Phonon-assisted exciton tunneling in $GaAs_xP_{1-x}$:N

D. Gershoni* and E. Cohen
Department of Physics and Solid State Institute, Technion-Israel Institute of Technology, Haifa 32 000, Israel

Arza Ron
Department of Chemistry and Solid State Institute, Technion-Israel Institute of Technology, Haifa 32 000, Israel
(Received 10 June 1987)

The low-temperature photoluminescence of $GaAs_xP_{1-x}$:N ($x \leq 0.07$) crystals has been studied under selective excitation into the nitrogen-related exciton band (N_X). The spectra consist of several features whose relative intensity depends on the excitation energy. Excitons created on nontransferring (terminal) states give rise to a sharp line (B') 0.9 meV below the exciting-laser line. Excitons in transferring states tunnel to lower-energy states by acoustic-phonon-assisted processes. This results in broad phonon sidebands. We introduce a model for exciton transfer and fit both the band shapes and their relative intensity. We thus find that the most probable tunneling process involves single-phonon emission and that the dominant interaction mechanism between excitons and zone-center acoustic phonons is the deformation potential. The fit to the experimental spectra excited at various energies in the N_X band yields the ratio between the densities of transferring and terminal states.

I. INTRODUCTION

The band of $1S$ excitons bound to impurities in alloy semiconductors is inhomogeneously broadened, reflecting the distribution of exciton binding energies.[1,2] This distribution is due to the random potential fluctuations produced by the local configurations of atoms around the impurity centers. It has been well established that excitons can tunnel between the localizing impurity sites. This gives rise to a shift between the absorption band and the luminescence band at low temperatures, as was first discussed by Mariette, Chevallier, and Leroux-Hugon[3] for excitons bound to nitrogen in $GaAs_xP_{1-x}$ (N_X band). Time-resolved experiments (in the subnanosecond range) confirmed that tunneling takes place,[4,5] and led Kash[6] to propose that it ceases when the exciton is trapped on a terminal state (where it can only recombine within its radiative lifetime). The density of terminal states (which are a subgroup of the total density of nitrogen-bound exciton states) has been measured[7] by selective excitation of luminescence and resonant Raman scattering for $GaAs_xP_{1-x}$:N.

In the present study we address ourselves to the energy dependence of the tunneling within the N_X band in indirect-gap $GaAs_xP_{1-x}$ ($x \leq 0.07$). The analysis of a series of selectively excited luminescence spectra indicates that the tunneling is accompanied by the emission of acoustic phonons. These are mainly zone-center phonons which interact with the exciton by the deformation potential (DP). An additional contribution comes from TA_X phonons. While the spectral shape of the densities of N-bound excitons and the subgroup of terminal states were previously determined,[7] to obtain their relative magnitudes we need an analysis of the tunneling processes.

The paper is laid out as follows. Section II describes the experimental procedure and results, Sec. III describes the model for exciton tunneling within the N_X band and the comparison between the calculated and observed spectra. A summary and comparison with other semiconductor alloys is given in Sec. IV.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Two bulk $GaAs_xP_{1-x}$ crystals were studied. One, with $x=0.02$, was doped with nitrogen to a level of about 10^{17} cm^{-3}. The other, with $x=0.07$, was nominally undoped but contained background nitrogen impurities at an estimated concentration of 10^{15} cm^{-3}. Luminescence spectra were excited with a dye laser, having a linewidth of 0.12 Å. The laser intensity impinging on the sample did not exceed 0.1 W/cm^2. The emission spectra were monitored with a double monochromator having a resolution of 0.05 Å. The crystals were immersed in pumped liquid He. Figure 1 shows the transmission spectrum of the $GaAs_{0.02}P_{0.98}$ crystal. Also shown is its photoluminescence spectrum excited above the band gap. The N_X band and its acoustic- and optic-phonon sidebands are typical of all indirect gap $GaAs_xP_{1-x}$:N crystals.[3,8] Figures 2 and 3 show a series of photoluminescence spectra (solid lines) which were selectively excited into the N_X band. In each series the exciting-laser intensity was kept constant and the spectra were drawn so that their relative intensity was preserved. There are three distinct spectral features (which we analyze in the following section). Just below the exciting-laser line is the B' line which is the radiative recombination of N-bound excitons in the $J=2$ state. These were resonantly excited into their $J=1$ state (the A' and B' lines are split by $\Delta E_{AB}=0.9$ meV). The band denoted FF is due to excitons which have tunneled from the resonantly excited states while emitting a low-q acoustic phonon. The band denoted N_X' is due to a simi-

