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Optical pumping in nitrogen-doped GaP

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We report on the results of optical-pumping experiments in GaP doped with the isoelectronic impurity nitrogen. In the first experiment we have measured the saturation of absorption at the A bound exciton as a function of pump intensity, using as the pump a pulsed dye laser tuned to the A line. The observed saturation behavior is in quantitative accord with a simple three-level system involving the A and B bound-exciton level and the N ground state. The second experiment involves measuring the absorption at the A line with a weak probe (a tunable dye laser) while the crystal is being pumped with an intense pump dye laser tuned above the indirect gap. In this case also the absorption saturates with increasing pump power and we can infer approximately 10% efficiency for the capture of excitons at N impurities. In this second experiment, a simple model predicts an amplification by a factor of 8.5 but none is observed. We conclude from these measurements that, when pumped above the indirect gap, the dominant excited state of N impurities in our crystal is a single electron trapped at N. We believe that this is caused by the presence of other impurities in the crystal and is not an intrinsic limitation of the system.

I. INTRODUCTION

The properties of the indirect semiconductor GaP in the presence of isoelectronic impurities substituted for P have been widely described.[1] In particular, the introduction of N into GaP results in an electron trap characterized by a short-range potential with ≈ 10-meV binding energy.[2] The nitrogen with an electron bound to it is in an excited state and in this state can bind a hole by approximately the same energy, giving rise to a bound-exciton complex. Depending on the electron-hole spin alignment, the bound exciton exists in one of two states: A $(J=1)$ and B $(J=2)$ with the radiatively allowed A state 0.8 meV higher in energy than the nonallowed B state. Thermal equilibration between the A and B levels occurs rapidly ($\sim 10^{-11}$ sec) so that the relative population in the A and B state is determined by the Boltzmann factor and level degeneracies.[3] The short range of the nitrogen potential sufficiently localizes the trapped electron so that its wave function in momentum space is spread over the Brillouin zone with significant amplitude at $k=0$. This results in a large oscillator strength for the A level of the bound-exciton complex and leads to a strong absorption peak[1] ($\sigma \sim 10^{-15}$ cm^2 at low temperatures) at 2.317 eV (see Fig. 1). This bound-exciton state is also responsible for the efficient green luminescence at room temperature,[4] and measurement of optical gain has also been reported in this indirect band-gap system.[5-7]

The optical properties of N in GaP have been investigated in great detail at low intensities.[2] We report here the results of our investigation of this system using an intense tunable dye laser. We have measured the absorption at the A level as a function of intensity and find that the absorption saturates (transmission approaches unity) in quantitative accord with the theory of a simple three-level system. No population inversion for the A state is possible when pumping directly at resonance with this level.

We have also performed another set of experiments using two dye lasers. A tunable weak laser is used to probe the absorption at the A level in the presence of an intense pump laser ($h\nu > E_g$). A simple three-level analysis of the bound-exciton system indicates that net gain due to stimulated emission at the A bound exciton is expected under these conditions. We find that the absorption of the probe saturates as we increase the pump intensity, but no net gain is observed.

II. EXPERIMENTAL TECHNIQUES

The material used for this investigation was epitaxially grown on GaP substrates and uniformly doped with N to a density of $\sim(0.5-1.0)\times 10^{18}$ cm^{-3}. In addition, the samples were doped with Zn and S to form p-n junctions for their intended uses as efficient room-temperature green-light-emitting diodes. The epitaxial layer thickness was typically 10^{-2} cm. The experimental results presented here were obtained on a single sample with $[\mathrm{N}] \sim 7\times 10^{17}$/cm^3 and $d \sim 100$ μm (the substrate was polished off). They are typical of the results obtained on all the samples examined. Nitrogen density was determined using Lightowlers's[8] results relating nitrogen concentration to the bound-exciton absorption line shape. High-resolution absorption measurements were made at 20 °K using a broad

