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Calculated emission intensity band M_0 from localised states due to disorder in $GaAs_{1-x}P_x$ alloys

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Abstract. A band of energy M_0 is observed in the photoluminescence (PL) spectra of indirect $GaAs_{1-x}P_x$ semiconductor alloys about 10–15 meV below the free exciton line. It is attributed to localised excitons by potential fluctuation due to the composition disorder. We propose a model calculation of emission intensity, which describes the localised exciton properties. We consider that the band energy M_0 corresponds to a critical energy E_μ which plays a role analogous to a mobility edge in an exponential tail of density of states $\rho(E) = \rho_0 \exp(E/E_0)$; $E < 0$. Taking into account thermal excitation above E_μ and the distribution of zero phonon radiative recombination rate W_0, we can model in a realistic way the evolution of PL decay as a function of composition, temperature and excitation power.

1. Introduction

Exciton localisation effects induced by a fluctuating random alloy potential in the indirect band-gap alloy $GaAs_{1-x}P_x$ have been studied by several authors [1–4]. We have shown [1, 2] that PL spectra of indirect band-gap alloys $GaAs_{1-x}P_x$ at low temperature ($T \simeq 2$ K) and very low excitation power ($\simeq 40$ mW cm^{-2}) are dominated by the zero-phonon localised exciton band (energy M_0) and its LA phonon replica (energy M_1) (figure 1). The M_0 band corresponds to radiative recombination of localised excitions with a density of states usually approximated by an exponential [1, 2, 5, 6]: $\rho = \rho_0 \exp(E/E_0)$. The relaxation of momentum conservation for these weakly localised indirect excitons is due to the effect of the alloy random potential on the radiative matrix elements [7].

Time-resolved studies [2] of resonant Raman scattering (RRS) and resonant photoluminescence (RPL) on the M_0 band provided a clear discrimination between non-resonant Raman processes (TO^Γ, LO^Γ) and processes resonating on localised exciton states. The increase of the lifetime (1–10 μs) when probing deeper states in the tail of localised excitons is due to a competition between essentially radiative recombination at a constant rate W_0 (see appendix) and energy transfer at a rate $W_{TR}(E)$ towards tail states. The position of the localised emission band is fixed by E_μ where $W_{TR}(E = E_\mu) = W_0$.

§ While writing the present paper, we have learned of the death of Professor M Zouaghi. We dedicate this work to him.

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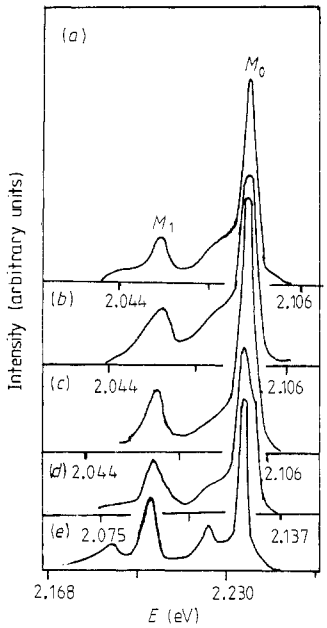

Figure 1. Luminescence spectrum of $GaAs_{1-x}P_x$ at $T = 2$ K and for excitation power $P = 40$ mW cm^{-2}: (*a*) $x = 0.51$, (*b*) $x = 0.52$, (*c*) $x = 0.56$, (*d*) $x = 0.61$, (*e*) $x = 0.85$. The band of energy M_1 is the LA phonon replica of that of energy M_0.

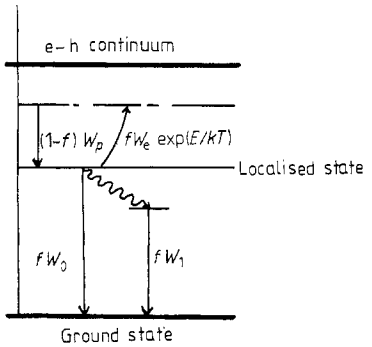

Figure 2. Schematic representation of excitonic transitions.

