Exciton thermalization in quantum-well structures

Massimo Gurioli, Anna Vinattieri, Juan Martinez-Pastor,* and Marcello Colocci
European Laboratory for Non Linear Spectroscopy and Department of Physics, University of Florence, Largo Enrico Fermi 2, 50125 Firenze, Italy
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We show that a unified picture, namely, thermalization within the inhomogeneously broadened exciton band, can be used to explain the excitonic photoluminescence (PL) spectra in quantum wells independently of the presence, or lack thereof, of the low-energy shift of the PL line with respect to the absorption peak (Stokes shift). The Stokes shift itself turns out to be a mere consequence of the thermal equilibrium with a quadratic dependence on the absorption linewidth and a linear dependence on the inverse of the excitonic temperature. The predictions are found to be in excellent agreement with careful measurements in GaAs/$Al_xGa_{1-x}As$ single-quantum-well structures.

I. INTRODUCTION

Excitons in low-dimensional semiconductor systems, in particular quantum-well (QW) structures, have attracted much interest in the past years due to their peculiar properties, which, making them different from bulk excitons, have permitted the realization of a new generation of electro-optic devices. The optical techniques, and in particular photoluminescence (PL),[1] are widely recognized as the most powerful tools not only for studying the intrinsic features of the confined excitons but also for characterizing the defect content and the sample quality.

So far two different approaches have been used for the analysis of the QW excitonic optical spectra, mainly depending on the presence, or lack thereof, of a redshift of the PL emission with respect to the fundamental absorption transition, usually referred to as the Stokes shift (SS). If the SS is negligible, a free-exciton picture is usually applied to the recombination kinetics in QW's. The exciton center-of-mass wave function is supposed to be delocalized over the whole QW plane and, as a consequence of the polariton effect, a very short lifetime is predicted[2-4] (often referred to as superradiance). The much longer PL decay times measured after nonresonant excitation[5-7] are then explained in terms of the thermalization between active and silent excitonic states, which gives rise to a temperature-dependent lifetime. On the contrary, the presence of a sizable SS is commonly assumed[8-11] as a direct proof of exciton trapping at interface defects, thus implying both localization of the exciton center-of-mass wave function and lack of thermalization. This picture has strong consequences on the whole recombination kinetics; in fact, apart from the trapping dynamics itself, the radiative lifetime is predicted[4] to increase by nearly one order of magnitude as a consequence of the reduction of the excitonic coherence length. We can therefore summarize the commonly accepted pictures as follows: the presence of a SS means exciton localization and lack of thermalization, while its absence is the signature of free excitons and, eventually, of a thermalized distribution.

In this paper we show that a unified picture, namely, thermalization within the inhomogeneously broadened exciton band, can be applied for explaining the whole phenomenology of the QW exciton optical spectra. We suppose that the recombining carriers, after momentum and energy relaxation, populate the excitonic states with a quasiequilibrium distribution described by an effective temperature T_C. Then, if the inhomogeneous broadening is small compared to the thermal energy KT_C, each exciton state has essentially the same thermal population: the PL reflects the absorption and the SS is not observable. On the contrary, if the excitonic linewidth exceeds the thermal energy, the low-energy side of the inhomogeneous exciton band is enhanced by the thermal population and a SS appears. On the basis of such a simple model we are able to find the general relationship between the SS, the photogenerated carrier temperature T_C, and the absorption linewidth Δ. In particular we predict that, for a given T_C, the SS is quadratic with Δ rather than linear, as recently claimed in Refs. 10 and 11.

We have performed a detailed study of the PL line shape in a set of good quality GaAs/$Al_{0.3}Ga_{0.7}As$ single-quantum-well (SQW) structures, with a Stokes shift ranging between 0 and 4.4 meV, by means of photoluminescence and photoluminescence excitation (PLE) measurements under low-power continuous-wave (cw) excitation. The thermalization of the photogenerated carriers is experimentally demonstrated, at all temperatures (1.8–120 K) and in all the QW's investigated independently of the SS values, by the presence in the PL spectra of free carrier and light-hole exciton recombinations. The equilibrium distribution, which necessarily follows the cw excitation, can then be described, with a very good approximation, by a thermal distribution. The resulting carrier temperature T_C is directly obtained from a fit of the PL free-carrier slope; we find that T_C is, in general, higher than the lattice temperature T_L. Only for resonant excitation at the heavy-hole (HH) exciton energy and/or high lattice temperatures does T_C correspond to T_L; in all other cases $T_C > T_L$. As a consequence, care has to be used when assuming that the low-temperature condition $KT_L \ll \Delta$ implies exciton trapping or when using the nominal lattice temperature T_L whenever comparing the

experimental data with theoretical predictions based on exciton thermalization. In fact the effective temperature T_C (not T_L) is the relevant parameter for describing the recombining exciton distribution.

We therefore correlate the value of the SS with the measured carrier temperature T_C. The experimental data are found to be in excellent agreement with the thermalization model for the SS origin in the whole range of investigated temperatures. Both the predicted temperature and linewidth dependence of the SS are nicely verified in all the QW's investigated. From our results it follows that the observed SS's can be unambiguously related to thermalization within the inhomogeneous distribution of the excitonic states, even when the measured SS and Δ largely exceed the lattice thermal energy KT_L.

The paper is organized as follows. Section II is devoted to the analysis of the consequences on the PL line shape of the thermal equilibrium hypothesis inside the inhomogeneous excitonic band; moreover the general relationship between the SS, the absorption linewidth, and the carrier temperature is derived. Details of the QW's investigated and the experimental setup are briefly reported in Sec. III. In Sec. IV we present and discuss the experimental results. The concluding remarks are given in Sec. V.

II. THEORY

Let us now discuss the effects of the thermalization hypothesis on the PL line shape of the SQW structure. If the photogenerated carriers are in thermal equilibrium at a temperature T_C, the PL spectrum will be essentially given by[12]

$$I_{\mathrm{PL}}(E)\approx\alpha(E)\exp\left\{-\frac{(E-E_0)}{KT_C}\right\}, \tag{1}$$

where the QW absorption spectrum $\alpha(E)$ is multiplied by the Boltzmann factor and the HH exciton transition energy E_0 is taken as a reference for the thermal distribution. Rewriting $\alpha(E)=\alpha_0(E)+\tilde{\alpha}(E)$, where $\alpha_0(E)$ and $\tilde{\alpha}(E)$ describe the absorption from the fundamental excitonic transition and from higher excited states, respectively, and assuming that $\alpha_0(E)$ has a Gaussian profile as a consequence of the QW inhomogeneities, Eq. (1) becomes

$$\begin{aligned} I_{\mathrm{PL}}(E)&\approx\alpha_0(E_0)\exp\left\{-\frac{(E-E_0)^2}{2\sigma^2}\right\}\exp\left\{-\frac{(E-E_0)}{KT_C}\right\}+\tilde{\alpha}(E)\exp\left\{-\frac{(E-E_0)}{KT_C}\right\} \\ &=\alpha_0(E_0)\exp\left\{-\frac{(E-E_0+\sigma^2/KT_C)^2}{2\sigma^2}+\frac{\sigma^2}{2(KT_C)^2}\right\}+\tilde{\alpha}(E)\exp\left\{-\frac{(E-E_0)}{KT_C}\right\}. \end{aligned} \tag{2}$$

The dominant contribution to the PL spectrum is therefore a Gaussian band with exactly the same linewidth as the absorption, but peaked at the energy $E_0'=E_0-\sigma^2/KT_C$. From the hypothesis of thermal equilibrium, which seems very reasonable under cw excitation, and the assumption of a Gaussian excitonic band, the Stokes shift $S=E_0-E_0'$ between the absorption and the PL lines is

$$S=\frac{\sigma^2}{KT_C}\cong 0.18\frac{\Delta^2}{KT_C}, \tag{3}$$

where $\Delta=2\sqrt{2\ln 2}\sigma$ is the full width at half maximum (FWHM) of the Gaussian absorption line.