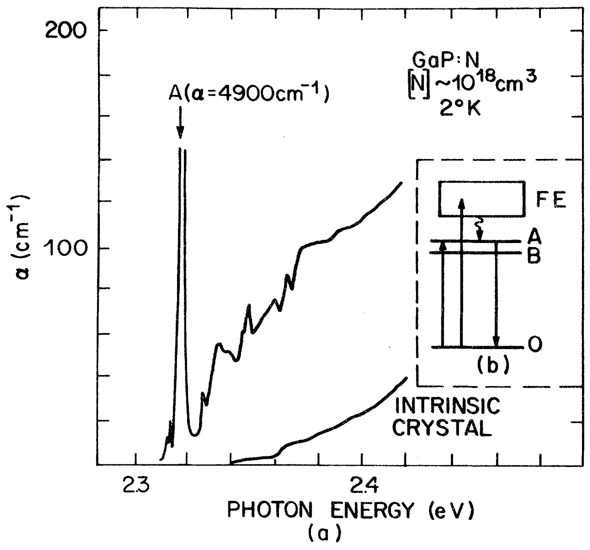

FIG. 1. Absorption spectrum of GaP in the vicinity of the A line for an intrinsic crystal (no N doping) and for a crystal doped with $\sim 10^{18}$ N/cm^3 [P. J. Dean, J. Lumin. 1, 2, 407 (1970)]. The inset shows the energy-level scheme relevant to this paper.

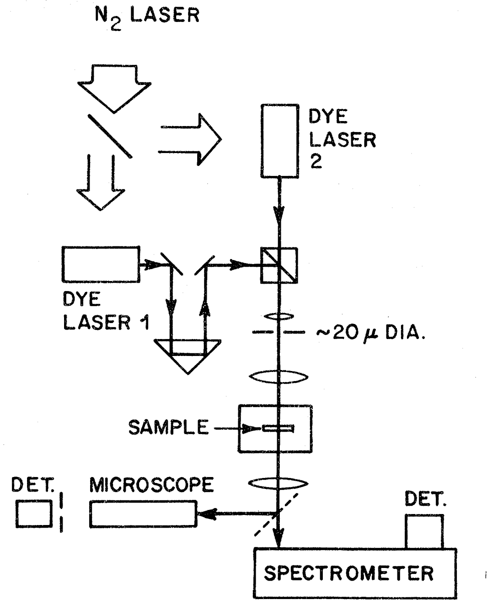

FIG. 2. Schematic diagram of experimental arrangement.

band fluorescence source and a double monochrometer to measure the spectrum of sample transmission. The bound exciton absorption was fitted to a Lorentzian line shape with 1.5 Å full width at half maximum and with an $(\alpha d)_{\max} \sim 7.6$ corresponding to a transmission of $\sim 5\times 10^{-4}$. Because of difficulties with fluorescence and scattered probe light, the minimum transmission measured with the dye laser in the optical pumping experiments was 5–10 times this value. Luminescence lifetime for the bound-exciton recombination line was also measured and found to be ≤ 20 nsec and to be weakly dependent on temperature between 10 and 40 °K, indicating that for these samples an efficient quenching mechanism competes with radiative recombination of the bound exciton[9] since in this temperature range much longer decay times have been measured for the bound excitons.[3]

The optical-pumping measurements were made with a nitrogen-laser-pumped dye laser. This system provided up to 10-kW output in a 5-nsec pulse at 30 pulses/sec with output line width ≤ 0.25 Å. By diverting a fraction of the nitrogen laser to pump a second dye laser, it was possible to generate two independently tunable lasers with typically 2–5 kW per beam. The experimental configuration is shown schematically in Fig. 2. As indicated on the figure, a delay was introduced in the probe beam so that sample absorption was measured after the pumping pulse was extinguished.

The lasers were focused through a nominally ~ 20-μm pinhole, and the light passing through this aperture (typically 85% of the incident beam) was refocused onto the sample. Taking account of surface reflections on the sample and on the optical components, the total power reaching the sample was reduced by approximately a factor of 5 over what was available at the laser. The light transmitted through the sample was collected and passed through a microscope system to project a magnified image of the spot at the sample onto an aperture set to pass only the relatively uniform central portion of the beam. In this way, effects due to variation of intensity in the transverse dimensions were minimized. The light passing through this aperture was focused into a spectrometer and then detected. The spectrometer was necessary to minimize the effects of background dye laser or sample fluorescence.

