

Phonon coherence and new set of sidebands in phonon-assisted photoluminescence

S.-J. XIONG^{1,2(*)} and S.-J. XU^{2(**)}

¹ *National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University - Nanjing 210093, PRC*

² *Department of Physics and HKU-CAS Joint Laboratory on New Materials The University of Hong Kong - Pokfulam Road, Hong Kong, PRC*

received 25 January 2005; accepted in final form 7 June 2005

published online 13 July 2005

PACS. 78.20.Bh – Theory, models, and numerical simulation.

PACS. 42.50.Ct – Quantum description of interaction of light and matter; related experiments.

PACS. 78.55.Et – II-VI semiconductors.

Abstract. – We investigate excitonic polaron states comprising a local exciton and phonons in the longitudinal optical (LO) mode by solving the Schrödinger equation. We derive an exact expression for the ground state (GS), which includes multi-phonon components with coefficients satisfying the Huang-Rhys factors. The recombination of GS and excited polaron states gives one set of sidebands in photoluminescence (PL): the multi-phonon components in the GS produce the Stokes lines and the zero-phonon components in the excited states produce the anti-Stokes lines. By introducing the mixing of the LO mode and environal phonon modes, the exciton will also couple with the latter, and the resultant polaron states result in another set of phonon sidebands. This set has a zero-phonon line higher and wider than that of the first set due to the tremendous number of the environal modes. The energy spacing between the zero-phonon lines of the first and second sets is proved to be the binding energy of the GS state. The common exciton origin of these two sets can be further verified by a characteristic Fano lineshape induced by the coherence in the mixing of the LO and the environal modes.

It has been recognized that the interactions of excitons with phonons in light-emitting materials lead to a number of interesting effects in optical properties, such as the phonon sidebands in photoluminescence (PL) spectra, the exciton dephasing and self-trapping [1–8]. Theoretically, the sideband structures caused by electron-phonon interactions for local excitons at deep centers were investigated using the Huang-Rhys model [9–11]. One set of Stokes lines (SLs) in PL, observed in the experiments, has been very successfully explained by the theories. However, there are some features in the experimental spectra associated with the interactions of excitons and phonons, such as complicated structure containing more than one set of phonon sidebands, anti-Stokes lines (ASLs), and Fano-like lineshape. Recently, the fabrication of nanostructures has renewed the study of this field, as the confinement in quantum dots

(*) E-mail: sjxiong@nju.edu.cn

(**) E-mail: sjxu@hkucc.hku.hk

much enhances the interaction between carriers and phonons. Such an enhancement has been experimentally observed [12,13]. Fomin *et al.* have proposed a nonadiabatic approach to interpret the unusual phonon sidebands observed in quantum dots [14]. Verzele *et al.* have indicated that the exciton-phonon bound states as a whole, called excitonic polarons, and the decaying of their phonon components into phonon thermostat have to be put under consideration in cases of strong exciton-phonon interactions [15].

In this letter, we present a unified theory to explain complicated structures of phonon sidebands in PL. The exact eigenstates and eigenenergies of excitonic polarons are obtained by solving the Schrödinger equation of an exciton interacting with LO mode. The obtained ground state (GS) contains multi-phonon components with coefficients strictly satisfying the Huang-Rhys factors, which gives the SLs including a ZPL. Meanwhile the zero-phonon components of the excited states can produce the ASLs. These SLs and ASLs form one set of sidebands. By introducing the mixing of LO mode and environal modes, another set emerges. The energy shift between two sets is determined by the strength of exciton-LO phonon coupling, and the coherence in the mode mixing results in specific Fano-like lineshape.

First, let us consider the interaction between an exciton and a LO mode,

$$H = \epsilon_0 a^\dagger a + \hbar\omega_0 b_0^\dagger b_0 + V_0 a^\dagger a (b_0^\dagger + b_0), \quad (1)$$

where a and b_0 are annihilation operators for exciton and for LO phonon, ϵ_0 and $\hbar\omega_0$ are their energies, respectively, and V_0 is the coupling strength between exciton and phonon. Here we regard the exciton as one quasiparticle, supposing that it has a large binding energy.