Note that, assuming a Gaussian line shape, the only effect of the thermalization inside the HH inhomogeneous band is the SS; neither the validity of the thermal equilibrium hypothesis nor the value of the carrier temperature T_C can be determined by the PL line shape analysis of the HH exciton band. However, this information is contained in the recombination from the higher excited states [described in Eq. (2) by the term proportional to $\tilde{\alpha}$] and can be extracted from the PL data if a high dynamic range is allowed by the experimental apparatus. We would also like to remark that, in the framework of the exciton trapping model for the SS origin,[10,11] the higher excited states are supposed to be empty; therefore the presence, or lack thereof, of PL emission from free carriers and/or light-hole excitons can be used as a test for discriminating between the trapping or the thermalization model.

It could be questioned whether a Gaussian profile is a realistic assumption for describing the HH absorption spectrum in QW's;[13] in fact different line shapes have been proposed recently. Due to the inhomogeneities arising from interface roughness, an asymmetric profile for the exciton absorption in QW's, with a Gaussian low-energy shape and an exponential high-energy tail, has been reported;[14,15] on the contrary, a standard Gauss-Lorentz profile has been used recently for the PL lineshape analysis.[12]

In any case, assuming an arbitrary line shape $\alpha_0[(E-E_0)/\Delta]$ for the HH exciton band, the Stokes shift will be determined by imposing equal to zero, for $E_0'=E_0-S$, the first derivative of $I_{\mathrm{PL}}(E)$, that is,

$$\frac{1}{\Delta}\alpha_0'\left[-\frac{S}{\Delta}\right]-\frac{1}{KT_C}\alpha_0\left[-\frac{S}{\Delta}\right]=0, \tag{4}$$

where $\alpha_0'(x)$ stands for the first derivative of $\alpha_0(x)$. Defining $G(x)$ as the logarithmic derivative of $\alpha_0(x)$ [i.e., $G(x)=\alpha_0'(x)/\alpha_0(x)$] one has, for the Stokes shift, the expression

$$S=-\Delta G^{-1}\left[\frac{\Delta}{KT_C}\right], \tag{5}$$

which, for Δ smaller than KT_C, becomes

$$S \cong \frac{\Delta^2}{KT_C} \frac{\alpha_0(0)}{\alpha_0''(0)} , \tag{6}$$

with α_0'' the second derivative of α_0. Therefore, even if Eq. (3) is indeed correct only for a Gaussian line shape, it is found that, at least for $\Delta < KT_C$ and apart from the numerical constant 0.18, the predicted dependences of the SS on both the temperature and the linewidth are valid independently of the exact absorption line shape. As an example, if $\alpha_0(x)$ were a hyperbolic secant, in the limit $\Delta \leq KT_C$, one would get for the Stokes shift $S \cong 0.14\Delta^2/KT_C$.

It is also worth stressing that Eq. (4) shows, as expected, that only the low-energy absorption profile determines the value of the Stokes shift at a given temperature. Even if the absorption line shape were asymmetric with a Gaussian shape only on the low-energy side, as predicted in Refs. 14 and 15, Eq. (3) would be still correct for any value of Δ/KT_C. At the same time Eq. (1) requires that the absorption low-energy tail has to vanish faster than exponentially; otherwise an infrared divergence of the PL spectrum would occur. In other words, a Gaussian-like low-energy profile of α_0 seems to be needed, thus strengthening the general validity of Eq. (3).

On the other hand, Eq. (3) predicts a divergence of the SS for vanishing T_C. The relaxation of the thermalization hypothesis for $T_C \rightarrow 0$ has been invoked in Ref. 15 for avoiding similar unphysical results. We believe instead that the divergence of the SS is mainly due to the unphysical assumption of an infinite distribution of the excitonic states [with energies even smaller (larger) than the exciton transition in the well (barrier) bulk material], while a cutoff is certainly needed for a better approximation to real samples. Even more relevant is the experimental finding, reported in Refs. 14 and 16 and observed in all the samples that we have investigated (see Sec. IV), that T_C is generally larger than the lattice temperature T_L, saturating to a finite value for decreasing T_L ($T_C \approx 20$ K for $T_L = 1.8$ K) and thus removing the SS divergence.

As far as the effects of the thermalization on the PL line shape for non-Gaussian broadening are concerned, it is easy to understand that a T_C-dependent high-energy profile will become apparent as soon as the HH exciton absorption spectrum decays slower than the Boltzmann factor. However, the slope of the excitonic PL high-energy tail, which also reflects the α_0 profile, cannot be directly used for estimating the effective carrier temperature and a PL line shape fit has to be used. On the other hand, T_C can be measured with better precision from the high excited-state recombination.

Concluding this section, a few remarks on previous theories for the SS's origin are certainly needed. The first model proposed interprets the Stokes shift in terms of exciton localization at interface defects,[8,9] assuming the value of the SS as a direct measure of the exciton binding energy at the trap. Moreover no general relationship between the SS and Δ is predicted, even if the two quantities originate by the same physical origin (i.e, the interface roughness). The SS is then supposed to decrease when the temperature is increased as a consequence of the thermally activated detrapping of the excitons.[9] The exact temperature variation of the SS therefore depends on the defect density,[9] and in general this gives rise to a nonlinear $1/T_C$ dependence of the SS. Furthermore, because of the presence of two PL peaks (free and localized excitons) with temperature-dependent amplitudes, the PL line shape, and in particular Δ, should also strongly depend on T_C.

Recently a topographical theory of the exciton optical spectra has been proposed, trying to demonstrate a universal relationship between the SS and the exciton absorption linewidth.[10,11] The photoluminescence is supposed to reflect the distribution of local minima (i.e., lateral regions of the QW thicker than all the neighboring ones) of the inhomogeneous distribution of the exciton states, under the main assumption that the photogenerated carriers are trapped at each minimum independently of its depth. This means a lack of thermalization of the recombining carriers and the low-temperature regime $KT_L \ll \Delta$ has been invoked[11] as a sufficient condition for its validity. Within this framework and assuming a Gaussian absorption spectrum, it has been shown[10,11] that the SS is linear with Δ with a coefficient of proportionality equal to 0.553, in agreement with a set of experimental data where a slope of 0.6 is found. Obviously this model does not consider the dependence of the SS on the temperature because its basic assumption is that the excitons are not in thermal equilibrium.

