Resonant Raman scattering on localized states due to disorder in $GaAs_{1-x}P_x$ alloys

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Resonant Raman scattering (RRS) and resonant photoluminescence (RPL) studies on localized exciton states due to disorder in indirect-band-gap $GaAs_{1-x}P_x$ alloys show that the RRS and RPL intensity is dominated by competition between radiative recombination at rate W_R and the energy transfer mechanism of excitons between states of the localization tail. The rate of change of the transfer probability $d[\ln(W_{tr})]/dE$ has been evaluated near the point where $W_{tr}=W_R$.

I. INTRODUCTION

The localization of excitons by random potential due to disorder in $GaAs_{1-x}P_x$ alloys was studied by Oueslati *et al.*[1] and other authors.[2–5] The M_0^X peak observed in photoluminescence (PL) spectra between free exciton (E_g^X) and donor-bound exciton (D_0^X) peaks is attributed to recombination of localized excitons, with a density of states usually approximated by an exponential:[6–8] $\rho=\rho_0\exp(E/E_0)$.

The PL spectra of indirect-band-gap alloys $GaAs_{1-x}P_x$ at low temperature (~2 K) and very low excitation power (~40 mW/cm^2) are dominated by the zero-phonon localized exciton peak M_0^X and its LA phonon replica M_1^X (Fig. 1). The relaxation of momentum

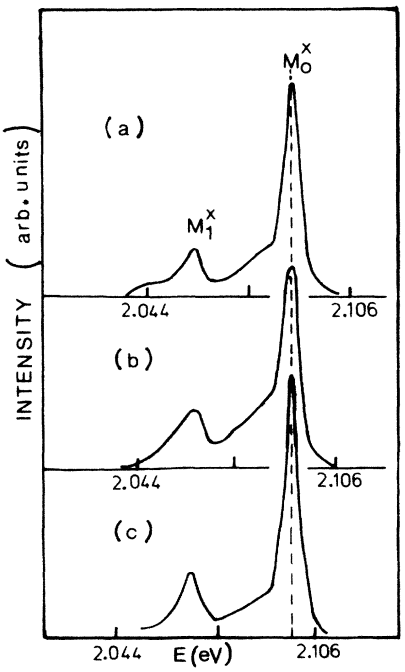

FIG. 1. Luminescence spectra of $GaAs_{1-x}P_x$ at $T=2$ K and for excitation power $P=40$ mW/cm^2. (a) $x=0.51$, (b) $x=0.52$, (c) $x=0.56$. M_1^X is the LA(M^X) phonon replica of M_0^X.

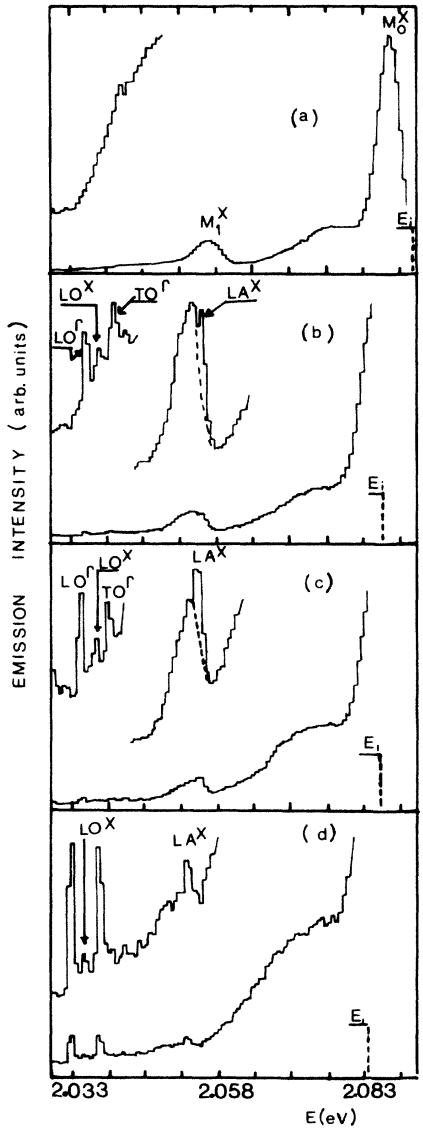

FIG. 2. Time-integrated emission spectra under selective excitation of $GaAs_{0.49}P_{0.51}$ at $T=2$ K. The exciting laser is tuned to the photon energy E_i shown by the dotted line: (a) $E_i=2.092$ eV, (b) $E_i=2.089$ eV, (c) $E_i=2.088$ eV, (d) $E_i=2.084$ eV. M_0^X and M_1^X are luminescence peaks. LA(X) and LO(X) are RRS peaks.

