Picosecond radiative decay of free and bound excitons and excitonic molecules in CdSe

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(Received 27 July 1994; revised manuscript received 7 September 1994)

Band-edge luminescence in photoexcited CdSe is known to show several interesting features due to radiative decay of free and bound excitons and excitonic molecules (biexcitons). In this paper, we report our experiments on the study of the time evolution of some of these processes in CdSe, using up-conversion luminescence spectroscopy with a time resolution of 2.5 ps. We obtain time-dependent luminescence spectra at two e-h pair excitation densities (estimated to be $n_0 = 8 \times 10^{16}$ and 8×10^{17} cm^{-3}). The role of hot biexciton dynamics in determining the time evolution of luminescence is evident. At low density ($n_0 = 8 \times 10^{16}$ cm^{-3}), the luminescence spectrum also reveals the time evolution of the bound exciton emission at long delays (> 200 ps). In addition, we obtain time-resolved luminescence of the longitudinal-optical phonon-assisted Stokes sidebands of the free exciton. The exciton and biexciton lifetimes are deduced to be 600 and 10 ps, respectively, on the basis of a theoretical model describing their coupled dynamics.

I. INTRODUCTION

Radiative recombination of photoexcited electron-hole (e-h) pairs in semiconductors such as CdS has been studied extensively in the past.[1] Depending upon the excitation density, different processes dominate the recombination luminescence of these e-h pairs. At low temperatures and low excitation densities, the edge emission spectrum is dominated by exciton recombination and exciton interactions with phonons and impurities. At higher excitation densities, the mutual interactions of the excitons become important.[2–4] One should then take into account the exciton-exciton collisions, formation of exciton molecules (biexcitons), and biexciton-biexciton interactions. The dynamics of processes such as energy relaxation of hot e-h pairs towards their respective band edges, formation of excitons and biexcitons from the initially excited hot free carriers, thermalization and cooling of exciton- and biexciton-energy distributions and the radiative decay of these excitations has been a topic of much interest. Considerable efforts have been devoted[5–6] in the case of materials such as CdS and CdSe to identify luminescence due to excitons, exciton-exciton collisions, biexcitons, electron-exciton interactions, etc., following the transformation of the free e-h pairs into excitons. At still higher densities, exceeding the Mott density, the e-h plasma effects dominate, screening out the excitonic states, at least near the surface, where the density due to one-photon generation is the highest. Rapid density reduction due to plasma expansion, recombination, and diffusion can make excitonic states possible once again, within $\sim$ 100–200 ps in some cases, as shown by Saito[7] for CdS and Frigo *et al.*[8] and Fujimoto *et al.*[9] for CdSe at high densities of 10^{18} to 10^{19} cm^{-3}. The study of the dynamics of these processes in II-VI semiconductors, especially in CdS, using time-resolved (TR) luminescence measurements has been the subject of intense research in the past[10]. In recent years, resonant optical nonlinearities in CdSe due to biexcitons and exciton-biexciton transitions have attracted attention.[11]

In addition to the processes listed above, it is well known that the exciton dynamics under low-density excitations is greatly influenced by its capture in an electrostatic potential well due to an impurity complex present in the semiconductor.[12] In II-VI semiconductors such as CdS and CdSe, for example, an exciton bound to a neutral donor (I_2) is known to have giant oscillator strength.[13] Optical bistability due to the bound exciton saturation[14] and quantum beats[15] due to the split states of the bound exciton have been observed in recent years. Several studies have been performed to determine the radiative lifetime of the I_2 bound exciton in CdS and CdSe using different techniques.[16,17] Although the bound exciton recombination (I_2) usually dominates the luminescence in CdS and CdSe at low excitation densities, the time evolution of the bound exciton luminescence with time from an initial low-density photoinjected e-h assembly has not been clearly demonstrated.

The picosecond time evolution of luminescence spectrum due to radiative annihilation of free and bound excitons and biexcitons, following ultrafast generation of high-density e-h pairs has been of great interest for some time.[7,18] The biexciton binding energy in CdSe is about 4 to 5 meV.[5,11] This may be compared with the value of 8.5 meV deduced for CdS,[5] $\sim$ 0.1 meV for GaAs and $\sim$ 1.0 meV for GaAs (Ref. 19) quantum wells. These values make studies of biexcitons possible in CdS and CdSe, but not in bulk GaAs. Such studies are of much relevance now with the renewed interest in the applications of II-VI semiconductors and their heterostructures.[20]

In this paper, we obtain the time-dependent energy distribution of the luminescence due to the excited e-h pairs in CdSe and demonstrate the emergence of the free and bound excitons and biexcitons with time. To our knowledge, such information was not available for CdSe previously. Our results are obtained by using up-conversion luminescence spectroscopy with 2.5-ps time resolution and the photoexcitation-correlation luminescence spectroscopy. We vary the excited e-h pair density n_0 in the range $\sim 8 \times 10^{16}$ cm^{-3} to 8×10^{17} cm^{-3}. We show that the time evolution of the luminescence is determined mainly by the biexcitons at high-density excitations ($\sim 8 \times 10^{17}$ cm^{-3}). At lower excitation densities ($\sim 8 \times 10^{16}$ cm^{-3}), time evolution of luminescence due to bound exciton recombination is also evident. In addition, we obtain the time-resolved luminescence spectrum of the 2-longitudinal-optical (LO) phonon related Stokes sideband of the free exciton near the polariton-knee region. An earlier study of such a spectrum[21] used a streak camera, with an effective time resolution of 70 ps. Using the time dependence of the luminescence due to biexcitons and the 1-LO phonon Stokes sideband of free excitons, we estimate the time constants associated with excitonic processes such as the formation and recombination of excitons and biexcitons. For this, we solve equations describing the coupled dynamics of the excitons and biexcitons within a simple model.

