Journal of Luminescence 38 (1987) 230–233
North-Holland, Amsterdam

RESONANT RAMAN SCATTERING AND EXCITON LOCALIZATION IN GaP:N AND $GaAs_xP_{1-x}$:N

D. GERSHONI
AT&T Bell Labs, Murray Hill, NJ, USA

E. COHEN, Arza RON
Solid State Institute, Technion, Haifa, Israel

M.D. STURGE
Dartmouth College, Hanover, NH, USA

We present a study of the luminescence and *resonant Raman scattering* (RRS) by optical phonons which are due to excitons bound to isoelectronic nitrogen impurities in GaP and in $GaAs_xP_{1-x}$. The exciton bands are inhomogeneously broadened. In GaP the broadening results from nitrogen centers which are perturbed by other distant impurities (V-band). In $GaAs_xP_{1-x}$ the N-bound exciton band reflects the random potential fluctuations in the alloy. Under resonant excitation at liquid He temperatures, strong Raman lines are observed involving the LO_Γ, TO_Γ phonons and a nitrogen-induced forbidden scattering by the zone-edge LO_X phonon. The LO_X RRS spectrum is shown to be determined mainly by the density of terminal states, namely, those N-bound excitons which do not tunnel to other sites within the A–B thermalization time. In GaP, this RRS shows a resonance which is strong in the V-band but is essentially missing at the peak of the A-line. This is interpreted as an indication of a fast dephasing rate within the A-line due to resonant transfer, as compared to slow tunneling between the perturbed centers.

1. Introduction

1.1. Isolated N-bound excitons

The spectroscopic properties of excitons bound to isoelectronic N impurities in GaP are well known [1]. The 1S state is split by e–h exchange into an upper $J=1$ state and a lower $J=2$ state. The corresponding transitions are designated A and B lines. The former is dipole allowed and the latter forbidden. Typical spectra are shown in fig. 1. The different symmetry of the two states results in different coupling to optical phonons. Both the $J=1$ and $J=2$ states couple to TO_Γ and LO_Γ phonons. However, only the $J=1$ state couples strongly to the LO_X phonon. This can be clearly observed in the photon sideband spectrum associated with either the A or the B lines.

Molenkamp and Wiersma [2] have measured by photon-echo experiments the decay time of the $J=1$ into the $J=2$ state: $\tau_{AB}=25$ ps at $T=1.5$ K. At higher temperatures, N-bound exciton thermalization into the free exciton band contributes to the dephasing rate. The radiative lifetimes of both the $J=1$ and $J=2$ states are very long compared to the inverse dephasing rates between these two states [3].

1.2. Spatial perturbations of N-bound excitons

We consider two types of microscopic environments of the nitrogen impurity which affect the properties of the bound exciton. In GaP, distant background impurities

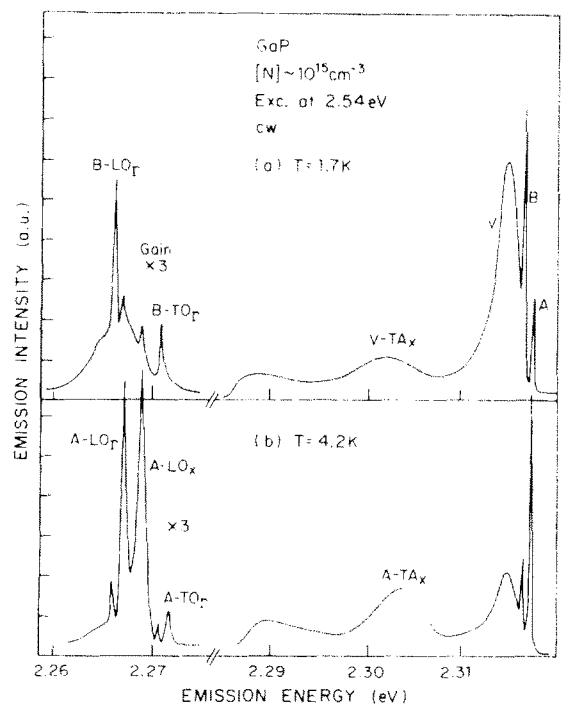

Fig. 1. The luminescence spectra of nominally undoped GaP:N. At 1.7 K the emission is due mostly to excitons in the $J=2$ state (B-line), while at 4.2 K the $J=1$ emission dominates. Note the different optical phonons sidebands.

