Exciton interaction with hot electrons in GaAs

I. Reimand and J. Aaviksoo
Institute of Physics, Tartu University, Riia 142, Tartu 50415, Estonia
(Received 22 October 1999)

The dynamics of exciton interaction with charge carriers in GaAs, excited by a cw light source and subjected to collisions with free carriers, which are independently created by a picosecond light pulse, is studied by a time-resolved dual-channel modulated luminescence correlation technique. The dynamics reveals a decreased exciton generation rate at a higher temperature of charge carriers and a strong exciton scattering on hot free carriers that heats the excitons and effectively quenches luminescence due to smaller exciton-photon coupling at an elevated temperature of excitons.

In spite of intense interest in excitons, some aspects of exciton dynamics are, due to their complexity, not yet well known. The dynamics of the formation of bound states, and more generally, exciton interaction with charge carriers, is one of these aspects. In recent years, several works[1–9] have been published on exciton formation and relaxation in quantum wells (QW's), which have greater exciton oscillator strength and binding energy compared to bulk material. In bulk, experiments are made with materials having a large exciton–LO-phonon coupling.[10] Only a few experimental works address exciton creation in bulk GaAs.[11,12] From theory, we know no comprehensive model with quantitative agreement. Therefore, every additional experimental feature could contribute to the overall understanding.

The current work presents some experimental results on exciton luminescence kinetics dependent on simultaneously generated charge-carrier properties. This work was initiated by a luminescence-quenching effect, we investigated earlier, due to the interaction between hot electrons and free excitons in bulk undoped GaAs.[11] Excitons generated by previous laser excitations were destroyed or heated by the next ongoing laser pulse, causing luminescence quenching. The effect had a strong dependence on the excitation energy and power.

EXPERIMENT

The sample was an ultrapure vapor-phase-epitaxy-grown GaAs sample with a residual donor concentration of about $10^{-12}\,\mathrm{cm}^{-3}$.[13] Luminescence was excited by two light sources: a synchronously pumped mode-locked cavity-dumped Styryl-8 dye laser and a semiconductor (diode) cw laser. The optical pulse duration was about 5 ps with a repetition rate of 4 MHz and spectral linewidth of 0.7 meV tunable at exciton energies and above. The semiconductor laser had a fixed wavelength of 815 nm with a linewidth of 0.1 nm (corresponding to an electron excess energy of 3 meV). The excitation power intensity was about 0.01–1 $\mathrm{W/cm}^2$ for the pulsed laser (time-averaged power) and 6 $\mathrm{W/cm}^2$ for the diode laser. Photoluminescence was measured at the temperature of 2 K. The semiconductor laser had a steplike modulation of 50 kHz, thus being a quasi-cw light source for our time scales. All the luminescence kinetics curves were recorded simultaneously into two channels (corresponding to the phase of cw laser modulation) by a time-correlated photon-counting system. The temporal and spectral resolution of the registering system was about 100 ps and 0.2 meV, respectively.

The chosen parameters of the modulation scheme of photon counting allow us to eliminate the effects of dead-time difference for each channel of photon counting (the modulation frequency is higher than the photon-count frequency) and slow time-scale laser drifts. Thus we can directly and quantitatively compare the luminescence intensities, depending on whether the diode laser is illuminating or not.

To the best of our knowledge, no one has ever reported using such an experimental setup for investigating exciton luminescence. Modulation schemes have been used for registering luminescence in the spectral domain.[4,9] Our experimental setup uses an idea similar to that in Ref. 4 in the *time domain* and gives us a new dimension for registering the processes. On the other hand, such an experiment is complementary to the four-wave mixing experiments with a preinjection of excitations,[14,15] but it registers inherently incoherent luminescence.

RESULTS

In Fig. 1, luminescence kinetics curves have been shown for three different pulse intensities. The pulse photon energy is E_g+15 meV, well below the optical phonon ($E_{\mathrm{LO}}=36$ meV) replica of the band (E_g is the electron conduction-band energy). The solid line marks the temporal dependence of luminescence when both (the diode and pulsed) lasers are exciting the crystal. The dashed line marks luminescence for the case in which the crystal is excited only by the pulsed laser.

