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Energy relaxation in quantum dots

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We present the results of energy relaxation calculations for electron-hole pairs confined in a quantum dot and in strong coupling with LO phonons (excitonic polarons). We show that despite the robustness of the polaron entity, its disintegration induced by the anharmonic decay of its LO phonon component can lead to an efficient energy relaxation. We compute the time-dependent photoluminescence signals associated with the ground-state excitonic polaron as well as the photoluminescence excitation signal and the energy loss rate of an excitonic polaron in a quantum dot. Our calculations clearly evidence the existence of dot parameters where the energy relaxation is inhibited.

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Despite intense researches since many years, the electronic properties of self-assembled quantum dots are still under debate. In particular, there is no consensus on how an electron-hole pair injected in the continuum of a dot relaxes its energy to reach its ground state before recombining radiatively. The use of models that are well established in bulk and quantum well structures, that is to say, the energy relaxation associated with the irreversible emission of LO phonons, has led to the concept of phonon bottleneck.[1,2] The latter arises from the impossibility for an electron-hole pair to emit optical phonons due to the discretization of its lower-lying states and of the very small dispersion of the LO phonons. Once the most efficient relaxation channel blocked, one is left with the emission of acoustical phonons which, however, becomes inefficient when the energy spacings between levels exceeds a few meV's. The phonon bottleneck was never shown to be as prevalent as was once predicted, although some dots with large electron and hole confinement did show inefficient energy relaxation (see, e.g., Refs. 3 and 4). It was recently realized[5–8] that the very notion of irreversible phonon emission is not applicable to quantum dots, because the size of the one-phonon continuum attached to, say, the ground electron state and into which the discrete excited state with zero phonon should irreversibly dissolve is much too small (and the Fröhlich interaction much too strong) to allow the Fermi golden rule to be applicable. In fact, the correct elementary excitations in quantum dots are the polarons.[5–10] When the dot contains electrons (e.g., from doping), one deals with electronic polarons.[5–8] When the dot contains one Coulomb-correlated electron-hole pair (in short, an exciton), it was shown[9,10] that the polaron concept fully applies. In the present paper we wish to show that the excitonic polaron (X_{POL}) formalism is able to describe the energy relaxation of a photoexcited dot. We shall show that the calculated energy loss rate of an X_{POL} can often be comparable to the single-particle one in quantum well structures. However, we shall also demonstrate that one may find (and even design) situations where the energy relaxation is hampered, a situation reminiscent of, but radically different from, the phonon bottleneck.

We consider strongly confining dots, such as the InAs/GaAs self-organized dots. These dots are modeled by truncated cones floating on a 1-ML-thick wetting layer. The dot typical dimensions are: $R \approx 10$ nm, $h \approx 3$ nm, basis angle $=30°$. The energy spacings (≈ 50 meV for the electrons, ≈ 20 meV for the holes) are comparable to the LO phonon energy (36 meV for GaAs LO phonons). Using a one-band envelope function approach and assuming a cylindrical symmetry for the confining potential, one finds the Coulomb-correlated electron-hole states to be labeled by the sum of the projections of the hole and electron angular momenta along the cone axis (for details see Ref. 10). While it is customary in bulk and quantum wells to consider the excitons to be weakly coupled to the optical phonons, the exciton-phonon interaction (Fröhlich term) in dots is diagonalized to give rise to the X_{POL}. Thus, there is no room left for X_{POL} desexcitation which are stationary eigenstates of the complete exciton-phonon Hamiltonian. Actually, what triggers the relaxation is the genuine instability of the LO phonons[8,10–14] associated with the anharmonicity of the lattice vibrations. We have already shown[10] that this mechanism induces a quick decoherence (a few ps at room temperature) of the fundamental recombination line of the quantum dots. We shall now show that the same LO instability leads often to an efficient energy relaxation.