Both these models assume that the SS reflects a trapping of the exciton at local defects of the QW structure and conversely that the absence of a measurable SS is a signature of free-exciton recombination. On the contrary, our model shows that the presence, or lack thereof, of the SS only depends on the relative magnitude of Δ and KT_C. Finally predictions similar to ours for the SS origin have been reported very recently in Refs. 12 and 15. Nevertheless it was claimed in Ref. 15, following Yang and co-workers,[10,11] that Eq. (3) is incorrect since the thermal equilibrium was supposed to be ineffective at very low temperatures; in Ref. 12, instead, no general relationship between the SS, Δ, and T_C was predicted.

III. EXPERIMENT

We have investigated several nominally undoped, $GaAs/Al_{0.3}Ga_{0.7}As$ SQW's belonging to different structures grown by molecular-beam epitaxy on undoped substrates at a temperature of the order of 600 °C. The nominal well widths are 40, 50, 60, 70, 120, and 180 Å; the QW's are separated by thick barriers (200–300 Å) in order to decouple the carrier wave functions. The PL and PLE measurements have been performed using a cw Ar^+ pumped Ti:sapphire laser as the excitation source; the excitation power used in all the measurements presented here was between 0.1 and 1 W/cm^2 (corresponding to a carrier density of about 10^7–10^8 cm^{-2}), except where different values are explicitly reported. The wavelength was tuned in and out of resonance with the fundamental excitonic transition, but always below the $Al_{0.3}Ga_{0.7}As$ barrier absorption edge. In the case of resonant excita-

tion, a nearly 90° scattering geometry was chosen with the incoming light at grazing incidence and the PL detection normal to the sample surface. This choice reduces the intensity of the Rayleigh scattering (RS) signal, which is mainly peaked in the direction of the reflected beam. However, due to the large index of refraction, this setup corresponds to a nearly backscattering geometry inside the crystal. The laser tuning was computer controlled; the accuracy of the excitation energy calibration was of the order of 0.2 meV. The PL signal was dispersed through a 60-cm double-grating monochromator (spectral resolution of 0.2 meV) and detected by standard photon counting techniques. The samples were mounted in a cryostat allowing to vary the temperature in the range 1.8–300 K.

IV. RESULTS AND DISCUSSION

We report our results discussing the experimental data in two separate sections. We report in Sec. IV A data referring to QW's without a SS and in Sec. IV B data from QW's where a measurable SS is observed; in fact it is common to consider these two sets of structures to be qualitatively different. Section IV C is devoted to a general discussion of the whole ensemble of data presented, showing that the apparently distinct phenomenologies are instead only different aspects of the same general picture.

A. QW's without SS

In this section we present the experimental data referring to two SQW structures of 120 and 180 Å, showing no measurable SS at very low lattice temperatures T_L. Actually, since the two samples show very similar behaviors, we will essentially refer to the 180-Å QW. The half width at half maximum (HWHM) of the PL and PLE lines turns out to be, at 1.8 K, as small as 0.22 and 0.28 meV for the 180- and 120-Å QW's, respectively, that is, two of the smallest values ever reported in the literature. These values are indeed comparable with the homogeneous linewidth of the exciton transition in QW's and it can be therefore questioned whether the discussion reported in Sec. III can be applied.

According to Hegarty *et al.*,[17] a sharp discrimination between homogeneous and inhomogeneous broadening can be obtained by measuring the enhancement of the RS at the HH resonance, which has been shown to be effective only for inhomogeneous lines. We report in Fig. 1 the PL spectrum of the 180-Å QW obtained by scanning the cw excitation energy around the HH exciton transition at 1.8 K. The hatched peaks represent the contribution from RS, as easily recognized from the line shape which reflects, as expected, the instrumental resolution. Very small contributions from RS are found outside the resonance region, due to a careful cleaning of the sample surface and alignment of the optical setup. On the other hand, a dramatic enhancement of the RS intensity is observed when the excitation approaches the HH exciton resonance. A huge signal from resonant Rayleigh scattering (RRS) requires the presence of some kind of disorder giving rise to an inhomogeneous broadening of the transition.[17,18] The intensities of the RRS (dots) and PL (squares) signals as a function of the excitation energy are reported in Fig. 2. The two curves show similar behaviors, both reflecting the absorption spectrum, apart from a small redshift of the RRS compared to the PLE curve ascribed in Ref. 17 to the dispersion of the homogeneous linewidth within the absorption profile. More important is the strong enhancement of the RS with respect to the PL, which makes the RS signal dominate the optical spectra as soon as the excitation energy is nearly resonant with the fundamental exciton transition.

At the same time, we find a strong dependence of the RRS on the lattice temperature, as shown in the inset of Fig. 2, where the peak values of the RRS and PL intensities are reported as a function of T_L. A strong decrease of the RRS is found when T_L is increased from 1.8 to 20 K, while the integrated PL intensity remains approxi-

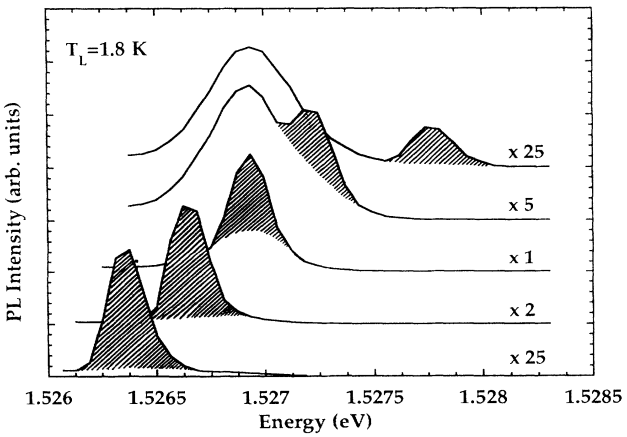

FIG. 1. PL spectra of the 180-Å QW at $T_L = 1.8$ K for different excitation energies showing a resonant enhancement of the RS (hatched areas) when the excitation is tuned across the HH exciton band. The relative scale factors of the PL spectra are also given in the figure.

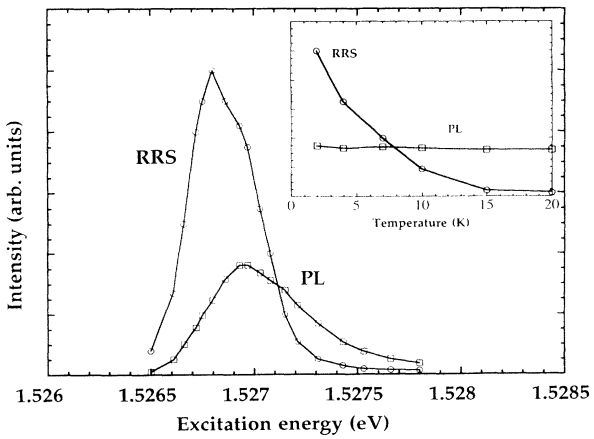

FIG. 2. Intensities of RRS (dots) and PL (squares) as a function of the excitation energy in the case of the 180-Å QW; the lines are only guides for the eye. In the inset the temperature dependence of the RRS and PL signals is reported.

mately constant in the same temperature interval. The RRS dominates the optical spectrum at the lowest temperatures while it is almost completely washed out at 10–20 K. As a consequence we can perform resonant excitation of the PL only for $T_L \geq 4$ K. A detailed analysis of the temperature dependence of the RRS, which contains very useful information on the exciton dephasing mechanisms, is outside the scope of this paper. Here we would only like to stress the inhomogeneous nature of the PL bands despite their extremely small HWHM's.