At the lowest pulse intensity [Fig. 1(a)] of 10 $\mathrm{mW/cm}^2$ (about 10^{14} excited electrons per cubic centimeter per pulse) a stationary luminescence is emitted by the crystal until the pulse fires. In response to the pulse, the luminescence momentarily (below the temporal resolution of the experiment) decreases and afterwards slowly relaxes to the stationary state. The integral of the ''hole'' in the luminescence is approximately 80% compared to the integral of luminescence when exciting only with the pulsed laser. In other words, the excited amount of electrons being able to create one registered exciton is able to eliminate 1.8 otherwise registered

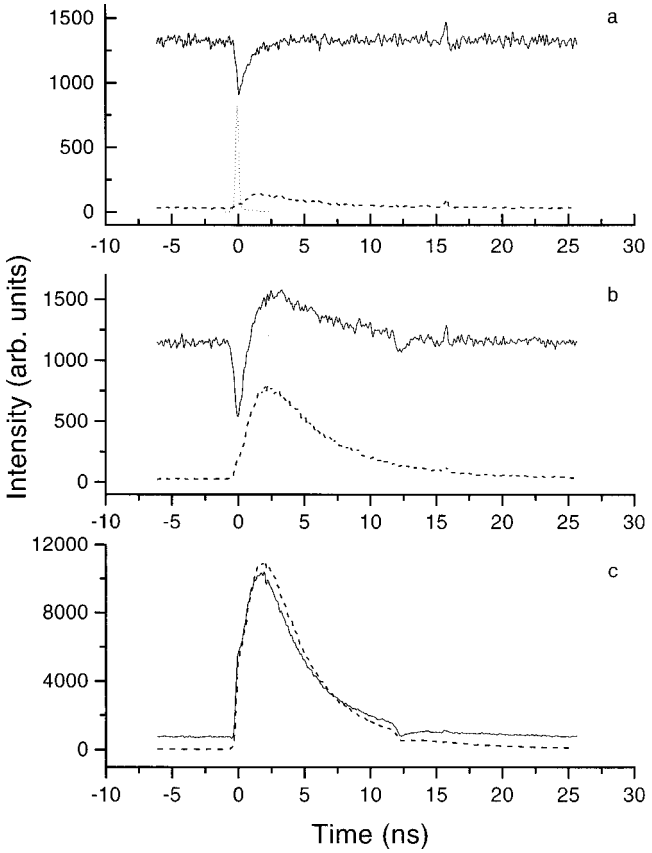

FIG. 1. Experiment: temporal behavior of the photoluminescence of the sample for excitation by the pulsed laser with (solid line) and without (dashed line) cw laser illumination in the case of three pulsed-laser intensities: (a) 0.01 W/cm^2, (b) 0.2 W/cm^2, and (c) 1 W/cm^2. The incident pulse is depicted by dots in (a).

excitons. The difference kinetics is shown in the upper part of Fig. 2.

It is remarkable that no maximum appears in the kinetics, although additional excitations were injected by pulse. Where do the excitons disappear? We can analyze whether the excitons were permanently destroyed or moved only temporarily out of sight—thrown into their evolution track (heated or ionized to charge carriers)—and will later also take part in luminescence.

If the excitons were destroyed, we can calculate the exciton decay time in the following way. The stationary number of excitons is determined by the balance between the generation rate (due to the diode laser), and lifetime τ_x of excitons. At the moment of the pulse an unknown process quickly changes the number of excitons. Then the system approaches the balance again, and, additionally, new excitons, generated by pulse, will play a role in the luminescence:

$$\frac{dN_1}{dt} = G_P(t) - \frac{N_1}{\tau_x},$$

$$\frac{dN_2}{dt} = G_S + G_P(t) - R(I)\,\delta(t) N_{2,\mathrm{stats}} - \frac{N_2}{\tau_x}.$$

Here N_1 and N_2 are the number of excitons created by pulsed laser only and by both lasers, respectively. G_P and G_S are the exciton generation rates from a pulsed and stationary