0022-2313/87/$03.50

perturb the N-bound exciton and increase its binding energy. This results in a broad emission band ("V-band") below the A, B lines (which are due to unperturbed nitrogen centers) [4]. In nominally undoped GaP, the density of such perturbed nitrogen centers is at least two orders of magnitude smaller than that of the unperturbed centers.

In $GaAs_xP_{1-x}$, the random distribution of As and P atoms sets up a random potential distribution which affects the binding energy of the exciton [5]. The resulting density of N-bound exciton states is Gaussian. In both cases of GaP and $GaAs_xP_{1-x}$, the N-bound exciton retains its splitting into $J=1$, 2 states as that of the unperturbed excitons in GaP [4,6]. The relative oscillator strengths of the corresponding A′ and B′ lines (obtained by selective excitation) is similar to those of the unperturbed excitons, as evidenced by their radiative lifetimes.

2. Experiment

RRS by optical phonons in nominally undoped GaP and in several $GaAs_xP_{1-x}$ crystals has been observed at $T=2$ K. Excitation was done with a dye laser operating either CW or in a cavity-dumped mode (with 7 ns pulse width). Fig. 2 shows a series of RRS spectra of GaP excited above

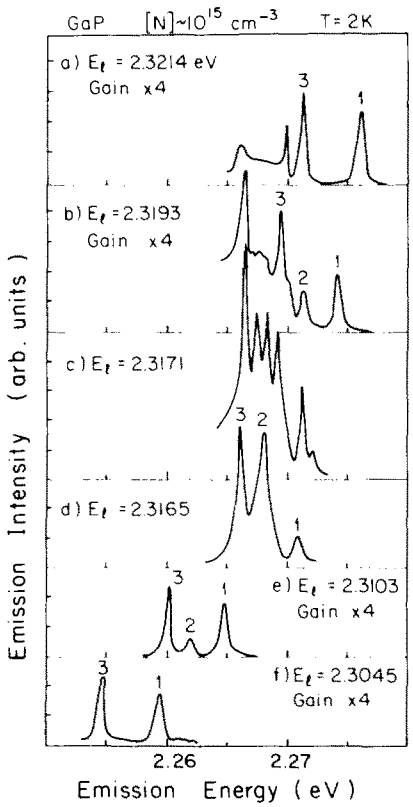

Fig. 2. Resonant Raman scattering spectra excited above the A-line (a, b), into the A-line (c) and into the V-band (d–f). Lines 1, 2, 3 correspond to TO_Γ, LO_X and LO_Γ, respectively.

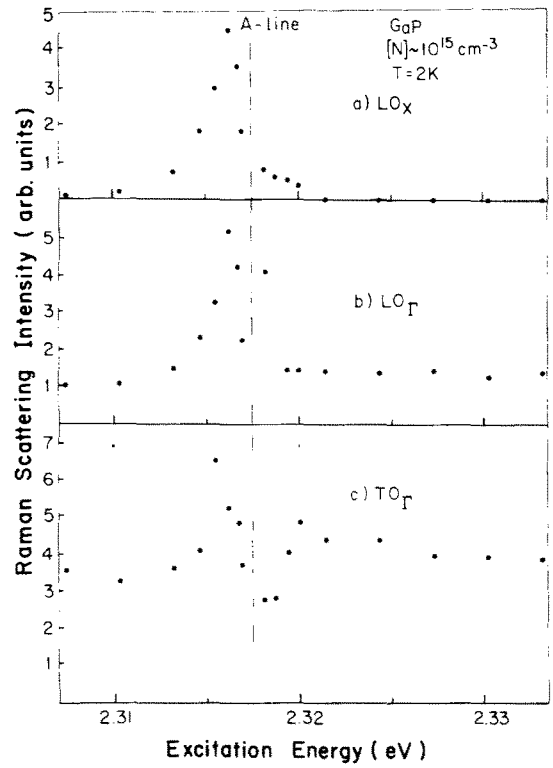

Fig. 3. The energy dependence of the RRS cross section for the three optical lines.

the A-line (a and b), at resonance with the A-line (c) and into the V-band (d–f). The lines marked 1, 2, 3 correspond to RRS by TO_Γ, LO_X and LO_Γ phonons, respectively. Fig. 3 shows the intensity of each of these RRS lines as a function of excitation energy in the spectral region of the A–B lines and the V-band.

