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Spontaneous photon echo from the (A^0,X) complex in CdS

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Abstract

The coherent and incoherent dynamics of the neutral acceptor bound exciton complex in CdS is investigated. A dephasing time T_2 of 700 ps and an energy relaxation time T_1 of 980 ps are found indicating pure dephasing processes due to impurity interactions. The dependence of the dephasing time T_2 on temperature and excitation density is discussed.

Energy relaxation processes of free and bound excitons in the wide band gap II–VI semiconductors are intensively studied by means of time resolved photoluminescence [1–4]. However, only few and contradictory information on the coherent dynamics is available, yet. Photon echo experiments yield coherence times T_2 of some hundred ps for the neutral acceptor bound exciton (A^0,X) in CdSe [5], whereas quantum beat and resonant Rayleigh scattering experiments of bound excitons in CdS yield a coherence time T_2 longer than a few ps only for the ionised donor bound exciton (D^+,X) [6]. A detailed knowledge of the coherent dynamics of bound excitons in single crystals would help to understand the influence of localisation on dephasing processes in mixed crystals [7].

In the present paper degenerate four-wave mixing (DFWM) experiments at bound exciton states in CdS are reported revealing a dephasing time T_2 of some hundred ps for the (A^0,X) complex. The influence of temperature and of excitation density I_{exc} on the dephasing processes is studied. Exciting laser pulses of 3 ps duration are provided by a synchronously pumped dye laser operating with Coumarin 102. The diffracted signal is detected time resolved by means of time correlated single photon counting using a multi-channel plate photomultiplier.

Fig. 1 shows time resolved the spontaneous photon echo from the (A^0,X) complex in CdS for different delays τ between the two input pulses. The two pulses indicated with #1 and #2 with constant intensity are the incoherently scattered input pulses, whereas the fast decaying third pulse indicated with #3 represents the photon echo. The shape of each pulse follows the apparatus response of the detection system, thus only an upper limit of about 10 ps for the full width at half the maximum of the photon echo pulse can be estimated. Fig. 1 clearly demonstrates the inhomogeneous broadening of the (A^0,X) resonance.

For an inhomogeneously broadened two level system the spontaneous photon echo signal obeys $I \propto \exp(-4\tau/T_2)$. However, the time integrated photon echo is found to decay non-exponential, see the insert in Fig. 2. With increasing delay time τ between the two incident pulses the decay of the photon echo becomes slower until for delay times

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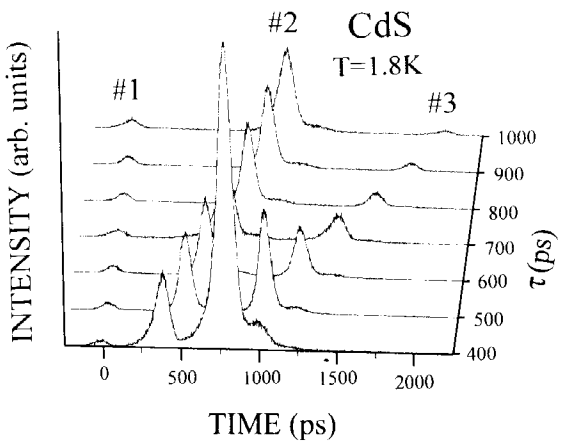

Fig. 1. Time resolved spontaneous photon echos from the neutral acceptor bound exciton complex (A^0,X) in CdS at $T = 1.8$ K and $I_{exc} = 600\,kW\,cm^{-2}$ in dependence on the delay time τ between the two incoming pulses.

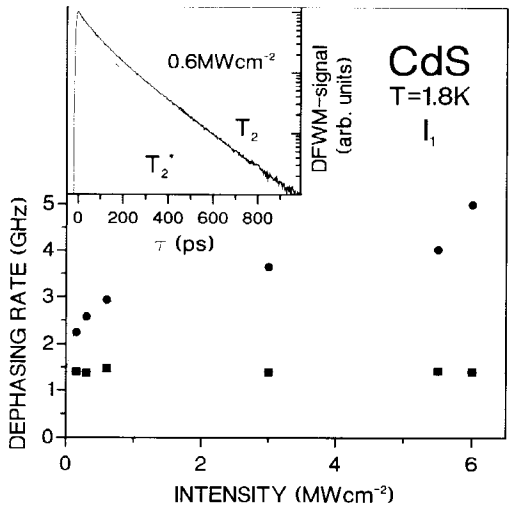

Fig. 2. The dephasing rates T_2^* for short delay times τ (circles) and T_2 for long delay times τ (squares) of the neutral acceptor bound exciton complex (A^0,X) in CdS at $T = 1.8$ K in dependence on excitation density. The insert shows the time integrated photo echon decay at 0.6 MW cm^{-2} and the two exponential fits giving T_2^* and T_2.

τ larger than about 500 ps an exponential decay is observed. Obviously, the dephasing rate is governed by a time dependent process. In order to discuss the dephasing rate two dephasing times T_2^* and T_2 are derived by independent exponential fits of the early part and of the late part of the photon echo decay, respectively. The main part of Fig. 2 gives the dephasing rates in dependence on excitation density. The early part (T_2^*, circles) becomes faster with increasing excitation density, whereas the decay for large delays (T_2, squares) is independent of excitation density. Thus, the excitation dependence indicates interactions with fast relaxing optical excited systems.