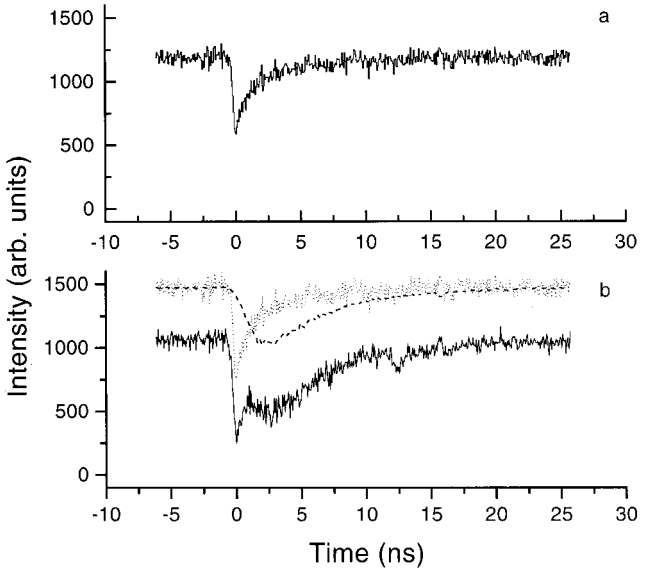

FIG. 2. Solid lines: temporal behavior of the photoluminescence difference at a low pulse intensity (0.01 W/cm^2, upper part) and intermediate intensity (0.2 W/cm^2, lower part). Dotted line represents the contribution of smaller exciton coupling with photons due to the exciton-temperature change; dashed line represents the contribution of the changed exciton-generation rate due to the electron-temperature change.

source, respectively, $R(I)$ is the number of lost excitons depending on the pulse intensity I, and $\delta(t)$ is the delta function. For the sake of simplicity we use stationary value of N_2, considering the number of lost excitons.

The solution gives us the number of excitons, proportional to our measured luminescence for either case:

$$N_1 = \exp\left(-\frac{t}{\tau_x}\right) \int G_P(t) \exp\left(\frac{t}{\tau_x}\right) dt,$$

$$N_2 = N_{2,\mathrm{stats}} \left[1 - H(t) R(I) \exp\left(-\frac{t}{\tau_x}\right)\right] + N_1.$$

Subsequently the difference of the two measured luminescence kinetics should give us a pure exponential curve. Consequently, we get exciton lifetime extracted from all other processes. $H(t)$ is the Heaviside function.

This idea holds in the zeroth-order approximation, assuming that the exciton generation function from the pulse-excited charge carriers $G_P(t)$ does not differ for different experiments (which means that the additional charge-carrier concentration, caused by pulse, is small compared to the stationary one). For testing of the applicability of the idea we subtracted the luminescence curves, corresponding to N_1 from N_2. In the pulse intensity range of 0.01 to 0.05 mW the character of the difference kinetics does not change essentially, indicating that using this idea at our lowest intensities is reasonable. The decay time fitted from the difference kinetics (assuming excitons were destroyed) is $\tau = 2$ ns.

If the excitons were not permanently destroyed (a part of ''lost excitons'' will return to the stationary state), then τ fitted from difference kinetics is a function of the exciton decay time τ_x and round-trip time τ_r. In the simplest case, when losses during the round trip are equal to the stationary