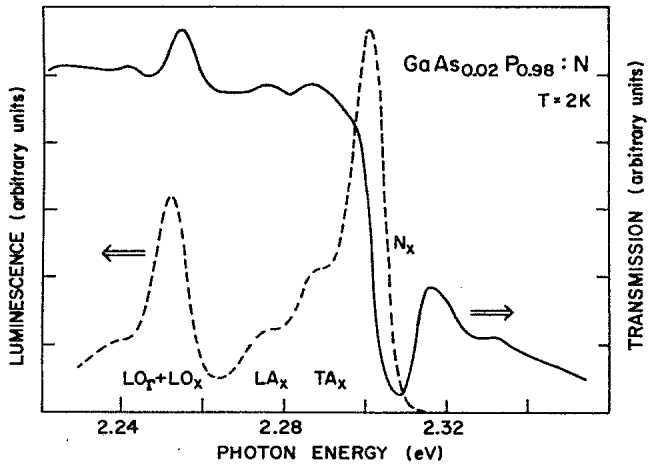

FIG. 1. The transmission and luminescence spectra of nitrogen-doped $GaAs_{0.02}P_{0.98}$. The luminescence was cw excited at 2.35 eV.

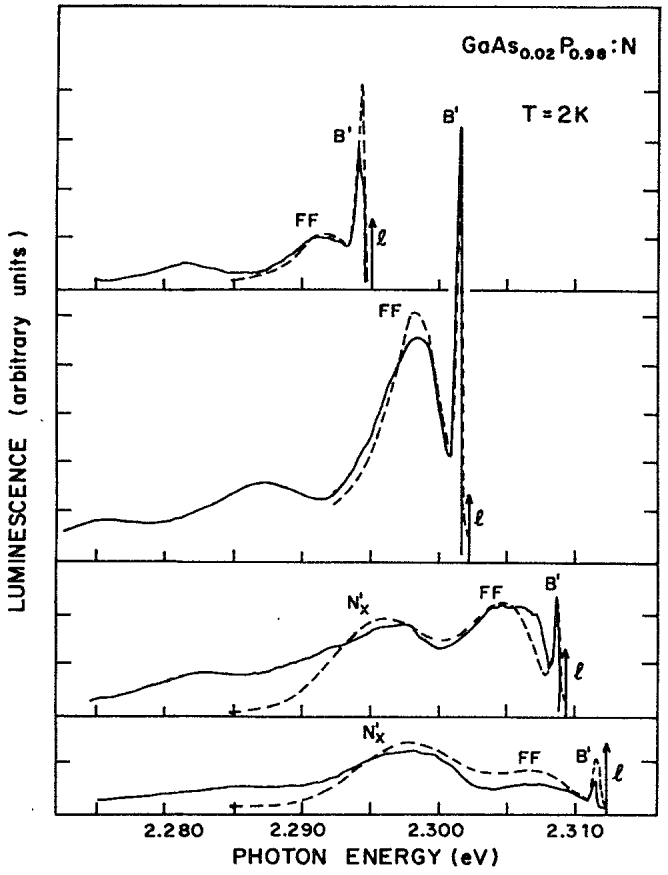

FIG. 2. Luminescence spectra of $GaAs_{0.02}P_{0.98}$:N selectively excited within the N_X band (solid curves). The gain in all spectra is the same. The results of the calculations detailed in Sec. III are shown in dashed curves. N'_X denotes transfer assisted by TA_X phonons.

