Time dynamics of free- and bound-exciton luminescence in CdSe under low- and high-intensity excitation

C. Gourdon and P. Lavallard
Groupe de Physique des Solides, Ecole Normale Supérieure, Tour 23, 2 place Jussieu, 75251 Paris, France

M. Dagenais*
GTE Laboratories, Inc., 40 Sylvan Road, Waltham, Massachusetts 02254
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A low-intensity direct measurement of the D^0X bound-exciton lifetime in CdSe is presented. A lifetime of 410 ps is measured, indicating a very large oscillator strength for this mostly radiative transition. The free-exciton lifetime is measured to be 1.4 ns, and is probably limited by trapping. At intensities of the order of 100 kW/cm^2, large changes of the time evolution of the luminescence intensity of both the free and bound excitons are observed. The bound-exciton luminescence appears almost instantaneously before decaying rapidly in the first 200 ps, and then the rate of decay slows considerably. This time behavior is believed to result from an interplay between stimulated emission and an induced absorption due to a self-broadening of free excitons at large densities.

I. INTRODUCTION

The time-integrated luminescence spectrum of a CdSe crystal is dominated by the well-known I_2 (impurity) line at 6805 Å corresponding to the recombination of an exciton bound to a neutral donor D^0X. Depending on the sample quality, one may also see a shoulder at higher energy corresponding to the recombination of the A free exciton and sometimes in between a line attributed to a surface exciton. A-LO and A-2LO phonon replicas can also be detected. The I_2-LO line is much weaker.

In this paper, we report the direct measurement of a bound-exciton lifetime. The lifetime of excitons bound to neutral donors in CdSe is measured to be 410±30 ps. This measurement was done at low intensity by directly exciting the bound-exciton resonance by a train of picosecond pulses and by studying the luminescence decay of the I_2-LO line using a synchronous-scanning streak camera. By exciting on the free-exciton resonance, a free-exciton lifetime of about 1.4 ns is obtained. By increasing the intensity of the exciting beam to intensities of the order of 100 kW/cm^2, it was found that the luminescence decay of both the free and bound excitons is dramatically altered. For instance, the luminescence from the bound exciton appears almost instantaneously, decay rapidly, and then slows considerably after about 200 ps. The final decay of the luminescence occurs on a time scale of several nanoseconds. Detailed complementary experiments have shown that the role of the biexciton luminescence can be discounted when interpreting the results. Stimulated emission is found to play a dominant role in decreasing the bound-exciton lifetime.

II. EXPERIMENTAL SETUP

The excitation source is a mode-locked dye laser synchronously pumped by an argon ion laser. The dye is DCM (4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4*H*-pyran). A dispersive element (Lyot filter) in the dye laser cavity narrows the pulse spectral width to about 0.2-nm full width at half maximum (FWHM). (Sometimes an intracavity étalon is used to further narrow the spectral width to less than 0.05 nm.) The pulse repetition rate is 82 MHz (pulse spacing 12 ns) and the pulse during is about 5–10 ps. The typical mean power is 10 mW. The CdSe samples are as-grown platelets, 5–30 μm thick, unintentionally doped. They are mounted strain-free in a liquid-helium cryostat pumped below the λ point. All the experiments are performed at about 2 K. The incident beam is focused on the sample to a spot diameter ($1/e^2$ points) of 160 μm. The c axis of the platelets lies in the plane of the sample. A half-wave plate followed by a polarizer insures a good polarization $\mathbf{E}\perp\mathbf{c}$ of the incident beam. A set of neutral-density filters is used to lower the incident power. Backward luminescence light is collected by an elliptic mirror and focused on the entrance slit of a double spectrometer. For taking the time-integrated luminescence spectra, a conventional photomultiplier coupled to a lock-in amplifier is used. For time-resolved spectroscopy, a double spectrometer operating in the subtractive mode to minimize pulse spreading is used in conjunction with a synchronous-scanning streak camera.[1] The spectrometer has a 3-nm/mm dispersion. A resolution of 0.1–0.3 nm is usually achieved. The streak camera is a Delli Delti model. The high frequency (41 MHz) sinusoidal voltage, which also drives the argon-laser mode locker, is frequency doubled, amplified and then applied to the deflection plates of the streak camera. Successive events occurring at the laser repetition rate are then superimposed on the image tube. An optical multichannel analyzer (OMA) is used to read out the spatial intensity distribution from the streak tube screen. A 30-ps time resolution is actually achieved. The broadening of the initial laser pulse (5–10 ps) is mainly due to pulse jitter. It could be reduced to about 20 ps by using a sinusoidal