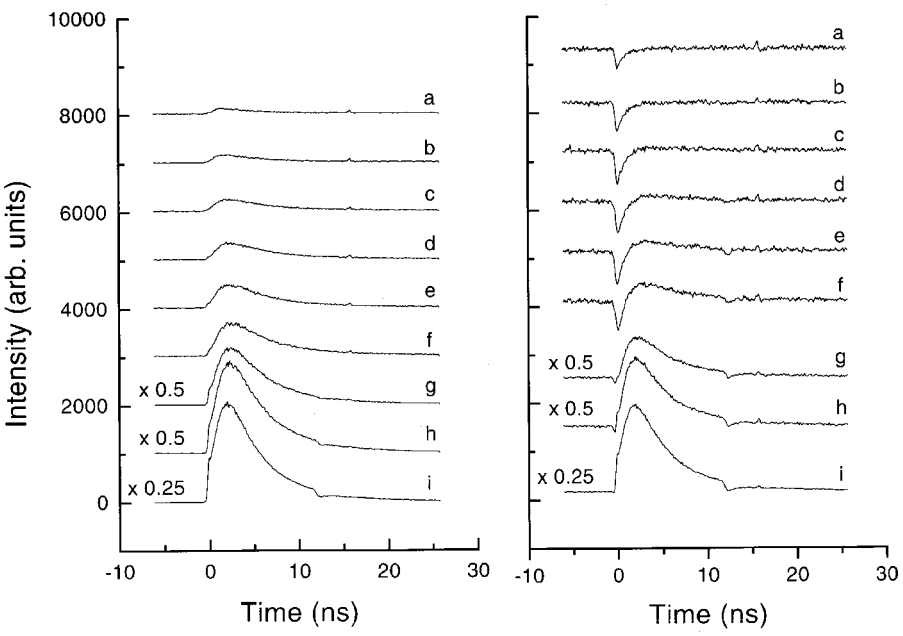

FIG. 3. A series of luminescence kinetics for different intensities of pulse excitation without (left part) and with (right part) cw background illumination. (a) 0.01 W/cm^2, (b) 0.03 W/cm^2, (c) 0.05 W/cm^2, (d) 0.08 W/cm^2, (e) 0.12 W/cm^2, (f) 0.15 W/cm^2, (g) 0.3 W/cm^2, (h) 0.5 W/cm^2, and (i) 0.8 W/cm^2. The excess energy of pulse excitation was 15 meV.

exciton losses, we will get $\tau^{-1}=\tau_x^{-1}+\tau_r^{-1}$. But in any case $\tau_x \geqslant \tau$. A qualitative analysis says that if losses during the round trip are smaller than those in the stationary case, then the luminescence kinetics excited by both lasers will always have a maximum.

On the other hand, we do have independent data for exciton decay time (measured on the same sample, where excitons were created directly by a laser pulse at a low intensity), $\tau_x \approx 4$ ns. Due to an essential difference between τ and τ_x, we can conclude that the excitons, disappearing from the luminescence band at the moment of an additional laser excitation, will be excited to a state with a higher energy (a hot exciton or a free charge-carrier pair) and will later return to their previous state. The absence of a maximum in luminescence (at excitation of both lasers) lets us conclude that the averaged losses (both nonradiative and radiative) at these upper states are larger than those in the stationary case.

At an intermediate intensity of 0.2 W/cm^2 [Fig. 1(b)] when excited both by a diode and pulsed laser, at the moment of pulse excitation the stationary luminescence also decreases, but later the luminescence grows higher than the stationary one. For the pulsed laser-only excitation, a steep rise of luminescence takes place followed by a slower component. In luminescence kinetics this steep steplike or even spikelike behavior is often attributed to an experimental artifact (scattered exciting laser pulse), but in the current experiment we do not see the feature on other simultaneously registered kinetics—indicating the real nature of the effect. We think that the steplike behavior may be caused by a small fraction of excitons created by a LO-phonon-mediated process (the initial high-energy distribution of the charge carriers generated by photons with an excess energy of 15 meV may have a sufficiently high-energy tail). The relative share of the steplike feature increases with the pulse intensity, as it should be in a bimolecular process, thus confirming the interpretation. The LO-mediated exciton generation is important in GaAs QW structures.[3,7] The Monte Carlo calculations of Selbmann *et al.*[16] predicted an essential share of the LO-phonon process in exciton creation also in bulk GaAs. In our earlier experiment,[11] we, as well as the authors of Ref. 12, have not seen distinct evidence of the LO-phonon-mediated exciton generation in bulk GaAs. This may be caused by the fact that in the experiments of Refs. 11 and 12 the excitation intensity is about an order of magnitude lower and the bimolecular process (depending on the carrier concentration as n^2) had too small a probability. In our earlier unpublished measurements, we often saw this spikelike behavior but attributed it to scattered laser light.

The difference kinetics in the case of an intermediate pulse intensity is shown in the lower part of Fig. 2. A two-component structure is clearly seen. At the moment of excitation, similar luminescence quenching occurs as in the low-intensity case. Later, another component, roughly proportional to the exciton luminescence signal, also reveals itself. We interpret the further component as a contribution of a smaller exciton coupling with photons due to an exciton temperature change (photons can be emitted only at $k \cong 0$, at an elevated temperature the share of such excitons decreases). The other component may be due to a changed exciton generation rate with an electron temperature increase.