conservation for these weakly localized indirect excitons is due to the effect of the alloy random potential on the radiative matrix elements. In a somewhat different situation, observation of one-phonon TA(X) and LA(X) peaks in nonresonant Raman scattering in similar alloys was attributed to "disorder activated TA(X) or LA(X) modes" [DATA(X), DALA(X)].[9]

Time-resolved studies of resonant Raman scattering (RRS) and resonant photoluminescence (RPL) with selective monochromatic excitation around the M_0^X peak are presented in Sec. II. They provide a clear discrimination between nonresonant Raman processes (TO, LO) and processes resonating on localized exciton states. Rather than invoking a "mobility edge" as in Ref. 5, we propose in Sec. III a model based upon a competition between recombination (rate W_R) and transfer towards deeper states [rate $W_{tr}(E)$].

II. EXPERIMENTAL RESULTS

RRS and RPL spectra were obtained in backscattering configuration. The samples were excited by a Rhodamine 6G dye laser (16 300–17 300 cm^{-1}). The excitation peak power was about 1 W/cm^2. For time-resolved measurement, the dye laser was chopped by an acousto-optic modulator (rise or fall time of 20 ns) and the signal was processed in single-photon counting mode.

The samples of $GaAs_{1-x}P_x$ are single crystals grown by metal-organic vapor-phase epitaxy,[10] and are nominally undoped, with a net carrier concentration $n \lesssim 10^{16}$ cm^{-3}.

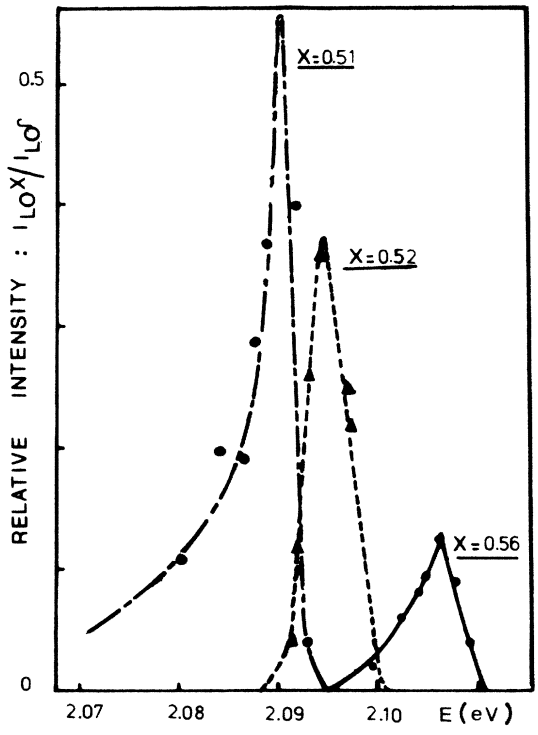

FIG. 3. Relative intensity of the LO(X) RRS line for various laser excitation energies, for different composition x in $GaAs_{1-x}P_x$ alloys.

Figure 2 shows the evolution of time-integrated spectra of $GaAs_{0.49}P_{0.51}$ with selective excitation energies E_i in the tail of localized exciton states. When E_i is above M_0^X [Fig. 2(a)], the spectrum is dominated by the localized exciton PL peaks M_0^X, M_1^X. As E_i decreases [Figs. 2(b), 2(c), and 2(d)] sharp Raman peaks emerge from the decreasing PL contribution. They are labeled TO(Γ) and LO(Γ) (center of Brillouin zone) and LA(X) (Ref. 11) and LO(X) (X point zone boundary). A careful examination shows that the intensity of TO(Γ) and LO(Γ) peaks is essentially independent of E_i: This is already an indication that these peaks are normal (i.e., nonresonant) Raman peaks. They can be used to normalize the intensity of LA(X) and LO(X) peaks, which depends strongly on E_i: This is shown on Fig. 3 where the ratio I LO(X)/I LO(Γ) is plotted as a function of E_i for three different compositions ($x = 0.51$, 0.52, and 0.56). These curves show a sharp resonance at an energy position a few meV above the peak of M_0^X. I LA(X)/I LO(X) shows a similar behavior. This is an indication that localized exciton states play a decisive role in the emission of LA(X) and LO(X) peaks.