signal directly derived from the dye-laser pulses as deflection voltage. The recorded spectra are corrected to take into account the sinusoidal deflection voltage and the intensity response of the OMA read-out system. For transmission experiments in a pump-probe configuration, two mode-locked dye lasers synchronously pumped by the argon laser are used. The probe beam has a rather broad spectral range (~ 3 nm), whereas the pump beam has a narrow spectral range (~ 0.2 nm). Both are focused on the sample to a spot diameter of 120 μm ($1/e^2$ points) and 30 μm, respectively. Only E$\perp$c transmitted light is detected. The probe intensity is highly attenuated by neutral-density filters to avoid self-induced effects.

III. LOW EXCITATION LEVEL

The lifetime of excitons bound to a neutral donor D^0X (the I_2 line) was measured by Henry and Nassau in CdS (Ref. 2) and Minami and Era in CdSe (Ref. 3) and found to be 500±100 ps and 500±50 ps, respectively. It should be mentioned that these measurements are not direct measurements. Henry and Nassau's phase-delay method implicitly assumes an exponential decay of the luminescence. Since only above-band-gap excitation was achieved in their experiments, they had to choose crystals with a free-exciton lifetime shorter than the bound-exciton lifetime. Therefore, the bound exciton are nearly instantaneously created and the I_2 luminescence decay actually corresponds to the bound-exciton lifetime. In the experiment of Minami and Era in CdSe, the bound exciton is also not directly created, but is probably generated in one of its excited states (rather than in its acoustic-phonon wing, as suggested by the authors). Other measurements of the bound-exciton lifetime in CdSe (Ref. 4) are questionable since the free-exciton role in bound-exciton formation is not clearly taken into account. We report here on the measurement of the bound-exciton lifetime by directly exciting the I_2 line and recording the phonon replica luminescence decay (Fig. 1). We find a D^0X lifetime of 410±30 ps in good agreement with Minami and Era. To our knowledge, this is the first direct measurement of the D^0X lifetime. We also observe the luminescence decay of D^0X when exciting either on the free exciton $A_{n=1}$ or on an excited state of D^0X. (We know from excitation spectra of the I_2 line[5] that there are at least two excited states of D^0X in the energy range between the I_2 line and the free-exciton energy.) To achieve a low excitation level on the $A_{n=1}$ state, we worked with the E parallel polarization (mixed mode) for which the absorption coefficient is much reduced. In the case of excitation on an excited state of D^0X, a three-level model well describes our results. The first level is the crystal ground state, the second one is the bound-exciton state with population density n_B and lifetime T_B, and the third one is the D^0X excited state with population density n and lifetime τ. We also take into account a transfer time t_2 from the third level to the second one. The rate equations then read

$$\frac{dn(t)}{dt}=-\frac{n(t)}{\tau}\ ,$$

$$\frac{dn_B(t)}{dt}=-\frac{n_B(t)}{T_B}+\frac{\tau}{t_2}\frac{n(t)}{\tau}=-\frac{n_B(t)}{T_B}+\frac{n(t)}{t_2}\ .$$

The bound-exciton-density time dependence is found to be

$$n_B(t)=\frac{n(0)}{t_2(1/\tau-1/T_B)}[\exp(-t/\tau)-\exp(-t/T_B)]\ .$$

When one of the decay times τ or T_B is much shorter than the other, the luminescence rising time is governed by the shorter time, whereas the decay time is dominated by the longer one. Therefore one must be very careful in interpreting decay-time measurements, especially when a poor time resolution prevents one from seeing the rising edge.