Nevertheless we should probably mention a very important implication of our findings upon a "hot" topic in the field of exciton recombination in QW's. Time-resolved PL experiments have shown recently that a very fast initial decay is observed when a resonant excitation at the HH exciton is used, but different interpretations have been proposed. On one hand, it has been argued in Refs. 19 and 20 that the cold photogenerated excitons recombine before thermalizing even if the occurrence of many processes upon comparable time scales complicates the analysis of the experimental results.[20] On the other hand, resonant Rayleigh scattering, which decays with the dephasing time, has been assumed in Ref. 18 as the main contribution responsible for the initial decay. One of the main differences between the two experiments is the lattice temperature, namely, $T_L = 1.8$ K in Ref. 18, while T_L was in the range 12–40 K in Ref. 20. We believe that the strong thermal quenching of the RRS we have reported here is very likely the principal origin of the apparent disagreement between the two assignments.

Let us now analyze in more detail the PL line shape. We report in Fig. 3 a semilogarithmic plot of the PL spectra of the 180-Å QW at two different lattice temperatures T_L, under both resonant (full lines) and nonresonant (dashed lines) excitations. Two features clearly emerge from these spectra. First of all, in spite of the low lattice temperature, recombination from both free carriers and light-hole (LH) excitons is observed, in addition to the main HH exciton peak, showing that the recombining carriers also populate the higher excited levels. As discussed in Sec. II this is a signature of thermalization among the different states. Second, at low T_L, the thermal distribution of the photoexcited carriers is very different, depending on the excitation energy E_{exc}. In fact, as shown in Fig. 3(a), an increase of 9 meV on E_{exc} produces a drastic increase of the population of both free carriers and LH excitons.

One can directly measure the carrier temperature T_C from the slope of the high-energy tail of the free-carrier spectrum and/or from the ratio of the heavy-hole to light-hole exciton peaks, if compared with the PLE spectrum. We find that, at low lattice temperatures and nonresonant excitation, T_C comes out higher than T_L, denoting an inefficient cooling of the photogenerated carriers, in agreement with previous investigations.[14,16] On the other hand, T_C approaches T_L when the lattice temperature is increased and finally $T_C \approx T_L$ for $T_L \geq 40$–50 K, as shown in Fig. 3(b); only for resonant excitation at the HH exciton energy does $T_C \approx T_L$ even at the lowest lattice temperatures.

A very convincing proof of the validity of the thermalization assumption is provided by comparing the PL spectra divided by the Boltzmann factor $\exp(-E/KT_C)$, with $T_C = T_L$ in the resonant case and T_C given by the population of the higher states for nonresonant excitation. An example for $T_L = 7$ K is given in Fig. 4; the mutual agreement is indeed very good. It should also be noted that the spectra in Fig. 4(b) very nicely agree with the experimental PLE spectrum, not reported in the figure to avoid confusion.

Our results also show that T_C does not depend on the excitation power P_{exc} as far as the low excitation regime is concerned. However, the physics dramatically changes when P_{exc} exceeds a few tens of W/cm^2, as shown in Fig. 5 for resonant excitation. Above this excitation intensity

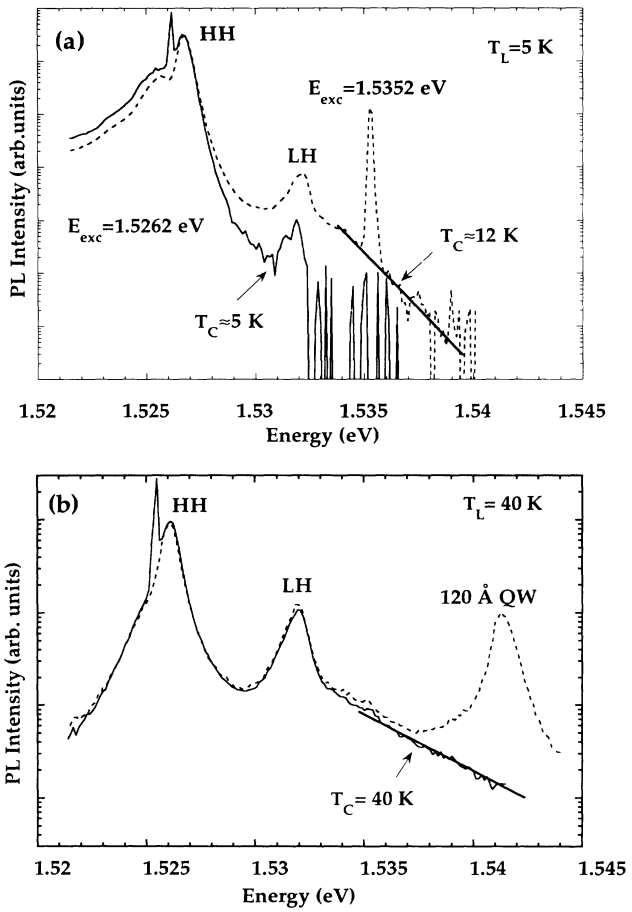

FIG. 3. Semilogarithmic plots of the PL spectra under resonant (full line) and nonresonant excitation (dashed line) of the 180-Å QW. The sharp peaks in the spectra correspond to the RS signals and mark the value of E_{exc}. The straight lines represent the best fit to the slope of the free carriers emission, from which we estimate the value of T_C. (a) $T_L = 5$ K and $E_{\text{exc}} = 1.5262$ and 1.5352 eV for resonant and nonresonant excitation, respectively. For $E_{\text{exc}} = 1.5262$, T_C has been estimated from the ratio of the HH and the LH recombination intensity. (b) $T_L = 40$ K and $E_{\text{exc}} = 1.5255$ and 1.7 eV for resonant and nonresonant excitation, respectively. Note that for $E_{\text{exc}} = 1.7$ eV the recombination from the 120-Å QW is also present. The excitation intensity is 0.5 W/cm^2.