Figure 4 shows time-resolved spectra in the case of an excitation energy near the peak M_0^X. As expected,

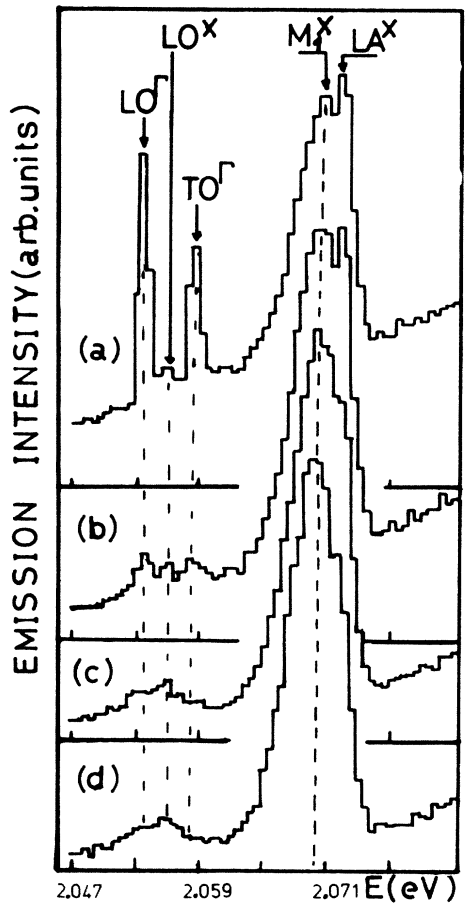

FIG. 4. Time-resolved luminescence spectra of $GaAs_{0.44}P_{0.56}$ obtained with 200-ns excitation pulse, at $T = 2$ K. Excitation energy $E_i = 2.091$ eV. Time origin is taken at the start of the excitation pulse ($t = 0$ μs). Delays are given in μs: (a) 0–0.19 μs, (b) 0.2–0.28 μs, (c) 0.29–0.39 μs, (d) 0.4–0.5 μs.

TO(Γ) and LO(Γ) phonon peaks are seen only during the excitation pulse (within our time resolution limited by the acousto-optic chopper). In contrast, LA(X) and LO(X) peaks (but with poorer signal-to-noise ratio) are still observed for a delay of at least 100 ns. When the excitation energy decreases, the lifetime of the LA(X) peak approaches the lifetime of localized exciton PL.

III. MODEL: COMPETITION BETWEEN RECOMBINATION AND ENERGY TRANSFER IN THE EXCITON BAND TAIL.

Since the time constant of our resonant process is so long (~ 100 ns), we discard any nonresonant contribution, and so we describe our model according to Fig. 5: The monochromatic excitation creates a localized exciton of energy E_S through a no-phonon absorption induced by random alloy potential. That exciton can either recombine with a probability W_R or make a transfer towards any exciton states of lower energy, with a probability W_{tr}.

Previous works[1,3] suggest that W_R corresponds essentially to radiative recombination involving no-phonon and phonon-assisted processes. For weakly localized excitons in indirect gap materials, one can show that W_R should be independent of localization, and hence of E (this is not so in direct-gap materials). This is consistent with the fact that the M_0^X line shape does not change with time delay after a pulsed excitation, except on its high-energy side, owing to energy transfer and thermal excitation at finite temperature. So we take W_R as a constant, independent of E. On the other hand, W_{tr} decreases rapidly when E decreases, since the exciton state is more localized, and the density of states available decreases. Of special interest is the energy E_{ME} such that

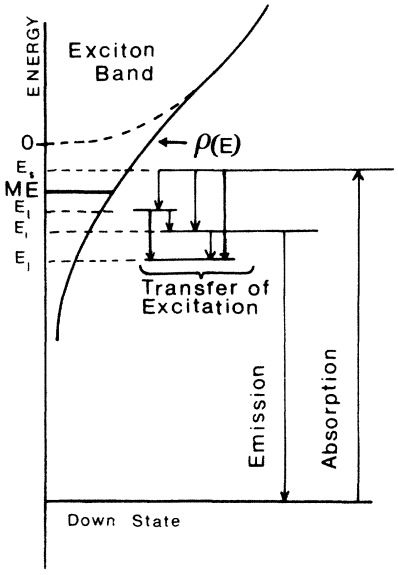

FIG. 5. Schematic representation of localized excitonic states and processes in $GaAs_{1-x}P_x$ alloys. $\rho(E)$ is the density of localized states. E is the energy of an excitonic state and is negative.

