Spontaneous photon echo from bound excitons in CdSe

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We have observed spontaneous photon echoes from acceptor bound excitons in CdSe. The I_1 line is inhomogeneously broadened to about 1 meV. The homogeneous linewidth is, at low temperature and low excitation density, found to be extremely small and is determined by the recombination lifetime $\tau_R = 500$ ps. The bound excitons have negligible interaction with phonons and interact only weakly with free excitons with a collision cross section $\sigma = 5.8 \times 10^{-13}$ cm^2. With increasing temperature, the dephasing of the bound excitons is determined by thermal release from the impurity bound state.

In recent years, nonlinear-optical spectroscopy has proved to be very powerful in the investigations of the initial relaxation mechanisms of photoexcited carriers in semiconductors.[1–4] Dephasing measurements of the nonlinear polarization associated with excitonic resonances in a number of III-V (Refs. 5 and 6) and II-VI (Refs. 7–9) semiconductors have been performed by degenerate-four-wave-mixing (DFWM) experiments with transform-limited spectral and temporal (picosecond) resolutions. In several of the excitonic resonances, the correlation traces of the coherently diffracted signal in a two-beam experiment have been well fitted with calculated correlation traces for a two-level system with inhomogeneous broadening.[9,10] The latter is caused by spatial potential fluctuations in the case of localized or bound excitons,[8] whereas for free (extended) excitons it is caused by spatial dispersion.[9] For such systems, the diffracted signal is, in fact, in the form of a photon echo,[9,10] which, however, is not easily time resolved for dephasing times in the picosecond or subpicosecond range. For free excitons, it has previously been found that, at low temperatures and at exciton densities where a nonlinear signal can be detected, dephasing is dominated by exciton-exciton interaction.[9] This is not the case for localized and bound excitons, where much larger dephasing times have been observed. Recently, directly resolved photon echoes have been observed in mixed crystals of $CdSe_xS_{1-x}$.[11,12] In the present paper we report the observation of photon echoes from impurity bound excitons in CdSe.

Rather thick (40–60-μm) platelets of CdSe, grown from the vapor phase, were mounted in a variable temperature liquid-helium cryostat. The photon echoes were excited by a synchronously pumped DCM dye laser system with pulse length $\tau_L \leq 10$ ps and the corresponding spectral width of $\Gamma_L \geq 1$ meV. The 82-MHz pulse train was split into two beams and directed onto the same focal spot of $\simeq 50$ μm in diameter on the sample with incident wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$. The DFWM signal was detected in the direction $2\mathbf{k}_2 - \mathbf{k}_1$ and analyzed spectrally and temporally, as a function of the delay between the two incoming pulses, by an optical multichannel analyzer system and a synchroscan streak camera, respectively.

Figure 1 shows the spectral behavior of the nonlinear signal. Two resonance peaks are observed. One peak at $\hbar\omega = 1.8197$ eV, i.e., in the M-band region,[7,9] only appears for a short delay τ between the incoming pulses, corresponding to a dephasing time of a few tens of picoseconds.[9] Another resonance at $\hbar\omega = 1.8185$ eV peaks for a larger delay and decays only slowly, which is typical for a photon echo with a long dephasing time of the individual oscillators. At even higher photon energies, a DFWM signal could not be detected in the forward direction of the present, rather thick, sample. Thus, we concentrate on the lowest resonance, which we identify as the I_1 line,[13] ascribed to excitons bound to neutral acceptors, from comparison with transmission and luminescence spectra in the same sample at 4.2 K.

That the DFWM signal in the I_1 resonance is indeed in the form of a photon echo is demonstrated by imaging simultaneously the transmitted pulses P_1 and P_2 (properly attenuated) and the signal P_s on the entrance slit of the streak camera. Figure 2 shows the three pulses for different delays τ between the incoming pulses, revealing that the signal appears as a photon echo with a further delay τ after the arrival of the second pulse.[9,10] The time resolution of about 35 ps in Fig. 2 was given by the streak camera and limited by jitter in the trigger circuit. Thus, we were not able to resolve any possible photon echo in the M band, displaying rapid dephasing in Fig. 1. Concentrating on the I_1 line, we investigated the decay of the photon echo as a function of the delay, $P_s(\tau)$, for different temperatures and light intensities. We shall use the results to discuss the mechanisms for damping, or dephasing, of bound excitons in comparison with free and localized excitons, that have previously been reported.[5–9,11,12]

The first conclusion from the photon echo results in Fig. 2 is that the I_1 line is indeed inhomogeneously broadened. From transmission and luminescence measurements, the linewidth is about 1 meV, leading to a free induction decay[10] with a characteristic time of about 2 ps. Thus, there is no noticeable increase in the duration of the photon echo pulse compared to the directly transmitted laser pulses. The homogeneous linewidth of the I_1 line, on the other hand, is much smaller, leading to a slow decay of the photon echo $P_s(\tau)$, at least at low