In the calculations we have neglected the interaction of the X_{POL} with the acoustical phonons as well as possible intradot Auger effects[15] that could arise, depending on the magnitude of the band offset, because a discrete excited X_{POL} state is superimposed on a continuum(s) that corresponds to the ejection of one particle to the benefit of the relaxation of the second. The energy and wave-function calculations have been performed within a basis spanned by the Coulomb-correlated pair states $|S_e S_h\rangle$, $|P_{e+} P_{h-}\rangle$, $|P_{e-} P_{h+}\rangle$, ... and their one-phonon and two-phonon replicas. Within these replicas (which are three-dimensional flat continuums) we keep only those particular linear combinations that diagonalize the Fröhlich interaction. This procedure considerably reduces the dimension of the Hamiltonian matrix to be diagonalized. Hence, after diagonalization, generic excited (e, energy ε_e) and less excited (or ground) (g, energy ε_g) excitonic polaron wave functions are in the simpler case

$$|\psi_e\rangle = \alpha_e |n_e,0\rangle + \sum_{\boldsymbol{q}} \beta_e(\boldsymbol{q}) |m_e,1_{\boldsymbol{q}}\rangle + \sum_{\boldsymbol{q}} \sum_{\boldsymbol{q}'} \gamma_e(\boldsymbol{q},\boldsymbol{q}') |p_e,1_{\boldsymbol{q}},1_{\boldsymbol{q}'}\rangle, \quad (1)$$

$$|\psi_g\rangle = \alpha_g |n_g,0\rangle + \sum_{\boldsymbol{q}} \beta_g(\boldsymbol{q}) |m_g,1_{\boldsymbol{q}}\rangle + \sum_{\boldsymbol{q}} \sum_{\boldsymbol{q}'} \gamma_g(\boldsymbol{q},\boldsymbol{q}') |p_g,1_{\boldsymbol{q}},1_{\boldsymbol{q}'}\rangle, \quad (2)$$

where the n's, m's, and p's label Coulomb-correlated electron-hole pair states.

The anharmonic decay of the LO phonons is governed by a Hamiltonian that does not involve the electron and hole degrees of freedom. Hence, using Eqs. (1),(2), the relaxation rate $\Gamma_{e\to g}$ from $|\psi_e\rangle$ to $|\psi_g\rangle$ due to this mechanism is

$$\Gamma_{e\to g} = \frac{1}{\tau_{pho}} \left[\left| \alpha_g \langle m_e | n_g \rangle \right|^2 \sum_{\boldsymbol{q}} \left| \beta_e(\boldsymbol{q}) \right|^2 + \left| \langle p_e | m_g \rangle \right|^2 \sum_{\boldsymbol{q}} \left| \beta_g(\boldsymbol{q}) \right|^2 \sum_{\boldsymbol{q}'} \left| \gamma_e(\boldsymbol{q},\boldsymbol{q}') \right|^2 \right] \quad (3)$$

In the spirit of a semiclassical approach, $1/\tau_{pho}$ is taken equal to the decay rate of LO phonons in bulk materials. One further assumption is that the route of the anharmonic decay is the same in the dots as in bulk material (i.e., LO→LO + TA). This restriction on the possible decay of the LO phonon part of the X_{POL} imposes a restriction on the possible $\varepsilon_e - \varepsilon_g$, namely that $\varepsilon_e - \varepsilon_g$ should fall[8] in the energy window (≈ 27 meV, ≈ 45 meV). Once $\Gamma_{e\to g}$ is calculated the transition rate for the reverse transition $\Gamma_{g\to e}$ follows from the thermal equilibrium of the thermostat,

$$\Gamma_{g\to e} = \Gamma_{e\to g} \exp[-\beta(\varepsilon_e - \varepsilon_g)] \quad (4)$$

With the knowledge of all transition rates, the set of coupled population equations can be solved if completed by initial conditions (which depend on the particular experiment one wants to model). Ultimately, the luminescence signal of the ground X_{POL} is proportional to the population n_0 of this state.