In Sec. II, we briefly describe the experimental procedure. The luminescence spectra showing evidence of transformation of the e-h plasma into biexcitons and bound excitons are presented in Sec. III, while the spectra due to the LO phonon-assisted exciton emission are discussed in Sec. IV. Section V is devoted to a study of the coupled dynamics of excitons and biexcitons based on simple rate equations for their densities. Section VI summarizes the main results.

II. EXPERIMENTAL PROCEDURE

Our experiments are performed by exciting CdSe crystals using pulses from a Nd-YAG (yttrium-aluminum-garnet) pumped dye laser (Rhodamine 6G dye) at a wavelength of 612 nm (photon energy of 2.026 eV) with a repetition rate of 76 MHz. The pulse width as given by an autocorrelator trace is 1.8 ps. As in a standard excite-probe optical arrangement, the beam is split into two parts, one part delayed with respect to the other with the help of a motorized delay stage. In the photoexcitation-correlation[22] (PEC) experiments, the two beams are chopped at different frequencies (235 and 196 Hz) and are focused on the sample with a lens at the same spot with a size of about 50 to 60 μm in diameter. The sample is mounted on a cold finger in a cryostat and maintained at 8 K. The time- and energy-resolved PEC signal is detected at the chopper sum frequency (431 Hz) using a 0.35-m monochromator, a photomultiplier tube detector, a current amplifier, and a lock-in amplifier. Both the beams are polarized perpendicular to the c axis of CdSe. The time-integrated (TI) luminescence is obtained in the same arrangement by blocking one of the beams and detecting the signal at the chopped frequency of the exciting beam. In the up-conversion (UC) measurements, the beams are not chopped. One of the beams excites carriers in the sample while the other is focused on a $LiIO_3$ crystal at the same spot where the luminescence from the sample is focused, as in a standard arrangement. The signal is detected using the 0.35-m monochromator and a photon counting setup. The time resolution of the UC measurement is about 2.5 ps while the energy resolution is about 2.5 meV. The maximum delay between pulses in the two beams possible in our measurements is 1 ns. All measurements are automated using a personal computer. The average intensity of the exciting beam in UC measurements is varied from 1.0 to 10 mW. Assuming an absorption depth of 0.2 μm, exciting beam spot size of 50 μm, and reflectivity of 0.2 in CdSe at 2.03 eV, an average intensity of 1.0 mW corresponds to an excited carrier density n_0 of 8×10^{16} cm^{-3} in our case (an underestimate of the spot size by 10 μm will reduce the density estimate by 30%).

III. BIEXCITON AND BOUND EXCITON LUMINESCENCE

Figures 1 and 2 show the time evolution of the luminescence spectra (discrete points) measured at two excitation intensities: 10 and 1 mW, corresponding to e-h pair densities n_0 of 8×10^{17} cm^{-3} and 8×10^{16} cm^{-3}, respectively. The peaks of the spectra are initially lo-

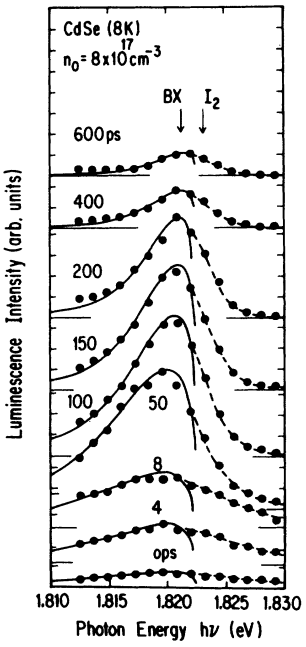

FIG. 1. The experimental TR luminescence spectra measured for 10-mW excitation (discrete points). Also shown are the theoretical fits (continuous curves) based on the hot biexciton model of Eq. (1). The dashed curves (not fits) are drawn to indicate other contributions due to bound excitons and biexciton collision broadening.

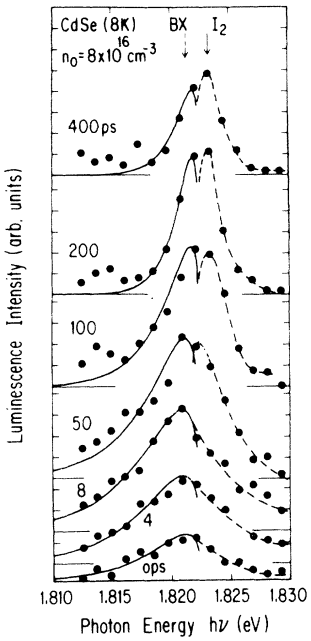

FIG. 2. The experimental TR luminescence spectra measured for 1-mW excitation (discrete points). Theoretical fits based on Eq. (1) (continuous curves) are also shown. The bound exciton is evident at long delays at 1.823 eV, as indicated by the dashed curves (not fits), drawn to guide the eye.