Fig. 4 shows a typical spectrum of $GaAs_{0.02}P_{0.98}$:N selectively excited into the N-bound exciton band. Under pulse excitation the RRS lines (designated ℓ-TO etc.) follow the laser time dependence while the rest of the spectrum has a long (≈ 2 μs) lifetime [6]. Similar spectra are observed for other crystal compositions.

3. Discussions

We now consider the RRS by the LO_X phonon which is induced by the N-bound excitons. Since only the $J=1$ state couples to this phonon, the RRS matrix element can be written as follows:

$$K_{\alpha\beta}(E_\ell, E_s) =$$
$$\langle g, 1_X | P_\alpha | (J=1, M_J), 1_X \rangle$$
$$\times \langle (J=1, M_J), 1_X | H_{el} | (J=1, M_J), 0_X \rangle$$
$$\times \langle (J=1, M_J), 0_X | P_\beta | g, 0_X \rangle$$
$$\times [(E_\ell - E_A + i\Gamma)(E_s - E_A + i\Gamma)]^{-1} \quad (1)$$

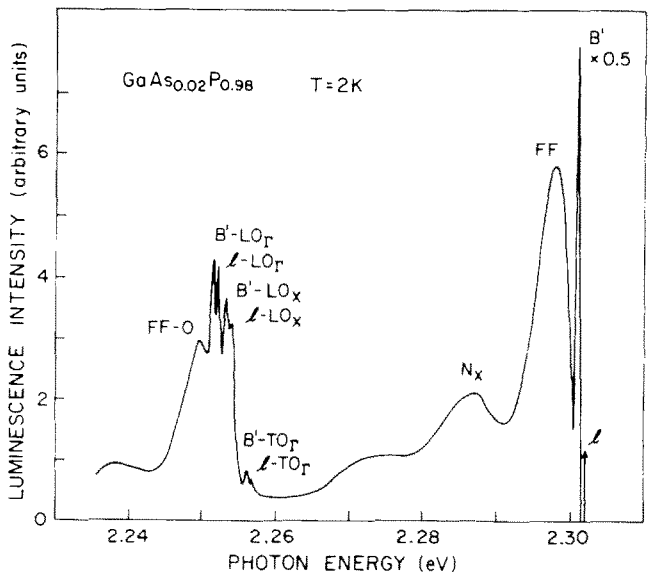

Fig. 4. A typical emission spectrum of $GaAs_{0.02}P_{0.98}$:N excited into the N-bound exciton band.

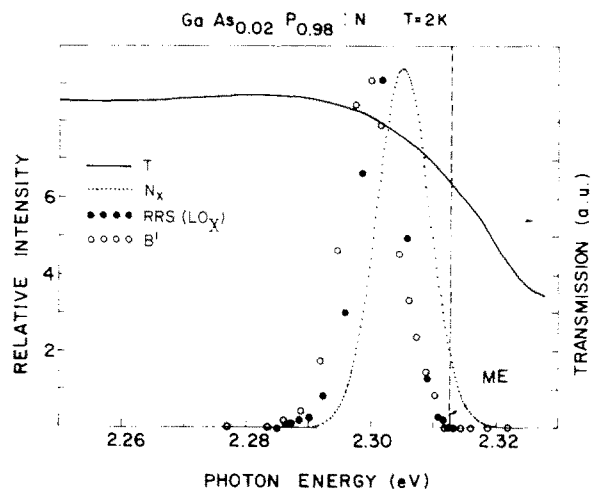

Fig. 5. A comparison between the density of terminal states (measured by the B' line intensity dependence on excitation energy) and the LO_X RRS spectrum. Also shown are the density of N-bound excitons (N_X band) extracted from the transmission spectrum and the part due to intrinsic excitons.