Before describing the results of these simulations for a low temperature ($T = 10$ K), let us first discuss the part played by the coulombic interaction in the simulations. One could in fact wonder whether it would not be possible to understand the energy relaxation of electron-hole (e-h) pairs in dots by means of single-particle polaronic model(s) where the relaxation takes place via one particle polaron while the other particle is merely a spectator (i.e., its quantum number does not change during one elemental relaxation event). This is impossible for several reasons. First, even in the absence of Coulomb coupling, e-h pairs become indirectly coupled via the Fröhlich interaction, in spite of the fact that the Fröhlich interaction of a pair with the phonons is the sum of the electron interaction and of the hole interaction: these are the same phonons that interact with the electron and with the hole. Second, the coulombic effects are quantitatively far from being negligible. In fact, even if Coulomb effects are very well taken into account perturbatively in quantum dots, they nevertheless produce sizable shifts (20–30 meV) of the e-h pairs (which have Coulomb unperturbed energies of ≈ 20–70 meV above the ground state). Therefore, due to the existence of an energy window for the relaxation, it can (and will) happen that a relaxation $e\to g$ is energetically possible for an interacting e-h pair while it would be forbidden if the Coulomb shifts were neglected or, symmetrically, a process seemingly allowed when neglecting Coulomb effect could turn out to be forbidden when these effects are accounted for. Along the same line, note that the magnitude of the $\Gamma_{e\to g}$ depends on the α, β, γ's. The latter result from the diagonalization of the Hamiltonian matrix and are thus influenced by the energies of the correlated pairs (in particular, in the vicinity of a crossing between two Fröhlich uncoupled e-h pair states). Thus, while a naive expectaction would lead to infer that one of the particles (say the hole) is a spectator of the relaxation of the other (the electron) in an elemental relaxation process, it is in fact an active spectator: the relaxation of the electron takes place in the Coulomb field of the hole (direct interaction) and is influenced by the Fröhlich-mediated electron-hole interaction. It is therefore qualitatively and quantitatively inaccurate to depict the energy relaxation of a pair in a dot by neglecting the Coulomb effects.

Before going to the details, let us point out the general trends on whether or not an X_{POL} will efficiently relax. We have found that X_{POL} with energies located in the vicinity of $2\hbar\omega_{\mathrm{LO}}$ from the ground state relax very efficiently. This is because their wave function contains one-phonon replica of less excited states which themselves enter in a resonant polaron interaction with the one-phonon replica of the ground state. To give an example, a X_{POL} state containing $\{|P_{e+}P_{h-},0\rangle + |P_{e-}P_{h+},0\rangle\}$ is Fröhlich admixed to another X_{POL} state that contains $|S_eP_{h\pm},1_{\boldsymbol{q}}\rangle$ or $|P_{e\pm}S_h,1_{\boldsymbol{q}}\rangle$. A first polaron disintegration brings the system to an X_{POL} that contains $|S_eP_{h\pm},0\rangle$ or $|P_{e\pm}S_h,0\rangle$, which themselves are strongly admixed with $|S_eS_h,1_{\boldsymbol{q}}\rangle$. A second polaron disintegration relaxes the system to the X_{POL} ground state that is mostly $|S_eS_h,0\rangle$. This efficient relaxation scheme recalls the two-phonon replicas of the exciton ground state often seen in bulk materials. It is important to stress that the physical relaxation mechanism is very different since in this case the relaxation process involves the emission of four phonons (two LO and two TA) and the energy of the intermediate state is very different from $\varepsilon_0 + \hbar\omega_{\mathrm{LO}}$ where ε_0 is the energy of the ground X_{POL}. Another general trend of the relaxation in quantum dots is that the relaxation gets more and more difficult when going to less excited states. This is hardly surprising in view of the discrete nature of the X_{POL} dot states. The latter is less important at high energy because the number of levels increases and, to some extent, it is always possible to find a level to which the system can relax. The possible cause of inefficient relaxation has to be traced back to the energy location of the first few X_{POL} excited levels. It turns out that most of these levels are optically inactive (or almost), making it difficult to detect them. Finally, it should be stressed that the relaxation efficiency increases with temperature. An energy relaxation bottleneck at low temperature is circumvented at elevated temperature because the blocked X_{POL} has a possibility to explore higher-energy states and to find an efficient path for cooling down.