$W_{tr}(E_{ME})=W_R$. For our problem, this point plays a role analogous to a mobility edge: Above E_{ME}, a localized exciton will transfer its energy towards deeper states; below E_{ME}, it will recombine. However, this has nothing to do with a genuine mobility edge, involving pure electronic (or excitonic) tunneling. We characterize the variation of W_{tr} by its logarithmic derivative $\alpha=(d/dE)[\ln W_{tr}(E)]$ at E_{ME}, since all important observations occur around E_{ME}. Hence we have

$$W_{tr}(E)=W_R \exp\alpha(E-E_{ME}) . \quad (1)$$

Then the density $N(E)$ of excitons at energy E is given by the following set of equations, at $T=0$ and in the low-excitation limit:

$$dN(E)/dt=G(E,t)+\sum_{\substack{E' \\ (E'>E)}} w(E'\rightarrow E)N(E') - [W_R+W_{tr}(E)]N(E) . \quad (2)$$

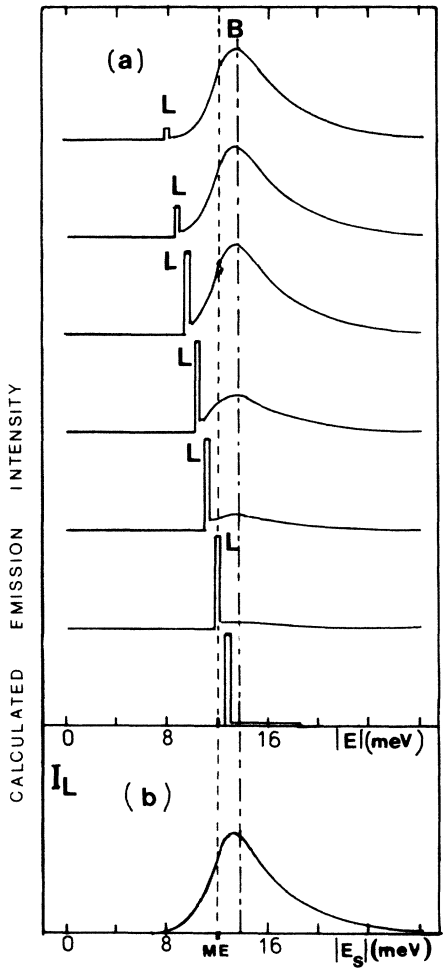

FIG. 6. (a) Calculated emission intensity computed from the model discussion in Sec. III [Eq. (2)] for different values of excitation energy E_i, in $GaAs_{0.49}P_{0.51}$. $E_i=E_g^X+E_S$ and $|E_S|=E_L$ (E_L denotes energy of line L). E_g^X is the excitonic band gap. E_S is negative. (b) Intensity of resonant line L for various excitation level energies $|E_S|$. I_L is measured from spectra of (a). E_S is negative.

$G(E,t)$ is the pump term, nonzero at $E=E_S$ and with an intensity proportional to the density of states at E_S. $w(E\rightarrow E')$ is also proportional to the density of final states:

$$w(E\rightarrow E')=\frac{1}{N}\exp(E'/E_0) \tag{3}$$

with a normalizing factor N such that

$$\sum_{\substack{E'\\(E'<E)}} w(E\rightarrow E')=W_{\mathrm{tr}}(E)\ .$$

Equations (2) were solved first in the steady state. Examples of such calculations are shown in Fig. 6, taking $\alpha^{-1}=1.25$ meV and $E_0=4$ meV. The spectrum of reemitted light [which goes as $W_R N(E)$] is shown as a function of excitation energy E_S in Fig. 6(a). Line L is the resonant peak corresponding to the LA(X) peak on Fig. 2 and band B corresponds to M_1^X luminescence: The main features of Fig. 2 are well reproduced. Fig. 6(b) shows the variation of the intensity of line L as a function of excitation energy E_S. This has to be compared with the experimental result in Fig. 3.

Equation (2) was also solved in the case of a pulsed excitation. Figures 7 and 8 show time-resolved spectra for a pulse positioned between 0 and 200 ns, for two different energies of excitation E_S. Figure 9 gives the time evolution of the intensities of line L and band B for three different values of E_S, near E_{ME}. As E_S decreases the lifetime of line L increases and tends towards the

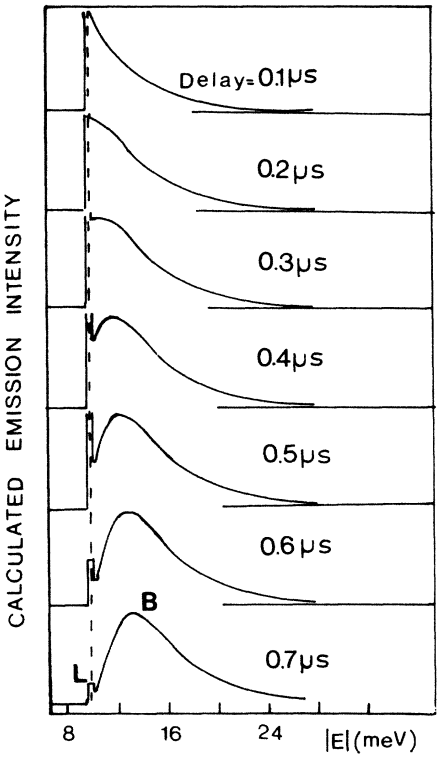

FIG. 8. The same as Fig. 7 except that $|E_S|=10$ meV.