Figure 2(a) shows the experimental bound-exciton luminescence decay and also a theoretical fit. We extract a bound-exciton lifetime T_B of 410 ps and an excited-state lifetime τ of 100 ps. This latter value is not very accurate since no deconvolution was made to take into account the incident pulse duration. When the free exciton is first excited, the D^0X excited-state lifetime can be neglected and a three-level model can still be used. Nevertheless, a better fit for early times is obtained with a four-level system (i.e., ground state, D^0X state, D^0X excited state, and free-exciton state). Figure 2(b) shows the experimental results and a theoretical fit. We use $T_B=410$ ps, $\tau=100$ ps, and obtain the free-exciton lifetime $T_E=1400$ ps. This last time may vary from sample to sample (from 950 to 1600 ps). We can obtain independently the free-exciton lifetime by directly creating the free exciton and recording the A-LO phonon-replica luminescence decay. We have measured $T_E=1400\pm100$ ps with the sample that was used for Fig. 3. It was noticed that the free-exciton lifetime is very sensitive to the value of the incident power. It increases with increasing incident power. Even at low intensity (about 30 $W\,cm^{-2}$) (Ref. 6) a weak fast-rising signal of unknown origin is often superimposed on D^0X time-resolved luminescence (Fig. 4). We checked very carefully that it is not due to some stray light from the exciting laser beam. One possibility is that it originates from bound excitons directly created through one of their short-

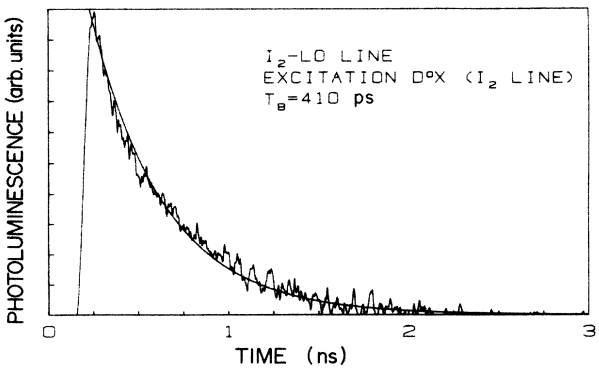

FIG. 1. I_2-LO time-resolved luminescence. The excitation is resonant on D^0X and is a low-intensity excitation. The solid line is an exponential fit with $T_B=420$ ps.

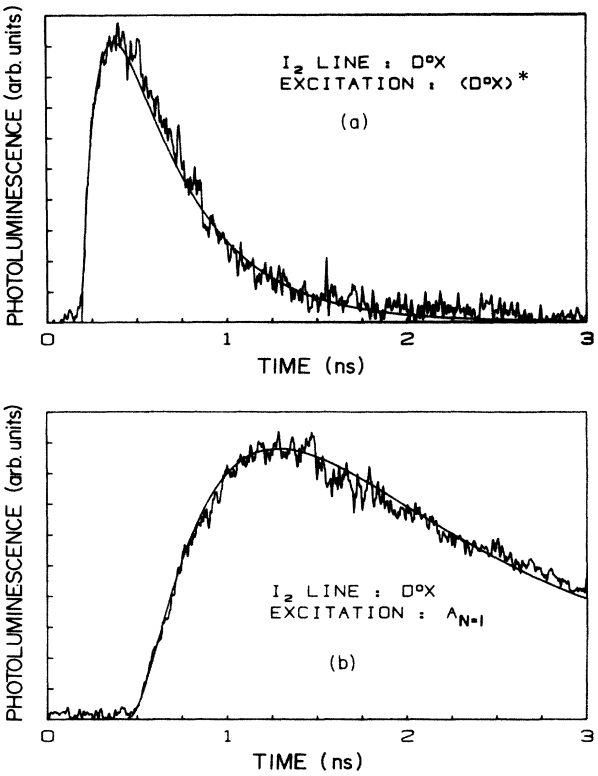

FIG. 2. I_2 time-resolved luminescence. (a) The excitation is on an excited state of D^0X and is at low intensity. The solid line is a theoretical fit with $T_B=410$ ps and $\tau=100$ ps (see text). (b) The excitation is on the free-exciton resonance and is a low-intensity excitation. The solid line is a theoretical fit with $T_B=410$ ps, $\tau=100$ ps, $T_E=1400$ ps (see text).