III. RESULTS AND DISCUSSION

A. Single-beam experiments: Saturation of A line absorption

We first discuss the results obtained by using a single dye laser to pump directly at the A line. Typical results for transmission through the sample as the dye laser grating is scanned are shown in Fig. 3 for three different pump intensities. The solid dots indicate the measured transmission at

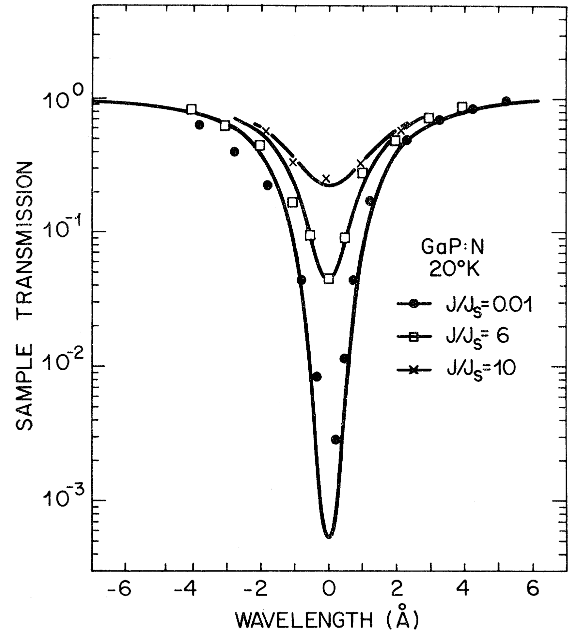

FIG. 3. Sample transmission spectrum at three different intensities. "0" on the horizontal scale corresponds to 5349.0 Å. The points are experimental; the solid curves are theoretical, as discussed in the text.

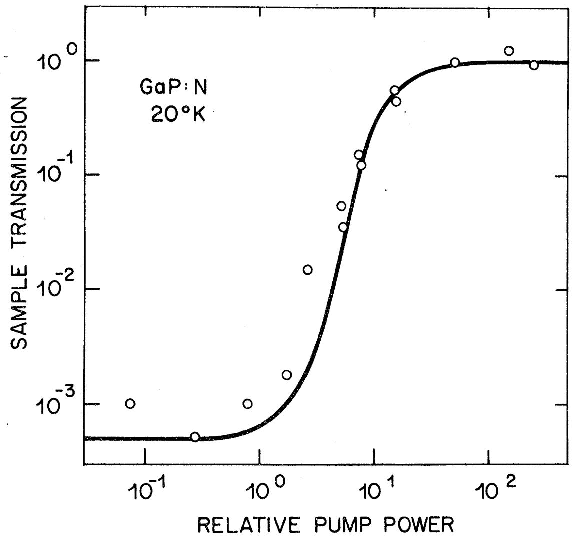

FIG. 4. Sample transmission vs incident pump power. The points are experimental and the solid curve is theoretical [Eq. (1)]. The highest pump power (last experimental point) was ≈ 200 W focused into ~ 30-μm diameter spot. $J_{\max} = 2.5 \times 10^{17}$ photons/cm^2. The theoretical curve is plotted for $J_s = 10^{15}$ photons/cm^2.

very low intensities. As the incident intensity is increased, the absorption saturates and sample transmission approaches unity. The variation of the transmission with pump power, measured at the peak of the bound exciton absorption, is plotted in Fig. 4 after correcting for the scattered laser light at low-pump intensities. The absorption begins to saturate when a significant fraction of the N impurity atoms are excited and, for the case when the bound exciton is the only excited state, vanishes when the fraction of N in the A excited state equals the fraction of N in the ground state. Under these conditions, stimulated emission exactly balances absorption, and further increases in pump intensity cannot produce any change in this population.

These qualitative ideas can be put in a more quantitative form using the energy-level diagram shown in the inset of Fig. 1. We review the analysis of saturable absorption applicable to these experiments in Appendix A and find, for the case of pumping directly at the A state, that the sample transmission varies as[10]

$$T = (J_s/J)\ln[1 + T_0(e^{J/J_s} - 1)], \qquad (1)$$

where J is the time integral of the incident photon flux, T_0 is the small signal transmission, and J_s is the "saturation parameter" defined in the Appendix. The solid curve in Fig. 4 was calculated using Eq. (1) with $T_0 = 5 \times 10^{-4}$. By fitting the data in this way, a value of J_s can be determined experimentally and, in turn, the product $(2 + \gamma/1 + \gamma)\sigma$ is determined. Taking account of the losses in optical components and measured spot size, we determine a value for σ of $\sim 10^{-15}$ cm^2, in agreement with that determined from small-signal-absorption measurements. It is interesting to note that the apparent variation of absorption line width in the scans of Fig. 3 results from the variation of σ with wavelength so that as the laser is scanned across the absorption line, the relative value of J/J_s varies.

