expression:

$$(\pi c T_2)^{-1}=(2\pi c)^{-1}\{\tau_{AB}^{-1}[n_{\mathrm{BE}}(\epsilon_{AB})+1] + \tau_{A_xA}^{-1}n_{\mathrm{BE}}(\epsilon_{A_xA})\}\ , \qquad (2)$$

where $n_{\mathrm{BE}}(\epsilon_{AB})$ stands for the Bose-Einstein occupation number for phonons of energy ϵ_{AB}, i.e., the difference in energy between A and B states, and τ_{AB} is the lifetime of state A due to *spontaneous* relaxation to B. The factor $\frac{1}{2}$ reflects the nonadiabatic nature of the dephasing mechanism.[27]

The interpretation of Eq. (2) is straightforward. It simply states that any phonon-mediated process that causes population to leave the A state will cause dephasing. At low temperature only spontaneous phonon emission can occur, so that the dephasing will be governed by the lifetime of the A state. At more elevated temperatures, also *stimulated*-phonon emission from A to B starts to occur, while at still higher temperatures phonon absorption will enable exciton detrapping from A to the bottom of the free-exciton continuum at A_x. These processes are similar to the (inverse) Orbach processes that have been shown[28] to cause spin relaxation.

As dephasing is a property of the oscillating macroscopic dipole present in the sample, phonon-scattering processes in the excitonic ground state would be equally capable of causing optical dephasing. However, since nitrogen in GaP is an isoelectronic substituent, there are no low-energy excitations possible in the ground state. For excitons, bound to neutral donor and acceptor impurities, one would, in contrast, certainly expect a contribution from ground-state excitations to the overall dephasing. We now turn to a discussion of the numerical values of the parameters in Eq. (2).

As three of the variables in this equation are now experimentally known ($\epsilon_{AB} = 7.1$ cm^{-1}, $\epsilon_{A_xA} = 83$ cm^{-1}, and $\tau_{AB} = 25.5$ ps), the only free parameter is τ_{A_xA}. From the fit, we deduce that $\tau_{A_xA} = 80 \pm 15$ fs. Knowledge of this quantity enables us to calculate the rate of bound-exciton—detrapping attempts[1] at a given temperature. This rate should not be confused with the one derived from luminescence-quenching experiments which encompasses only those detrapping events that lead to nonradiative decay. This explains why the latter decay rate is always smaller[7] than the one obtained from the photon-echo experiments. With regard to the interpretation of τ_{A_xA} itself, we note the following: Using Fermi's golden rule for the calculation of the overall rate of bound-exciton—detrapping attempts, Γ_{A_xA}, we arrive at the following expression:

$$\Gamma_{A_xA} = \frac{2\pi}{h} \sum_k{}' \,|\langle \Psi_k, n(\epsilon_{A_xA}) - 1 \,|\, A^\dagger b \,|\, \phi_N, n(\epsilon_{A_xA}) \rangle|^2 = \frac{2\pi}{h} \sum_k{}' \,|\langle \Psi_k \,|\, A^\dagger \,|\, \phi_N \rangle|^2 n_{\mathrm{BE}}(\epsilon_{A_xA}) = (1/\tau_{A_xA}) n_{\mathrm{BE}}(\epsilon_{A_xA}) \,, \tag{3}$$

which defines τ_{A_xA}. The phonon-annihilation operator b lowers the occupation number $n(\epsilon_{A_xA})$, while the operator $A^\dagger$ symbolizes the change of a bound exciton with wave function ϕ_N into a free exciton, denoted by Ψ_k (for an exciton with wave vector k). As we assume detrapping to the bottom of the free-exciton band only, the summation over k must be restricted to those k values that have concomitant energies close to the bottom of the band. This is a reasonable approximation for the low (as compared with ϵ_{A_xA}) temperatures involved in our study. For higher temperatures one would have to include detrapping to energetically higher states of the free-exciton band in Eqs. (2) and (3).

On the other hand, the value for τ_{AB}^{-1} is known from the low-temperature-echo experiment. The observation that the same prefactor can also explain the observed dephasing up to 15 K is a strong argument supporting our identification of the echo-decay time at 1.5 K as the population-relaxation time. At still higher temperatures, exciton detrapping becomes the dominant dephasing mechanism due to its much larger prefactor ("cross section").

As is evident from the quality of the fit, nonadiabatic processes account for all of the observed dephasing. This is the same situation as encountered in molecular mixed crystals;[10] adiabatic dephasing processes are negligible as soon as nearby resonant levels are present.