living excited states lying in the exciton region. Although the signal is too weak to be discernible on a time-integrated spectrum, a time-resolved measurement indicates that the luminescence spectrum of the fast-rising signal is broader than the I_2 line. In addition, on the low-energy side of the I_2 line, the time decay of the fast-rising signal is much shorter than the time decay of the I_2 line; it is nearly as short as the laser pulse. This rules out the above hypothesis. We also rule out the possible role of Raman effects, since the spectrum is

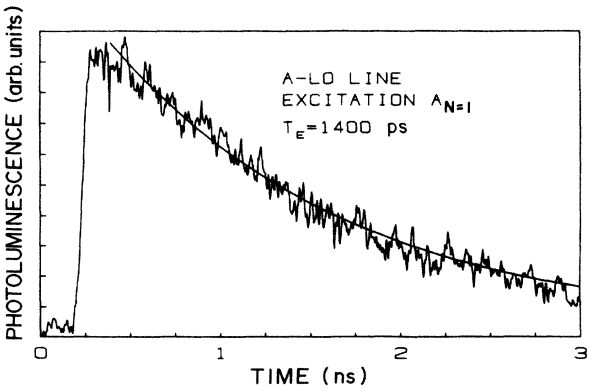

FIG. 3. A-LO time-resolved luminescence at low-intensity excitation. The solid line is an exponential fit with $T_E=1400$ ps.

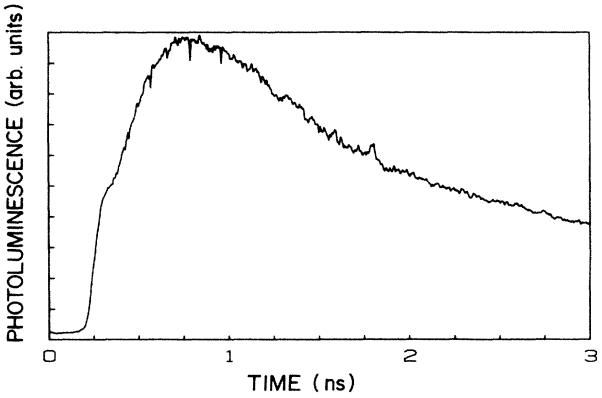

FIG. 4. I_2 time-resolved luminescence showing a weak unknown fast-rising signal at early times. The excitation is on the free-exciton resonance.

broad and does not depend on the exact wavelength of the incident light. Another possibility is that this additional signal is due to some luminescence light from exciton polaritons scattered along their dispersion curve from the bottleneck down to the energy region of the I_2 line. However, even though the lifetime of these states is very short, the luminescence time decay should not be shorter than that of the polaritons from the bottleneck which feed these states.

IV. HIGH EXCITATION LEVEL

At "high" excitation level (typically 100 kW/cm^2), the bound-exciton luminescence time behavior drastically changes. When the exciting-beam energy lies in the energy range between the excited state of D^0X and the free exciton, the bound exciton appears to be created instantaneously (in a lapse of time corresponding to the pulse integral). The luminescence signal initially decays much faster than previously (within 150–200 ps) and then slows considerably. Its rate of decay becomes comparable to the free-exciton decay at long times. This behavior is shown in Figs. 5(a) and 5(b). The A-LO phonon-replica time behavior also changes. The decay becomes longer with a characteristic time of 2.5–2.7 ns, probably as a result of the filling of traps. We have investigated several mechanisms to explain the initial fast decrease of the I_2 luminescence.

