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Degenerate four-wave mixing at bound excitons in II–VI semiconductors

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Abstract

The coherent and incoherent dynamics of bound exciton complexes in CdS are investigated by means of degenerate four-wave mixing and differential transmission spectroscopy. We observe dephasing times T_2 up to 800 ps for the (A^0, X) complex and up to 150 ps for the forbidden A_F exciton. The dephasing times T_2 are found to be generally shorter than expected from the energy relaxation times T_1. Pure dephasing processes not connected with exciton or phonon scattering are found and discussed in view of impurity interactions and nuclear spin-flip processes.

1. Introduction

The first step in the relaxation of an excited electronic system like bound excitons in semiconductors is the loss of coherence due to dephasing processes. Thus, the study of dephasing processes yields information on basic interactions at the investigated system. Most dephasing processes in semiconductors take place on a fs or ps time scale and are connected either with a continuum of electronic states or with the scattering of quasiparticles [1]. These processes are expected to depend on the degree of localization of the investigated system. However, the influence of the localization on dephasing processes is still an open question [2].

Energy relaxation processes of free and bound excitons in wide band-gap II–VI semiconductors are intensively studied by means of time resolved photoluminescence [3–5]. However, only little and contradictory information on the coherent dynamics is available yet. On the one hand, using transient four-wave mixing, dephasing times T_2 of several hundred ps could be determined only for the neutral acceptor bound exciton (A^0, X) in CdSe [6] and CdS [7]. On the other hand, a dephasing time of 300 ps has been found for the ionized donor bound exciton (D^+, X) in CdS [8] by means of quantum beat spectroscopy, whereas no quantum beats have been observed for the deeper bound exciton complexes. Detailed knowledge of the coherent dynamics of bound excitons in single crystals would help to understand the basic dephasing processes of localized systems in semiconductors.

In the present paper we investigate nonlinear effects and dephasing processes of excitonic states in CdS by means of degenerate four-wave mixing (DFWM). The dephasing times are found to be too short to result exclusively from energy relaxation, indicating pure dephasing processes. Phonon and exciton scattering are intensively investigated in ref. [7] and can be excluded under

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suitable experimental conditions. Here, possible dephasing processes of excitonic complexes due to impurity interactions and nuclear spin-flip processes are discussed.

2. Experimental procedure

The samples used for the measurements are high-quality platelets of CdS with thicknesses between 10 and 20 μm. The samples are selected for excellent surfaces and appropriate I_1 absorption.

The excitation source for the DFWM experiments is a dye laser synchronously pumped by a mode-locked and frequency-tripled Nd : YAG laser providing pulses of about 3 ps duration. Using Coumarin 102, the dye laser is tunable between 460 and 510 nm with an energy resolution of 250 μeV. The laser beam is split into two beams with one chopped at 1.5 kHz. Neutral glass filters are used to adjust the laser power. Changes in the probe beam transmission as well as the first order diffracted signal are detected using photo-diodes allowing the simultaneous recording of the differential transmission spectra (DTS) and the DFWM signal, respectively.

3. Experimental results

Fig. 1 gives representative absorption and emission spectra of the investigated CdS platelets in the near band gap region which are typical for high quality CdS samples [9]. In the polarization, $E \perp c$ transitions involving A excitons are allowed. Two different neutral acceptor bound exciton complexes produce an I_1 doublet around 2.5357 eV with an energy splitting of 190 μeV. Around 2.546 eV, several I_2 transitions corresponding to excitons bound at different neutral donors are observed. These absorptions are situated on a tail of the A exciton absorption but dominate the luminescence spectrum. In the polarization $E \| c$ instead of the strong A exciton absorption the forbidden (A_F) and the longitudinal (A_L) A exciton are clearly resolved in absorption as well as in emission. B excitons bound at a