Due to mixing of X and Γ states by random potential, the decay of the emission intensity is nonexponential. The distribution of decay rates was given as $P(W_0) = \langle W_0 \rangle^{-1} \exp(-W_0/\langle W_0 \rangle)$; where $\langle W_0 \rangle$ is the mean phononless radiative rate. The one-phonon radiative decay rates W_1 involving momentum-conserving phonons is independent of the degree of disorder since it is not sensitive to the mixing of X and Γ states.

In this paper, we propose a model calculation of emission intensity of the luminescence bands M_0 and M_1 studied in [1, 2].

2. Model calculation

2.1. Integrated emission intensity

The integrated emission intensity of the phononless band coming from localised states in the tail can be approximate by the following expression:

$$I(M_0) \sim \int_0^{\infty} \int_{-\infty}^{0} W_0 P(W_0) \rho(E) f(E, W_0, T, t)\, \mathrm{d}W_0\, \mathrm{d}E \tag{1}$$

where W_0 is the zero-phonon radiative recombination rate. Its statistical distribution was given as [7]: $P(W_0) = \langle W_0 \rangle^{-1} \exp(-W_0/\langle W_0 \rangle)$; where $\rho(E)$ is the localised density of states, usually approximated by an exponential: $\rho(E) = \rho_0 \exp(E/E_0)$, and

$f(E, W_0, T, t)$ is the occupation probability of the states at energy E and at the time t. The function f satisfies the rate equation (figure 2)

$$\mathrm{d}f/\mathrm{d}t = W_\mathrm{p}(1-f) - \{W_0 + W_1 + W_\mathrm{e}\exp[(E-E_\mu)/kT]\}f \tag{2}$$

where W_p is the pump rate. The rate of phonon assisted process W_1 does not depend on the degree of disorder. W_e is the thermal excitation rate. (E_μ will be defined in § 2.3.)

2.1.1. Steady state case: $\mathrm{d}f/\mathrm{d}t = 0$. Equation (2) gives

$$f(E, W_0, T) = B/(B + W_0/\langle W_0\rangle + \langle R_0\rangle + \langle R_\mathrm{e}\rangle) \tag{3}$$

where $B = W_\mathrm{p}/\langle W_0\rangle$; $\langle R_0\rangle = W_1/\langle W_0\rangle$, $\langle R_\mathrm{e}\rangle = (W_\mathrm{e}/\langle W_0\rangle)\exp[(E-E_\mu)/kT]$ and

$$\langle W_0\rangle \sim \int_0^\infty W_0 P(W_0)\,\mathrm{d}W_0.$$

For very low temperatures, at which $\exp[(E-E_\mu)/kT] \ll 1$, the zero-phonon integrated emission intensity is given by

$$I(M_0) \sim \int_0^\infty \frac{BW_0\exp(-W_0/\langle W_0\rangle)}{\langle W_0\rangle(B + \langle R_0\rangle + W_0/\langle W_0\rangle)}\,\mathrm{d}W_0. \tag{4}$$

Equation (4) can be written as

$$I(M_0) \sim B\langle W_0\rangle\,\mathrm{e}^y\left(\mathrm{e}^{-y} - y\int_y^\infty \frac{\mathrm{e}^{-V}}{V}\,\mathrm{d}V\right) \tag{5}$$

with $y = B + \langle R_0\rangle$ and $V = (W_0/\langle W_0\rangle) + B + \langle R_0\rangle$. For $y > 0$, the exponential integral has the following form [8]:

$$I(y) = \int_y^\infty \frac{\mathrm{e}^{-V}}{V}\,\mathrm{d}V = E_1(y)$$

$$E_1(y) = -\gamma - \log y - \sum \frac{X^n}{nn!} \qquad y > 0 \tag{6}$$

$$E_1(y) = \mathrm{e}^y\left(\frac{0.711093}{(y+0.415775)} + \frac{0.278518}{(y+2.29428)} + \frac{0.010389}{(y+6.2900)}\right) \qquad y > 10 \tag{7}$$

where $\gamma = 0.5772\ldots$ is Euler's constant.