At a high pulse intensity of 1 W/cm^2 [Fig. 1(c)], no initial decrease takes place. Instead, at the first moment, a steplike rise in luminescence is found for both cases. A striking fact is that the maximum luminescence intensity, if exciting with both light sources, is lower than if exciting only with a pulsed laser. The character of difference kinetics (not shown) does not change, compared with the intermediate pulse intensity, except that the slower component reveals a different (slower) form than the corresponding pulsed-only luminescence. This seems to be natural, considering the bimolecular process of exciton formation and the reduced exciton-generation rate at a higher carrier temperature.

In Fig. 3, a series of kinetics relations depending on the pulse intensities are shown. At higher excitation intensities another hole in the luminescence kinetics is pronounced (at 12 ns delay). The second hole originates from the excitation

by a replica of the laser pulse (due to a imperfection of the cavity dumper), which has approximately 1.5% of the main pulse intensity.

For comparison, similar experiments were performed with the photon energy of the pulsed laser tuned into the exciton energy zone and below the exciton resonance energy. In the case of exciting excitons directly by laser pulse, no significant changes in the luminescence kinetics' shape, depending on the background lightening, were found. In this case, however, the rise of the luminescence is so fast that the quenching effect could be hidden under it. In the case of exciting the crystal below the exciton resonance, the stationary luminescence was totally unaffected by the presence of the pulsed laser. This case rules out the possibility of a direct interaction between the laser pulse and the excitons created by the diode laser.

In Fig. 4, the number of lost excitations (N_{lost}) depending on N_{pulsed} is shown, calculated by formula:

$$N_{\mathrm{lost}} = N_{\mathrm{stationary}} + N_{\mathrm{pulsed}} - N_{\mathrm{both}},$$

where $N_{\mathrm{stationary}}$ is the integral of stationary luminescence when excited only with a diode laser, N_{pulsed} is the integral of luminescence when excited only with a pulsed laser, and N_{both} is the integral when both excitations are in use. We do not have an explanation to the dependence, but it is interesting to note that N_{lost} depends on N_{pulsed} as square root. The dotted line in Fig. 4 marks the dependence $N_{\mathrm{lost}} = a + b(N_{\mathrm{pulsed}})^{1/2}$.

To model the interaction of charge carriers and excitons including thermal exchange, we used the following set of Boltzmann rate equations for particle concentrations n and mean energies E (subscripts eh and x denote charge carriers and excitons, respectively):

$$\frac{dn_{eh}}{dt} = G - \frac{n_{eh}}{\tau_{eh}} - \sigma n_{eh}^2,$$

$$\frac{dn_x}{dt} = -\frac{n_x}{\tau_x} + \sigma n_{eh}^2,$$

$$\frac{2}{3k}\frac{dE_{eh}}{dt} = GT_g - \frac{n_{eh}}{\tau_{eh}}T_{eh} - \left\langle \overline{\frac{dE_{eh}}{dt}} \right\rangle_{\mathrm{ph}} - \sigma n_{eh}^2 T_{eh} + \gamma n_{eh} n_x (T_x - T_{eh}),$$

$$\frac{2}{3k}\frac{dE_x}{dt} = -\frac{n_x}{\tau_x}T_x - \left\langle \overline{\frac{dE_x}{dt}} \right\rangle_{\mathrm{ph}} + \sigma n_{eh}^2 (T_{eh} + T_B) - \gamma n_{eh} n_x (T_x - T_{eh}).$$

Here T_g is the charge-carrier temperature at excitation and T_B is the temperature corresponding to the Rydberg energy of the exciton. $\langle \overline{dE}/dt \rangle_{\mathrm{ph}}$ is the mean energy-loss rate of a particle in all the scattering processes on phonons (for charge carriers we considered the deformation potential and piezoelectric-LA-phonon and polar-LO-phonon scattering; for exciton deformation potential LA-phonon scattering, the corresponding rates were taken from the literature.[17,18] γ denotes the probability of an exciton to lose energy by colliding with a charge carrier (we considered the thermal exchange, not exciton dissociation). For γ we used the hydrogen-electron collision efficiency $\gamma_0 = 20a_0(h/m_e)$, taken from Ref. 19, multiplied by the mean energy exchange fraction at collision, $2m_e/(m_e+m_x)$:

$$\gamma = 40a_0 \frac{h}{m_e + m_x}.$$

a_0 is the Bohr radius of an exciton.

