Picosecond-luminescence study of exciton formation dynamics in CdSe

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We make a direct determination of the time constant for free-exciton formation in CdSe at 8 K by measuring the picosecond time-resolved luminescence at a longitudinal-optical-phonon-assisted Stokes sideband of the free exciton. This method allows us to obtain the time evolution of the total exciton population, in contrast to measurements of luminescence due to $\vec{K}=\vec{0}$ excitons. The free-exciton formation time constant is found to be 7–10 ps, independent of the exciting photon energy within a few LO-phonon energies above the band-gap energy at the carrier excitation density of $\approx 6\times 10^{16}$ cm^{-3}. The results suggest rapid carrier thermalization and energy relaxation in the continuum before exciton formation, rather than hot exciton formation by the geminate electron-hole pairs followed by a cascade emission of LO phonons by the excitons. [S0163-1829(96)52316-7]

The dynamics of exciton formation has been a subject of much interest for some time. Experiments to investigate this have been carried out for several material systems having exciton binding energy large enough for the exciton formation process to dominate over exciton ionization at the temperature of measurements. These materials include, for example, CdS,[1,2] GaAs/Al$_x$Ga$_{1-x}$As quantum wells (QW's),[3,4] Cd$_x$Zn$_{1-x}$Te/ZnTe QW's,[5] etc. Different models have been proposed[1–3, 6] to describe the process of exciton formation in these systems by photoexcited electrons and holes.

If the excitons formed by the electrons and holes near their band edges have a small enough wave vector $\vec{K}$ so that they can couple to photons, the exciton luminescence time evolution should be directly related to the exciton formation time. The rate of such a direct formation of excitons with small $\vec{K}$, however, is substantially reduced due to various kinematic selection rules. The excitons formed from free electron-hole (*e-h*) pairs are expected to have a large $\vec{K}$ vector.[3] These excitons have to relax to small $\vec{K}$ values before they can undergo radiative decay. Thus, direct determination of the exciton formation time from the time evolution of the small $\vec{K}$ exciton luminescence is in general not possible.

While an exciton with a large $\vec{K}$ cannot emit a photon directly, it may couple to a photon via LO-phonon emission. A direct measurement of the exciton formation dynamics can be made for those material systems for which the exciton–LO-phonon coupling is large and leads to excitonic transitions to the photonlike polariton branch via emission of one or more LO phonons. It is known[7] that the luminescence spectra at these exciton Stokes sidebands reflect the exciton distribution in $\vec{K}$. Such sidebands can be easily seen for materials like CdS and CdSe but usually not for GaAs (bulk or QW's). Time-resolved luminescence energy spectra due to a LO-phonon-assisted Stokes sideband can provide direct information on the free-exciton dynamics, as was shown by Snoke and co-workers,[8] who studied the relaxation of nonthermal energy distributions of excitons, resonantly photoexcited in Cu_2O. In this paper, we determine the time evolution of the total exciton density following an initial excitation of free electron-hole pairs in CdSe at 8 K by a laser pulse. For this, we measure the spectrally integrated up-conversion (UC) luminescence at the A_1-2LO Stokes sideband of the free exciton (A_1) associated with the A valence band of CdSe. The free electron-hole pair density (n_0) excited per pulse is estimated to be about 6×10^{16} cm^{-3}. The time resolution in these experiments is about 3 to 3.5 ps. We find that the exciton formation time constant is about 7–10 ps at 8 K, irrespective of the exciting photon energy within a few LO phonon energies above the band gap energy.

Figure 1 shows the continuous wave (cw) photoluminescence (PL) spectrum for CdSe taken at 8 K with He-Ne laser. The various well-known prominent PL peaks,[9] due to free excitons (A_1), excitons bound to a neutral donor (I_2), and

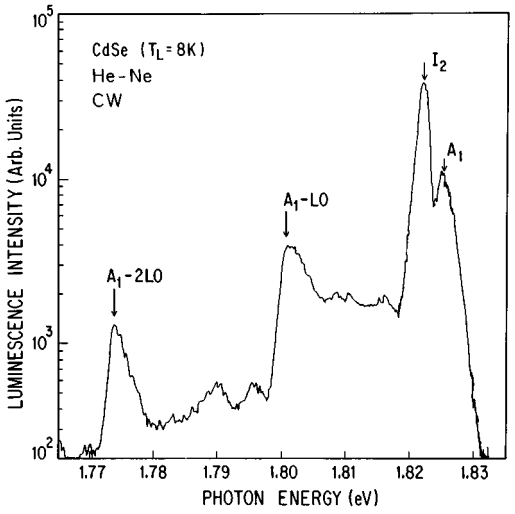

FIG. 1. CW luminescence spectrum in CdSe at 8 K showing the various prominent luminescence lines.