The zero-phonon integrated emission $I(M_0)$ is given by

$$I(M_0) \sim B\langle W_0\rangle\,\mathrm{e}^y[1 - yE_1(y)].$$

Using the same procedure used for deriving $I(M_0)$, the one-phonon integrated emission intensity is described by

$$I(M_1) \sim \int_0^\infty \int_{-\infty}^0 W_1 P(W_0)\rho(E) f(E, W_0, T)\,\mathrm{d}W_0\,\mathrm{d}E$$

$$I(M_1) \sim BW_1 y\,\mathrm{e}^y\,E_1(y).$$

The calculated ratio of $I(M_1)$ and $I(M_0)$ is given by

$$R = I(M_1)/I(M_0) = \langle R_0\rangle yE_1(y)/[1 - yE_1(y)]. \tag{8}$$

We present in figure 3, the calculated ratio $R = I(M_1)/I(M_0)$, using equation (8) and

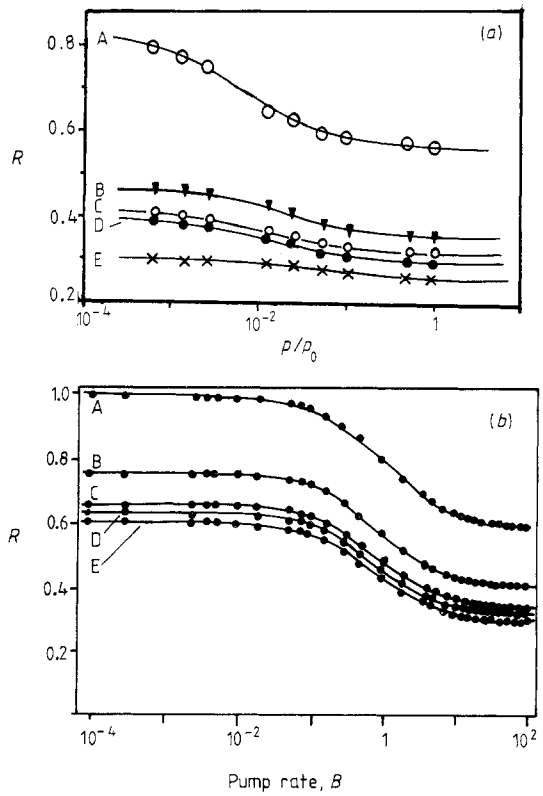

Figure 3. Intensity ratio $R = I(M_1)/I(M_0)$ as a function of excitation power for different compositions x: curves A, $x = 0.85$; curves B $x = 0.61$; curves C, $x = 0.56$; curves D, $x = 0.52$; curves E, $x = 0.51$. (*a*) experimental curves; $P_0 \simeq 10\ \mathrm{W\ cm^{-2}}$, $T = 5$ K. (*b*) calculated curves.

experimental values of R, versus the excitation power represented by B, for different values of $\langle R_0 \rangle$ given in table 1. Note that at $y = 10$, the two parts of the curve obtained by using equations (6) and (7) link smoothly. R increases with increasing composition x and presents two stages with a maximum at lower B values and a minimum at higher B values.

2.1.2. Pulsed excitation case. We first deal with out of saturation case, where B is relatively small. We consider a laser pulse defined as

$$B = \begin{cases} 0 & t \leqslant -\tau \\ B & -\tau < t \leqslant 0 \\ 0 & t > 0 \end{cases}$$

The coupled rate equation (2) can be written as

$$\mathrm{d}f/\mathrm{d}t = \langle W_0 \rangle [B/(B + A) - f](B + A) \tag{9}$$

with $A = W_0/\langle W_0 \rangle + \langle R_0 \rangle + \langle R_e \rangle$.