For bimolecular coupling constant σ we used a formula from Ref. 20, which we modified for the case when the temperature of the charge carriers differs from that of the lattice. To our knowledge, this is the only model describing the exciton creation cross section depending on (carrier effective) temperature (in three dimensions). In our calculations the essential feature was the temperature behavior of the cross section $\sigma \propto T_e^{-1.5}$, which follows from the acceptable assumption of the charge-carrier Boltzmann distribution. For two-dimensional case in QW, the dependence $\sigma \propto T_e^{-1}$ is used by Ref. 6.

In Fig. 5 the calculated kinetic curves are presented. The model qualitatively explains the experimental features. At a low pulse intensity no maximum appears in the luminescence with a cw background excitation. At a high excitation the luminescence without a background cw excitation has a higher intensity than the one with that. We could not find an opportunity for the model to take into account the proposed LO-phonon-mediated exciton creation mechanism, so the model does not reproduce the initial steep rise.

COMPARISON WITH THE RESULTS OF OTHER AUTHORS

The results of our experiment are related to excitation-induced dephasing (EID) experiments, made by four-wave mixing (FWM) techniques with a preinjection of incoherent excitations.[14,15] The authors of Refs. 14 and 15 determine the exciton dephasing rate $1/T_2$ depending on the concentration of the additionally injected excitations. They indicate that exciton–free-carrier scattering is 10 times as efficient as exciton-exciton scattering. As the FWM experiment measures the phase-coherence dephasing, it says nothing explicit about the energy (heat) exchange, but the heat exchange in

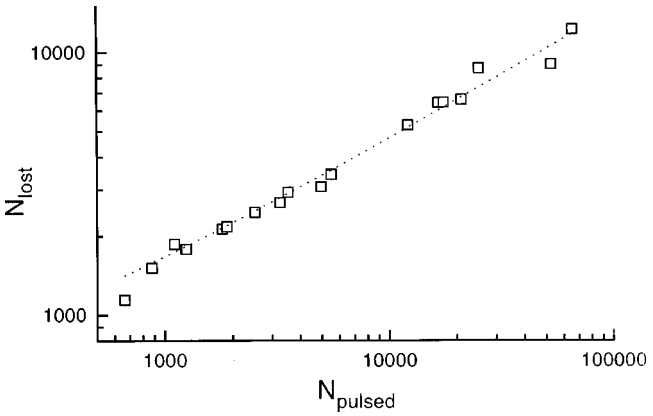

FIG. 4. Open squares: fraction of excitons ''getting lost'' when an additional cw excitation is present, compared to the luminescence intensity for the pulsed excitation. With the dotted line a fit $q \propto \sqrt{N_{\mathrm{pulsed}}}$ is shown.