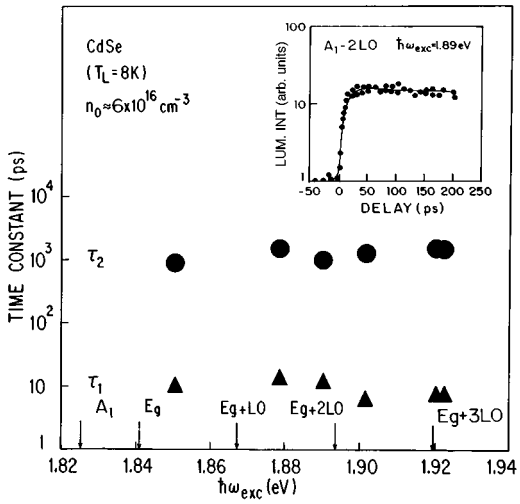

FIG. 2. The exciton luminescence rise and decay times obtained for different excitation wavelengths near the band edge from the time evolution of the A_1-2LO line, using measurements such as the one shown in the inset, as an example.

the LO-phonon-assisted Stokes sidebands of the free and bound exciton are identified in Fig. 1. For time-resolved up-conversion luminescence measurements, we use a Nd-YAG (yttrium aluminum garnet) pumped DCM dye laser with a pulse width of about 2.5 to 3 ps as given by an autocorrelator and a repetition rate of 76 MHz. The exciting photon energy is varied in the range 1.85 eV to 1.92 eV, near the CdSe band edge E_g (=1.841 eV at 8 K). The signal is detected using a cooled bialkali photomultiplier tube (with a dark count of less than 1 per sec) and a standard photon counting setup. The sample is mounted on a cold head in a closed cycle He refrigerator at 8 K. The intensity of the laser beam focused on the sample to a spot of about 50 μm is 1 mW, with the excited carrier density (n_0) per pulse estimated to be about 6×10^{16} cm^{-3}. The monochromator slits are opened to 200 μm, corresponding to a spectral width of about 5 meV.[10] The total PL signal thus detected at the A_1-2LO Stokes sideband of the free exciton is expected to be related to spectral integration of the major part of the exciton kinetic-energy distribution.

Figure 2 (inset) shows the time evolution of the UC PL of the A_1-2LO sideband at the laser photon energy of 1.89 eV, as an illustration. A rapid initial rise and then a slow decay of the signal is evident.[11] Figure 2 (inset) also shows a fit to the data based on a double exponential form $A[\exp(-t/\tau_2)-\exp(-t/\tau_1)]$ where τ_1 and τ_2, respectively, determine the characteristic rise and decay time constants of the A_1-2LO luminescence intensity, and hence of the formation and population decay of free excitons. The time constant τ_2 is rather large, of the order of 1000 ps. The long exciton lifetime ensures enough time for the excitons to attain a thermalized energy distribution via exciton-exciton collisions before their recombination. Figure 2 shows the rise time τ_1 measured at different wavelengths of the exciting photons. The rise time τ_1 is seen[12] to be about 7 to 10 ps. No dramatic oscillatory behavior of the UC PL rise time is seen in Fig. 2 as the exciting photon energy ($\hbar\omega$) varied within a few times the LO-phonon energy (=26.5 meV) above the band edge. To understand the insensitivity of τ_1 to variation in $\hbar\omega$ we need to consider the dynamics of the *e-h* pairs as they form excitons.

We may briefly recall the various models proposed in the past for the exciton formation process. In one picture, the geminate electron-hole pair emits an LO phonon to form a hot exciton with high kinetic energy. The subsequent relaxation occurs via a cascade emission of LO phonons by the hot excitons. This process should lead to sharp lines in hot luminescence and excitation spectra.[1] Such a behavior in fact has been seen in the case of CdS and CdSe crystals with small exciton lifetime at low excitation densities.[13–15]

It may be mentioned that although GaAs is a polar semiconductor and the *e-h* correlation is enhanced in GaAs QW's, hot exciton effects have not been seen so far in GaAs or GaAs QW's. In such cases, the excited carriers may first undergo energy-momentum relaxation in their respective bands before forming excitons. Here, exciton formation is mainly bimolecular with random binding of electrons and holes via phonon emission or carrier-carrier interaction, rather than forming hot excitons from geminate *e-h* pairs, resonant with free-carrier bands. (This mode of exciton formation has been shown to be valid also for materials where the exciton–LO-phonon coupling is weak, as in Si.[6]) In the model proposed for low-density excitations in GaAs QW's,[16] the correlation of the geminate *e-h* pair is lost due to phonon scattering. The holes, with a smaller share of the exciting photon excess energy, rapidly relax to the top of the valence band. The electrons relax towards the conduction-band edge by emitting a cascade of LO phonons. The electron and hole then form an exciton via LO-phonon energy emission, if energetically possible, or else via other mechanisms, such as acoustic-phonon emission or carrier-carrier scattering. The oscillations seen by Blom *et al.*[16] in the exciton luminescence rise time in narrow GaAs QW's as the exciting photon energy is varied have been interpreted to be due to whether the electrons and holes near their band edges can form excitons via LO-phonon emission or not.