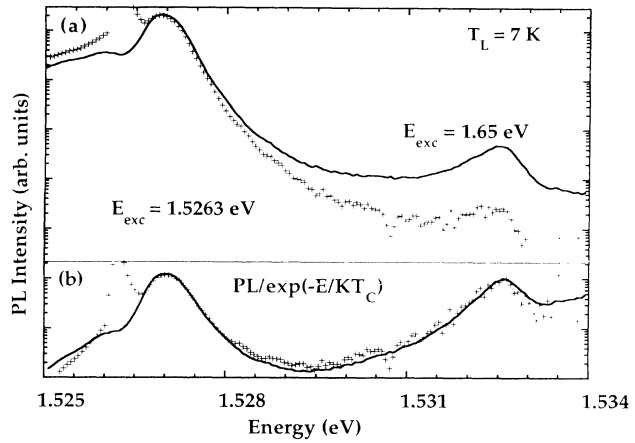

FIG. 4. Semilogarithmic plots of the PL spectra, under resonant (crosses) and nonresonant excitation (solid line) of the 180-Å QW at $T_L=7$ K. (a) Experimental spectra. (b) PL spectra after division by the thermal factor $\exp[-(E-E_0)/KT_C]$. For the resonant excitation case we have found $T_C=T_L=7$ K. For the nonresonant case $T_C=12$ K has been obtained from the slope of the free carriers emission, as in Fig. 3(b); as shown in the figure, good agreement between the two spectra is obtained after division by the Boltzmann factor. The excitation intensity is 0.5 W/cm^2.

we find both a relevant heating of the excitons and a broadening of the PL line shape.

B. QW's with SS

Here we consider the results from the QW's with thicknesses ranging between 40 and 70 Å, showing a SS in the range of 0.8–4.4 meV at low T_L; the HWHM's of the PLE excitonic lines are in the range 1.4–3.7 meV, clearly denoting an inhomogeneous broadening. Let us illustrate the phenomenology observed by considering the 40-Å QW; the other structures show very similar behaviors. The comparison, at $T_L=1.8$ K, between the nonresonant PL (solid line) and the PLE (dashed line) spectra is reported in Fig. 6. The continuum edge and

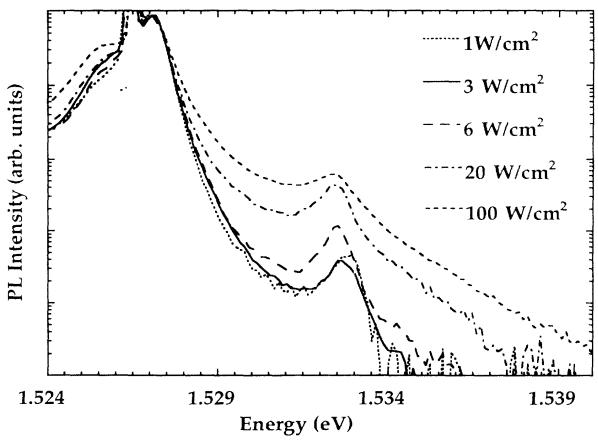

FIG. 5. PL spectra of the 180-Å QW as a function of the excitation intensity for resonant excitation at $T_L=10$ K.

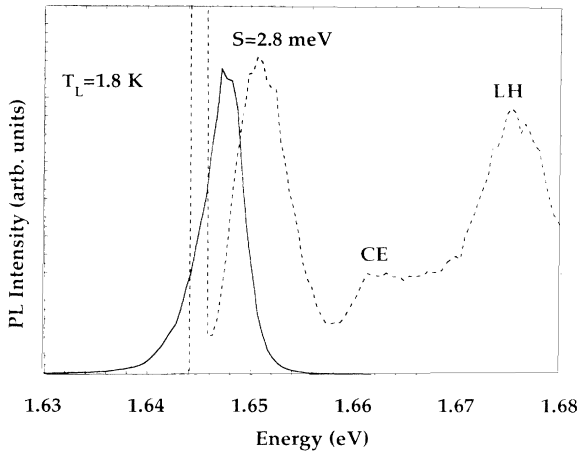

FIG. 6. Comparison between the PL (full line) and PLE (dashed line) spectra for the 40-Å QW at $T_L=1.8$ K. We find a SS of 2.8 meV. Note that the continuum edge (CE) and the light-hole (LH) exciton recombination are resolved in the PLE spectrum.

the light-hole exciton are clearly resolved in the PLE spectrum and indicated in the figure. The measured SS is $S=2.8$ meV while the absorption linewidth is $\Delta=6$ meV; therefore the low-temperature conditions $KT_L \ll S$ and Δ are largely verified. Following common belief and the picture of Refs. 10 and 11 one should conclude that the PL reflects exciton trapping and a lack of thermalization. Note also that the ratio $S/\Delta=0.47$ is in fair agreement with the prediction of Refs. 10 and 11.

Nevertheless we now demonstrate that the trapping model cannot be applied. The semilogarithmic plot of nonresonant PL spectra at four different lattice temperatures is reported in Fig. 7, where for the sake of simplicity the different curves have been shifted so that the PL maxima occur at the same energy. Besides the main peak both the free carriers and light-hole exciton emissions are resolved in the PL spectra, as shown by the comparison with the PLE spectrum reported in Fig. 6. The presence of recombination from high excited levels is, as discussed previously, in contrast with the exciton trapping model and denotes a thermal distribution of the photogenerated carriers among different states.

The slope of the high-energy tail of the free-carrier emission spectrum (together with the ratio of the heavy-hole to light-hole exciton peaks) directly provides the carrier temperature T_C. The straight lines in Fig. 7(a) are the best fits to the experimental data; the values obtained are given in the caption and the estimated accuracy is of the order of 10%. In analogy with the results of Sec. IV A, we find that, at low lattice temperatures, T_C turns out to be higher than T_L. It should be stressed that in our experiments the photogenerated carrier density ($\sim 10^8$ cm^{-2}) is comparable or even smaller than the usual values in cw measurements; heating of the lattice does not certainly occur, as the resonant PL with similar P_{exc} in the 120- and 180-Å QW's demonstrated [see Figs. 3(a) and 4]. Moreover we find that T_C does not change when the excitation power is decreased by a factor 10. At the same time, in QW's with a sizeable SS the resonant exci-

tation with zero excess of energy for photogenerated carrier, which as shown before for QW's without SS ensures $T_C = T_L$ even at the lowest T_L, is complicated by the fact that the PL peak lies on the low-energy side of the absorption spectrum. Resonant excitation on the low-energy side of the PL produces a very weak PL intensity and the RRS completely dominates the measured spectrum.

In order to emphasize the validity of the thermal equilibrium hypothesis, we report in Fig. 7(b) the same spectra of Fig. 7(a) divided by the Boltzmann factor $\exp\{-E/KT_C\}$; the curves are shifted to facilitate the comparison. The mutual agreement of the four plots is rather good, even if the contribution from the higher excited states seems to be somehow higher at low T_L. However, one has to consider the large amplification of the experimental data when normalizing for the thermal population. For example, in the case of curve (4), referring to $T_L = 1.8$ K and $T_C = 21$ K, the amplification of the free-carrier recombination with respect to the low-energy side of the HH exciton is of the order of 10^{10}; in fact the 10% indetermination on T_C has a big effect on the high-energy side of the spectra. At the same time, we find that the relative contribution of the free carriers and LH excitons, with respect to the HH excitons, is higher the lower is the lattice temperature, also in the PLE spectra.

The plots reported in Fig. 7(b), as stated by Eq. (1), should reflect the QW absorption: indeed, they agree rather well with the measured PLE spectra. This also suggests the possibility of measuring the absorption spectrum of the QW's by simply performing accurate PL measurements (i.e., with a high dynamic range). It turns out, for instance, that an estimate of the excitonic binding energy from the onset of the free-carrier spectrum[21] can be obtained from PL experiments instead of using the commonly adopted techniques (PLE, reflection, transmission on a substrate etched sample, etc.), which require tunable sources.