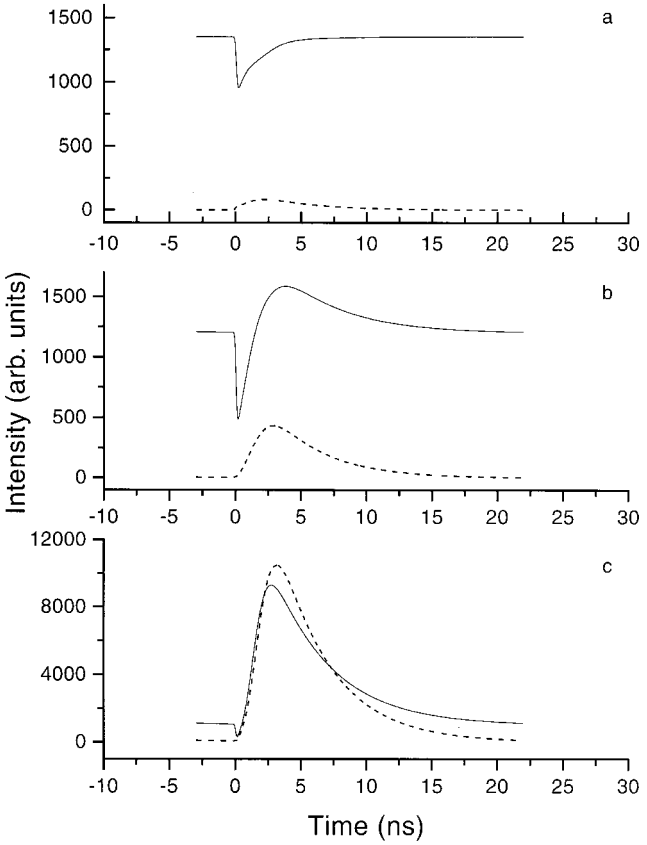

FIG. 5. Model calculations based on the Boltzmann rate equations (see text): temporal behavior of the photoluminescence of the sample for excitation by the pulsed laser with (solid line) and without (dashed line) cw laser illumination in the case of different pulsed laser intensities: (a) low pulse intensity, (b) intermediate pulse intensity, and (c) high intensity.

exciton–free-carrier scattering is evident. Our experiment, measuring the incoherent part of the secondary emission, thus gives some complementary information to FWM EID experiments.

Robert *et al.*[21] have also seen a significant energy exchange between the charge carriers and excitons. They have even concluded a thermodynamic equilibrium with equal temperatures and chemical potentials of the subsystems. In a bulk crystal, we cannot apply the method of Ref. 21 to check these ideas.

To the authors' knowledge, the most comprehensive calculation of the involved processes was published in Ref. 16 using the Monte Carlo ensemble method for solving the Boltzmann rate equations for coupled free carriers and excitons. The authors of Ref. 12 report a good accordance of the experimental data with the calculations (except for the calculation conclusion about the exciton creation through a LO phonon). In the theoretical consideration, however, no process was involved for the charge-carrier–exciton heat exchange and for the exciton dissociation depending on the charge-carrier distribution. Based on our experiment and on the FWM results of Ref. 14, we note, however, that exciton dephasing processes should play an important role in the experimental results of Ref. 12 as well. These processes do reveal themselves in a less evident way, retarding the onset of luminescence until the hot charge carriers are cooled down. However, the Monte Carlo ensemble approach, used by the authors of Refs. 12 and 16, after including the thermal exchange between excitons and carriers, is evidently a more appropriate method for trying to quantitatively fit the experimental results.

Piermarocchi *et al.*,[8,22] calculating exciton creation dynamics in QW, also neglect the heat exchange effect while operating with hot charge-carrier distributions with quite a high concentration up to $n=10^{12}$ cm^{-2} (the corresponding bulk concentration would be $n=10^{18}$ cm^{-3}). We think that one should expect an essential influence of exciton dephasing on carriers.

Aschkinadze *et al.*[4] have also investigated the exciton heat exchange with charge carriers in GaAs QW's. A very interesting result was obtained, revealing exciton *cooling* by the carriers (although the carriers were initially generated at a high temperature). We think that in their experiment, the excitons, created directly in the exciton band, had normally a higher effective temperature, compared with the carriers' effective temperature, which was established dynamically in the process of charge-carrier generation and their energy relaxation.

Baars and Gal,[9] in their modulation experiment on exciton creation in GaAs QW's, detected a broadening and blueshift of the exciton line depending on the excitation intensity of the charge carriers. They have attributed the exciton broadening to exciton-carrier scattering and the blueshift to a quantum-confined Stark effect. We think that if there is an effective exciton-carrier scattering (as they propose), then the carriers may heat excitons as well, with a blueshift of the exciton line. Certainly, a detailed analysis of the origin of the blueshift is needed to establish the contributions of each process.

SUMMARY

Exciton luminescence quenching in bulk GaAs was investigated using a different experimental technique. This technique gives complementary information for the FWM experiments with preinjection of excitations, studying excitation-induced dephasing in semiconductors.