For Hamiltonian (1), the m -th eigen-wavefunctions can be written as

$$\Psi_m = \sum_n c_{m;n} \frac{a^\dagger (b_0^\dagger)^n}{\sqrt{n!}} |0\rangle, \quad (2)$$

where n is the number of phonons of the LO mode in the corresponding component, and $|0\rangle$ is the vacuum. Since there is only one exciton state included, in the polaron wavefunctions the phonon and exciton parts are separable and the calculation is within the adiabatic scheme [16]. For this exciton state the operator $a^\dagger a$ in Hamiltonian (1) takes value 1 and can be treated as a c -number. Using operator $b_{00} \equiv b_0 + \frac{V_0}{\hbar\omega_0}$, the Hamiltonian becomes

$$H = \epsilon_0 + \hbar\omega_0 b_{00}^\dagger b_{00} - \frac{V_0^2}{\hbar\omega_0}.$$

From it one can get the eigenenergies as

$$E_m = \epsilon_0 + m\hbar\omega_0 - \Delta_0, \quad (3)$$

with $\Delta_0 \equiv \frac{V_0^2}{\hbar\omega_0}$ being the binding energy of the excitonic polaron, and E_0 is the GS energy. The coefficients in eq. (2) satisfy the following iteration relations:

$$[(m-n)\hbar\omega_0 - \Delta_0]c_{m;n} = V_0\sqrt{n}c_{m;n-1} + V_0\sqrt{n+1}c_{m;n+1}. \quad (4)$$

For the GS, the coefficients are related with each other by

$$c_{0;n+1} = \frac{-\Delta_0 c_{0;n}}{\sqrt{n+1}V_0} \quad \text{for } n \geq 0. \quad (5)$$

From these relations, we can find the coefficients

$$c_{0;n} = \frac{(-1)^n S^{n/2}}{e^{S/2} \sqrt{n!}}, \quad (6)$$

with S being the Huang-Rhys factor $S = \frac{V_0^2}{\hbar^2 \omega_0^2} \equiv \frac{\Delta_0}{\hbar \omega_0}$. Considering that the n -th component in GS $\Psi_{m=0}$ is associated with n phonons, $|c_{0;n}|^2$ gives the intensity of a phonon sideband at energy $E_0 - n\hbar\omega_0$. This is as predicted by the Huang-Rhys theory.

For excited states Ψ_m with $m > 0$, the coefficients can be obtained by the following iteration relations:

$$c_{m;n+1} = -\frac{c_{m;n}}{\sqrt{n+1}V_0D_{m;n}}, \quad \text{for } n = 0, 1, 2, \dots, \quad (7)$$

where

$$D_{m;n+1} = \frac{1}{\Delta_0 - (m-n-1)\hbar\omega_0 - (n+1)V_0^2D_{m;n}},$$

with the initial value

$$D_{m;0} = \frac{1}{\Delta_0 - m\hbar\omega_0},$$

and by the normalization. Although the eigenenergy of state Ψ_m with $m > 0$ is higher than E_0 , it should have a finite occupation rate as long as the photon energy of the excitation laser is high enough [17]. In order to calculate the PL spectrum of the polaron states, we must know the population of each state. For simplicity, we assume that all the states with energies less than the laser energy E_{laser} have the same occupation rate. The intensity of PL at photon energy ϵ is proportional to

$$\rho(\epsilon) = \sum_m \sum_n |c_{m;n}|^2 \theta(E_{\text{laser}} - E_m) \delta(\epsilon - E_m + n\hbar\omega_0). \quad (8)$$