D. Temperature dependence of the echo intensity

As mentioned in the preceding section, the echo-signal intensity decreases upon raising the sample temperature. This can be explained by a decrease in efficiency of the bottleneck in the process of accumulation. In our case this bottleneck is the B state, whose lifetime can be shortened through thermal communication with the A and A_x states.

Hesselink and Wiersma[14] showed that the echo-enhancement factor γ, which arises from the accumulation effect, can be expressed as

$$\gamma = \frac{e^{-\Theta/T_1}[2(1-e^{-K_B\Theta}) - \beta] + \beta e^{-K_B\Theta}}{2(1-e^{-K_B\Theta})} \,. \tag{4}$$

Here, Θ is the time span between consecutive pulse pairs, T_1 is the population-relaxation time of the upper state, and K_B is the decay rate out of the bottleneck level. The constant β, which determines the population efficiency of the bottleneck, can be set equal to 1 in the present case. Moreover, we have Θ (about 10 ns) $\gg T_1$ (about 25 ps). As at 1.5 K the B-level lifetime is on the order of μs, we then certainly have $K_B\Theta \ll 1$. From luminescence-quenching measurements (*vide infra*) we find that at temperatures up to 15 K we still have $K_B\Theta \lesssim 1$. We thus find

$$\gamma \approx \frac{1}{2\Theta}(K_B^{-1}) \,. \tag{5}$$

The echo polarization is measured as the pump-induced transparency which is observed by the probe beam. This leads to a modified Lambert-Beer equation describing the signal intensity.[14] However, the induced transparency is always small as compared with the intrinsic absorption of the sample. Therefore the echo intensity is always proportional to γ, and we find

$$I_{\mathrm{echo}} \propto K_B^{-1} \,. \tag{6}$$

From the principle of detailed balance, applied to the level scheme in Fig. 2, we find the following expression for K_B, the rate out of bottleneck B, as a function of temperature T:

$$K_B(T)=\frac{K_{B0}+K_{A0}g(A/B)e^{-\epsilon_{AB}/k_BT}+k_{A_x0}g(A_x/B)e^{-\epsilon_{A_xB}/k_BT}}{1+g(A/B)e^{-\epsilon_{AB}/k_BT}+g(A_x/B)e^{-\epsilon_{A_xB}/k_BT}}\;. \tag{7}$$

Here, K_{IO} represents the rate out of state I in the absence of communication with any electronic level, other than the ground state, but including communication with nearby nitrogen sites. The factor $g(I/J)$ gives the ratio of the degeneracies of states I and J. Since we want to compare the relative echo-intensity changes as a function of temperature, we introduce a ratio R_E defined as

$$\begin{aligned}R_E&=\left[\frac{I_{\text{echo}}(T=1.5\text{ K})-I_{\text{echo}}(T)}{I_{\text{echo}}(T)}\right]=\left[\frac{K_B^{-1}(T=1.5\text{ K})-K_B^{-1}(T)}{K_B^{-1}(T)}\right]\\&=\left[\frac{K_{A0}}{K_{B0}}g(A/B)\right]_E e^{-\epsilon_{AB}/k_BT}+\left[\frac{K_{A_x0}}{K_{B0}}g(A_x/B)\right]_E e^{-\epsilon_{A_xB}/k_BT}\;.\end{aligned} \tag{8}$$

Here, $I_{\text{echo}}(T)$ is the echo intensity at temperature T.

The experimental data are plotted as the crosses in Fig. 5, together with a fit according to Eq. (8). As is evident from the figure, the biexponential deactivation of the intensity is well established. In the fit we used the values for ϵ_{AB} (7.1 cm^{-1}) and ϵ_{A_xB} (90 cm^{-1}) that were obtained from the absorption spectrum. The quality of the fit confirms the identification of the B level as the bottleneck state. From the data, we find