The measured Stokes shifts at various temperatures are reported in Fig. 8 as a function of $1/KT_C$, with T_C measured from the slope of the free-carrier recombination, as shown in Fig. 7; the error bars correspond to an uncertainty of 0.3 meV on the SS's and 10% on T_C. The data reported in Fig. 8 refer to nonresonant excitation (≈ 50

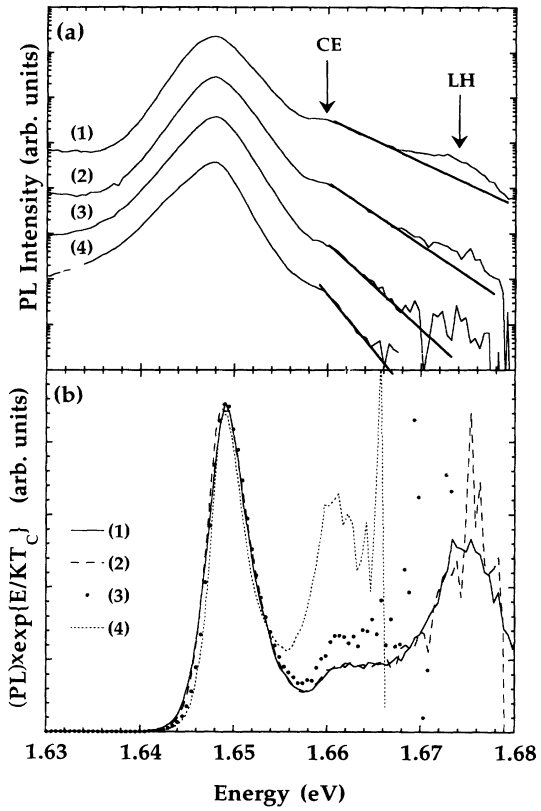

FIG. 7. PL spectra of the 40-Å QW at four different lattice temperatures: curve (1), $T_L = 50$ K and $T_C = 52$ K; curve (2), $T_L = 30$ K and $T_C = 38$ K; curve (3), $T_L = 10$ K and $T_C = 26$ K; curve (4), $T_L = 1.8$ K and $T_C = 21$ K. (a) Semilogarithmic plot for evidencing the recombination from the high excited states: the arrows indicate the energy positions of the continuum edge and of the light-hole excitation, respectively, as measured by the PLE spectrum (Fig. 6). The straight lines are fits for estimating the carrier temperature T_C. (b) The same PL spectra as in (a) divided by the Boltzmann factor $\exp\{-E/KT_C\}$.

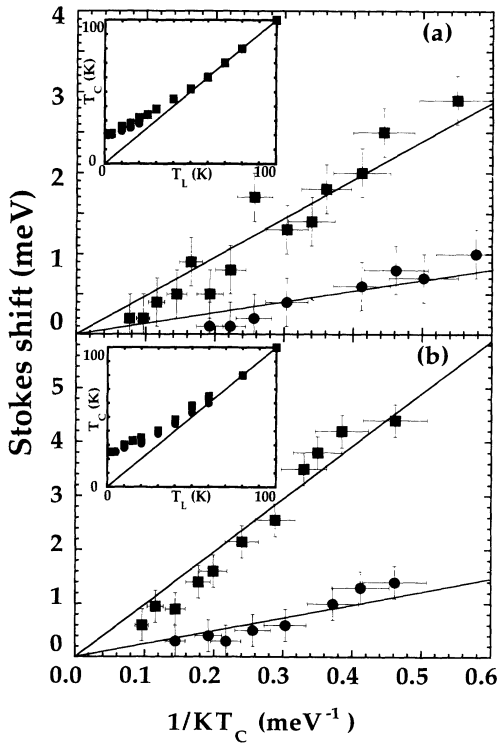

FIG. 8. Measured Stokes shift as a function of $1/KT_C$ for nonresonant excitation (≈ 50 meV above the HH transition). (a) Squares and dots refer to the 40- and 60-Å QW's, respectively; (b) squares and dots refer to the 50- and 70-Å QW's, respectively. The error bars correspond to an uncertainty of 0.3 meV on the SS and of 10% on T_C. The straight lines are the best fits to the experimental data assuming $S = \beta^2/KT_C$. In the insets we report the dependence of T_C on T_L; note the saturation toward a nearly constant value around $T_C = 20$ K, in all cases, when decreasing T_L.

meV above the HH transition) and the dependence of T_C on T_L is shown in the insets where the straight lines are $T_C = T_L$. At low T_L the carrier temperature T_C seems to saturate at a constant value independently of T_L; decreasing T_L below 4 K, no significant change of T_C occurs. On the contrary, T_C approaches T_L when increasing the lattice temperature, typically for $T_L \geq 50-60$ K.

The linear dependence of S on $1/KT_C$, predicted by Eq. (3), is clearly demonstrated for all the QW's investigated. Note that, as stressed in Sec. II, the assumption of thermal detrapping of excitons from the interface defects, suggested in Ref. 9, gives rise to a nonlinear $1/T_C$ dependence of the SS. At the same time, in the framework of the detrapping model, a strong variation in the PL line shape of the HH recombination is expected with the appearance, for a given range of T_L, of two different lines (free and localized excitons), contrary to our experimental findings (see, for instance, Fig. 7). The straight lines in Fig. 8 represent the best fit $S = \beta^2/KT_C$ to the experimental data, and the fitting parameter β, reported in Table I, turns out to be, as predicted by Eq. (3), in good agreement with the standard deviation σ obtained from a Gaussian fit of the PLE excitonic lines. Actually the experimental line shapes are not Gaussian; in particular we find that the HH exciton peaks are asymmetric with a more prominent high-energy tail.[21] This feature is in qualitative agreement with the predictions reported in Refs. 14 and 15, where a Gaussian low-energy tail and an exponential high-energy profile are expected as a consequence of the interface roughness. We have shown in Sec. II that Eq. (3) is valid even if only the low-energy side of the absorption is Gaussian-like and this explains the agreement between β and σ. We also want to emphasize that the agreement concerns values of the SS's, at low T_L, ranging between 4.4 and 0.8 meV and an interval of lattice temperatures T_L from 1.8 to 120 K.

Finally we report in Fig. 9 the dependence of the SS on σ^2, at $T_C \approx 30$ K (which corresponds to different values of T_L for different QW's) together with the linear behavior given by Eq. (3) and the square-root prediction of Refs. 10 and 11. Again, the agreement of the experimental data with Eq. (3) is very good and the quadratic dependence of the SS on the absorption linewidth is clearly proved.