The solution of equation (9) is

$$f = f_0\, \mathrm{e}^{-A\langle W_0 \rangle t} \tag{10}$$

where

$$f_0 = [B/(B + A)]\{1 - \exp[-\langle W_0 \rangle (B + A)\tau]\}. \tag{11}$$

Using the expression (10) for $f(E,\ W_0,\ B,\ t,\ \tau)$, and taking into account

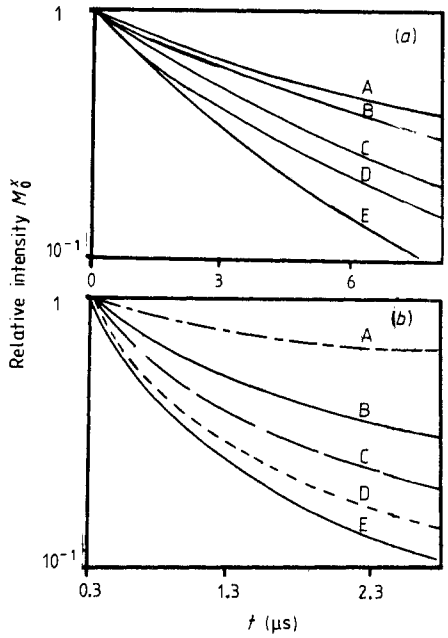

Figure 4. Time dependence of the intensity of the M_0 band in $GaAs_{1-x}P_x$: curve A, $x = 0.85$; curve B, $x = 0.61$; curve C, $x = 0.56$; curve D, $x = 0.52$; curve E, $x = 0.51$. (*a*) calculated curves. (*b*) experimental curves at $T = 2$ K and $P = 10$ W cm^{-2}.

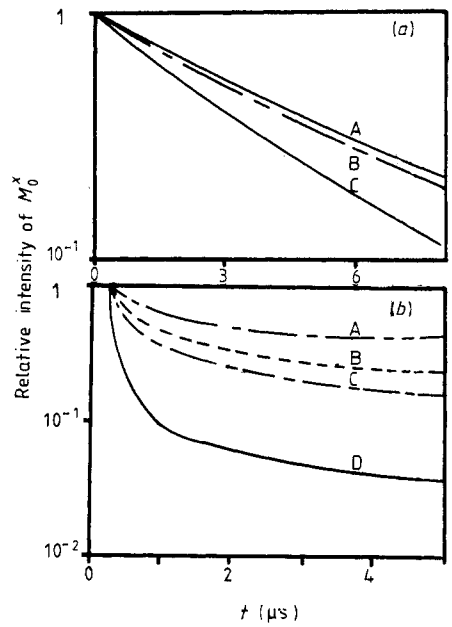

Figure 5. Time dependence of the intensity of the M_0 band in $GaAs_{0.15}P_{0.85}$ for different excitation powers. (*a*) calculated curves: curve A, $B = 10^{-1}P$; curve B, $B = 10^{-2}P$; curve C, $B = 10^{-3}P$. (*b*) experimental curves, $T = 2$ K, $P_0 = 10$ W cm^{-2}: curve A, $P = 10^{-3}P_0$; curve B, $P = 10^{-2}P_0$; curve C, $P = 10^{-1}P_0$; curve D, $P = P_0$.

$\exp[(E - E_\mu)/kT)] \ll 1$, the integrated emission intensity without phonon assistance (1) is then given by

$$I(M_0) \sim \frac{B\,e^{-W_1 t}}{\langle W_0\rangle} \int_0^\infty \frac{W_0 \exp[-(1 + \langle W_0\rangle t)(W_0/\langle W_0\rangle)]}{(B + W_0/\langle W_0\rangle + \langle R_0\rangle)}\,dW_0 \tag{12}$$

which can be written as

$$I(M_0) \sim \frac{B\langle W_0\rangle}{(1 + \langle W_0\rangle t)}\,e^{-W_1 t}\left(e^{-y} - y\int_y^\infty \frac{e^{-V}}{V}\,dV\right)e^{y} \tag{13}$$

with $V = (B + W_0/\langle W_0\rangle + \langle R_0\rangle)(1 + \langle W_0\rangle t)$ and $y = (B + \langle R_0\rangle)(1 + \langle W_0\rangle t)$.