It should be noted that the above pictures, in which the carriers initially relax mainly due to a cascade emission of LO phonons, may be valid only for low-density excitations. In these cases, the carrier-carrier scattering rate is relatively insignificant compared to the LO-phonon interaction of electrons and holes, either in geminate form or in uncorrelated conditions. At sufficiently high excitation densities, on the other hand, the *e-h* correlation within the geminate pairs may be lost due to carrier-carrier interactions and carriers may rapidly form a hot thermalized energy distribution within a few tens of fs. Such a hot carrier assembly in polar semiconductors then cools mainly via LO-phonon emission, the typical time for one LO-phonon emission being about a few hundreds of fs. The carriers then approach their respective band edges (within one LO-phonon energy) in a few ps by phonon emission, before they can form excitons.

The first possibility that the *e-h* pairs in our experiments can form hot excitons immediately after excitation can be ruled out as follows. After their formation, the hot excitons rapidly emit LO phonons to form excitons with smaller kinetic energies, which then thermalize among themselves via exciton-exciton collisions.[1] A calculation of the average time required by the hot excitons in CdSe to emit one LO phonon

leads to an estimate of about 300 fs, based on known exciton–LO-phonon Fröhlich coupling[17] in CdSe. Thus, the exciton sideband luminescence rise time, after emission of a few (in our case three at most) LO phonons by the hot excitons, is expected to be of the order of 1 ps and excitation energy dependent. However, the measured rise time is about one order larger (about 10 ps), and independent of the excitation energy.

The other possibility is that the carriers rapidly form a thermalized distribution and undergo energy relaxation via LO-phonon emission before forming excitons. The excitation carrier density used in our experiments ($\approx 6\times 10^{16}$ cm^{-3}) is large enough for the carriers to rapidly form such a thermalized energy distribution via carrier-carrier scattering.[18,19] The correlation of the geminate *e-h* pair is thus lost. The carriers cool within a few ps by emitting LO phonons and attain energies close to the band edge before forming excitons at nonzero $\vec{K}$. The A_1-2LO PL rise time in such a case will not have a significant dependence on the energies at which the *e-h* pairs were initially excited, if the exciton formation rate is smaller than the rate of carrier energy relaxation via LO-phonon emission. We believe that this is what happens in our experiments and Fig. 2 provides the typical time constant for formation of excitons by the *e-h* pairs near the band edge. This is deduced here to be about 7 to 10 ps for CdSe at 8 K for $n_0 = 6\times 10^{16}$ cm^{-3}. We should mention here that the role of carrier-carrier scattering should be increasingly unimportant (when compared with the carrier–LO-phonon coupling) as the carrier density is reduced to $\leqslant 10^{15}$ cm^{-3}. In that case, one might be able to observe the possible dependence of the exciton formation time on the exciting photon energy, especially for CdSe samples with a small exciton lifetime.[1,2,13] Time-resolved luminescence measurements at such low carrier densities may be performed using the streak camera technique. However, this technique may not have the desired time resolution of ≈ 1 ps. On the other hand, although the up-conversion luminescence measurement can have ps time resolution, it is rather difficult to use it at the required low excitation densities.

The measured value of 7–10 ps in our experiments is rather too small for exciton formation via acoustic-phonon emission by the carriers, which in CdSe should typically take several tens of ps.[20] Exciton formation by LO-phonon emission requires that the *e-h* pairs lose 26.5 meV (the LO-phonon energy in CdSe) to form an exciton with a binding energy of about 15 meV in CdSe. Thus the *e-h* pairs should have excess energy at least of the order of 10 to 20 meV for exciton formation by LO-phonon emission. In the presence of such hot carriers, the initial exciton formation and the associated carrier density decay will be rapid. Subsequently, as the hot carriers cool, the exciton formation and free-carrier-density decay will be much slower, if controlled by acoustic-phonon interactions. Whether the LO-phonon-emission process can explain our experimental results can be examined when a detailed calculation of the rate of exciton formation due to LO-phonon emission becomes available. We should, however, point out that LO-phonon emission is not possible for carrier excitation close to E_g, as in the case of some of the data points in Fig. 2. Since τ_1 is not energy dependent within the range of excitation photon energy used, the process of LO-phonon-assisted exciton formation appears to be rather unimportant in our case. The precise mechanism by which free *e-h* pairs form bound pairs in our experiments is not fully clear at present. The role of Auger-type carrier scattering in exciton formation process remains to be investigated. A calculation of rate of exciton formation by a distribution of *e-h* pairs via different mechanisms is in progress.