(i) At high excitation level, the time-integrated luminescence spectrum is modified (cf. Fig. 6). The I_2 line is broadened and a background luminescence appears in the energy range between the I_2 line and the free-exciton energy. We therefore looked for the existence of another line superimposed on the I_2 line. It has often been reported in the literature that a new line (the M line) appears at high excitation level as a low-energy shoulder of the I_2 line. In the case of CuCl, the origin of the new line is ascribed to the recombination of an excitonic molecule that leaves one excitonic polariton and one photon. In wurtzite II-VI compounds, the M line is still a matter of controversy.[7] It is known that the ratio of M-line luminescence over the I_2-line luminescence can be increased by carefully selecting the

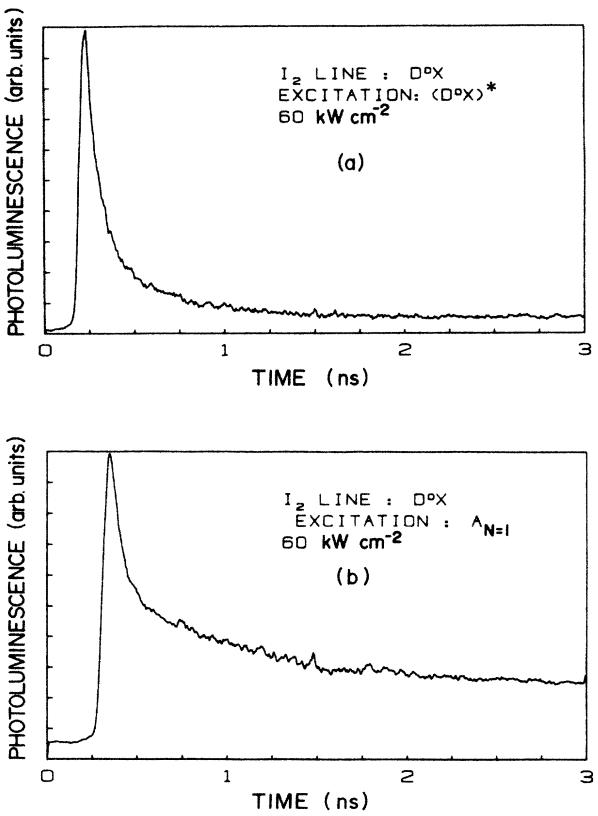

FIG. 5. I_2-line time-resolved luminescence. The excitation is at "high" intensity and is (a) on an excited state of D^0X, and (b) on the free-exciton resonance.

emergence and polarization angle of luminescence.[8] This is achieved by using a narrow slit perpendicular to the c axis and a polarizer parallel to the c axis. In this particular configuration, the I_2 line luminescence, which is more strongly E⊥c polarized than the M line, is highly attenuated and the M line shows a small low-energy shift. We have recorded the time-integrated luminescence spectra in the two configurations (E⊥c and k⊥c, E∥c), but no difference was observed. This was the first evidence against the hypothesis of the M line. Another experiment gave us more arguments against this hypothesis. The lifetime of the excitonic molecule is generally assumed to be short and of the order of hundreds of ps.[9] By placing a slit followed by a photomultiplier on the phosphor screen at the output of the streak camera, we were able to record the luminescence spectra for different time delays after the excitation pulse. At zero time delay (within 50 ps) as well as at 1-ns time delay after the excitation pulse, the two spectra are almost identical, the second one being a little broader. Therefore, we conclude that the very fast decay of the I_2 line within the first 150 ps is not due to an M line superimposed on an I_2 line. The luminescence signal at any time after the pulse belongs to the same line.

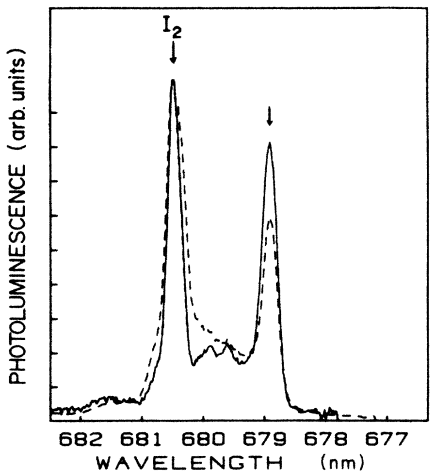

FIG. 6. Low (——) and high (— — —) intensity time-integrated luminescence spectra. The line under the arrow is the stray light due to the exciting laser beam on the free-exciton resonance.