cated approximately at 1.82 eV. The peaks and the low-energy tails of the spectra shift towards the right (high-energy side) with time but the high-energy tails hardly shift with time beyond 50 ps. The spectra are broad in the initial stages but the full width at half maximum (FWHM) decreases rapidly, from over 10 meV at 8 ps to about 5 meV at 200 ps in Fig. 1. It is even narrower in Fig. 2 (less than 4 meV at 200 ps). It may be noted that while the luminescence in the high-density case ($n_0 = 8 \times 10^{17}$ cm^{-3}) evolves into a peak at about 1.822 eV after long delays, the corresponding peak in the case of low-density ($n_0 = 8 \times 10^{17}$ cm^{-3}) luminescence is at a higher energy (1.823 eV). It has been shown in the past,[1-6,16,23] on the basis of PEC and other measurements, such as the intensity dependence of luminescence, that the luminescence peaks occuring at energies about 4 to 5 meV below the free exciton energy (1.827 eV) in CdSe are due to the biexciton and bound exciton (I_2) annihilation. It is expected that, at high densities, the exciton-exciton interaction is strong enough for efficient formation of biexcitons, whereas at low densities, the rate of formation of bound excitons may be comparable. Our time resolved measurements (Figs. 1 and 2) indeed show the time evolution of the luminescence due to biexcitons at $n_0 = 8 \times 10^{17}$ cm^{-3} and reveal emission due to bound excitons at $n_0 = 8 \times 10^{16}$ cm^{-3}, following the initial band to band photoexcitation of e-h pairs.

Figures 1 and 2 show a comparison with a simple biexciton emission line shape given by[4]

$$I(\nu) = A' \sqrt{\epsilon_M} \exp(-\epsilon_M / kT_M) \ , \tag{1}$$

where $\epsilon_M = \hbar^2 k_M^2 / 4m_x = E_x^0 - E_{bM} - h\nu$, $h\nu$ is the energy of the emitted photon, $E_x^0 = E_g - E_{bx}$ is the exciton ground-state energy, E_{bx} and E_{bM}, respectively, are exciton and biexciton binding energies, $\vec{k}_M$ is the biexciton momentum wave vector, and m_x is the exciton effective mass. The literature values of E_{bM} are quoted to be 4 meV (Ref. 5) to 5 meV (Ref. 11). We have used $E_{bM} = 4.5$ meV in our calculations. The agreement of the low-energy side of the spectra with the behavior predicted within the above simple model of hot biexciton emission (continuous curves) appears to be reasonably good. A more detailed analysis of the time-resolved luminescence spectra for various excitation densities on the basis of an improved model of biexciton luminescence line shape has been performed recently[23] to obtain the hot biexciton effective temperature T_M and its time dependence as the biexcitons cool. We may only mention that T_M is deduced to be about 50 K initially but drops to $\sim$ 15 K in 400 ps. The hot biexciton energy relaxation rates have been obtained from the biexciton cooling rates and compared with theoretical calculations based on biexciton energy loss due to phonon emission via Fröhlich, deformation potential, and piezoelectric interactions.

Since the biexciton ground-state energy in CdSe is smaller than the bound exciton energy only by 1 meV or so,[5] a line shape analysis of the complete spectra using only a biexciton model is not adequate. The emission spectra on the high-energy side of the peaks in Figs. 1 and 2 will have some effects of the bound exciton recombination in addition to those of the collision broadened biexciton emission spectrum. This is relatively more important for low excitation densities and long delays as in Fig. 2, although even in this case, the spectra on the lower-energy side of the bound exciton are expected to be predominantly due to the biexciton decay.

It is seen in Fig. 2 that the peak of the spectra measured at the low excitation density ($n_0 = 8 \times 10^{16}$ cm^{-3}) shifts from 1.82 eV at generation to the energy expected for the bound exciton (1.823 eV) beyond 200 ps. This clearly shows that although the low-energy tail of the luminescence spectra is due to biexcitons, the luminescence at 1.823 eV for long delays evolves into that predominantly due to bound exciton radiative recombination for $n_0 = 8 \times 10^{16}$ cm^{-3}.

It is known that the energy relaxation of the photoexcited hot e-h pairs (at low lattice temperatures) occurs, first due to rapid optical phonon emission, when permitted energywise, and then by slow emission of acoustic phonons. The carriers can take several tens of picoseconds to reach their respective band edges. It is interesting, however, to note that although the carriers are generated in our experiments by photons with energy of 2.026 eV, the spectra of Figs. 1 and 2 at $t = 0$ ps show that some of the e-h pairs have already relaxed in energy at $t = 0$ ps (within our time resolution $\sim$2.5 ps) to recombine and emit photons at near-band gap energies at about 1.82 eV (in the wavelength range $\sim$ 680 to 682 nm) while the fundamental one particle band gap energy[24] E_g of CdSe at 8 K is 1.843 eV. This is, of course, not incon-