Using the solution of exponential integration given above, equation (13) becomes

$$I(M_0) \sim [B\langle W_0\rangle/(1 + \langle W_0\rangle t)]\,e^{-W_1 t}[1 - y\,e^{y}E_1(y)]. \tag{14}$$

The same calculation gives the one-phonon integrated emission intensity

$$I(M_1) \sim BW_1\,e^{-W_1 t}\,y\,e^{y}\,E_1(y). \tag{15}$$

Equations (14) and (15) show that the decay of calculated intensities $I(M_0)$ and $I(M_1)$ is non-exponential. As it has been observed experimentally [1], the decay of $I(M_0)$ and $I(M_1)$ is faster when the composition goes from $x = 0.85$ to $x = 0.51$ (figure 4). It

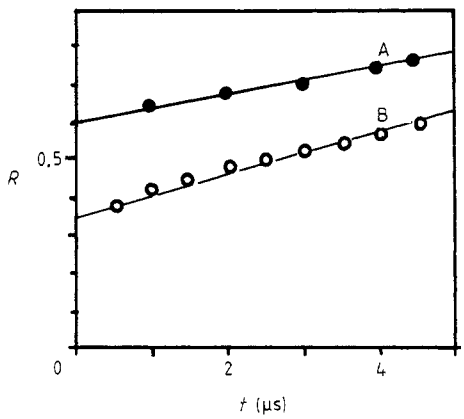

Figure 6. Intensity ratio $R = I(M_1)/I(M_0)$ as a function of delay time in $GaAs_{1-x}P_x$: A, $x = 0.85$; B, $x = 0.52$ at $T = 2$ K and $P_0 = 10$ W cm^{-2}.

Table 1.

x	0.51	0.52	0.56	0.61	0.85
W_1 (ms^{-1})	95	56	47	36	34
$\langle W_0 \rangle$ (ms^{-1})	284	160	131	83	57
$\langle R_0 \rangle$	0.33	0.35	0.36	0.43	0.6

becomes even faster with increasing excitation power and is still non-exponential at saturation corresponding to high power excitation B (figure 5).

We now deal with the situation at saturation, for which $B \gg \langle R_0 \rangle$ and $B \gg (W_0/\langle W_0 \rangle)$. Here equation (12) becomes

$$I(M_0) \sim (e^{-W_1 t}/\langle W_0 \rangle) \int_0^\infty W_0 \exp[-(1 + \langle W_0 \rangle t)(W_0/\langle W_0 \rangle)]\, dW_0$$
$$\sim e^{-W_1 t}/(1 + \langle W_0 \rangle t)^2. \tag{16}$$

Under the same conditions, we get

$$I(M_1) \sim \langle R_0 \rangle e^{-W_1 t}/(1 + \langle W_0 \rangle t) \tag{17}$$

The expressions for $I(M_0)$ and $I(M_1)$ given by equations (16) and (17), which show non-exponential decay, are similar to those calculated in [7]. Using equations (16) and (17), we find a linear dependence on time for the calculated ratio $R = I(M_1)/I(M_0)$

$$R = W_1 t + W_1/\langle W_0 \rangle = W_1 t + \langle R_0 \rangle. \tag{18}$$

Figure 6 shows experimental values of R for $x = 0.85$. The fitting curves using equation (18) gives experimental measurements of $\langle W_0 \rangle$ and W_1 represented in table 1, for several values of x.

$\langle W_0 \rangle$ becomes important compared to W_1 as x goes to 0.51. In this case, the Γ and X bands are close together, favouring the zero-phonon radiative recombination processes. The increase of W_1 and $\langle W_0 \rangle$ when x decreases reflects the fact that W_1 varies as $[E(\Gamma) - E(X)]^{-2}$, and $\langle W_0 \rangle$, which is affected by disorder, varies as $x(1-x)[E(\Gamma) - E(X)]^{-2}$.