The first kind of experiments we model is the time-resolved photoluminescence from the ground X_{POL} state $I_{\mathrm{PL}}(t)$ at $T = 10$ K. The signal is proportional to the popula-

tion of the ground state but only the zero-phonon part contributes to this signal. The initial condition (source term) is a δ pulse that populates some particular excited X_{POL}. One has to include in the rate equations the radiative damping of each of the excited states. Since the excitonic polaron wave function contains parts with zero, one, and two phonons, they can give rise to luminescence with zero phonon or to replicas red shifted by $\hbar\omega_{\mathrm{LO}}$ or $2\hbar\omega_{\mathrm{LO}}$, where $\hbar\omega_{\mathrm{LO}}$ is the optical phonon energy. The radiative rate of a level $|\psi_e\rangle$ with $n=0$ emission of optical phonons is written as

$$\frac{1}{\tau_{e0}} = \frac{1}{\tau_0}\frac{|\langle\varnothing|n_e\rangle|^2}{|\langle S_e|S_h\rangle|^2}|\alpha_e|^2, \tag{5}$$

where we took $\tau_0 = 1\,\mathrm{ns}$ for the $S_e \rightarrow S_h$ transition. The same state $|\psi_e\rangle$ can also give rise to an emission shifted by $\hbar\omega_{\mathrm{LO}}$ or $2\hbar\omega_{\mathrm{LO}}$ from $|\psi_e\rangle$. The associated radiative frequencies are

$$\frac{1}{\tau_{e1}} = \frac{1}{\tau_0}\frac{|\langle\varnothing|m_e\rangle|^2}{|\langle S_e|S_h\rangle|^2}\sum_{\boldsymbol{q}}|\beta_e(\boldsymbol{q})|^2,$$

$$\frac{1}{\tau_{e2}} = \frac{1}{\tau_0}\frac{|\langle\varnothing|p_e\rangle|^2}{|\langle S_e|S_h\rangle|^2}\sum_{\boldsymbol{q},\boldsymbol{q}'}|\gamma_e(\boldsymbol{q},\boldsymbol{q}')|^2. \tag{6}$$

Note that the luminescence other than the ground state one can be viewed as an effective ''nonradiative'' decay channel. Hence, besides the luminescence rise time, the magnitude of the luminescence signal witnesses whether relaxation is or is not efficient in a particular dot.

Figure 1 shows the calculated $I_{\mathrm{PL}}(t)$ curves for several dot parameters (h/R is kept equal to 0.1 and R is varied). Figure 1 clearly shows the increasing difficulty of an excited X_{POL} to relax towards the ground state when its wave function contains less and less phonon component (see insert of Fig. 1), i.e., when the dot parameters are changed in such a way as moving away from an anticrossing. In fact, the luminescence rise time is smaller when the dot parameters are such that the two-phonon replica of the ground state is the nearer from the level that is excited at $t=0$. Note the overall good relaxation on the upper branch of the two-phonon anticrossing, as witnessed from the magnitude of the maximum reached by $I_{\mathrm{PL}}(t)$. For these dot parameters, the relaxation is at least as efficient as the recombination from the intermediate levels. Increasing the dot radius and following the lower branch of the two-phonon anticrossing [Fig. 1(b)], one finds a different physical situation. While the luminescence rise time does not become very long, $I_{\mathrm{PL}}(t)$ remains very small at all times. This behavior reflects a situation where the excited state, populated at $t=0$ empties more efficiently to an intermediate level which is not (or faintly) coupled to the ground state. Hence, a tiny fraction of the population reaches the ground state, but most of it contributes to the luminescence of this excited state. It is therefore lost for the ground-state luminescence. This situation corresponds to an energy relaxation bottleneck.