The measurements illustrated in Figs. 3 and 4 were made at 20 °K but are typical of results obtained at lower temperatures. At 2 °K the linewidth is somewhat narrower so that σ is larger, but γ also varies with temperature, and we observe little change in the saturation intensity. At higher temperature, σ decreases as the line broadens, with corresponding increase in the power required to saturate the bound-exciton absorption.

B. Two-beam experiments

For these measurements, the crystal was excited by a strong pump laser tuned above the indirect energy gap. Sample transmission was approximately 50% at the pump laser wavelength

($\lambda \sim 4880$ Å), allowing nearly uniform pumping of the crystal. The probe laser was continuously tunable in the region of *A* line absorption (~ 5350 Å or 2.317 eV), and its intensity was kept small enough not to affect saturation of the nitrogen centers. In these measurements, the pump beam generates free excitation in the volume pumped and some fraction of this excitation is trapped at the nitrogen centers. Unlike pumping at the bound-exciton transition, there is no limit to the fraction of nitrogen centers which can be excited, and population inversion with respect to the bound-exciton transition occurs when the number of nitrogen centers in the *A* excited state exceeds the number in the ground state. Taking account of level degeneracy, the maximum gain available if all the nitrogen centers were excited into the bound exciton states is $g = \alpha_0/(1+\gamma)$ ($\sim 2.2\ \text{cm}^{-1}$ at 20 °K for $[\text{N}] = 5 \times 10^{17}$), while if some fraction $(1-f)$ of the nitrogens are in another excited state, this gain would be reduced by f. A detailed analysis of the variation of absorption of the probe beam expected for a pump generating n_x free excitons is given in Appendix A where we find for $f = 1$,[10]

$$\alpha = \frac{-\alpha_0}{1+\gamma}\left[1 - (2+\gamma)e^{-c' n_x \Delta t}\right], \tag{2}$$

where Δt is the pumping pulse width, and c' is the probability for trapping an exciton at the nitrogen impurity. For the case $f = 0$ (no bound exciton),

$$\alpha = \alpha_0 e^{-c' n_x \Delta t}, \tag{3}$$

reflecting the exponential decrease in the population of unexcited nitrogen centers as the pump intensity increases.

The absorption traces obtained with the pump on and pump off are shown in Fig. 5 for the same probe intensities. Variation of the sample transmission at the wavelength of peak absorption versus pump intensity is shown in Fig. 6. We see a significant decrease in absorption when the pump is turned on. It was found that careful alignment of the two laser beams was required to insure good overlap of the beams at the sample. Similar results were obtained for pump wavelengths varying from 5150 to 4700 Å. A small shift to lower energy in peak absorption (~ 0.5 Å) is evident, and an increase in the broad feature at lower energies, over that calculated for a Lorentzian line, is also observed. While this feature of the spectrum is reproducible and present in all the samples examined, the actual increase in absorption is quite small. The origin of this feature is not known at present, and we will not consider it further at this time.

Clearly the data show no evidence of net gain, even at the highest pump power used here (5×10^7 W/cm^2). Equations (2) and (3) have been plotted in Fig. 6, for comparison to the data, by fitting the point at which the probe transmission corresponds to that for half the nitrogen centers excited ($T = T_0^{1/2}$), assuming $f = 0$. As shown in the figure, if the bound exciton was the only excited state of the nitrogen center, a net amplification of 8.5 is predicted. Since the measurement sensitivity is such that an amplification as low as 20% could have been detected, we conclude that f is less than 0.1.