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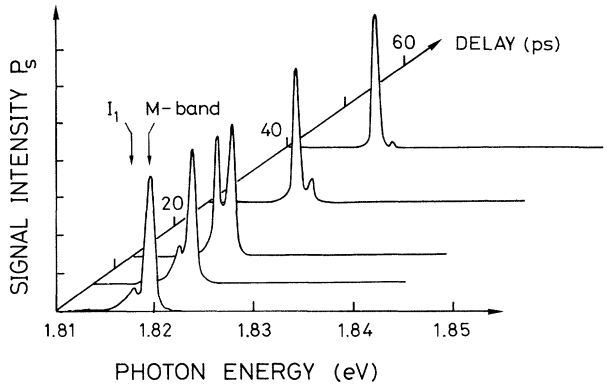

FIG. 1. Excitation spectra, at 4.2 K, of the integrated DFWM signal intensity P_s in the direction $2\mathbf{k}_2-\mathbf{k}_1$ for different delays τ between the two incident laser pulses P_1 and P_2.

temperatures. Figure 3 shows $P_s(\tau)$ for two different temperatures, revealing a strong temperature dependence. From an inhomogeneously broadened two-level system we expect,[9,10] for delays much larger than the pulse width, $P_s \propto \exp(-4\tau/T_2)$, from which we can determine the dephasing time T_2.

Figure 4 plots the dephasing rate $1/T_2$ versus temperature T. It is seen that above 10 K, the dephasing rate rises very rapidly. The solid curve in Fig. 4 is, in fact, a fit by the function

$$1/T_2=\gamma+\nu_0\exp(-E_a/kT) \tag{1}$$

with $\gamma=1.6\times10^9$ s^{-1}, $\nu=3.0\times10^{11}$ s^{-1}, and $E_a=5.6$ meV. The latter activation energy is equal to the binding energy of the I_1 bound exciton.[13] We therefore conclude that with rising temperature the dephasing of the I_1 line is determined by thermal release of the bound excitons. The homogeneous linewidth at low temperature $h\gamma\simeq10^{-3}$ meV is so small that the exciton-phonon interaction is negligible in the bound state. This is in contrast to the situation with free and localized excitons.[8,9,12] Another dephasing mechanism is by collisions with free excitons.[9] This is investigated by varying the intensity of the laser pulses and thereby the exciton density.

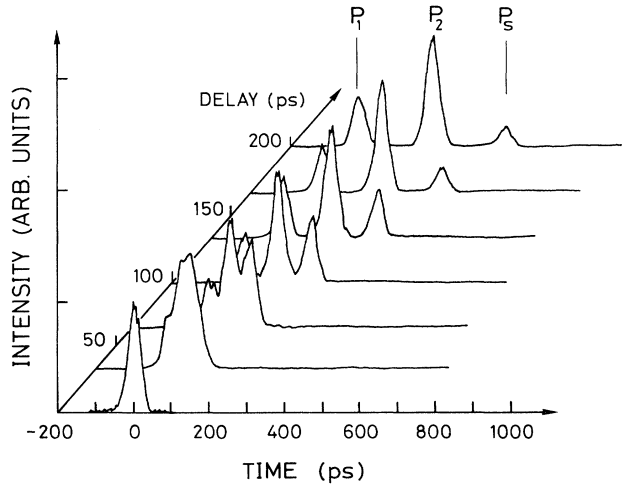

FIG. 2. Incident laser pulses P_1 and P_2 and photon echo P_s for different delays τ between P_1 and P_2. $T=4.2$ K and the laser is resonant with the I_1 line.

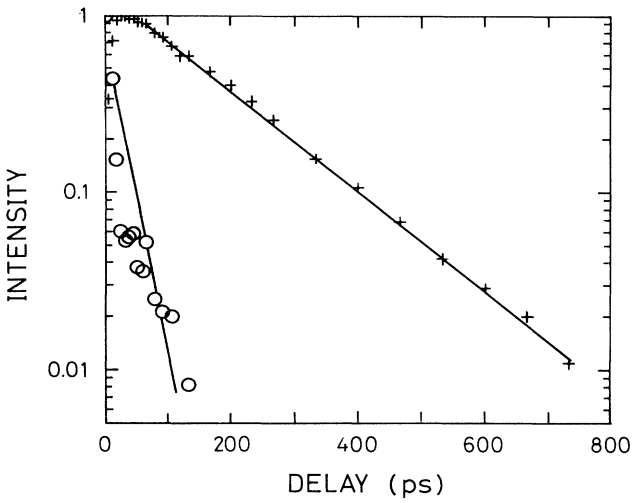

FIG. 3. Integrated signal intensity P_s as a function of delay τ between the incident pulses P_1 and P_2, resonant with the I_1 line, for $T=2$ K (+) and $T=17.5$ K (○). The exponential decays are given by $P_s \propto \exp(-4\tau/T_2)$ as discussed in the text.