sistent with a picture in which the free e-h pairs rapidly form hot excitons and biexcitons, even before their complete energy relaxation has taken place. On the other hand, the possibility that the observed luminescence is due to hot e-h plasma with a renormalized, reduced band gap due to many-body effects should be examined. We believe that the luminescence spectra in Figs. 1 and 2 originate from both these mechanisms, the plasma contributing in the initial stages but the excitonic processes dominating after some delay. In the present case, the tail on the high-energy side of the broad luminescence peak seen in the initial stages cannot be due to biexcitons but is due to hot free carriers. This is confirmed[25] by a separate, detailed study of the high-energy tails of the luminescence spectra which show a $\exp(-h\nu/kT_c)$-like behavior ($h\nu$ is the photon energy, T_c is the effective carrier temperature). On the other hand, we find that the complete spectra beyond the initial stages ($\geq$ 50 ps) cannot be fully explained by the plasma model. It can be shown on the basis of a calculation of the spontaneous emission line shape due to e-h plasma recombination[26] that the luminescence spectra of a hot plasma is much broader than the FWHM of the peaks seen in Figs. 1 and 2. For example, the expected width for the e-h plasma emission band is about 35 meV (20 meV) even at a small plasma temperature T_c of 100 K (50 K) for 8×10^{17} cm^{-3} (4×10^{17} cm^{-3}) whereas the spectra in Figs. 1 and 2 have much smaller widths of 5 meV or less for $\geq$ 50 ps. Furthermore, the luminescence spectrum of a hot e-h plasma generally has an asymmetric shape with a longer high-energy tail, while the measured spectra are asymmetric with a longer tail on the low-energy side of the peaks, the high-energy side hardly changing with time beyond 50 ps.

In view of these considerations, the picture of carrier relaxation consistent with our data is the following. Although the estimated carrier density at excitation in our experiments is comparable to or somewhat greater than the Mott density of about 10^{17} cm^{-3} in CdSe,[8] the actual carrier density away from the surface is smaller. Moreover, effects such as the e-h plasma expansion, diffusion, and recombination further reduces the density with time. Thus, while the e-h plasma processes dominate initially, especially near the surface, luminescence due to the excitonic processes are superposed on the plasma emission and dominate at later stages as the plasma transforms into excitons and biexcitons. A similar conclusion was reached in the case of CdS by Saito and Gobel[7] who found, using their luminescence measurements and transient grating data, that the e-h plasma could be supported only up to about 100–200 ps and the e-h pairs rapidly transform into biexcitons. Evidence of very rapid formation of excitons and biexcitons following initial e-h plasma generation was provided by Hulin *et al.*[18] in the case of CuCl. (This is in contrast with the luminescence results[27] obtained for GaAs and $In_xGa_{1-x}As$, where it is possible to study hot e-h plasma and its approach towards equilibrium with the lattice for well over 100 ps, the exciton and biexciton binding energies being very small.)

The TR luminescence at 1.823 eV (680.1 nm) in Fig. 3

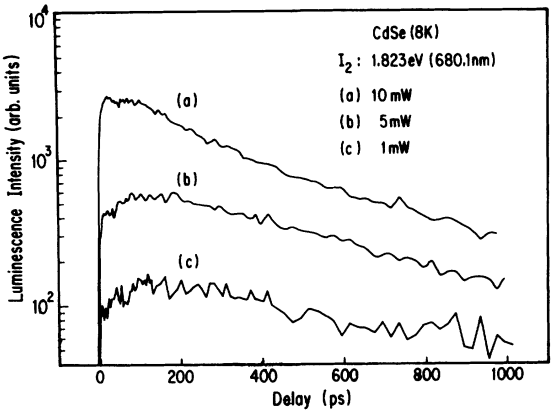

FIG. 3. The time dependence of luminescence taken at 1.823 eV corresponding to the the bound exciton (I_2) energy showing the intensity dependence.

[corresponding to the bound exciton (I_2)] shows that the initial rising part and the peak region has a dependence on the excitation density. The signal rises for about 50 ps. The time dependence for delays beyond 400 ps appears to have an exponential behavior. The nonexponential part of the decay before 400 ps seen for 10 mW appears to dimimish as the excitation density decreases, as is evident in Fig. 3 which compares the time evolution of the luminescence obtained at average excitation intensity of 10, 2.5, and 1.0 mW. As the excitation intensity decreases, the I_2 luminescence decay tends to a single exponential behavior. The luminescence decays with a time constant of 565, 585, and 800 ps for 10, 2.5, and 1.0 mW, respectively.[28] The dependence of the decay rate on the excitation intensity may be a result of the reduced electron and free exciton collisions with the bound excitons as the excited e-h pair density is made smaller.

The TR luminescence shown in Fig. 4 is taken at 1.8214

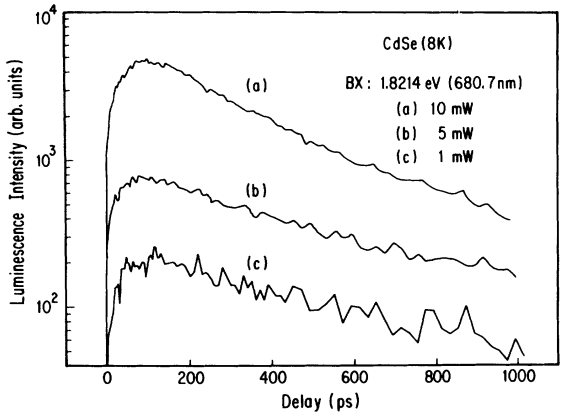

FIG. 4. The TR luminescence at 1.821 eV corresponding to the biexciton energy (M band) taken at different excitation densities.

eV (680.7 nm) for 10, 2.5, and 1.0 mW at a wavelength expected for the biexciton emission. The luminescence here rises to its peak in about 75 ps. It shows an exponential decay beyond 400 ps with a time constant of 420, 660, and 730 ps, respectively for 10, 2.5, and 1.0 mW. Once again, the time evolution is seen to depend upon the excitation density.