The luminescence peaks produced by the GS Ψ_0 consist of a ZPL at energy $E_0 = \epsilon_0 - \Delta_0$ and a number of SLs at energies $E_0 - n\hbar\omega_0$. This ZPL originates from the zero-phonon component ($c_{0;0}$) of the GS state while the remaining lines are from the components ($c_{0;n>0}$) with more than one phonon. The intensities of the SLs relative to the ZPL follow a Poisson distribution predicted by the Huang-Rhys theory. Other eigenstates $\Psi_{m>0}$ will produce sidebands at $\epsilon_0 - \Delta_0 + (m-n)\hbar\omega_0$ with $n \geq 0$. The $n = m$ component will intensify the ZPL peak by simultaneous emission of m LO phonons. The $n > m$ components in the radiative recombination will enhance the intensity of the corresponding SLs. Meanwhile, the components with $n < m$ may produce the ASL peaks above the ZPL. The relative intensity of the ASL is $\rho_{m;m-n}/\rho_{m;m} = \frac{S^n (m)!}{n! 2^m (m-n)!}$.

The population assumed in eq. (8) corresponds to the situation just after the illumination and without any relaxation. The relaxation, mainly via the nonradiative processes of absorption and emission of phonons in the bath modes, can greatly change the population. It is known that besides the LO mode, there are a large number of bath phonon modes in solids. Although these bath modes do not directly interact with the exciton, they may have crucial influence on phonon components of the polaron states. This influence and the resultant relaxation can be accounted for using the following Hamiltonian of the mode mixing:

$$H_1 = \sum_{\lambda} g(b_0^\dagger b_\lambda + \text{H.c.}) + \sum_{\lambda} \hbar\omega_\lambda \left(b_\lambda^\dagger b_\lambda + \frac{1}{2} \right), \quad (9)$$

where λ is the mode index of bath phonons, and g is the strength of the mixing. For simplicity, g is assumed to be the same for all bath modes and the dispersion relation ω_λ is continuous with a constant density of states between energies 0 and W . For a pure harmonic phonon system without exciton, the mixing terms should vanish as all the phonon modes are orthogonal to

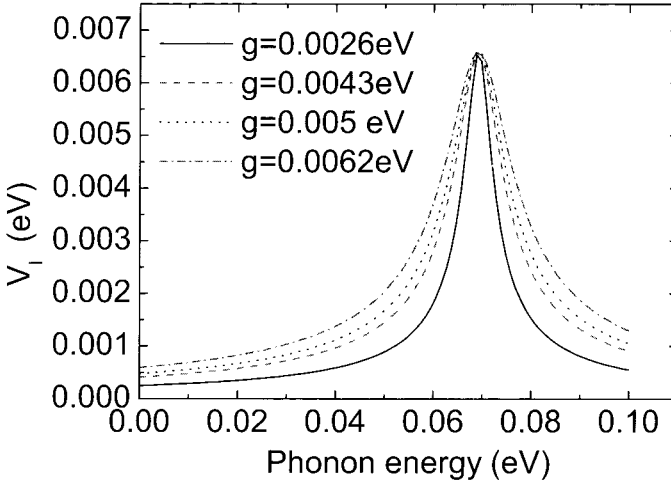


Fig. 1 -- Coupling strength V_l as a function of phonon frequency.

each other. The formation of the excitonic polaron states, however, violates the orthogonality between the LO and bath modes, and thus creates the mixing terms. It is this mixing that makes the LO phonons in polaron state Ψ_m decay into the continuum of bath modes. From Hamiltonian (9), the orthogonal modes become

$$b_l = \frac{\hbar\omega_l - \hbar\omega_0}{\sqrt{g^2 + (\hbar\omega_0 - \hbar\omega_l)^2}} b_\lambda + \frac{g}{\sqrt{g^2 + (\hbar\omega_0 - \hbar\omega_l)^2}} b_0, \quad (10)$$

with frequency ω_l determined by solving the equation

$$\hbar\omega_l = \hbar\omega_0 + \sum_\lambda \frac{g^2}{\hbar\omega_l - \hbar\omega_\lambda}. \quad (11)$$

The resultant set of orthogonal modes $\{l\}$ will couple with the exciton at a strength

$$V_l = \frac{g}{\sqrt{g^2 + (\hbar\omega_0 - \hbar\omega_l)^2}} V_0. \quad (12)$$

Figure 1 shows the phonon frequency dependence of V_l . It can be seen that most of the modes $\{l\}$ are still weakly coupled to the exciton except for those modes with frequencies $\omega_l \sim \omega_0$. As mentioned earlier, this results in not only the broadening of the peaks in the first set but also the creation of the second set of the phonon sidebands.