C. General discussion

As previously remarked, it is widely believed that the recombination dynamics in QW structures with and without the SS are qualitatively different: the SS is usually supposed to manifest the exciton localization at a given defect with a lack of thermalization, while a zero SS is associated with thermally distributed free excitons. We believe that the data presented in Secs. IV A and IV B show, on the contrary, a strong analogy between the two kinds of situations. In both cases (QW with and without the SS) the same physics applies, namely, thermalization of the photogenerated carriers inside the inhomogeneous exciton band. Therefore the presence of a sizeable SS only depends on a quantitative difference connected both to the degree of disorder in the QW layers and to the QW thickness; a similar disorder induces a larger inhomogeneous broadening the thinner the QW. As an example, for both the 120- and 180-Å QW's investigated the SS's estimated from Eq. (3) for $T_C = 4$ K are smaller than 0.05 meV, that is, smaller than our instrumental resolution. The SS remains, therefore, a probe of the sample quality; the general relationship with the other standard quality test Δ is established by Eq. (3), but a measurable SS does not necessarily imply exciton trapping, as claimed in the previous models for the origin of the SS. In particular, the value of the SS does not simply correspond either to the exciton binding energy at the defects[8,9] or to simple geometrical properties of the well;[10,11] it also reflects the dynamical behavior of the photogenerated carriers.

Obviously inside the inhomogeneous band there are states which correspond to localized exciton wave functions. As shown in Refs. 10 and 11, assuming a Gaussian broadening, the distribution of localized states is still a Gaussian function, shifted by $0.6^*\Delta$ on the red side of the absorption line. This means that the localized states are distributed along the whole absorption profile, even in the high-energy side, but they essentially dominate the low-energy tail of the inhomogeneous exciton band. One could also introduce the concept of mobility edge as the energy where the densities of localized and delocalized states are equal. Therefore, even in the thermalization picture, if $KT_C < \Delta$ (note that T_C, and not T_L, is the relevant parameter), excitons mainly populate states below the mobility edge and then the PL essentially arises

TABLE I. Comparison between the parameter β obtained from fitting the linear dependence of the SS on $1/KT_C$ and the standard deviation σ given by a Gaussian fit of the PLE spectra. The two values coincide within the errors, in agreement with the predictions of Eq. (3).

QW (Å)	β (meV)	σ (meV)
40	2.2±0.1	2.3±0.2
50	3.1±0.1	3.2±0.2
60	1.2±0.2	1.2±0.2
70	1.6±0.2	1.6±0.2

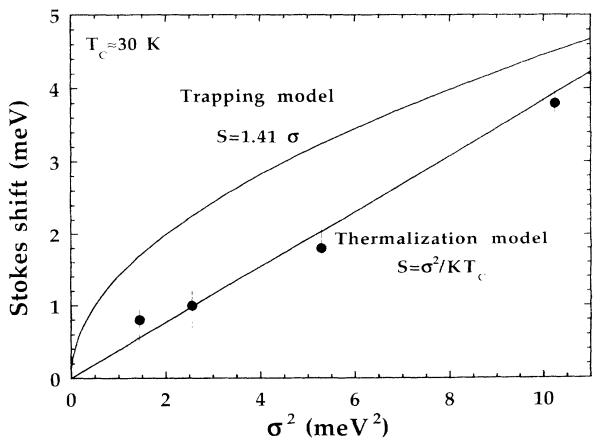

FIG. 9. Measured Stokes shifts at $T_C = 30$ K as a function of the standard deviation σ obtained from a Gaussian fit of the PLE excitonic lines. The straight line demonstrates the quadratic dependence of the SS on σ.

from localized excitons and shows a large SS. On the contrary, in the opposite regime ($KT_C > \Delta$), the PL is mainly due to recombination of delocalized excitons and the SS turns out to be small.

Therefore, even within our model, it is partially true that a large (small) SS is a signature of recombination from localized (free) excitons, as commonly believed, while it is completely wrong to assume a lack of thermalization as a consequence of the presence of a SS. Moreover, at each temperature, the thermalization assumption requires the coexistence of both kinds of excitons and this has strong consequences on the recombination properties. One of them is the general relationship of the SS on Δ and KT_C discussed in this paper, which is very different from the one derived from the trapping model. A second important consequence is expected in the recombination kinetics leading to the increase of the excitonic radiative lifetime and the smoothing of its temperature dependence on temperature. This has been calculated in Ref. 4 considering only one discrete localized level; the predictions seem to be in agreement with the experimental findings.[22] Obviously further effort is needed to completely elucidate this point.

It is probably worth comparing now our results with the findings of Refs. 10 and 11. There a linear dependence of the SS on the absorption linewidth was derived assuming a nonthermal exciton distribution (i.e., exciton trapping at each local minima). The agreement with the experimental data was rather good, especially for ZnSe QW's where the SS's and FWHM's were in the range 20–100 meV.[10,11] We believe that in structures with large SS's the local minima are very deep and therefore the hypothesis of trapping is probably a better approximation than thermal equilibrium. However, we have shown that the validity of exciton trapping rather than thermalization (and vice versa) is experimentally testable and therefore it should be demonstrated case by case, as we have done for the QW's investigated. Moreover, the geometrical model[10,11] neither considers the well-known temperature dependence of the SS nor can be applied when the SS is comparable with the thermal energy KT_C; in fact T_C, and not T_L, is the relevant parameter. Since for nonresonant excitation and low T_L the carrier temperature T_C can be much higher than T_L, it is rather difficult to assess *a priori* the validity of a nonthermal rather than a thermal model. Indeed we have shown that even SS's much larger than the lattice thermal energy KT_L are eventually due to thermalization inside the inhomogeneous excitonic band.

Let us go back to the difference between T_C and T_L. We find that in the case of nonresonant excitation T_C turns out to be larger than T_L for $T_L \leq 40$–60 K, depending on the QW, while $T_C = T_L$ at higher temperatures. This observation, which is in good agreement with previous findings,[14,16] implies that the relaxation of the carriers from the initial distribution to a high-T_C quasithermal distribution is very fast on the recombination time scale, probably through the emission of longitudinal optical phonons. The subsequent cooling, governed by acoustical phonons, turns out to be much less efficient and unable, except at high T_L, to cool down the carrier distribution to the lattice temperature. The temperature T_C of the recombining carriers is somehow determined by the ratio of the characteristic recombination and cooling times τ_{rec} and τ_{cool}, respectively; only in the limit $\tau_{cool}/\tau_{rec} \ll 1$ can we expect $T_C = T_L$. Time-resolved experiments of carrier cooling show[23] indeed that, at low T_L, τ_{cool} is in the range of hundreds of picoseconds, namely, on the same order of magnitude as τ_{rec}.

The carrier temperature T_C is obviously a measure of the excess of energy per carrier. Therefore one can expect T_C to be independent of the excitation power P_{exc}, as far as the carrier-carrier interaction does not play a major role, since by increasing P_{exc} only the number of carriers increases, but not their excess of energy. The observed dependence of T_C on P_{exc} agrees with this picture: in the low excitation limit we find that T_C does not change when varying P_{exc}. Our data also seem to indicate the threshold for carrier-carrier nonlinearities in the range of $P_{exc} \approx 10$ W/cm^2; for higher excitation powers, a rather important heating of the recombining carrier has been found, even in the case of resonant excitation (see Fig. 5). It is also worth noting that under resonant excitation the photogenerated excitons have no excess energy to dissipate by phonons and therefore an effective T_C higher than T_L cannot be fully ascribed to a nonefficient exciton-phonon interaction. In fact we believe that Auger-like processes are most likely responsible for the phenomenology reported in Fig. 5.