IV. LO PHONON-ASSISTED FREE EXCITON LUMINESCENCE

Figure 5 (curve *a*) shows the TI luminescence taken at a beam intensity of 4 mW for wavelengths beyond 1.8074 eV (686 nm). Also shown is the corresponding PEC spectrum in Fig. 5 (curve *b*) taken at a delay of 200 ps. Using the results of Fig. 5, we determine the longitudinal-optical phonon energy ($\hbar\omega_{LO}$) of $\sim$ 26.5 meV in CdSe. The LO phonon Stokes sidebands of the I_2 luminescence (at 1.823 eV or 680.1 nm) are identified in Fig. 5 at 1.7966 eV (690.1 nm) (I_2-LO) and 1.7699 eV (700.5 nm) (I_2-2LO) using the PEC spectrum. If most of the excited *e-h* pairs relax to form free excitons (with density n_f), we have a linear relationship: $n_f \sim n_0$. The recombination luminescence of the exciton in its ground state (A_1) and the phonon replica A_1-LO (1.801 eV or 688.4 nm) and A_1-2LO (1.774 eV or 698.9 nm) seen in the TI luminescence spectrum of Fig. 5 (curve *a*), therefore, do not show corresponding peaks in the PEC spectrum. The TI luminescence peak at A_1-3LO is much broader than the peaks at A_1-LO and A_1-2LO and perhaps has a more complex origin, as suggested by the small negative PEC signal at A_1-3LO. With $\hbar\omega_{LO} \approx 26.5$ meV, the wavelength positions of these phonon replica lead to the determination of the free exciton wavelength of 1.827 eV (678.7 nm). The bound exciton has a binding energy of 4 meV, as shown by the relative positions of the phonon replica of A_1 and I_2.

The luminescence due to the free exciton polaritons is usually not efficient. The emission due to its LO phonon-assisted recombination, however, can escape the semiconductor surface. Luminescence peaks due to some of these phonon Stokes sidebands are already identified in Fig. 5. It is known[21,29] that the exciton dynamics can be determined by studying the TR luminescence at these phonon replica. The time evolution of the luminescence at the A_1-LO energy is shown in Fig. 6 at 10 mW. The luminescence initially rises rapidly, reaching its peak in only about 5 ps. It then shows a rapid fall with an approximate time constant of 50 ps. It has an exponential decay after 200 ps with a time constant of 650 ps.

The line shape of the A_1-2LO band is expected to reflect the exciton energy distribution more directly than the A_1-LO band.[21,29] We have studied the time evolution of the luminescence spectrum in the A_1-2LO region in some detail for the 10-mW excitation. This is seen in Fig. 7(a). The TI luminescence (for 4 mW) showing the peak at A_1-2LO is also shown for comparison [Fig. 7(a)]. It is seen that the free exciton related signal emerges from the background in about 100 ps following the initial *e-h* pair excitation. The background signal has a relatively rapid decay with time. This is brought out more clearly in Fig. 8 where the time dependence of the luminescence is shown at a few photon energies. The associated time constants of the approximate double exponential decay behavior of the luminescence in the A_1-2LO region at various energies are shown in the inset of Fig. 8. There are several points of interest here. First, the rapid initial decay takes place with a time constant of about 40 ps irrespective of the wavelength. The time evolution beyond 100 ps, however, takes place with a highly energy-dependent time constant. We note that a clear peak is seen in the polariton luminescence decay time constant at the A_1-2LO energy (Fig. 8, inset). The signal at the A_1-2LO energy shows a 600 ps decay time constant whereas that on its either side decays faster, with a time constant of about 300 ps. Many years ago, Toyozawa[29] argued that the polariton lifetime should reach a maximum at about

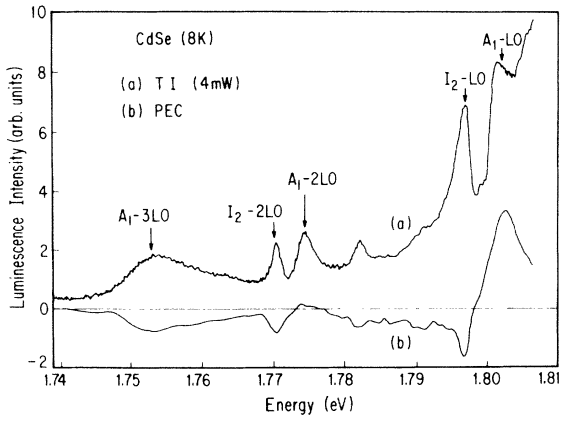

FIG. 5. The TI and PEC (at 200 ps) luminescence spectra showing various features due to LO phonon-assisted excitonic processes.