To give a clarification, we can divide the modes $\{l\}$ into two groups: P_1 includes modes with $\omega_l \sim \omega_0$ which strongly couple with the exciton; P_2 includes the remaining modes weakly coupled to the exciton. Because the modes in P_1 with frequencies in the vicinity of ω_0 have coupling strength of about V_0 with the exciton, the formed polaron states will produce the first set of phonon sidebands including broadened ZPL, SLs and ASLs, as already discussed above. It should be noted that the ZPL is centered at the GS eigenenergy E_0 which lowers with increasing g due to an increase of the mode number in group P_1 as seen from fig. 1. Now we turn to discuss the modes in P_2 . For a mode l in this group, it has a weak coupling with the exciton, *i.e.*, $V_l \sim 0$, so the binding energy of the relevant polaron state is approaching zero.

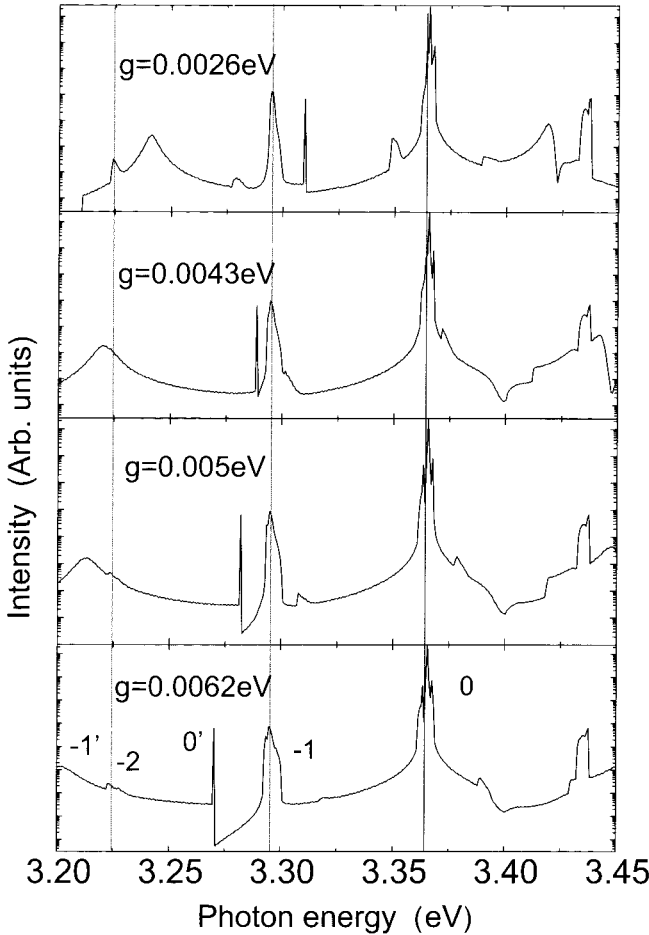


Fig. 2 – Relative intensity as a function of photon energy when H_1 is included. In the simulation 1000 modes uniformly distributed in a band from 0 to 0.1eV are included. $V_0 = 0.0078$ eV, $\epsilon_0 = 3.366$ eV, and $\hbar\omega_0 = 0.069068$ eV.