In conclusion, we report a direct determination of the exciton formation time in CdSe at 8 K at an excitation density of 6×10^{16} cm^{-3}. This is deduced from the time evolution of the 2LO Stokes sideband of the free exciton using picosecond up-conversion luminescence measurements. The time constant, obtained to be 7–10 ps, is not sensitive to excitation photon energy near the band edge, suggesting rapid carrier thermalization and energy relaxation in the continuum before exciton formation.

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[1] S. Permogorov, Phys. Status Solidi B **68**, 9 (1975).

[2] R. Planel, A. Bonot, and C. Benoit a' la Guillaume, Phys. Status Solidi B **58**, 251 (1973).

[3] T. C. Damen, J. Shah, D. Y. Oberli, D. S. Chemla, J. E. Cunningham, and J. M. Kuo, J. Lumin. **45**, 181 (1990); Phys. Rev. B **42**, 7434 (1990).

[4] B. Dareys, X. Marie, T. Amand, B. Baylac, J. Barrau, I. Razdobreev, M. Brousseau, and D. Dunstan, Solid State Commun. **90**, 237 (1994).

[5] R. P. Stanley, J. Hegarty, R. Fischer, J. Feldaman, E. O. Göbel, R. D. Feldman, and R. F. Austin, Phys. Rev. Lett. **67**, 128 (1991).

[6] J. Barrau, M. Heckmann, and M. Brousseau, J. Phys. Chem. Solids **34**, 381 (1973); J. Barrau, M. Heckmann, J. Collet, and M. Brousseau, *ibid.* **34**, 1567 (1973).

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

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

[9] D. G. Thomas and J. J. Hopfield, Phy. Rev. **128**, 2135 (1962).

[10] The UC signal at the A_1-2LO wavelength being rather weak, mapping of the energy distribution of the excitons was not possible in these experiments.

[11] At high enough excitation intensities, the time evolution at the A_1-2LO PL line first shows, after the initial rise, a rapid decay before a more gradual fall of the PL intensity. Presumably, this initial decay of the A_1-2LO PL at high intensities is related either to a rapid biexciton formation by the excitons or to some other process giving a rapidly decaying PL background at the A_1-2LO wavelength. At lower intensities, as used in our experiments, this initial rapid decay of the PL is not seen.

[12] The change in these numbers remains within the experimental uncertainties ($\sim$10 to 15%) even after deconvolution of the time evolution for the time resolution of about 3.5 ps.

[13] E. F. Gross, S. A. Permogorov, V. V. Travnikov, and A. V. Selkin, Fiz. Tverd. Tela (Leningrad) **14**, 1388 (1972) [Sov. Phys. Solid State **14**, 1193 (1972)].

[14] The competing picture in which the sharp luminescence lines

are attributed to Raman scattering has also been considered (see Refs. 1 and 13). The distinction between the two processes is not possible if the exciton dephasing time and the exciton lifetime are similar (Ref. 15). In some cases, the Raman scattering picture has been shown to be inconsistent with the observations of luminescence quenching by nonradiative channels (Ref. 1).

[15] Y. Toyozawa, J. Phy. Soc. Jpn. **41**, 400 (1976); Y. Toyozawa, A. Kotani, and A. Sumi, *ibid.* **42**, 1495 (1977).

[16] P. W. M. Blom, P. J. van Hall, C. Smit, J. P. Cuypors, and J. H. Wolter, Phys. Rev. Lett. **71**, 3878 (1993).

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

[18] This density, however, is smaller than the Mott density estimated to be about $\sim 10^{17}$ cm^{-3} in CdSe (Ref. 19). Rapid initial carrier diffusion, as described by Frigo *et al.* (Ref. 19) may reduce the density even further.

[19] N. J. Frigo, H. Mahr, and D. J. Erskine, IEEE J. Quantum Electron. **QE18**, 192 (1982).

[20] S. S. Prabhu, Ph.D. thesis, University of Bombay, 1995. A theory of exciton formation via acoustic-phonon emission in GaAs QW's leads to a time constant of the order of a few hundred ps, as shown by A. Thilagam and J. Singh, J. Lumin. **55**, 11 (1993).