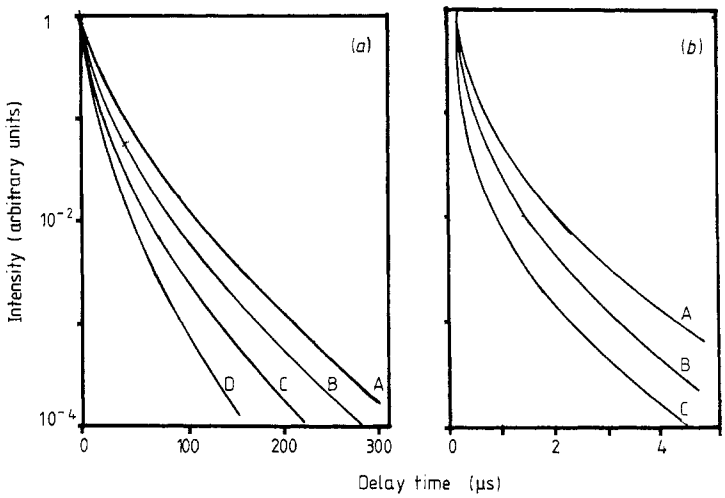

Figure 7. Time dependence of the intensity of the M_0 band in $GaAs_{0.44}P_{0.56}$ for different temperatures T. (*a*) calculated curves: curve A, $T = 0.1$ K; curve B, $T = 2$ K; curve C, $T = 4$ K; curve D, $T = 6$ K. (*b*) experimental curves: curve A, $T = 4.3$ K; curve B, $T = 5.2$ K; curve C, $T = 6.4$ K, all with $P = 10$ W cm^{-2}.

2.2. *Temperature dependence of* M_0 *decay*

When T increases, the condition $\exp[(E - E_\mu)/kT] \ll 1$ is no longer true for useful values of E. In this case, the rate equation was integrated numerically. In figure 7, we show the time decay of M_0 emission at four different temperatures. This figure has to be compared with figure 8 of [4]. A very good fit was obtained, using $\langle W_0 \rangle$ and W_1 values already determined (table 1). So, the variation of the decay with temperature can be understood only in terms of thermal excitation of the tail states above the energy E_μ where $\tau_t \gg \tau_r$, where τ_t and τ_r are the transfer and radiative relaxation times, respectively. That T-dependence is found to be quite sensitive to the value of E_0.

2.3. *Line shape of emission band* M_0

For the model calculation, we assume that for each emitted photon energy E in the band M_0 the intensity can be written as

$$I(E) \sim \rho(E) f(E, T, t). \tag{19}$$

In the steady case equation (13) becomes

$$I(E) \sim \rho_0 \exp(E/E_0)/\{1 + a_R + a_e \exp[(E - E_\mu)/kT]\} \tag{20}$$

with $a_R = W_0 + W_1/W_p$ and $a_e = W_e/W_p$.

The maximum of the band M_0 corresponding to $(dI/dE) = 0$ gives an approximate solution

$$E_{max} = -nKT + E_\mu. \tag{21}$$

K is the Boltzmann constant and E_μ corresponds to the energy position of the band M_0 at $T = 0$ K. We have $n \simeq 8$ [1].

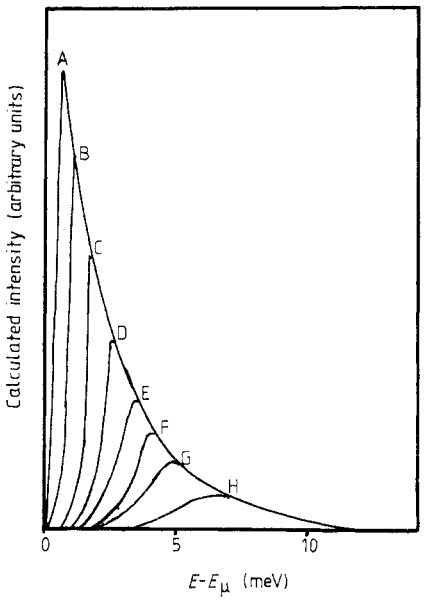

Figure 8. Calculated band shape of M_0 at different temperatures T. E_μ is taken as the energy origin.

Combining (20) and (21) with $(dI/dE) = 0$, we find that a_e has the following form:

$$a_e = bT \qquad b = (K e^n/E_0).$$

The intensity $I(E)$ becomes

$$I(E) \sim \rho_0 \exp(E/E_0)/\{1 + bT \exp[(E - E_\mu)/kT]\}. \tag{22}$$

Figure 8 shows calculated M_0 band-shape using equation (22) for different values of the temperature T. We have used experimental values [1, 2]: $E_0 = 3.2$ meV, $n = 8$ corresponding to the composition $x = 0.51$ and $k = 0.086$ meV K^{-1}. E_μ is taken as the energy origin. As shown by figure 7 and reported by our experimental results [1], the position of the M_0 band shifts to lower energy with increasing T.