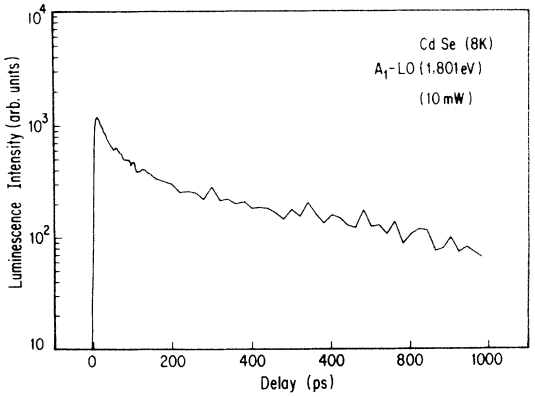

FIG. 6. The TR luminescence at 1.801 eV corresponding to one-LO phonon Stokes sideband of the free exciton ground state (A_1).

the transverse exciton energy, showing the so-called polariton bottleneck effect, due to reduced phonon scattering near the polariton-knee region. We should mention that unlike this, a steplike behavior was seen for CdS by Wiesner and Heim[30] at the transverse exciton energy in their delayed-coincidence photon counting experiments with a 300-ps time resolution. This was explained[31] to be consistent with the polariton bottleneck effect on the basis of a two-exponential behavior for the exciton population, symmetric in the filling and decay rates. Whether the difference between this and our results is due to impurities creating bound excitons in our case in addition to exciton-phonon scattering is not clear at present. The possibility that the free exciton-polaritons can be formed

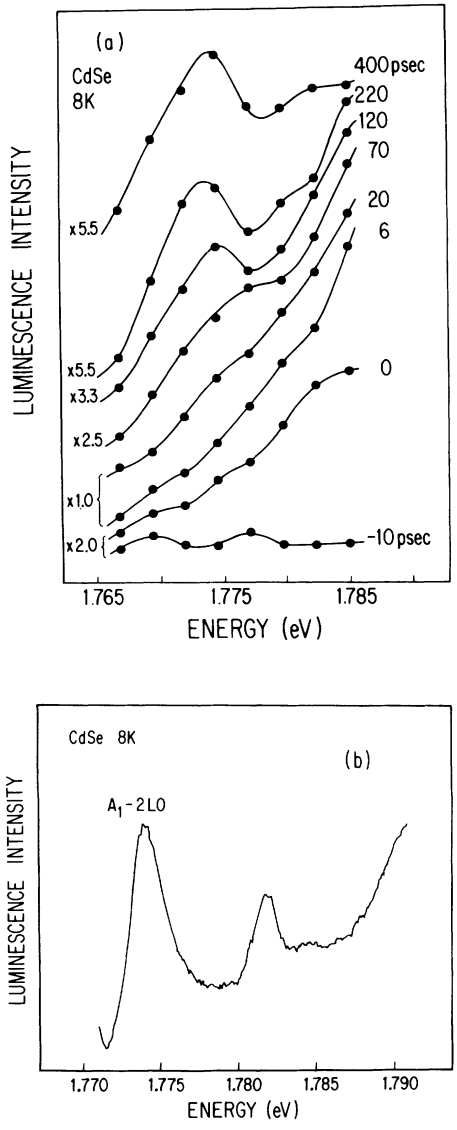

FIG. 7. The time- and energy-resolved luminescence spectrum (at 10-mW excitation) showing the evolution of the A_1-2LO luminescence at 1.774 eV (a). Also shown is the corresponding TI luminescence spectrum (b).

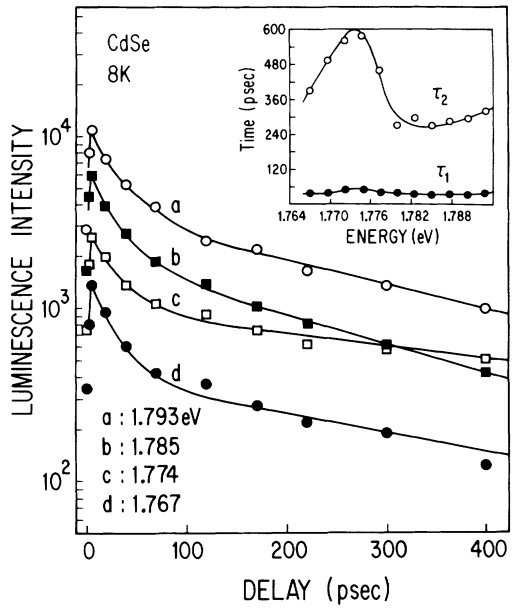

FIG. 8. The TR luminescence at various energies near the A_1-2LO region. The inset shows the early and long time effective decay time constants for different energies.

at a large wave vector (and kinetic energy) and with a nonthermal energy distribution is often considered. The excitons may subsequently thermalize among themselves and relax towards the knee in the polariton dispersion curve. This in fact has been demonstrated in the case of Cu_2O by Snoke *et al.*[32] who studied the phonon-assisted luminescence of the exciton after a resonant creation of the excitons. The data of Fig. 8 does not provide the necessary clear evidence to infer the relaxation of a highly nonequilibrium, nonthermal exciton distribution shifting towards the knee at 1.774 eV from an initial higher kinetic energy of excitons at formation during the period of the evolution studied (from about 100 ps up to 1000 ps) and within the energy resolution used ($\sim$ 2.5 meV) in our experiments. Energy resolution better than this and a low-density excitation to minimize the background effects and to probe the initial period ($<$ 100 ps) is required to address the question of the time evolution of the exciton-energy distributions.