$$\left[\frac{K_{A0}}{K_{B0}}g(A/B)\right]_E=2.8\pm0.2$$

and

$$\left[\frac{K_{A_x0}}{K_{B0}}g(A_x/B)\right]_E=9500\pm1000\;.$$

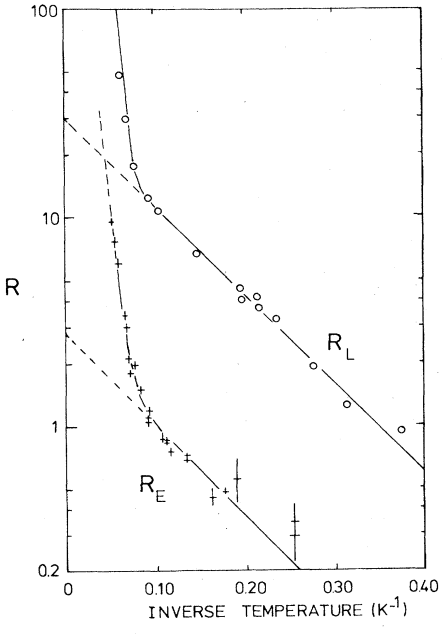

FIG. 5. $\log_{10}$-vs-$1/T$ plot of echo-intensity ratio R_E and luminescence-lifetime ratio R_L. Note that the two curves are similar but displaced, thus establishing similar activation energies, but different prefactors in the quenching expression, Eq. (4).

Additional information on B-state relaxation can be obtained from luminescence-quenching measurements. Note that, in contrast with echo measurements, these data are not sensitive to communication between neighboring sites, as the luminescence lifetime is an intrinsic property of a single excitation. The photon echo, in contrast, is both in intensity and in lifetime, a property of an ensemble of excitations.

We performed luminescence-quenching experiments on the same crystals we used for the photon echoes (nitrogen concentration 1.4×10^{16} atoms cm^{-3}). In this case, absolute rates are obtained. From a curve fitting similar to the ones performed previously,[6,7] we obtain a low-temperature relaxation rate $K_{B0}=(1.0\pm0.2)\times10^6\ \text{s}^1$. For a comparison with the echo-intensity data, however, it is more convenient to consider

$$R_L=\left[\frac{K_L^{-1}(T=1.5\text{ K})-K_L^{-1}(T)}{K_L^{-1}(T)}\right]$$

as a function of inverse temperature (K_L is the inverse of the luminescence lifetime). R_L should obey the same functional temperature dependence as the one given in Eq. (7) for R_E. In the most general case all indices E in this equation should be replaced by L. As is clear from the open circles in Fig. 5, R_L again exhibits the biexponential activation, with the same values for the exponential constants as the ones that were found for R_E. However, the prefactors

$$\left[\frac{K_{A0}}{K_{B0}}g(A/B)\right]_L \text{ and } \left[\frac{K_{A_x0}}{K_{BO}}g(A_x/B)\right]_L$$

are both a factor of 10.5 ± 1 larger than their counterparts describing the echo intensity. Since this factor is the same for both prefactors, we must conclude that the discrepancy arises from the fact that different values of K_{B0} determine the echo intensity and luminescence lifetime. As $(K_{BO})_L \approx 10^6$ s^{-1} was obtained from the quenching studies, we conclude that $(K_{BO})_E \approx 10^7$ s^{-1}.

Apparently there exists, even at the lowest temperature, a process which decreases the bottleneck effectiveness of the *B* state. Since this evidently cannot be a lifetime-shortening process, we propose excitation energy transfer to be responsible for the discrepancy of a factor 10. Such a process would destroy the accumulated frequency grating in the sample but not influence the luminescence lifetime. As the temperatures involved are very low, as compared with the exciton-trapping energy of 10.3 meV (120 K), we can rule out phonon-assisted exciton detrapping as the cause of excitation transfer. A similar temperature argument allows us to exclude also the possibility of excitation transfer from the *B* state to the energetically higher *A* state.

Several other mechanisms have been proposed to explain excitation transfer in solids. The best known is probably the *multipolar* electrostatic coupling, which was suggested originally by Förster[29] and extended by Dexter.[30] Since in GaP:N the *B* line corresponds to a dipole-forbidden transition, we can rule out the contribution of dipole-dipole coupling to excitation transfer. Moreover, since the internitrogen separation in the sample we used for the echo-intensity study is, on the average, 415 Å, we can also ignore higher-multipole interactions.

A *tunneling* process seems much more likely to be the cause of energy transfer. As the bound exciton is of the Wannier-Mott type, its radius is quite large. Using the effective masses of electron and hole, given by Vink,[31] we calculate a Bohr radius of some 30 Å. Therefore the exciton at a given site can have a considerable overlap in wave function with another site in its environment, thus allowing tunneling of the excitation. A similar mechanism has been invoked by Wiesner *et al.*[32] to explain nonresonant energy transfer between N-N—pair lines. Here, tunneling times on the order of tens of nanoseconds were observed for distances of some hundred angstroms. Thus, it is not unreasonable to propose a similar mechanism in our case.