The quenching effect consists of two contributions: a decreased exciton coupling with photons due to an exciton temperature change and a changed exciton-generation rate due to an electron-temperature change. The effect can be explained qualitatively using the Boltzmann rate equations, if the exciton heating by the charge carriers is taken into account. The steep luminescence onset, often attributed to an experimental artifact, may be evidence of a LO-phonon-mediated exciton-creation process.

ACKNOWLEDGMENTS

We gratefully thank V. V. Travnikov and V. V. Rossin for their contribution to the theoretical model and for providing us with the sample. The present work has been supported by Estonian Science Foundation Grant No. G2338.

[1] T. C. Damen, J. Shah, D. Y. Oberli, D. S. Chemla, J. E. Cunningham, and J. M. Kuo, Phys. Rev. B **12**, 7434 (1990).
[2] J. Kusano, Y. Segawa, Y. Aoyagi, S. Namba, and H. Okamoto, Phys. Rev. B **40**, 1685 (1989).
[3] P. W. M. Blom, P. J. van Hall, C. Smit, J. P. Cuypers, and J. H. Wolter, Phys. Rev. Lett. **71**, 3878 (1993).
[4] B. M. Ashkinadze, E. Linder, E. Cohen, Arza Ron, and L. N. Pfeiffer, Phys. Rev. B **51**, 1938 (1995).
[5] J. Kovač, H. Schweizer, M. H. Pilkuhn, and H. Nickel, Phys. Rev. B **54**, 13 440 (1996).
[6] R. Kumar, A. S. Vengurlekar, S. S. Prabhu, J. Shah, and L. N. Pfeiffer, Phys. Rev. B **54**, 4891 (1996).
[7] M. Gulia, F. Rossi, E. Molinari, P. E. Selbmann, and P. Lugli, Phys. Rev. B **55**, R16 049 (1997).
[8] C. Piermarocchi, F. Tassone, V. Savona, A. Quattropani, and P. Schwendimann, Phys. Rev. B **55**, 1333 (1997).
[9] T. Baars and M. Gal, Phys. Rev. B **57**, 3974 (1998).
[10] S. S. Prabhu, A. S. Vengurlekar, and J. Shah, Phys. Rev. B **53**, R10 465 (1996).
[11] J. Aaviksoo, I. Reimand, V. V. Rossin, and V. V. Travnikov, Phys. Rev. B **45**, 1473 (1992).
[12] M. Gurioli, P. Borri, M. Colocci, M. Gulia, F. Rossi, E. Molinari, P. E. Selbmann, and P. Lugli, Phys. Rev. B **58**, R13 403 (1998).
[13] V. G. Golubev, Yu. V. Zhilyaev, V. I. Ivanov-Omskii, G. R. Markaryan, A. V. Osutin, and V. E. Chelnokov, Fiz. Tekh. Poluprovodn **21**, 1771 (1987) [Sov. Phys. Semicond. **21**, 1074 (1987)].
[14] L. Shultheis, J. Kuhl, A. Honold, and C. W. Tu, Phys. Rev. Lett. **57**, 1635 (1986).
[15] A. Honold, L. Shultheis, J. Kuhl, and C. W. Tu, Phys. Rev. B **40**, 6442 (1989).
[16] P. E. Selbmann, M. Gulia, F. Rossi, E. Molinari, and P. Lugli, Phys. Rev. B **54**, 4660 (1996).
[17] J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures* (Springer, Heidelberg, 1996).
[18] *Semiconductors Probed by Ultrafast Laser Spectroscopy*, edited by R. R. Alfano (Academic, Orlando, 1984), Vol. 1.
[19] C. Erginsoy, Phys. Rev. **79**, 1013 (1950).
[20] V. N. Avakumov, V. I. Perel, and I. N. Yassievich, Zh. Eksp. Teor. Fiz. **78**, 1240 (1980) [Sov. Phys. JETP **51**, 626 (1980)].
[21] D. Robert, X. Marie, B. Baylac, T. Amand, M. Brousseau, G. Baquet, G. Debart, R. Planel, and J. M. Gerard, Solid State Commun. **95**, 287 (1995).
[22] C. Piermarocchi, F. Tassone, V. Savona, A. Quattropani, and P. Schwendimann, Phys. Rev. B **53**, 15 834 (1996).