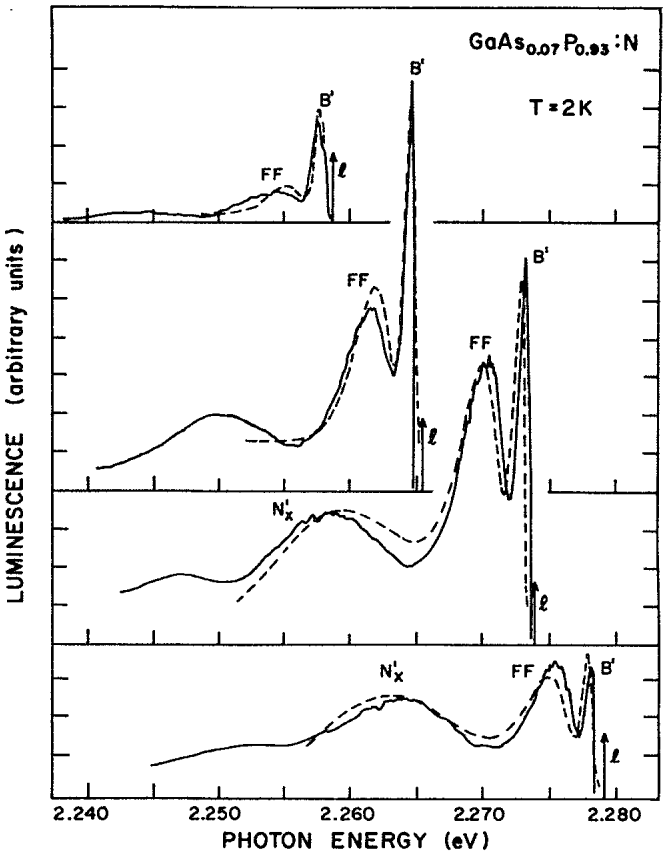

FIG. 3. Same as Fig. 2 but for $GaAs_{0.07}P_{0.93}$ (nominally undoped).

lar process but the emitted acoustic phonons are from the Brillouin-zone edge (TA_X).

III. MODEL AND DISCUSSION

According to our present understanding[5–7] of N-bound excitons in $GaAs_xP_{1-x}$, an exciton selectively created at an energy E_a (within the N_X band) can be either in a terminal or in a transferring state. (A schematic description is shown in Fig. 4.) An exciton in a terminal state with E_a will recombine radiatively with a lifetime τ_R. The probability of it tunneling out of a terminal state within τ_R is negligible. At the same energy E_a there are states from which the exciton can transfer into lower-energy states E_b, while emitting an acoustic phonon (at $T=0$). The tunneling rate is given by[9]

$$W_{ab}=\frac{4\pi}{\hbar}J^2(R_{ab})\frac{|M(E_{ab})|^2 f(E_{ab})\rho(E_b)}{E_{ab}^2}, \qquad (1)$$

$E_{ab}=E_a-E_b$, $J(R_{ab})$ is the overlap integral between the two exciton sites separated by R_{ab}, $f(E_{ab})$ is the phonon density of states at energy E_{ab}, and $\rho(E_b)$ is the density of excitonic states. The form factor of the exciton–acoustic-phonon DP interaction is given by[10]

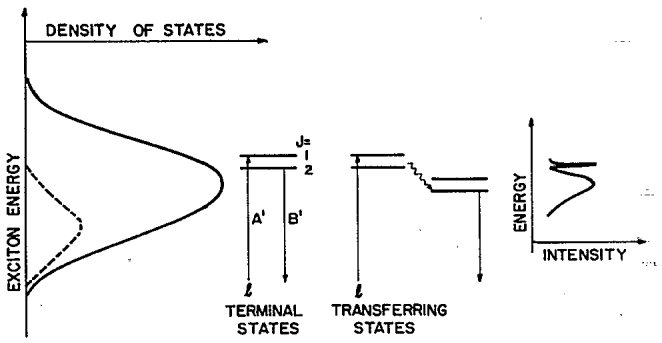

FIG. 4. A schematic description of the densities of exciton states: $\rho(E)$, solid curve; $\rho'(E)$, dashed curve. Also shown are the dynamic processes which the exciton undergoes in a transferring and a terminal state. The spectrum on the right shows the B' line and FF band, which are observed under selective excitation.

$$|M^{\mathrm{DP}}(q)|^2=\frac{\hbar q}{2g v_l}(\varepsilon_c\alpha_e-\varepsilon_v\alpha_h)^2 , \tag{2}$$

$q=E_{ab}/\hbar v_l$ is the wave vector of the emitted zone-center acoustic phonon and v_l is its velocity. ε_c is the (averaged) conduction-band DP (ε_v is the corresponding one for the valence band). g is the crystal density.

$$\alpha_{e,h}=\left[1+\left[\frac{m_{h,e}qa_B}{2M_X}\right]^2\right]^{-2} , \tag{3}$$

where m_e (m_h) is the electron (hole) effective mass, M_X is the exciton translatory mass, and a_B is its Bohr radius.