As the activation of R_E remains neatly biexponential over the whole temperature range, we can assume that the excitation-transfer rate of 10^7 s^{-1} is not very strongly dependent on temperature. This is a further indication that excitation tunneling may take place. For several other transfer processes that have been proposed,[33] one predicts strong temperature dependences, as they involve the exchange of (virtual) phonons. Moreover, these mechanisms cannot contribute at the lowest temperature, as they do not contain any temperature-independent terms.

For a proper assignment of the transfer mechanism, much more experimental work is needed. It will be necessary to know the temperature dependence, if any, and concentration dependence of the excitation-transfer phenomenon. An ideal experiment to measure these parameters directly would be to perform a three-pulse stimulated-photon-echo experiment on the *A* line. One expects[34] a biexponential decay, where the short component measures the T_1 of the *A* state, while the long component is directly determined by the energy-transfer rate out of the *B* state.

Finally, we want to discuss in some more detail why and how excitation tunneling effects the echo. As mentioned in the experimental section, the accumulated echo is stimulated from a frequency grating in the ground state of the transition under study. The fringe spacing (in energy units) of this grating is inversely proportional to the separation (in time) of the two pulses that create the grating.[14] Furthermore, it is known[33] that excitation tunneling still can take place if there is an energy mismatch ΔE between the exciton-absorption energies at neighboring sites. It is obvious that such quasiresonant energy transfer will partially destroy the grating, thus leading to a decrease of echo intensity. Energy transfer pertaining to ΔE intervals small compared with the inhomogeneous linewidth, however, will affect finely grained frequency gratings (long pulse separation) more strongly than coarsely grained ones. Thus, such processes would lead to a shortening of the observed echo decay.[22] This is in contrast with our observation that the two-pulse and accumulated echoes yield identical decay times. One has to realize that, while the grating is accumulated in the inhomogeneous profile of the *A* transition, the excitation transfer occurs in the *B* state. In general, the inhomogeneous profiles of optical transitions belonging to different electronic states do not seem to be correlated,[35] as is evident from fluorescence-line-narrowing[36] and hole-burning[37] experiments. Applied to the accumulated echo in GaP:N, this means that excitation transfer over a specific ΔE interval for the *B* transition (ΔE can even be zero) can be accompanied by excitation transfer over the complete inhomogeneous profile of the *A* line, thereby leading to a decrease in echo intensity, but not affecting the echo-decay time.

IV. CONCLUSIONS AND SUGGESTIONS

We have shown that new information on optical dynamics in semiconductors can be obtained from optical-coherent-transient studies. In this paper accumulated photon echoes provided us with detailed information on the relaxation and dephasing phenomena associated with the upper bound-exciton state in GaP:N. From the data we find a (25.5 ± 0.5)-ps relaxation time for the decay from the *A* to the *B* state which can be explained in terms of a strong orbit-lattice interaction. Optical dephasing of the *A* line was shown to be of a nonadiabatic nature and can be understood as arising from inverse Orbach processes[28] involving the *B* state and, at higher temperatures, thermal detrapping into the free-exciton band.

We stress that information on relaxation processes within the inhomogeneous linewidth can only be obtained through nonlinear spectroscopic measurements, and not, e.g., by luminescence-quenching methods. From a comparison of echo-intensity with luminescence-quenching data, we conclude that excitation-tunneling processes occur in the *B* state of the system studied.

As mentioned previously, a three-pulse stimulated-photon-echo study should yield important information on energy transfer in the present system. Related but more elaborate techniques[38] could be used to study the processes governing the broadening in the biexciton lines that occur at higher excitation densities in GaP:N.

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[1] P. J. Dean and D. C. Herbert, in *Excitons,* edited by K. Cho (Springer, Berlin, 1979), p. 55.

[2] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).

[3] E. C. Lightowlers, J. S. C. North, and O. G. Lorrimor, J. Appl. Phys. **45**, 2191 (1974).

[4] Y. Yafet and D. G. Thomas, Phys. Rev. **131**, 2405 (1963).

[5] H. Mathieu, L. Bayo, J. Camassel, and P. Merle, Phys. Rev. B **22**, 4834 (1980).

[6] J. D. Cuthbert and D. G. Thomas, Phys. Rev. **154**, 763 (1967).

[7] M. D. Sturge, E. Cohen, and K. F. Rodgers, Phys. Rev. B **15**, 3169 (1977).