3. Conclusion

The calculation model of the emission band intensity $I(M_0)$ from localised exciton states in an exponential tail reproduces our previous experimental results [1, 2] and describes very well the evolution of $I(M_0)$ with varying experimental parameters. These parameters are temperature, excitation power, time and composition x of alloys. The approximations made are justified if one considers the orders of magnitude of the different experimental parameters.

Appendix

The wavefunction of a weakly localised exciton (localisation energy smaller than exciton Rydberg) can be written

$$\Phi = \sum_k A_k \psi_{\mathrm{FE},k} \tag{A1}$$

where $\psi_{\mathrm{FE},k}$ is the wave function of a free exciton of wavevector $\boldsymbol{k}$ in its ground state. In terms of electron and the hole states φ_v and φ_c, $\psi_{\mathrm{FE},k}$ can be written

$$\psi_{\mathrm{FE},k} = \sum_l B_{k,l} \varphi_{vl} \varphi_{c,l+k}. \tag{A2}$$

In an indirect gap material, no-phonon optical transitions are treated by second-order perturbation, involving a vertical optical transition, and a scattering by potential fluctuations in the alloy, modelled by $V = \Sigma_j V(\boldsymbol{R}_j)$. In this approximation, the matrix element for a no-phonon process reads:

$$H_{\text{no-phonon}} = \sum_j \sum_k A_k \sum_l B_{kl} \langle \varphi_{v,l} | H_{\mathrm{opt}} | \varphi_{c,l} \rangle \langle \varphi_{v,l} | V_j | \varphi_{c,l+k} \rangle / \Delta. \tag{A3}$$

Assuming slow variation of $\mathrm{M}_0 = \langle \varphi_{v,l} | H_{\mathrm{opt}} | \varphi_{c,l} \rangle$ and Δ, and writing $\langle \varphi_{v,l} | V_j | \varphi_{c,l+k} \rangle = V_k \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j}$, we get

$$M_{\text{no-phonon}} = \frac{\mathrm{M}_0}{\Delta} \sum_{j,k} A_k V_k \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j} \sum_k B_{kl}. \tag{A4}$$

Noting that $\Sigma B_{kl} = F_{\mathrm{FE},k}(0)$, the envelope function of the free exciton and considering that the perturbing potentials are short ($V_k = V$), we arrive at

$$M_{\text{no-phonon}} = \frac{\mathrm{M}_0}{\Delta} V F_{\mathrm{FE}}(0) \sum_{jk} A_k \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j} \tag{A5}$$

When taking $|M_{\text{no-phonon}}|^2$, the term coming from $|\Sigma_{jk} A_k \, \mathrm{e}^{\boldsymbol{k}\cdot\boldsymbol{R}_j}|^2$ will take a wide distribution of values depending on the particular distribution of $\boldsymbol{R}_j$. Writing it as

$$\sum_{jklq} A_k A_q^* \, \mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{R}_j - \boldsymbol{q}\cdot\boldsymbol{B}_l)}$$

one can notice that its mean value comes from the terms such that $j = l$ and $\boldsymbol{k} = \boldsymbol{q}$, namely

$$\sum_{jk} A_k A_k^* \sim N. \tag{A6}$$

Since $\Sigma_k A_k A_k^* = 1$, one gets

$$\langle |M_{\text{no-phonon}}|^2 \rangle = (\mathrm{M}_0^2 \, \Delta) V^2 |F_{\mathrm{FE}}(0)|^2 N. \tag{A7}$$

So, the mean value $\langle W_0 \rangle$ does not depend upon the exciton localisation provided the localisation is weak (equation A1).

In the case of phonon-assisted transition, it can be shown that the coherence in the sum over k in equation (A3) is lost, because for each term, a different phonon is emitted.

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[8] Abramovitz M and Stegun I A *Handbook of Mathematical Functions* (expression 5.1.11 on p 229 for equation (6) and asymptotic form of $E_1(y)$ given on p 250 for equation (7))