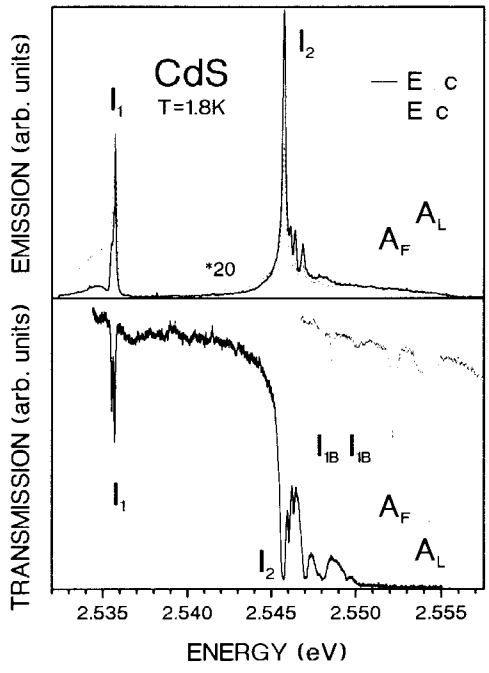

Fig. 1. Polarized absorption and emission spectra of CdS at $T = 1.8$ K.

neutral acceptor (I_{1B}, I'_{1B}) are observed in absorption only. However, the interpretation of weak emission lines in the same spectral region in terms of ionized donor bound exciton complexes is not clearly established to date.

CdS exhibits strong nonlinearities in the near band-gap region correlated with excitonic processes. Fig. 2 shows the energy dependence of the DTS as well as of the DFWM signals for fixed delays τ between the two incoming pulses of 10 ps (dotted traces) and 60 ps (full traces) recorded with the pulse polarizations perpendicular to the crystal c-axis. Strong signals are observed at the bound exciton resonances. Both I_1 and I_2 show saturation leading to a long-living induced transmission. Nevertheless, all fine structures are situated on a broad induced absorption band following the tail of the A exciton absorption (see Fig. 1), probably connected with excited state absorption of free excitons. The induced absorption in the energy region between I_1 and I_2 disappears very fast. Strong DFWM signals occur for the different bound exciton complexes (I_1, I_2) and

additional weak signals are observed for the I_3 and on the low energy side of the I_2 resonance. The strong absorption starting at the I_2 resonance influences the DFWM signal, leading to a small energy shift between the DTS and the DFWM signals of I_2. DFWM signals of the A_F and the A_L exciton are observed using light pulses polarized parallel to the crystal c-axis (not shown in Fig. 2). It should be noted that the separate investigation of the different bound exciton transition becomes possible using a narrow bandwidth laser system as done in this study.

Comparing the spectra taken at delays τ of 10 and 60 ps, it is apparent that only the I_1 bound exciton complex has a dephasing time longer than a few 10 ps. Corresponding spectra for the polarization $\boldsymbol{E} \parallel \boldsymbol{c}$ show a resolvable dephasing process for the forbidden A_F exciton too. Fig. 3 depicts transients of the DFWM signal for the I_1, the I_2, and the A_F resonances recorded at an excitation density of 0.5 MW cm^{-2} giving a reasonable signal-to-noise ratio. Only for the I_1 complex and for the forbidden A_F exciton does the signal extend noticeably beyond the autocorrelation function of the exciting laser pulses, indicating extremely fast dephasing processes for most of the excitonic states. Time-resolved investigations of the photon echo of I_1 prove the inhomogeneous broadening of the I_1 resonance [7]. For an inhomogeneously broadened two-level system, the DFWM signal decays with $I \propto \exp(-4t/T_2)$. However, the time-integrated photon echo signal of the I_1 resonance is non-exponential (Fig. 3). Photon echo experiments in dependence of the excitation density [7] demonstrate that the *fast early part* results from interactions with a time-dependent bath, probably free excitons, and that the exponential part at longer delays gives the dephasing time of the investigated system. We determine dephasing times T_2 between 550 and 800 ps for the (A^0, X) complex depending on the investigated crystal. The DFWM signal observed for the A_F exciton resonance shows a fast part following the autocorrelation of the exciting laser pulses and a slower exponential decay yielding

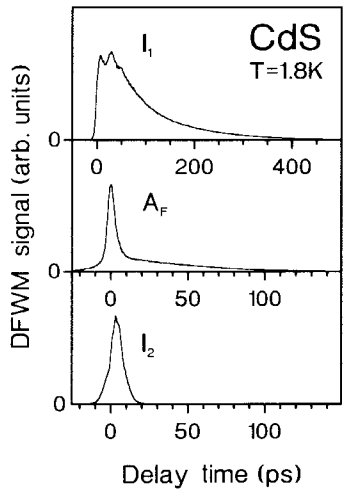

Fig. 3. Transients of the DFWM signals observed for the (A^0, X) (I_1) and the (D^0, X) (I_2) bound exciton complexes ($\boldsymbol{E} \perp \boldsymbol{c}$) and the A_F exciton in CdS ($\boldsymbol{E} \parallel \boldsymbol{c}$) at $T = 1.8$ K. Notice the changed time scale for I_1.