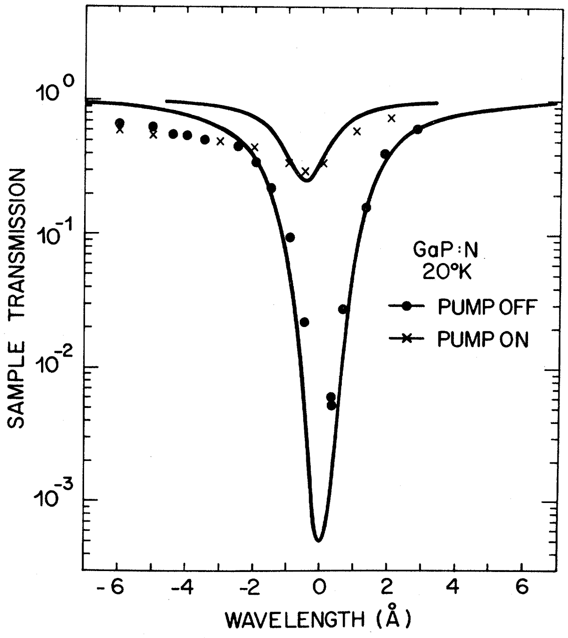

FIG. 5. Transmission spectrum near the *A* line obtained with the probe beam for the pump beam on and off. The pump beam was at 4880 Å.

In the analysis of these measurements, we have taken the direct approach of relating the expected gain to the measured absorption. This approach takes advantage of the fact that the stimulated emission cross section of the *A* level just equals the absorption cross section, and the principal assumption in the calculation is that the bound-exciton states included in the model completely describe the excited states of the N impurity. Nonradiative decay out of any of these states to the ground state does not alter our conclusions, since this form of deexcitation merely competes with radiative and increases the pumping rate required to maintain a given fraction of the N atoms in an excited state. The presence of losses (optical absorption or scattering) in the sample cannot account for the nonobservation of gain. Any such loss would be expected to be nonresonant and therefore contribute equally off the *A* line as on resonance. In the presence of such a loss, the total transmission through the sample at the *A* line wavelength would increase over that off the *A* line due to amplification by the excited N atoms. By scanning the probe wavelength, we determine that this is not the case. In addition, scanning the probe insures that there is no broadening of the *A* bound-exciton state with corresponding decrease in gain as the absorption is reduced.[11] The possibility of excited-state absorption out of the bound-exciton state competing with stimulated emission, that is, the probability for direct absorption out of the bound-exciton state being greater than the probability for stimulated emission, can also be ruled out since such a process would also not be expected to be resonant and would be evidenced by increased off-resonance absorption in the scanned-probe-wavelength measurements. Because the complete saturation of absorption implies that the population of nitrogen centers in the ground state is negligible, and the absence of gain implies a negligible fraction of the excited nitrogen centers are in the *A* bound-exciton state, we must conclude that the nonobservation of amplification implies the nitrogen atoms are in an excited state not included in the model, and one which is not connected to the ground state by the probe energy.

While these absorption measurements provide no insight into this alternative excited state, we can rule out certain possibilities. Pairing of the nitrogen centers is known to result in formation of new electronic levels, the *NN* levels, in heavily doped GaP, but there is no evidence of *NN* line absorption in the small-signal-absorption spectrum for the sample studies in agreement with what is expected at the nitrogen concentration used.[2] However, one might consider what happens for high densities of excited nitrogen centers. The model for bound-exciton formation on nitrogen impurities is that first an electron is trapped, followed by a hole trapping. Therefore, we view our results to imply that electrons are effectively trapped on the nitrogen impurities, but not the holes. This could be due to intrinsic effects in which at the density of excitation, the holes are no longer bound as tightly to individual excited nitrogen centers, with resulting broadening or shifting of the bound-exciton level. We reject this possibility because at the density of nitrogen centers used $[\mathrm{N}] \sim 5 \times 10^{17}$, and even for the case of all nitrogens excited, banding of the bound holes is highly unlikely.[12]

While there is no spectroscopic evidence of an alternative excited state involving just an electron bound to the nitrogen, Dean *et al.*[13] have shown the existence of such an excited state for the isoelectronic impurity Bi (which traps a hole first) for which only a single carrier is bound to the isoelectronic center. Our measurements represent the first suggestion that such a possibility exists for the N impurity.