In other words, the eigenenergy of the polaron state is very close to the bare exciton energy ϵ_0 . Thus, the ZPL produced by the zero-phonon component in this state almost located at ϵ_0 , higher than the ZPL of the first set by an energy about $\epsilon_0 - E_0$. The intensity of the ZPL in the second set should be much stronger than that of the ZPL in the first set since the ZPL intensity is proportional to the number of involved phonon modes. Because of the evident dispersion of the bath modes in group P_2 , it can be expected that the ZPL of the second set is wider than that of the first set. The energetic position of the one-phonon sideband in the second set ranges from ϵ_0 (the ZPL position) to $\epsilon_0 - W$. The transition probability of this sideband is found to be

$$p_{10;1} \propto \frac{(\hbar\omega_l - \hbar\omega_0 + g)^2}{g^2 + (\hbar\omega_0 - \hbar\omega_l)^2}. \quad (13)$$

From eq. (13), it can be easily known that $p_{10;1}$ reaches its maximum value for $\hbar\omega_l = \hbar\omega_0 + g$ and the minimum for $\hbar\omega_l = \hbar\omega_0 - g$. When the phonon frequency is increased from $\hbar\omega_0 - g$ to $\hbar\omega_0 + g$ the intensity of the sideband rapidly increases. However, as the phonon frequency

is further increased over $\hbar\omega_0 + g$ the sideband intensity slowly decreases. This results in a typical Fano asymmetric lineshape. As a matter of fact, one can rewrite eq. (13) into a standard Fano lineshape function $\alpha_l = (\tilde{\epsilon} + 1)^2/(\tilde{\epsilon}^2 + 1)$ with $\tilde{\epsilon} = (\hbar\omega_l - \hbar\omega_0)/g$. Here the Fano asymmetry parameter is the unity [18]. Since the mixing between LO-mode and λ -mode (which forms the l mode components in the polaron states, illustrated in eq. (10)), introduced by H_1 , is coherent, an interference between the optical transitions associated with the two phonon components in the l mode will occur. That is the origin of Fano interference in the phonon-assisted luminescence.

By diagonalizing the whole Hamiltonian $H + H_1$, one can calculate the PL spectrum by

$$\rho(\epsilon) = \sum_m \sum_{\{n_l\}} |c_{m;\{n_l\}}|^2 \left(\prod_l \alpha_l^{n_l} \right) \theta(E_{\text{laser}} - E_m) \delta \left(\epsilon - E_m + \sum_l n_l \hbar\omega_l \right), \quad (14)$$

where E_m and $c_{m;\{n_l\}}$ are eigenenergy and eigenfunction of the whole Hamiltonian. As the relaxation processes have been partially taken into account, the calculated results are not sensitive to the upper limit in the summation of eq. (14). In fig. 2, we plot the PL spectrum obtained from a numerical calculation. As expected, there are two ZPL peaks, $0'$ and 0 , belonging to the first and second set, respectively. In each set, there are several SLs and ASLs. The SLs are red-shifted from their corresponding ZPL by integer times $\hbar\omega_0$. In the second set, the energy distance between the first ASL and the ZPL is $\hbar\omega_0$. In the first set, however, this energy distance is not exactly $\hbar\omega_0$ and is dependent of g , because the positions of ZPL and ASL in the first set are just the energies of GS and some excited states which contain not only the LO phonons but also the phonons of other modes. The Fano interference features are partially smeared by the summation in eq. (14), but they can still be seen near some peaks. These results catch the main features observed in experiment [19].

In summary, by reconsidering the exciton-phonon interaction and decaying of LO phonons we can conclude that there are two sets of phonon-assisted peaks: one is from excitonic polaron states of the phonon modes with frequencies $\omega_l \sim \omega_0$, and the other is from polaron states of the remaining bath phonon modes. The latter set was not properly considered in previous theories and was usually assigned to be the first set because it may include the strongest "ZPL" peak. The common exciton origin of these two sets of phonon sidebands can be further verified by the characteristic energy difference between them determined by the exciton-LO phonon coupling strength, and by the specific Fano lineshape reflecting the coherence in the phonon mode mixing. Together with the experimental observation, the present theory may give a new and better understanding of the complicated structures in the phonon-assisted luminescence spectrum.

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This work was supported in HK by HK RGC CERG Grant (No. HKU 7036/03P), in Nanjing by National Foundation of Natural Science in China Grant Nos. 60276005 and 10474033, and by the China State Key Projects of Basic Research (2005CB623605).

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