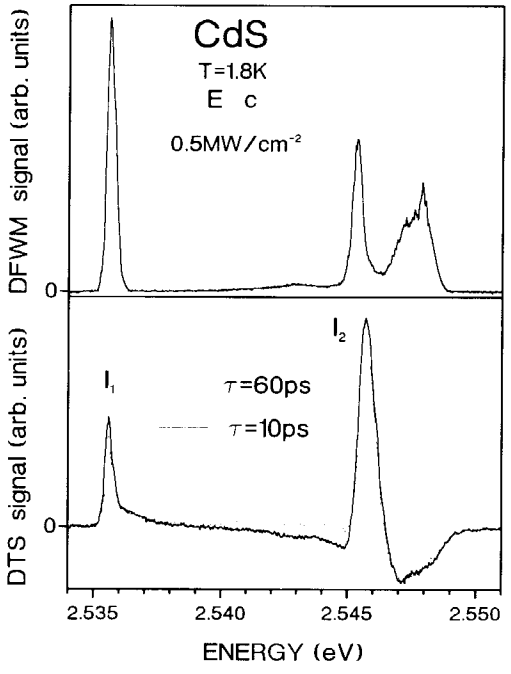

Fig. 2. Differential transmission (DTS) and degenerate four-wave mixing (DFWM) signals in dependence on the excitation energy in the band-gap region of CdS at $T = 1.8$ K and two different delays τ between the two incoming pulses. The exciting light pulses are polarized perpendicularly with respect to the crystal c-axis.

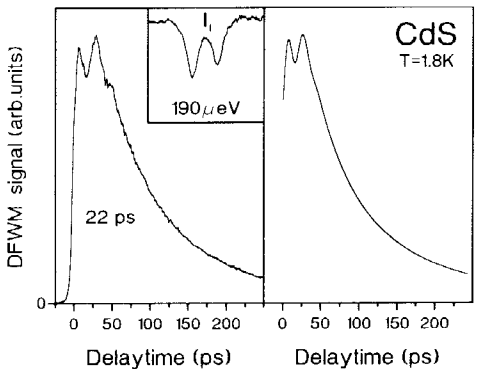

Fig. 4. Experimental (left side) and calculated (right side) DFWM signals of the (A^0, X) bound exciton complex in CdS showing polarization interference. The inset gives a high resolution absorption spectra showing the two involved I_1 absorptions.

dephasing times T_2 between 100 and 150 ps depending on the investigated sample. DFWM excitation spectra show that the *fast component* is not resonant with the A_F exciton.

On the left-hand side, Fig. 4 shows enlarged the modulation in the early part of the time integrated photon echo signal observed for the (A^0, X) resonance. Such modulation can either result from quantum beats or from polarization interference [10]. The beating has been observed for a sample showing two clearly resolved I_1 resonances, as is obvious from the high resolution absorption spectrum depicted in the insert. The beat period of 22 ps corresponds well to the energy difference between the two I_1 resonances of 190 μeV. These beats are absent in crystals showing only a single or two poorly resolved I_1 resonances, proving that the beats result from polarization interference caused by the simultaneous excitation of two independent (A^0, X) complexes. Recently, polarization interference between the (A^0, X) and the (D^0, X) complexes in CdSe has been reported [11]. On the right-hand side, Fig. 4 shows the beating of the time-integrated photon echo signal calculated for a system consisting of two inhomogeneously broadened oscillators. Using the energy splitting and the FWHMs determined from the absorption spectrum, good agreement with the experimental results is obtained. The fast decay of the beating results from the inhomogeneous broadening of the two oscillators.