A cw photoluminescence excitation spectrum (PLE) consists of detecting the ground-state photoluminescence signal

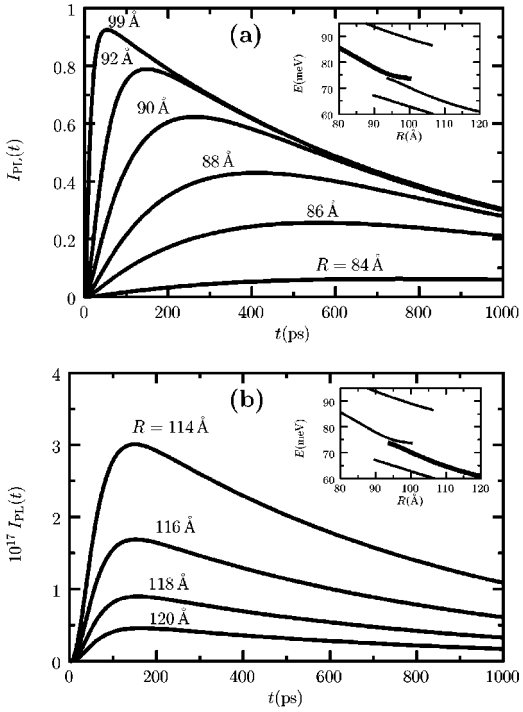

FIG. 1. Calculated $I_{\mathrm{PL}}(t)$ curves for varying dot parameters ($h/R=0.1$). The upper (lower) panel corresponds to dot parameters such that the energies of the photoexcited X_{POL} are on the upper (lower) branch of the two phonon anticrossing (thick lines on the inset). $T=10$ K. Note that the vertical scale in (b) has been strongly dilated.

when continuously exciting the dot at an increasing energy (e.g., by a dye laser). Hence, the PLE signal is a complicated convolution between the system's ability to absorb light and its relaxation capability to make an excited X_{POL} reaching the ground state. In quantum well structures, PLE very often mimics absorption while, in bulk materials, the presence of nonradiative decay channels reveals relaxation resonances, often associated with the irreversible emission of LO phonons, when a particular relaxation mechanism is able to bring an excited carrier to the band bottom, bypassing the other decay channels. Note that in bulk and quantum wells there is no possible radiative decay but at the band edges.

To calculate the PLE spectrum we compute the ground excitonic polaron population when varying the energy of the cw excitation. The creation rate of a given excited state $|\psi_e\rangle$ is proportional to the radiative rate $1/\tau_{e0}$. The radiative rate for each level is written as in the calculation of $I_{\mathrm{PL}}(t)$. Figure 2 shows a comparison between absorption and PLE spectra when varying the dot parameters. One sees a clear evidence of an energy relaxation bottleneck in large dots. While for $R<11\,\mathrm{nm}$, PLE spectra resemble absorption spectra (with more lines than predicted in the bare exciton model due to the presence of excitonic polarons), there exists a pronounced difference at larger R. An inefficient energy relaxation takes place in bigger dots because the lower-lying excited X_{POL} become too close in energy from the ground X_{POL} state (decreased size quantization). They consequently move out from the energy window where polarons can relax and very little of the excitation reaches the ground state.