$E_i(E_s)$ is the incoming (outgoing) photon energy, $E_i - E_s = \hbar\omega_X$, E_X is the energy of the $(J=1, M_J)$ state of the N-bound exciton, g is the crystal ground state, Γ is the damping factor which is a measure of the dephasing rate of the $J=1$ states including the RRS. For isolated N-bound excitons, at $T=0$, the damping rate is determined by the A–B thermalization rate:

$$\Gamma_0 = 1/\pi c \tau_{AB} \approx 0.03 \text{ meV} . \tag{2}$$

When we introduce resonant tunneling between states with equal energy, or phonon-assisted tunneling into sites with lower energy, the damping factor becomes:

$$\Gamma = (1/\pi c)(1/\tau_{AB} + 1/\tau_t) . \tag{3}$$

$1/\tau_t$ is the tunneling rate. It depends on the spatial separation between the participating sites as well as on their energies [7]. The density of all N-bound excitons can be subdivided into subsets with different damping factors:

$$\rho(E) = \int_{\Gamma_0}^{\Gamma} \rho(E, \Gamma)\, d\Gamma . \tag{4}$$

The density of states with the lowest value of Γ is just that of terminal states, namely, those from which no tunneling occurs within τ_{AB} [8]:

$$\rho_0(E) = \rho(E, \Gamma_0) . \tag{5}$$

Then, the RSS cross section is given by [9]:

$$\sigma_{LO_X}(E_i, E_s) = \int dE_X \int d\Gamma\, |K_{\alpha\beta}(E_i, E_X)|^2 \rho(E_X, \Gamma)$$

$$= C \int dE_X \int d\Gamma\, \Gamma \rho(E_X, \Gamma)/[(E_i - E_X)^2 + \Gamma^2] . \tag{6}$$

In the constant C we have lumped together all the terms which are independent of the energies E and E_X. If we now assume that the major contributing to the scattering comes only from terminal states then

$$\sigma_{LO_X}(E_i) \approx C \int dE_X \frac{\Gamma_0 \rho_0(E_X)}{(E_i - E_X)^2 + \Gamma_0^2} \approx \rho_0(E) . \tag{7}$$

Fig. 5 shows $\sigma_{LO_X}(E_i)$ normalized to the same peak value as the spectrum of the B' line intensity which measures the density of terminal states. The two curves are virtually identical. This corroborates the underlying assumption of eq. (7).

The situation for GaP:N is more complex. The σ_{LO_X} spectrum (fig. 3a) peaks below the A-line. Actually, under resonant excitation into this line (fig. 2c), the optical phonon sidebands are identical with the spectrum observed under above gap excitation. Also, the intensity of these sidebands is only twice as strong as the RRS lines obtained by selective excitation into the V-band. Therefore, the contribution of the A-line to the LO_X RRS is much smaller than that expected if all N-bound excitons were isolated. The majority of nitrogen impurities are sufficiently close to each other that they introduce large dephasing rates due to resonant tunneling.

4. Summary

We have shown that RRS by LO_X phonons which is induced by excitons bound to N impurities is a sensitive tool for differentiating between transferring and non-transferring (terminal) states. Our results indicate that in GaP:N, the photon echo signal, reported in ref. [2], is also due to the subset of terminal states. An outstanding problem is the observations of the tunneling rates between the transferring states.

Acknowledgement

This study was supported by the US–Israel Binational Science Foundation.

References

[1] P.J. Dean and D.C. Herbert, in: Excitons, ed. K. Cho (Springer, Berlin, 1979) p. 55.
[2] L.W. Molenkamp and D.A. Wiersma, Phys. Rev. B32 (1985) 8108.
[3] J.D. Cuthbert and D.G. Thomas, Phys. Rev. 154 (1967) 763.
[4] D. Gershoni, E. Eohen and A. Ron, J. Lumin. 34 (1985) 83.
[5] H. Mariette, J. Chevallier and P. Leroux-Hugon, Phys. Rev. B21 (1980) 5706.
[6] D. Gershoni, E. Cohen and A. Ron, Phys. Rev. Lett. 56 (1986) 2211.
[7] T. Holstein, S.K. Lyo and R. Orbach, in: Laser Spectroscopy of Solids, eds. W.M. Yen and P.M. Selzer (Springer, Berlin, 1981) chap. 1.
[8] Note that this definition is more restricted than that required for energy transfer, as described in ref. [6].
[9] R.M. Martin and L.M. Falicov, in: Light Scattering in Solids, ed. M. Cardona, Topics in Applied Physics, Vol. 8 (Springer, Berlin, 1980).