E.g. the scattering of free excitons at the (A^0,X) complex leads to shorter bound exciton coherence times with increasing excitation densities. This model implies that the corresponding dephasing rate is proportional to the density of free excitons. Thus, it is to be expected that the dephasing rate is no longer constant but decreases with the decay of the free exciton concentration after the exciting pulse resulting in a non-exponential decay of the photon echo signal. Time resolved photoluminescence measurements give a free exciton lifetime of 100 ps in the investigated sample, which is sufficiently short to explain deviations from an exponential photon echo decay as observed in our experiments. Therefore, we take the non-exponential photon echo decay as a hint for efficient exciton scattering. Thus, exciton scattering contributes to T_2^* but not to T_2 determined for long delays τ. T_2 is determined to be (700 $\pm$ 50) ps for the (A^0,X) complex at $T = 1.8$ K in the investigated sample.

The excitation density dependence of T_2^* shows, even at excitation densities of 0.1 MW cm^{-2}, an efficient generation of free excitons which saturates at higher excitation densities. This behaviour indicates an impurity correlated two step generation process at low excitation densities and two photon absorption at higher excitation densities. Indeed, anti-Stokes luminescence of excitons is observed exciting resonantly the I_1. In contrast to the present results mono-exponential photon echo decays are observed for the (A^0,X) complex in CdSe even at high excitation densities giving a linear increase of the dephasing rate with exciton density [5].

Fig. 3 represents the temperature development of the dephasing rate $1/T_2$. At temperatures above 7 K a drastical increase of the dephasing rate occurs, indicating a strong interaction of the (A^0,X) complex with phonons. An analysis of the

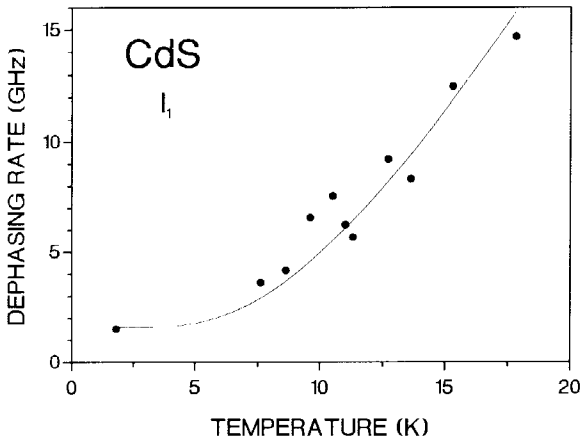

Fig. 3. Temperature dependence of the dephasing rate T_2 of the neutral acceptor bound exciton complex (A^0,X) in CdS at $I_{exc} = 0.5\,MW\,cm^{-2}$.

temperature dependence shows that resonant one-phonon transitions involving low frequency acoustical phonons explain this development. For resonant one-phonon transitions a temperature development of the transition rate W as

$$W = W_0 \coth\left(\frac{\hbar\omega}{2kT}\right) \tag{1}$$

is expected with W_0 the spontaneous transition rate. The full line in Fig. 3 gives a fit of the temperature dependent changes of the dephasing rate $(1/T_2)$ using Eq. (1), $W_0 = 29\,GHz$ and $\hbar\omega = 2.5\,meV$. For example stimulated Raman experiments [8] locate the first excited state of the (A^0,X) complex 2.5 meV above the ground state. The good agreement of this fine structure splitting and the phonon energy $\hbar\omega$ deduced from the temperature dependence, Fig. 3, confirms the interpretation in terms of resonant one-phonon transitions. A similar temperature dependence of the dephasing rate of the (A^0,X) complex in CdSe has been explained with a thermally activated ionisation process, an explanation which obviously does not hold in the case of CdS. The binding energy of the (A^0,X) complex in CdS is about three times larger than that of the investigated (A^0,X) complex in CdSe corresponding to a stronger localisation of the bound exciton which leads to an enhanced interaction with acoustical phonons. However, Fig. 3 demonstrates that phonon induced processes do not limit the dephasing time T_2 observed at $T = 1.8\,K$.

Interactions of an electronic system can either result in energy relaxation processes, characterised by T_1, or in pure phase relaxation processes, characterised by T_2', both contributing to the dephasing time T_2 accessible in coherent experiments:

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2'} \tag{2}$$

The presented experimental results demonstrate that the dephasing time T_2 of the (A^0,X) complex in CdS is not limited by phonon induced processes or the scattering of free excitons using appropriate experimental conditions. This implies that the dephasing results from energy relaxation processes ($T_2 = 2T_1$). However, the dephasing time $T_2 =$ 700 ps is considerably shorter than expected from the energy relaxation time $T_1 = 980$ ps measured by time resolved photoluminescence under comparable experimental conditions at the same crystal. This indicates even for a localised system like a bound exciton pure phase relaxation processes which are not connected with free exciton or phonon scattering.

A possible explanation is an interaction with other impurity centres. In general, in doped crystals a reduction of bound exciton lifetimes due to the introduction of competing relaxation channels or the screening of the Coulomb interaction [9] is observed. The present results show that similar interactions lead to even more pronounced phase relaxation processes. It is obvious that the interaction between different impurity centres depends critically on their localisation. This explains why for the strongly localised (A^0,X) complex a dephasing time T_2 of 700 ps is observed, whereas our experiments give an upper limit of 30 ps for the dephasing time T_2 of the less localised neutral donor bound exciton complex (D^0,X) in spite of an energy relaxation time T_1 of 300 ps.

In conclusion, the presented experimental results demonstrate dephasing times T_2 of some hundred ps for the acceptor bound exciton complex (A^0,X) in CdS, which are still too short to be limited by energy relaxation processes. Neither phonon nor exciton scattering is found to contribute to the dephasing process at liquid He temperatures and

low excitation densities. However, impurity interactions could explain the dependence of the dephasing rate on the localisation of the bound exciton complex. At higher excitation densities and higher temperatures the scattering of free excitons and resonant one-phonon transitions between the fine structure states of the (A^0,X) complex, respectively, are found to determine the dephasing.

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