By comparing the pump intensity required to saturate the bound-exciton absorption in this two-beam measurement to that required in the single-beam experiment, we can determine the relative efficiency for excitation when pumping above the band gap. While the experiment is slightly different due to the time delay in the probe beam, so that the absorption is measured after the pumping pulse, we find that approximately ten times the pump intensity is required to excite the same number of nitrogen centers when pumping above the band gap as for pumping directly on the *A* line. This implies a capture efficiency of ~10% for conversion of the free excitation created by the pump laser into excited nitrogen centers.

IV. CONCLUSIONS

We have measured the saturation of absorption at the *A* line in GaP doped with isoelectronic nitrogen. When pumping directly at the *A* line, we find that the absorption saturates in quantitative accord with a simple three-level system. However, when pumping above the band gap, no net gain is observed, contrary to expectations. We conclude that this is because the dominant excited

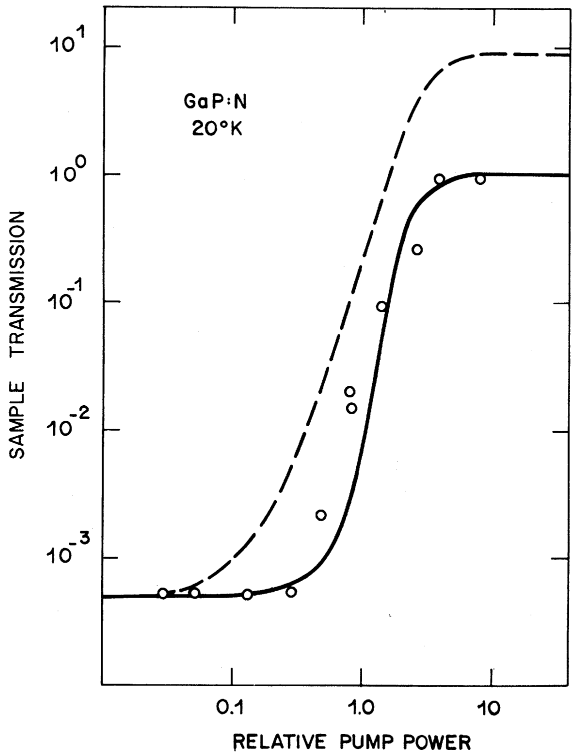

FIG. 6. Sample transmission vs pump power. The last experimental point corresponds to ≈ 500 W focused into 30-μm diameter spot.

state of the N atoms in our crystals is a single electron trapped at the N atom. This is not an intrinsic limitation of the GaP:N system but appears to be due to the presence of other impurities in the crystal.

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APPENDIX A

Analysis of optical pumping into the bound-exciton state can be done by straightforward application of coupled rate equations governing relaxation of the excitation in the crystal and the interaction of the incident photons with the impurity. Taking N_0 to be the density of unexcited nitrogen centers, the rate equations governing the relative population of excited nitrogen centers are

$$\frac{dN_A}{dt}=\sigma\phi(N_0-N_A)-\frac{N_A}{\tau_A}-\Gamma(N_A-N_B)-\frac{N_A}{\tau'}, \qquad \text{(A1)}$$

$$\frac{dN_B}{dt}=-\frac{N_B}{\tau_B}-\Gamma'(N_B-N_A)-\frac{N_B}{\tau'}, \qquad \text{(A2)}$$

$$N=N_0+N_A+N_B=N_0+N_A(1+\gamma), \qquad \text{(A3)}$$

where σ is the cross section for absorption of a photon ($\sigma \sim 10^{-15}$ cm^2 at 20 °K), and ϕ is the photon flux density. For equilibrium, the rate of thermal excitation from B to A, Γ' just compensates for the rate of relaxation from A to B, Γ to maintain $\gamma=N_B/N_A=\frac{5}{3}e^{+\Delta/kT}$, where $\Delta=0.8$ meV, the energy separation between A and B levels. The factors with lifetime τ' are included to indicate the possibility of relaxation into a complex other than a bound-exciton state. Equations (A1)–(A3) can be combined to yield

$$\frac{dN_A}{dt}=\frac{\sigma[N-(2+\gamma)N_A]\phi}{1+\gamma}-N_A\frac{1}{1+\gamma}\left(\frac{1}{\tau_A}+\frac{\gamma}{\tau_B}+\frac{1+\gamma}{\tau'}\right). \qquad \text{(A4)}$$