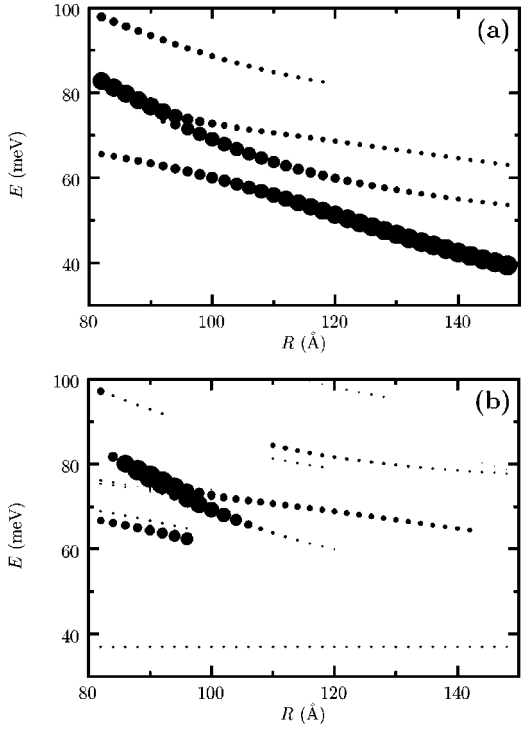

FIG. 2. Calculated absorption (upper panel) and PLE (lower panel) peaks versus dot parameters ($h/R=0.1$), the area of the dots is proportional to the magnitude of the absorption or PLE signal. $T=10$K.

Another indicator of the relaxation efficiency is the energy loss rate (E_{LR}) of an excitonic polaron. To compute its time evolution we take initial conditions identical to the $I_{\mathrm{PL}}(t)$ spectra and at each time we compute

$$\langle E\rangle=\sum_i \varepsilon_i n_i(t), \quad E_{\mathrm{LR}}(t)=\frac{-d\langle E\rangle}{dt}, \tag{7}$$

where n_i is the population of the ith X_{POL} level. $E_{\mathrm{LR}}(t)$ includes two contributions, the radiative one ($\approx\varepsilon_{\mathrm{gap}}/\tau_0$) and the one related to the X_{POL} relaxation. The latter varies widely, depending on whether the relaxation is fast or inefficient. Figure 3 shows the $E_{\mathrm{LR}}(t)$ curves when the dot parameters are changed, as in Fig. 1, to move on the upper

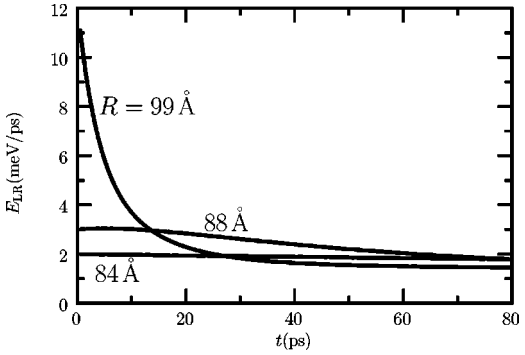

FIG. 3. Calculated $E_{\mathrm{LR}}(t)$ curves for several dot sizes. $T=10$ K.

branch of the two-phonon anticrossing. Again, one sees a larger E_{LR} at early time close from the anti-crossing while E_{LR} decreases when there is less and less admixture in the X_{POL} wave function with the one-phonon replicas of (predominantly dark) less excited states. At long time all E_{LR} reache the radiative value corresponding to the ground-state optical recombination. The magnitude of E_{LR} is interesting. Namely, it is of the same order of magnitude as found for holes at $T_{eff}\approx 100$ K in modulation-doped quantum wells (see, e.g., Ref. 16). Therefore, it appears that, while of radically different nature than that which prevails in bulk materials and heterostructures, the energy relaxation can be quite efficient in quantum dots. This is due to the small decay time of the optical phonons (36 meV/10 ps) which, in turn, induces an efficient relaxation channel for the X_{POL}. On the other hand, there exist situations where the relaxation, while fast at early stage, slows down when the system reaches the lower-lying excited polaron states. Such situations are found in the bigger dots where the polaron disintegration becomes energetically impossible.

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