For piezoelectric interaction (PE) between the exciton and the zone-center acoustic phonon, the form factor is[10]

$$|M^{\mathrm{PE}}(q)|^2=\left[\frac{e}{\kappa}\right]^2\frac{e_{14}}{2gqv_t}(\alpha_e-\alpha_h)^2 . \tag{4}$$

e_{14} is the piezoelectric coefficient. The parameters used in the calculations detailed below are summarized in Table I. Those for the alloys were interpolated from the values reported for GaAs and GaP. Since the exciton interacts mainly with LA phonons via the DP, and mainly with TA phonons via the PE interaction, we take the corresponding sound velocities in Eqs. (1) and (4).

Now, the exciton can tunnel between transferring states until it is trapped on a terminal state. We describe these dynamic processes by considering the rate equations for the probabilities $P_a(t)$ and $P_f(t)$ of finding the exciton on a transferring state (a) or on a terminal state (f) at time t:

TABLE I. The parameters used in calculating the exciton–acoustic-phonon interaction.

	GaP	GaAs	$GaAs_xP_{1-x}$ $x=0.02$	$GaAs_xP_{1-x}$ $x=0.07$
$\varepsilon_c/\varepsilon_v$	-1.38[a]	-1.32[a]	-1.38	-1.38
$V_l(10^5$ cm/s)	6.342[b]	5.142[c]	6.318	6.258
$V_t(10^5$ cm/s)	3.748[b]	3.027[c]	3.734	3.698
$\frac{m_e}{m_e+m_h}$	0.60[d]	0.70[c]	0.6	0.6
a_B (Å)	40[e]	72[e]	33±4	33±4

[a]D. L. Camphausen, G. A. Nevill-Connel, and W. Paul, Phys. Rev. Lett. **26**, 184 (1971).
[b]R. Weil and W. Groves, J. Appl. Phys. **39**, 4049 (1968).
[c]S. Adachi, J. Appl. Phys. **58**, 871 (1985).
[d]G. Beni and T. M. Rice, Solid State Commun. **23**, 871 (1977); P. Lawaetz, Phys. Rev. B **4**, 3460 (1971).
[e]These are the effective-mass values. The value quoted for $GaAs_xP_{1-x}$ is obtained by our fit to the data.

$$\frac{dP_f(t)}{dt}=-\frac{P_f(t)}{\tau_R}+C\sum_{b\ (E_b>E_f)}W_{bf}P_f(t) , \tag{5}$$

$$\frac{dP_a(t)}{dt}=-\frac{P_a(t)}{\tau_R}-C\left[\sum_{b\ (E_a>E_b)}W_{ab}+\sum_{f\ (E_a>E_f)}W_{af}\right]P_a(t)+C\sum_{b\ (E_b>E_a)}W_{ba}P_b(t) . \tag{6}$$

The constant C contains all the common factors which appear in the previous equations, so that it actually measures the tunneling rate in units of τ_R^{-1}. In writing rate equations for the probabilities $P_a(t)$ of finding the exciton in a state with a given energy E_a we make the simplifying assumption that E_{ab} and R_{ab} are uncorrelated ("microscopic disorder"). This means that W_{ab} dependence on E_{ab} comes only through the variation of M^{DP} and M^{PE} with E_{ab}.