4. Discussion

For some systems a significant influence of exciton localization on dephasing processes has been found [2]. For these systems the dominating factor is the reduction of relaxation channels with increasing localization. Thus, it can be expected that excitons localized at a single impurity forming atomic-like electronic systems show no comparable fast dephasing processes. Indeed, recent quantum beat [8] and DFWM [6,7] experiments as well as the present results show dephasing times of some hundred ps for bound exciton complexes in the wide band gap II–VI semiconductors. Without pure dephasing processes only energy relaxation contributes to the dephasing time T_2, then given by $T_2 = 2T_1$. In this paper, T_2 times are determined for bound exciton complexes which are always shorter than expected from pure energy relaxation processes. For example, the dephasing time T_2 of the (A^0, X) complex of about 700 ps is considerably shorter than expected from the energy relaxation time T_1 of 980 ps measured by time resolved photoluminescence spectroscopy. This discrepancy is even more pronounced for the (D^0, X) complex. DFWM experiments in dependence on sample temperature and excitation density show a strong interaction with resonant acoustical phonons and free excitons [6,7]. However, at low temperature and moderate excitation density, both processes do not contribute any longer to the dephasing. Thus, there is evidence for an additional dephasing process of bound exciton complexes.

Excluding exciton and phonon scattering, pure dephasing processes of bound exciton complexes could be due either to impurity interactions or to nuclear spin-flip processes of the surrounding host ions. Time-resolved photoluminescence measurements show that higher impurity concentrations can alter even the energy relaxation times [12] and, e.g., the dephasing of excited Cr ions in Al_2O_3 results from nuclear spin-flip processes of

neighbouring ions [13]. It is obvious that the interaction of a bound exciton complex with other impurities as well as with surrounding spins depends critically on its localization. With increasing extension of its wave function, the bound exciton probes larger areas of the crystal leading to a faster dephasing. This is in good agreement with our experimental results. Only the impurity interaction depends on the defect concentration, making the dephasing time T_2 dependent on the investigated crystal. Our experiments show only a small variation of the dephasing time of the (A^0, X) complex in CdS, caused either by slightly different impurity concentrations or by the different chemical nature of the neutral acceptor. It has to be noted that we expect the investigated crystals to be very similar, since they are grown using the same equipment and selected for a suitable I_1 absorption. Thus, no unambiguous distinction between the two dephasing processes is possible at this point.

It is interesting to compare the results of linear quantum beat [8] and DFWM experiments yielding apparently contradictory results in the case of bound exciton complexes in CdS. Quantum beat experiments, in principle, do not probe the "optical" coherence between the ground and excited states of a system, but the "quantum" coherence between two nearby excited states, which means that additional relaxation processes between the two excited states would decrease the measured dephasing time. Further on, a magnetic field is used to generate and tune the two excited states. The magnetic field alters the electronic states and can directly influence dephasing processes [13]. Thus, DFWM experiments give more reliable results, since they work in each two-level system showing absorption. This means that a short DFWM signal proves a short dephasing time, whereas a missing quantum beat signal can have different reasons.

Our DFWM experiments indicate extremely short dephasing times for the (D^0, X) as well as for the weaker bound exciton complexes. In contrast, the quantum beat experiments give a dephasing time of 300 ps for the weakly bound (D^+, X) complex [8]. This indicates either a much lower impurity concentration or an influence of the magnetic field on the dephasing process by stabilization of the nuclear spins. In both cases, the (D^0, X) and the (A^0, X) complexes should possess even longer dephasing times. However, no quantum beat signals have been observed for the neutral donor or acceptor bound exciton complexes. The lack of a quantum beat signal can have many different reasons, especially considering the complicated level structure of bound exciton complexes formed at neutral donors or acceptors.

Completely different is the situation in the case of the forbidden A_F exciton, showing a comparatively long dephasing time between 100 and 150 ps. In general, generating free excitons, exciton–exciton collisions lead to a dephasing on a fs time scale [1]. However, the forbidden exciton has only a small dipole moment, and thus experiences a weaker interaction with other electronic excitations.

5. Conclusion

DFWM spectroscopy is an appropriate technique to study coherent processes in the near band-gap region of semiconductors. The presented experimental results demonstrate dephasing times T_2 of several hundred ps for the acceptor bound exciton (A^0, X) complex in CdS, which are still too short to be limited by energy relaxation processes. Neither phonon nor exciton scattering contributes to the dephasing process under the experimental conditions used in this work [7]. However, impurity interactions or nuclear spin-flip processes in the surroundings could explain the dependence of the dephasing rate on the localization of the bound exciton complex. Additionally, for the forbidden A_F exciton, dephasing times longer than 100 ps are observed.

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7. References

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