Figure 5 shows the dephasing rate $1/T_2$ as a function of exciton density N_x, as estimated from the absorbed laser pulse intensities. We observe a small linear rise of the scattering rate of the form

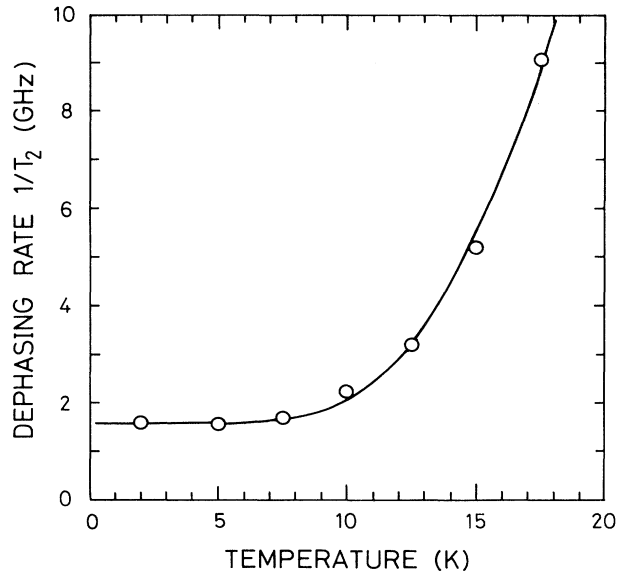

FIG. 4. Dephasing rate $1/T_2$ of the bound exciton transition (I_1 line) as a function of temperature T. The points are experimental, and the curve is fitted by Eq. (1), as discussed in the text. The exciton density $N_x\simeq2.4\times10^{14}$ cm^{-3}.

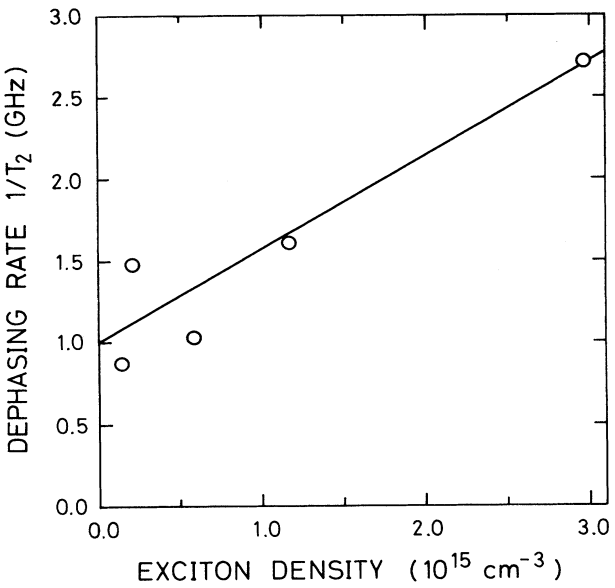

FIG. 5. Dephasing rate $1/T_2$ as a function of excition density N_x at 4.2 K. The linear fit is given by Eq. (2) in the text.

$$1/T_2=\gamma_0+v\sigma N_x \tag{2}$$

with $\gamma_0=1.0\times10^9$ s^{-1} and where $v=10^6$ cm s^{-1} is the thermal velocity of excitons. We then find the scattering cross section for collisions between free and bound excitons $\sigma=5.8\times10^{-13}$ cm$^2\simeq0.6\pi a_x^2$, where $a_x=54$ Å is the exciton Bohr radius in CdSe.[14] This cross section is about ten times smaller than the cross section previously found for collisions between free excitons.[9]

The dephasing rate remaining at low density and low temperature then has to be due to recombination of the acceptor bound excitons. From the above, we find the recombination lifetime $\tau_{I_1}=\frac{1}{2}/\gamma_0=500$ ps. This is in good agreement with calculations on the radiative recombination lifetime of acceptor bound excitons in semiconductors[15] as expected, since Auger recombination of bound excitons is usually negligible compared to radiative recombination in wide-gap semiconductors like CdSe. The photon echo experiment thus provides a direct measurement of the radiative lifetime of acceptor bound excitons in CdSe. This is not easily obtained from luminescence decay measurements, because of the simultaneous capture of free (long-lived) excitons.[15]

In summary, the photon echo experiments have revealed interesting details about the acceptor bound excitons in CdSe, their interactions with phonons, free excitons, and their radiative recombination lifetime that are otherwise not easily accessible.

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