There are two densities of exciton states in the set of coupled-rate equations (5) and (6): the density of all N-bound exciton states $\rho(E)$ and that of terminal states $\rho'(E)$. We know their spectral shapes from absorption measurements [which yield $\rho(E)$] and from the energy dependence of the B' line intensity and resonant Raman scattering by LO_X phonons [which yield $\rho'(E)$]. $\rho(E)$

TABLE II. The Gaussian parameters of the nitrogen-bound exciton densities of states.

x	Mean ρ (eV)	$\Delta\rho$ (meV)	Mean ρ' (eV)	$\Delta\rho'$ (meV)
0.02	2.306±0.001	6.9±0.7	2.302±0.001	5.4±0.5
0.07	2.271±0.004	15^{+5}_{-2}	2.269±0.001	10.0±1

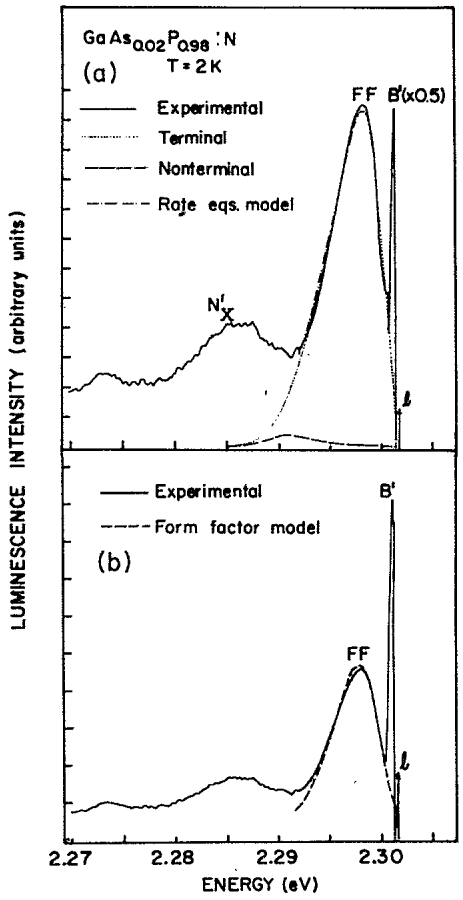

FIG. 5. (a) A comparison between the measured FF band and that calculated by solving the set of coupled-rate equations. (b) The same spectrum with a fit obtained with the spectral shape of the deformation potential interaction form factor.

and $\rho'(E)$ are approximated by Gaussians[7] with parameters given in Table II. Their ratio

$$\eta_1 = \int \rho(E)dE \Big/ \int \rho'(E)dE$$

will be determined by the fit to the experimental data.

Our goal is to calculate the spectral shapes of the series of spectra shown in Figs. 2 and 3 with a single set of parameters. Due to the computational complications introduced by such a problem, we first solved the set of Eqs. (5) and (6) to fit a single spectrum obtained by selective excitation into the N_X band. Figure 5(a) shows an example of such a fit to the FF band. The separate contributions of the terminal and transferring states to the emission intensity are shown in the figure. It is clear that the contribution of transferring states to the luminescence intensity is negligible. From the values of parameters which gave the best fit it became clear to us that (1) most of the tunneling occurs through the DP coupling mechanism, and (2) the transfer rate C is very fast in comparison with the inverse radiative lifetime[4] ($C\tau_r > 10^4$), which is equivalent to only one phonon-assisted exciton-tunneling process. In other words, excitons created by selective excitation into a subset of transferring states and tunnel directly to terminal states by emission of zone-center acoustic phonon give rise to the FF band. The above conclusions allow to greatly simplify the calculation procedure. There is essentially no need to solve the coupled-rate equations. In Fig. 5(b) we present such a fit using the simplified approach. It can be seen that although this fitting procedure required only one free parameter, the exciton Bohr radius a_B, no considerable degradation in the fit quality is observed. We obtained a value of 33±4 Å for this parameter in excellent agreement with Leroux-Hugon and Marriete[11] who obtained a value of 32 Å by fitting the transfer rates of excitons bound to nitrogen in heavily doped GaP:N. We would like to remark also that the fit was extremely insensitive to the parameter $\varepsilon_c/\varepsilon_v$.

Using the above approximation we now turn to calculate simultaneously the spectral shapes of the series of spectra shown in Figs. 2 and 3. In considering this larger spectral range one has to take into account yet another transfer mechanism, namely, zone-edge phonon-assisted exciton tunneling into lower-energy terminal states. This mechanism manifests itself in the line denoted N'_X and it evolves tunneling of excitons into lower-lying states by emitting zone-edge transverse-acoustic (TA_X) phonon. While we know the explicit dependence of the exciton-phonon interaction on the phonon wave vector q for zone-center acoustic phonons, we do not known it for TA_X phonons. We, therefore, describe their contribution to the transfer processes by a Gaussian function denoted $N'_X(E)$. The parameters defining this function are the mean TA_X-phonon energy $\langle \hbar\omega_{TA} \rangle$ and the width of this band. Both are obtained by the fitting procedures.