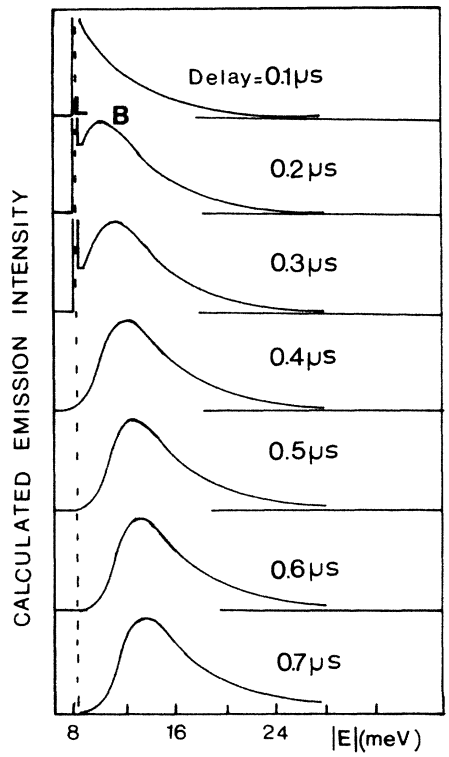

FIG. 7. Time-resolved calculated emission intensity computed from the model discussed in Sec. III [Eq. (2)] for various delays. Here $E_0=4$ meV, $\alpha=1.25$ meV^{-1}, $|E_S|=+8.5$ meV, $|E_{\mathrm{ME}}|=+12$ meV.

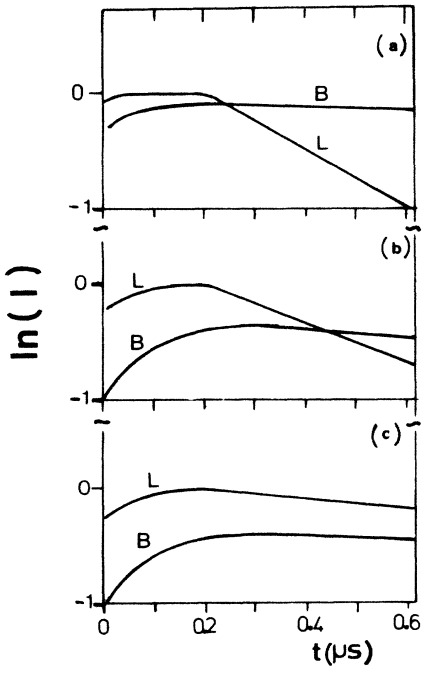

FIG. 9. Calculated intensity of band B and line L plotted logarithmically vs time for different excited level energies: (a) $|E_S|=+8.5$ meV, (b) $|E_S|=+10$ meV, and (c) $|E_S|=+12$ meV, $|E_{\mathrm{ME}}|=+12$ meV.

lifetime of band B. This is obvious from (2) since for $E=E_S$ the lifetime of line L is $[W_R+W_{tr}(E_S)]^{-1}$. So, these experiments give a direct access to $W_{tr}(E)$ in a narrow region of width α^{-1} around E_{ME}.

Let us point out that the two parameters E_0 and α entering into the model play a very different role upon the line shapes of Figs. 7 and 8: E_0 fixes essentially the low-energy shape of the line; α determines the steepness of the high-energy cutoff.

IV. CONCLUSION

RRS experiments have shown that only LA(X) and LO(X) modes are resonant with localized exciton states in $GaAs_{1-x}P_x$ alloys with an indirect band gap. This is a confirmation that these states are dominated by X point contributions, a fact which is also in agreement with the order of magnitude of their lifetime, in the μs range.[1-3]

Time-resolved RRS experiments have shown the increasing lifetime of these resonant peaks, approaching the M_0^X lifetime when probing deeper states in the tail of localized excitons.

We have explained these results through a competition between recombination, essentially radiative at constant rate W_R, and energy transfer towards tail states at a rate $W_{tr}(E)$, and we have obtained the rate of change of $W_{tr}(E)$ near the energy position E_{ME}, where $W_{tr}(E_{ME})=W_R$; E_{ME} plays a key role in fixing the position of localized exciton emission spectrum.

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