[8] P. Hu, S. Chu, and H. M. Gibbs, in *Picosecond Phenomena II,* edited by R. M. Hochstrasser, W. Kaiser, and C. V. Shank (Springer, Berlin, 1980).

[9] R. T. Harley and R. M. Macfarlane, J. Phys. C **16**, L1121 (1983).

[10] (a) L. W. Molenkamp and D. A. Wiersma, J. Chem. Phys. **80**, 3054 (1984); (b) W. H. Hesselink and D. A. Wiersma, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems,* edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983).

[11] W. H. Hesselink and D. A. Wiersma, J. Chem. Phys. **73**, 648 (1980).

[12] K. Duppen, L. W. Molenkamp, and D. A. Wiersma, Physica **127B**, 349 (1984).

[13] Ph. de Bree and D. A. Wiersma, J. Chem. Phys. **70**, 790 (1979); Ph. de Bree, Ph.D. thesis, University of Groningen, The Netherlands, 1981.

[14] W. H. Hesselink and D. A. Wiersma, J. Chem. Phys. **75**, 4192 (1981).

[15] W. H. Hesselink and D. A. Wiersma, Chem. Phys. Lett. **56**, 227 (1978).

[16] D. G. Thomas, M. Gershenzon, and J. J. Hopfield, Phys. Rev. **131**, 2397 (1963).

[17] J. J. Hopfield, P. J. Dean, and D. G. Thomas, Phys. Rev. **158**, 748 (1967).

[18] E. Cohen and M. D. Sturge, Phys. Rev. B **15**, 1039 (1977).

[19] H. de Vries and D. A. Wiersma, J. Chem. Phys. **80**, 657 (1984).

[20] R. W. Olson, H. W. H. Lee, F. G. Patterson, and M. D. Fayer, J. Chem. Phys. **76**, 31 (1982).

[21] See, e.g., A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1934).

[22] R. M. Macfarlane and R. M. Shelby, Opt. Commun. **45**, 46 (1983); L. W. Molenkamp and D. A. Wiersma, J. Chem. Phys. (to be published).

[23] K. Duppen (unpublished).

[24] S. Chu and S. Wong, Phys. Rev. Lett. **48**, 738 (1982); **49**, 1292 (1982).

[25] R. Romestain (private communication).

[26] D. E. McCumber and M.D. Sturge, J. Appl. Phys. **34**, 1682 (1964).

[27] C. Cohen-Tannoudji, in *Frontiers in Laser Spectroscopy,* edited by R. Balian, S. Haroche, and S. Liberman (North-Holland, Amsterdam, 1977), Vol. 1.

[28] B. di Bartolo, *Optical Interactions in Solids* (Wiley, New York, 1968), Chap. 15; E. A. Harris and K. S. Yngvesson, J. Phys. C **2**, 990 (1968).

[29] Th. Förster, Ann. Phys. (Leipzig) **2**, 55 (1948).

[30] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

[31] A. T. Vink, J. Lumin. **9**, 159 (1974).

[32] P. J. Wiesner, R. A. Street, and M. D. Wolf, Phys. Rev. Lett. **35**, 1366 (1975).

[33] T. Holstein, S. K. Lyo, and R. Orbach, in *Laser Spectroscopy of Solids,* edited by W. M. Yen and P. M. Selzer (Springer, Berlin, 1981).

[34] J. B. W. Morsink, W. H. Hesselink, and D. A. Wiersma, Chem. Phys. **71**, 289 (1982).

[35] H. W. H. Lee, C. A. Walsh, and M. D. Fayer, J. Chem. Phys. (to be published).

[36] R. Flach, D. S. Hamilton, P. M. Selzer, and W. M. Yen, Phys. Rev. B **15**, 1248 (1977); H. J. Griesser and U. P. Wild, J. Chem. Phys. **73**, 4715 (1980); E. I. Al'shits, R. I. Personov, and B. M. Kharlamov, Chem. Phys. Lett. **40**, 116 (1976).

[37] S. Voelker and R. M. Macfarlane, IBM J. Res. Dev. **23**, 547 (1979); R. W. Olson, H. W. H. Lee, F. G. Patterson, M. D. Fayer, R. M. Shelby, D. P. Burum, and R. M. Macfarlane, J. Chem. Phys. **77**, 2283 (1982).

[38] K. Duppen, D. P. Weitekamp, and D. A. Wiersma, Chem. Phys. Lett. **106**, 147 (1984); **108**, 551 (1984).