(ii) Then we looked for stimulated effects. We used a cylindrical lens to focus the laser light on the sample with oblique incidence. We then focused the luminescence light coming either from the center or exiting from the edge of the sample on the entrance slit of the spectrometer. Almost no difference in the time-integrated spectra around the I_2 line was observed. In the second configuration the spectrum was slightly broader, but we know from the previous experiment that this broadening corresponds to long-time rather than early-time luminescence.

No difference with time-resolved spectra was expected since the whole exciton system must decay with the same time behavior wherever the luminescence light comes from. This was experimentally confirmed. Then we excited the sample with two spherical lenses: first with a 25-cm focal length lens and then with a 5-cm focal length lens. The ratio of the diameter of the two laser spots on the sample was verified to be of order 5. Stimulation of emitted light is expected to occur in the first configuration where the transverse dimension of the spot is larger. For comparable intensities (incident power divided by spot area) in the two configurations, D^0X time-resolved luminescence recorded with the 25-cm lens shows the early fast decay component, whereas the one taken with the 5-cm lens does not. This result is taken as strong evidence for stimulated emission.

(iii) Finally we investigated the effect of a "high-density" free-exciton population by recording the transmission spectrum of the sample. We knew from previous work that the transmission spectrum of a thin CdSe platelet is strongly modified in the A exciton region at moderate incident power.[10] We performed a pump-probe experiment with two synchronously pumped mode-locked dye lasers. We recorded the transmission of a weak probe with a rather broad spectral width under excitation by a narrow-spectral-width pump beam. The pump-beam energy position lies either on the D^0X excited state or on the free exciton. In both cases, the transmission spectrum in the free-exciton region is broadened and the transmitted intensity decreases (Fig. 7).

The broadening of this transmission spectrum under high excitation is a clear indication that the free-exciton

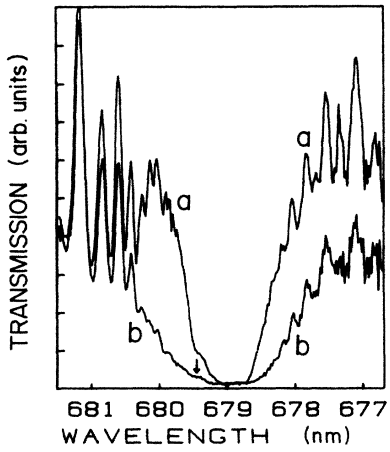

FIG. 7. Transmission under excitation: (a) probe before pump, (b) probe 140 ps after pump. The pump wavelength is indicated by the arrow and corresponds to an excited state of D^0X. Fabry-Perot transmission fringes can easily be observed.

damping coefficient increases. In this case, elastic and inelastic collisions between free excitons are probably the most efficient sources of broadening. These changes in the transmission spectrum might affect the I_2-line region. They seem to be instantaneous with regard to the time resolution of our experiment (about 50 ps) and they last for more than 1 ns. It is possible that stimulated emission is very rapidly quenched because of increasing absorption. Yet little change is seen in the I_2-line region in transmission because the probed depth is only of the order of the inverse of the absorption coefficient (a few micrometers) whereas for stimulated emission the active length is of the order of the spot diameter.

From the transmission experiments we can also tentatively explain the very fast rise of D^0X luminescence at high intensity. The excited states of the bound exciton are broadened and their lifetime reduced due to exciton scattering. Thus wherever the excitation lies, from the first excited state of D^0X to the free-exciton region, bound excitons are always created almost instantaneously through a very short-lived excited state. The lengthening of the free-exciton lifetime at high excitation is certainly due to saturation of long-living traps.

V. CONCLUSION

In conclusion, the D^0X bound-exciton lifetime in CdSe at low intensity is measured to be 410 ps, indicating a very large oscillator strength. A free-exciton lifetime of 1.4 ns is also extracted. When the excitation intensity is increased, the luminescence decay of the bound exciton is strongly affected. We show that it is due to stimulated emission. In the same experimental conditions, the transmission spectrum in the exciton region is highly modified by exciton collisions. Reabsorption can then occur and stop stimulated emission after a few tens of picoseconds.

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*Present address: Department of Electrical Engineering, University of Maryland, College Park, MD 20742.

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