V. COUPLED DYNAMICS OF EXCITONS AND BIEXCITONS

In a simplified picture, the *e-h* pairs, after their initial creation, relax to form excitons. The exciton density decays due either to various recombination processes or to formation of biexcitons. The biexcitons, in turn, can disintegrate, leaving behind excitons. The dynamics of the excitons and biexcitons is, therefore, coupled. The time dependence of the biexciton density (n_B) is governed by[1]

$$dn_B/dt = C(n_f)^2 - n_B/\tau_B \ , \qquad (2)$$

where C determines the biexciton formation rate, n_f is the free exciton density, and τ_B is the biexciton lifetime. The dynamics of free exciton density n_f may be described approximately by

$$dn_f/dt = G - n_f/\tau_f - 2C(n_f)^2 + n_B/\tau_B \ , \qquad (3)$$

where G is the exciton formation rate [$G \approx (n_0/\tau_1) \times \exp(t/\tau_1), \tau_1$ determines the exciton formation time] and τ_f is the exciton lifetime. The framework of Eqs. (2) and (3) is based on the assumption that (1) the effects of carrier-exciton, exciton-biexciton, and biexciton-biexciton collisions are not important, (2) all the excited e-h pairs are assumed to first form free excitons, (3) the biexcitons are assumed to be formed only from free excitons, and (4) the role of bound excitons in the exciton dynamics is relatively less important. Since Eqs. (2) and (3) are coupled, the time evolution of the biexciton luminescence is expected to depend on the free exciton dynamics. We normalize Eqs. (2) and (3) with respect to the excitation carrier density n_0 and estimate the various parameters in these equations by comparing their numerical solutions with the measured time dependence of the biexciton and exciton luminescence intensities. We obtain the total time-resolved biexciton luminescence by integrating the spectra of Fig. 1. This is shown in Fig. 9. We assume that the biexciton density n_B has the same time dependence. The time dependence of the exciton density n_f is taken to be given by that of the A_1-LO luminescence (Fig. 6). Figure 9 shows that the above simple model [Eqs. (2) and (3)] fits the data at 10 mW for the exciton and the biexciton luminescence time dependence reasonably well. The small difference between the data and the model for early times may be due to effects such as phonon-assisted emission by the e-h plasma, electron-exciton interactions etc., not included in the model. From this fit, we obtain the free exciton formation time τ_1 to be 5 ps and its lifetime τ_f of 600 ps. The biexciton lifetime τ_B is determined to be 10 ps. Although the data in Fig. 9 shows that the biexciton luminescence decay time constant obtained by a simple exponential fit to the data is 240 ps, its lifetime τ_B ($\sim$ 10 ps) is much smaller. It is thus clear that the decay behavior of the biexciton luminescence in Fig. 9 is in fact determined by the availability of the free excitons for biexciton formation, hence, to a large extent, by the free exciton lifetime and not as much by the biexciton recombination rate itself. The biexciton decay time constant $\tau_B \approx 10$ ps deduced above for CdSe is comparable to a previous estimate of 17 ps for CdS by Baumert (quoted by Saito[7]).

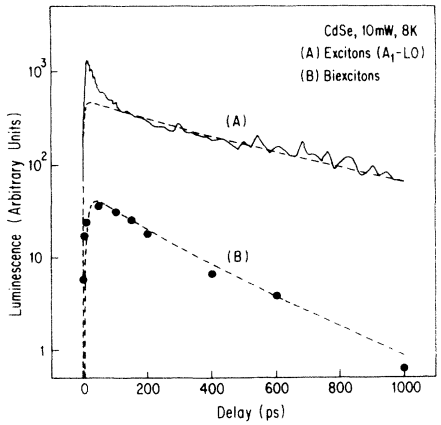

FIG. 9. The solutions (dashed curves) of the coupled dynamics of the exciton and biexciton densities [based on Eqs. (2) and (3)] are compared with the data (continuous curves for excitons and discrete points for biexcitons) at 10-mW excitation.

VI. CONCLUSION

In conclusion, we have performed a time-resolved study of luminescence in CdSe photoexcited by picosecond laser pulses. Depending upon the density of excited e-h pairs, the luminescence spectrum is expected to be dominated by different processes such as formation and radiative decay of e-h plasma, free and bound excitons, biexcitons, etc. Using time-integrated and time-resolved measurements of the luminescence spectra at densities varying from $\sim 8 \times 10^{16}$ cm^{-3} to 8×10^{17} cm^{-3}, we demonstrate the time evolution of the free e-h pairs into hot biexcitons at high densities. The role of bound excitons in the luminescence time evolution becomes evident at low densities. A simple model of the time dynamics of free excitons and biexcitons leads to the estimates of the exciton and biexciton lifetimes of approximately 10 ps, and 600 ps, respectively.

ACKNOWLEDGMENT

This work was partly supported by the NSF under Grant Nos. INT-9022623 and INT-9201350.