The explicit expression used for the fluorescence intensity at photon energy E when selectively excited into the N_X band at energy E_l is given by

$$I(E,E_l) = \left[\int \rho'(E')dE'\right]^{-1} \rho'(E_l) B(E-(E_l-\Delta E_{AB}),\sigma_B) + [N(E_l)]^{-1} \left[\frac{\rho(E_l)-\rho'(E_l)}{\int [\rho(E')-\rho'(E')]dE'}\right] \frac{\rho'(E)}{\int \rho'(E')dE'} [F^{DP}(E_l-E)+\eta_2 F^{PE}(E_l-E)+\eta_3 N'_X(E_l-E)] \quad (7)$$

in Eq. (7). We denote by $B(E,\sigma_B)$ the line shape of the B' line: a Gaussian centered at E and width of σ_B. The normalized spectral shapes of the DP interaction form factor are given by

$$F^{DP}(E_{ab}) = \frac{|M^{DP}(E_{ab})|^2}{\int |M^{DP}(E_{ab})|^2 dE_{ab}}, \quad (8)$$

TABLE III. The parameters obtained from the best fit to the selective excitation luminescence spectra.

x	η_1	η_2	η_3	$\langle\hbar\omega_{TA}\rangle$	Δ_{TA}
0.02	6.0±2.2	0.01±0.01	2.7±1.3	17.0±3.0	7.1±2.8
0.07	7.0±3.0	0.07±0.07	3.9±1.4	18.6±2.2	7.6±3.0

and a similar expression for F^{PE}. η_2 is the ratio between the two interactions coupling strengths and η_3 is the TA_X coupling strength relative to DP coupling strength at $q\sim 0$. The function $N(E_l)$ is an overall normalizing factor for all three types of tunneling processes:

$$N(E_l)=\left[\int \rho'(E)dE\right]^{-1}\int_0^{E_l}[F^{DP}(E_l-E)+\eta_2 F^{PE}(E_l-E)+\eta_3 N'_X(E_l-E)]\rho'(E)dE\ . \tag{9}$$

Note that the two exciton densities of states are introduced normalized.

We have fitted all the spectra shown in Figs. 2 and 3 with the parameters given in Table III. We must note that for excitation energies into the lower part of the N_X band (the two lowest energies in Figs. 2 and 3), the TA_X phonon sideband is due to phonon-assisted radiative recombination and not to tunneling followed by emission. The reason is that $\langle\hbar\omega_{TA}\rangle$ is larger than the width of $\rho(E)$. Therefore, these sidebands have not been included in the model fitting.