The excess of energy per photogenerated carrier pair $\Delta E = E_{exc} - E_0$ instead plays a very important role in determining T_C at low T_L. In fact T_C decreases with decreasing excitation energy and $T_C = T_L$ for resonant excitation at the fundamental transition E_0. On the other hand, we find that the increase of T_C with E_{exc} tends to saturate for large excesses of energy ΔE, very likely due to the efficient relaxation through LO phonons. Finally an increase of T_C when decreasing the well thickness L_W was also reported in Ref. 16, where this behavior was explained in terms of the well-known increase of the excitonic oscillator strength. We find that, at low T_L, T_C is in fact smaller in the larger wells (120 and 180 Å) than in the thinner wells (40–70 Å): nevertheless the values of T_C among the latter do not seem to follow any regular behavior with L_W. Indeed only the intrinsic radiative lifetime of excitons changes with L_W while the experimental values for the recombinations time are rather scattered,[5–7] even in nominally similar QW's.

V. CONCLUDING REMARKS

We have demonstrated that a unified picture, namely, thermalization of the photogenerated carriers inside the inhomogeneous exciton band, can be applied to the excitonic recombination in QW's, independently of the presence, or lack thereof, of a sizable SS. In this framework we were able to explain the origin of the SS and also establish its dependence on both the temperature and the absorption linewidth. The experimental data are found to be in excellent agreement with our model.

We also would like to remark that our discussion has only concerned cw measurements, where a quasiequilibrium distribution is necessarily reached. As stressed in Ref. 13, the carrier kinetics is more complicated in time-resolved experiments where, as an example, the SS is found to continuously increase with time.[24] This effect, which is completely out of the model presented in Refs. 10 and 11, can be explained in the framework of our approach by using in Eq. (3) a time-dependent carrier temperature T_C. This implies the assumption of an adiabatic cooling following a sequence of thermal quasiequilibrium exciton distributions during the relaxation process and should be obviously verified by time-resolved PL measurements.

At the same time it is well known that one of the most dramatic consequences of thermalization is the huge increase of the effective excitonic lifetime. Instead of the short free-exciton lifetimes predicted by the theoretical models[2-4] (≈ 12 ps for a 100-Å GaAs/$Al_{0.3}Ga_{0.7}As$ QW) much longer values are commonly measured by time-resolved luminescence spectroscopy[5-7] due to thermalization among radiative and nonradiative exciton states resulting in an effective radiative time which increases linearly with temperature. We clearly demonstrate that excitons reach a thermal distribution even at the lowest lattice temperatures but, for nonresonant excitation and low lattice temperatures, T_C turns to be higher than T_L. Our results therefore suggest that low-power resonant excitation at the HH band provides the best conditions for studying not only the initial exciton recombination kinetic related to the intrinsic radiative lifetime, as recently reported,[18-20] but also the subsequent regime, namely, the recombination of the thermalized distribution of excitons.

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*Permanent address: Departament de Física Aplicada, Universitat de València, 46100 Burjassot, Valencia, Spain.

[1]See, for instance, M. A. Herman, D. Bimberg, and J. Christen, J. Appl. Phys. **70**, R1 (1991).
[2]E. Hanamura, Phys. Rev. B **38**, 1228 (1988).
[3]L. C. Andreani, F. Tassone, and F. Bassani, Solid State Commun. **77**, 641 (1991).
[4]D. S. Citrin, Phys. Rev. B **47**, 3832 (1993).
[5]J. Feldmann, G. Peter, E. O. Gobel, P. Dawson, K. Moore, G. Foxon, and R. J. Elliott, Phys. Rev. Lett. **59**, 2337 (1987).
[6]M. Gurioli, A. Vinattieri, M. Colocci, C. Deparis, J. Massies, G. Neu, A. Bosacchi, and S. Franchi, Phys. Rev. B **44**, 3115 (1991).
[7]J. Martinez-Pastor, A. Vinattieri, L. Carraresi, M. Colocci, Ph. Roussignol, and G. Weimann, Phys. Rev. B **47**, 10 456 (1993).
[8]G. Bastard, C. Delalande, M. H. Meynadier, P. M. Frijlink, and M. Voos, Phys. Rev. B **29**, 7042 (1984).
[9]C. Delalande, M. H. Meynadier, and M. Voos, Phys. Rev. B **31**, 2497 (1985).
[10]F. Yang, M. Wilkinson, E. J. Austin, and K. P. O'Donnell, Phys. Rev. Lett. **70**, 323 (1993).
[11]Wilkinson, F. Yang, E. J. Austin, and K. P. O'Donnell, J. Phys. Condens. Matter **4**, 8863 (1992).
[12]J. Humlíček, E. Schimdt, L. Bočánek, R. Švehla, and K. Ploog, Phys. Rev. B **48**, 5241 (1993).
[13]J. A. Kash, Phys. Rev. Lett. **71**, 1286 (1993); F. Yang *et al.*, *ibid.* **71**, 1287 (1993).
[14]R. F. Schnabel, R. Zimmermann, D. Bimberg, H. Nickel, R. Lösch, and W. Schlapp, Phys. Rev. B **46**, 9873 (1992).
[15]R. Zimmermann and E. Runge, J. Lumin. (to be published).
[16]C. Colvard, D. Bimberg, K. Alavi, C. Maierhofer, and N. Nouri, Phys. Rev. B **39**, 3419 (1989).
[17]J. Hegarty, M. D. Sturge, C. Weisbuch, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **49**, 930 (1982).
[18]H. Stolz, D. Schwarze, W. von der Osten, and G. Weimann, Phys. Rev. B **47**, 9669 (1993).
[19]B. Deveaud, F. Clerot, N. Roy, K. Satzke, B. Sermage, and D. S. Katzer, Phys. Rev. Lett. **67**, 2355 (1991); B. Sermage, B. Deveaud, K. Satzke, F. Clerot, C. Dumas, N. Roy, D. S. Katzer, F. Mollot, R. Planel, M. Berz, and J. L. Oudar, Superlatt. Microstruct. **13**, 271 (1993).
[20]A. Vinattieri, J. Shah, T. C. Damen, D. S. Kim, L. N. Pfeiffer, and L. J. Sham, Solid State Commun. **88**, 189 (1993); J. Phys. IV **3**, C5-27 (1993).
[21]M. Gurioli, J. Martinez-Pastor, M. Colocci, A. Bosacchi, S. Franchi, and L. C. Andreani, Phys. Rev. B **47**, 15 755 (1993).
[22]M. Colocci, M. Gurioli, and J. Martinez-Pastor, J. Phys. IV **3**, C5-3 (1993).
[23]K. Kash, J. Shah, D. Block, and A. C. Gossard, Physica B **134**, 189 (1985).
[24]Y. Masumoto, S. Shionoya, and H. Kawaguchi, Phys. Rev. B **29**, 2324 (1984).