[1] C. Klingshirn and H. Haug, Phys. Rep. **70**, 315 (1981).
[2] E. Hanamura and H. Haug, Phys. Rep. **33C**, 209 (1977).
[3] H. Haug, Festkörperprobleme **XXII**, 149 (1982); S. Nikitine, in *Excitons at High Density*, edited H. Haken and S. Nikitine (Springer-Verlag, Berlin, 1975).
[4] M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura, *Excitonic Processes in Solids* (Springer-Verlag, Berlin, 1986).
[5] H. Shionoya, H. Saito, E. Hanamura, and O. Akimoto, Solid State Commun. **12**, 223 (1973); H. Saito, H. Shionoya, and E. Hanamura, *ibid.* **12**, 227 (1973).
[6] J. Bille, Festkörperprobleme **XIII**, 111 (1973); H. Butner *ibid.* **XIII**, 145 (1973); D. Magde and H. Mahr, Phys. Rev. Lett. **24**, 890 (1970).
[7] H. Saito, J. Lumin. **30**, 303 (1985); H. Saito and E. O. Gobel, Phys. Rev. B **31**, 2360 (1985).
[8] N. J. Frigo, H. Mahr, and D. J. Erskine, IEEE J. Quantum Electron. **QE-18**, 192 (1982).
[9] J. G. Fujimoto, S. G. Shevel, and E. P. Ippen, Solid State Commun. **49**, 605 (1984).

[10]T. Daly and H. Mahr, Solid State Commun. **25**, 323 (1978); T. Kobayashi, Y. Segawa, and S. Namba, *ibid.* **31**, 253 (1979); M. Hayashi, H. Saito, and S. Shionoya, *ibid.* **24**, 833 (1977); H. Saito, M. Hayashi, and S. Shionoya, *ibid.* **24**, 837 (1977); M. Hayashi, H. Saito, and S. Shionoya, J. Phys. Soc. Jpn. **44**, 582 (1978).

[11]C. Dornfeld and J. M. Hvam, IEEE J. Quantum Electron. **QE-25**, 904 (1989).

[12]C. Benoit a la Guillame, J. M. Debever, and F. Salvan, Phys. Rev. **177**, 567 (1969); D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).

[13]E. I. Rashba and G. E. Gurgenishvili, Fiz. Tverd. Tela (Leningrad) **4**, 1029 (1962) [Sov. Phys. Solid State **4**, 759 (1962)].

[14]M. Dagenais and W. F. Sharfin, J. Opt. Soc. Am. **2**, 1179 (1985).

[15]K. H. Pantke, P. Schillak, J. Erland, V. G. Lyssenko, B. S. Razbirin, and J. M. Hvam, Phys. Status Solidi B **173**, 91 (1992); H. Stolz, *ibid.* **173** 99 (1992).

[16]M. Jorgensen and J. M. Hvam, Appl. Phys. Lett. **44**, 460 (1983).

[17]C. Gourdon, P. Lavallard, and M. Dagenais, Phys. Rev. B **37**, 2589 (1988); T. Steiner and M. L. W. Thewalt, Can. J. Phys. **63**, 1207 (1985); F. Minami and K. Era, Soild State Commun. **53**, 189 (1985); C. H. Henry and K. Nassau, Phys. Rev. B **1**, 1628 (1970).

[18]D. Hulin, A. Mysyrowicz, A. Migus, and A. Antonatti, J. Lumin. **30**, 290 (1985).

[19]D. V. Lovering, R. T. Phillips, G. J. Denton, and G. W. Smith, Phys. Rev. Lett. **68**, 1880 (1992).

[20]*Proceedings of the Vth International Conference on II-VI Compounds, Tamano, Japan, 1991*, special issue of J. Cryst. Growth **117**, 1 (1992).

[21]Y. Masumoto and S. Shionoya, Phys. Rev. B **30**, 1076 (1984).

[22]See for example, B. Johnson and T. C. McGill, J. Appl. Phys. **63**, 2077 (1988).

[23]A. S. Vengurlekar, S. S. Prabhu, S. K. Roy, and J. Shah, Phys. Rev. B **50**, 8348 (1994).

[24]*Data in Science and Technology*, edited by O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. b (Springer-Verlag, Berlin, 1982), p. 207.

[25]A. S. Vengurlekar, S. S. Prabhu, S. K. Roy, and J. Shah, *Ultrafast Phenomena IX* (Springer-Verlag, Berlin, in press).

[26]See, for example, S. Tanaka, H. Saito, H. Yoshida, and S. Shionoya, in *Semiconductors Probed by Ultrafast Laser Spectroscopy*, edited by R. R. Alfano (Academic Press, Orlando, 1984).

[27]K. Kash, J. Shah, D. Block, A. C. Gossard, and W. Wiegmann, Physica B **134**, 189 (1985).

[28]Ideally, data up to a few ns are required to deduce such time constants conclusively. Our experimental conditions limit the maximum delay possible to 1 ns.

[29]Y. Toyozawa, Prog. Theor. Phys. Suppl. **12**, 111 (1959).

[30]P. Wiesner and U. Heim, Phys. Rev. B **11**, 3071 (1975).

[31]F. Askary and P. Y. Yu, Phys. Rev. B **31**, 6643 (1985).

[32]D. W. Snoke, D. Braun, and M. Cardona, Phys. Rev. B **44**, 2991 (1991).