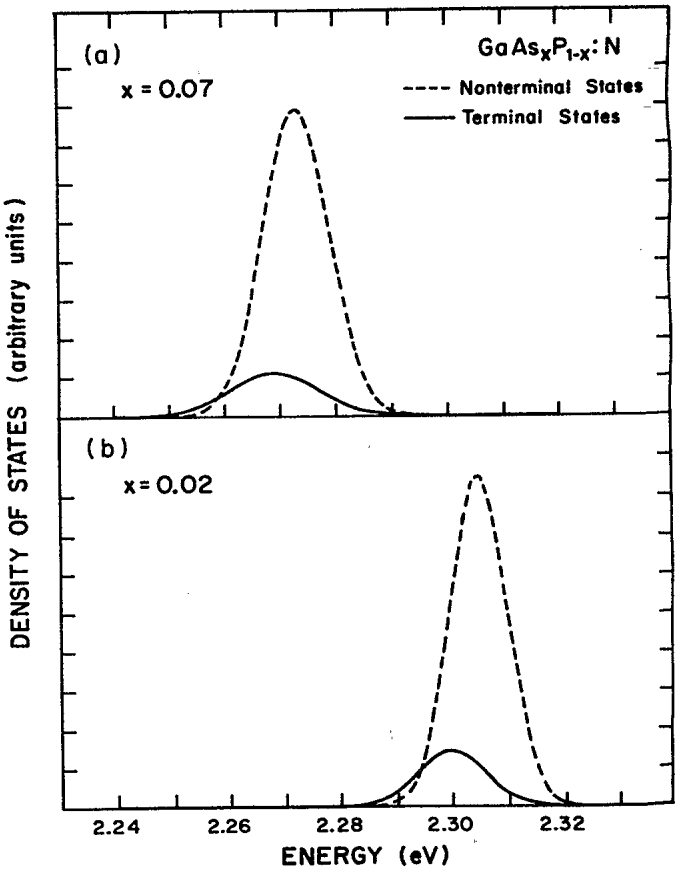

FIG. 6. The transferring (broken curve) and terminal (solid curve) density of exciton states obtained by fitting the series of luminescence spectra shown in Figs. 2 and 3 for $GaAs_xP_{1-x}$ with $x=0.02$ and 0.07, respectively.

Several conclusions can be drawn from this fit. (i) For tunneling assisted by zone-center phonons (FF bands), the main contribution comes from the DP interaction ($\eta_2\sim 0$). (ii) The FF bands have a comparable intensity to the N'_X bands. Yet the density of zone-center acoustic phonons is much smaller than that of zone-edge phonons. Therefore, the exciton DP interaction with zone-center phonons is much stronger than that with zone-edge phonons. (iii) The fit yields $\eta_1\sim 6$–7, which is comparable to that obtained by Kash[6], namely, $\eta_1\sim 15$. Figure 6 shows the appropriate densities of states for the two crystals.

IV. SUMMARY

In this study we describe a model for the tunneling processes of excitons bound to N impurities in $GaAs_xP_{1-x}$. The model is based on the existence of transferring and terminal excitation states and on the energy dependence of the exciton-acoustic phonon interaction. Using this model we calculated the spectra obtained by selective excitation into the N_X band. An adequate fit is obtained both for the spectral shapes and for the relative intensities of the observed B' line which results from excitons created on terminal states and the bands which are due to exciton tunneling. These results, together with the direct measurement of the density of terminal states[7] and the radiative decay curves,[4,5] provide a comprehensive understanding of exciton dynamics in indirect-gap $GaAs_xP_{1-x}$. In particular they show that the most probable transfer process involves single-phonon emission, and they determine the relative abundance of transferring and terminal states.

It should be noted that the mechanism of exciton trapping into terminal states may account also for some unresolved problems in direct-gap CdS_xSe_{1-x}.[9,12] In these crystals, multiple-phonon-assisted tunneling processes have been observed. Under pulse excitation the decay curves were nonexponential. This observation may reflect a distribution of transfer rates into terminal states.

ACKNOWLEDGMENT

This study was supported by the US-Israel Binational Science Foundation, Jerusalem, Israel.

*Present address: AT&T Bell Laboratories, Murray Hill, NJ 07974.

[1]R. J. Nelson, in *Excitons,* edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), p. 319.
[2]O. Goede, D. Henning, and L. John, Phys. Status Solidi B **96**, 671 (1979).
[3]H. Mariette, J. Chevallier, and P. Leroux-Hugon, Phys. Rev. B **21**, 5706 (1980).
[4]J. H. Collet, J. A. Kash, D. J. Wolford, and J. Thompson, J. Phys. C **16**, 1283 (1983).
[5]H. Mariette, J. A. Kash, D. J. Wolford, and A. Marbeuf, Phys. Rev. B **31**, 5217 (1985).
[6]J. A. Kash, Phys. Rev. B **29**, 7069 (1984).
[7]D. Gershoni, E. Cohen, and Arza Ron, Phys. Rev. Lett. **56**, 2211 (1986).
[8]D. J. Wolford, B. G. Streetman, S. T. Lai, and M. V. Klein, Solid State Commun. **32**, 51 (1979).
[9]E. Cohen and M. D. Sturge, Phys. Rev. B **25**, 3828 (1982).
[10]W. Ulbrich and C. Weisbuch, in *Light Scattering in Solids III,* edited by M. Cardona and G. Guntherodt (Springer-Verlag, New York, 1982), p. 207.
[11]P. Leroux-Hugon and H. Mariette, Phys. Rev. B **30**, 1622 (1984).
[12]J. A. Kash, Arza Ron, and E. Cohen, Phys. Rev. B **28**, 6147 (1983).