In the energy-saturation limit (pumping pulse shorter than the time for relaxation to the ground state), the second term in Eq. (A4) can be neglected, yielding

$$\frac{dN_A'}{dt}=\left(\frac{2+\gamma}{1+\gamma}\right)\sigma\phi N_A', \qquad \text{(A5)}$$

where $N_A'=N-N_A(2+\gamma)$. This result is coupled to the expression for optical absorption,

$$\frac{d\phi}{dx}=-\sigma\phi(N-N_A') \qquad \text{(A6)}$$

Equations (A5) and (A6) can be solved for the transmission of the pump signal through the sample as a function of the integrated flux incident on the sample $J_0=\int\phi\,dt$ to yield[14]

$$T=J_s/J_0\ln[1+T_0(e^{J_0/J_s}-1)], \qquad \text{(A7)}$$

where $J_s=\phi\tau=\{[(2+\gamma)/(1+\gamma)]\sigma\}^{-1}$ corresponds to the integrated flux density at which the transmission begins to increase due to saturation, and T_0 is the initial small-signal transmission $e^{-\sigma Nd}$. The factor $(2+\gamma)/(1+\gamma)$ results from inclusion of stimulated recombination out of the A level in Eq. (A1). For large values of γ (low temperatures), the fraction of bound excitons in the A level is small, and this factor approaches unity. At 20 °K $\gamma \sim 2.5$, and a significant fraction of the bound excitons can be maintained in the A level, providing the bound exciton does not relax into a third excited state not included in this analysis, in a time short compared to the radiative lifetime of the bound-exciton state.

In analyzing the two-beam experiments, certain simplifications are possible. The probe pulse was delayed ~5 nsec with respect to the pumping pulse and was of low enough intensity so that the variation of excited nitrogen atoms during the probe transmission through the sample is negligible. In addition, the pump wavelength was chosen so that ~50% of the pump signal was transmitted, resulting in nearly uniform pumping of the sample. Taking N^* to be the number of excited nitrogen centers, the variation of N_0, the unexcited nitrogen is determined by considering $N=N_0+N^*$ and writing

$$\frac{dN^*}{dt}=c'n_xN_0-\frac{N^*}{\tau}, \qquad \text{(A8)}$$

where n_x is the density of free excitation due to the pump, and c' determines the rate at which this excitation excites the nitrogen atoms. Solving for N_0 assuming N^*/τ is negligible during the measurement,

$$N_0=Ne^{-c'n_x\Delta t}. \qquad \text{(A9)}$$

The absorption of the probe beam is related to $\alpha=+\sigma(N_0-N_A)$. Consider how this quantity varies in the two limits; first, when $N_A=0$, corresponding to fast relaxation out of the bound-exciton state or the excitation of a different excited state of the nitrogen impurity; and second, when $N_A=[1/(1+\gamma)](N-N_0)$, corresponding to equilibrium between the A and B levels for excited nitrogen atoms and no other possible excited states. In the first case, the probe beam measures the population of unexcited N atoms and $\alpha=+\sigma Ne^{c'n_x\Delta t}$. For the second case, stimulated emission must be included to yield $\alpha=[-\sigma N/(1+\gamma)][1-(2+\gamma)\times e^{-c'n_x\Delta t}]$, and the probe signal should be amplified when the density of free excitons n_x is such that $n_x \geqslant (1/c'\tau)\ln(2+\gamma)$.

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[10] We have tacitly assumed that the energy limit, rather than the steady-state limit, of the rate equations is applicable. For the case where the bound excitons relax radiatively, the relaxation times are greater than our pumping pulse width for crystal temperatures $\lesssim 40$ °K, and the energy limit assumption is clearly valid. For the samples measured, the luminescence lifetimes are shorter than radiative but still longer than the pumping pulse width.

[11] To reduce the effective amplification below our detection limit by broadening, the *A* exciton linewidth would have to exceed 3 meV (7 Å). In order for sample heating to result in this degree of broadening, the sample temperature would have to rise to 90 °K, at which point the absorption peak would have shifted ∼20 Å to longer wavelengths (Ref. 8). There is no evidence in our data to suggest that these effects are present; therefore, sample heating cannot explain our result.

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