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Acceptor bound biexcitons in ZnSe and CdS

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Abstract

We report on degenerate-four-wave-mixing experiments mainly based on biexcitonic processes near the bandgap of CdS and ZnSe. Broadband femtosecond-excitation is applied in order to coherently create free and bound excitons as well as free and bound biexcitons in the sample. Using the results of nonlinear quantum beat spectroscopy the binding energies of the free and acceptor bound biexciton in CdS and ZnSe are determined.

1. Introduction

Gain mechanisms in ZnSe-based blue-green-laser diodes are discussed in the framework of biexcitonic processes [1]. However, the identification of free and bound biexcitons in ZnSe is still ambiguous, although free biexciton complexes are well known [2,3] in several II–VI semiconductors. The occurrence of biexciton complexes leads to a renormalization of the polariton dispersion curves [4]. Bound biexciton complexes have been first reported for indirect semiconductors [5,6]. Here, they have large binding energies compared to those of free and bound excitons, so that the radiative annihilation of the bound multiexciton complex leads to photon energies smaller than those of bound excitons. In direct semiconductors, the luminescence of a bound multiexciton complex has been observed in CdTe [7] and CdS [8] in the energy range of the bound excitons. In ps nonlinear quantum beat spectroscopy

(NQBS) in CdSe a biexciton bound to a neutral acceptor A^0 has been identified [9]. Extending the investigations to broadband femtosecond-experiments, a mixture of coherently excited states near the bandgap of semiconductors occurs leading to complex interference effects [10].

In this contribution, we present degenerate-four-wave-mixing experiments (DFWM) in the self-diffraction geometry near the bandgap of CdS and ZnSe. In particular, we report on NQBS of the forward and backward scattered DFWM signal which allows us to identify the creation of free biexcitons M in a two-step absorption via the free exciton state X as well as of the (A^0, M) state in a two step-absorption via the (A^0, X) state.

2. Samples and experimental setup

The CdS samples used are nominally undoped single crystal platelets of about 15 μm thickness with the c -axis in the sample plane. They are selected for $\sim 30\%$ absorption at the (A^0, X) -reso-

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nance. The investigated ZnSe samples are high-quality p-type MBE-grown epilayers. The p-doping is performed with a nitrogen-plasma source resulting in net acceptor concentrations around 10^{16} cm^{-3} determined by CV-profiling. For transmission experiments the ZnSe samples are glued onto quartzglass before the GaAs substrate is removed by selective wet chemical etching. The $3.8 \mu\text{m}$ thick sample has subsequently been released from the quartzglass for strain-free investigations.

DFWM-measurements are performed with a frequency doubled passive mode-locked Ti:sapphire laser providing pulses of 150 fs pulsewidth. The DFWM-signal in dependence on the delay time is spectrally dispersed in a double monochromator and detected time-integrated by an optical-multichannel-analyzer.

3. Experimental results and discussion

DFWM investigations in the femtosecond-range are performed to study coherent effects in CdS and ZnSe. DFWM transients for different detuning δE around the I_1 -resonance is seen in the left part of Fig. 1. The lower right part of Fig. 1 shows the beat energies extracted from a Fourier analysis of the transients on the I_1 -resonance in CdS. Here, we find beat energies corresponding to the energy of the TA-phonon, the A_F -exciton and to an energy lying

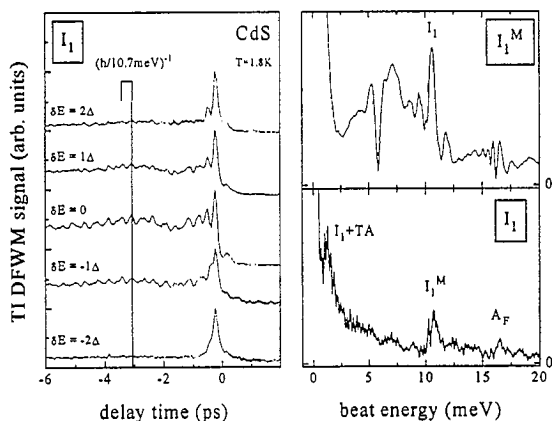


Fig. 1. Left part: DFWM transients for different detunings δE around the I_1 -resonance in CdS ($\Delta = 110 \mu\text{eV}$). Right part: Fourier analysis of the DFWM transients at the spectral positions of the I_1 - (bottom) and the I_1^M -resonance (top).

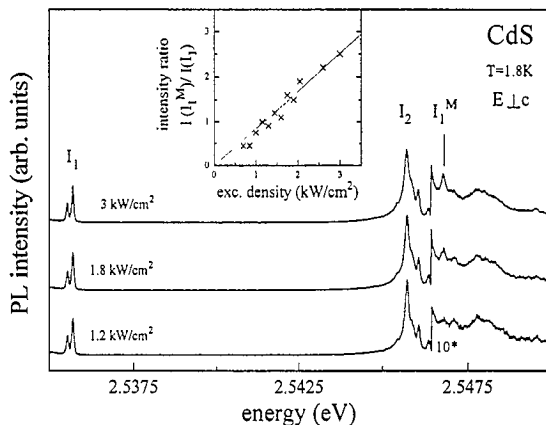


Fig. 2. Luminescence of CdS under cw-excitation with the 476 nm line of an Ar-laser. The inset shows the intensity ratio of the I_1^M - to the I_1 -line in dependence on excitation density.

closely above the I_2 -resonance (radiative recombination of an exciton bound to a neutral shallow donor). In analogy to previous NQBS results in CdSe [9] we want to label this resonance with I_1^M indicating the formation of a biexciton bound to a neutral acceptor. This is supported by the fact that the Fourier analysis of the DFWM transient at the I_1^M resonance exhibits a sharp peak at the beat energy corresponding to the I_1 resonance (upper right part of Fig. 1).

The I_1^M beats dominate the DFWM transients (left part of Fig. 1) recorded at I_1 and show no phase shift for different detunings. This indicates a common state of the involved polarizations [11] and demonstrates that the (A^0, X) state is involved in the I_1^M -polarization.

An emission line labelled I_1^M has been found by Razbirin [8] et al. under intense laser excitation in CdS. Since there the energetic position of this I_1^M -line has not been given accurately enough, we also performed intensity dependent luminescence measurements at our samples: A superlinear rise of the I_1^M line was found giving strong evidence for a correlation with the high density excitonic system (Fig. 2). Furthermore, the energetic distance to the I_1 -line was determined to $11.08 \pm 0.05 \text{ meV}$, a value which agrees well with the observed beat energy between I_1 and I_1^M of $10.7 \pm 0.3 \text{ meV}$. Our results thus identify the common state of the beating polarizations to be the (A^0, X) -state, the uppermost state as the (A^0, M) -ground state or at least one of its excited states.

To illustrate this, Fig. 3 shows a level scheme for the free biexciton (right part) and the biexciton bound to an impurity centre (left part). The beating polarizations are established by the electric field of the incoming pulses between the ground state and the intermediate level and between the intermediate level and upper level in both cases. If quantum beats of the polarizations are observed, their common state has to be initially occupied as has been shown in Ref. [11]. Accordingly, the first broad band excitation pulse establishes both, a population of (A^0, X) -complexes and the beating polarizations. The second pulse then gives rise to a polarization emitting photons in the direction $2k_2 - k_1$. The beat energies observed in the DFWM-experiments are $E^{\text{beat}} = E_x - E_m$ and $E_c^{\text{beat}} = E_{mc} - E_{xc}$ for the free and the bound biexciton, respectively (Fig. 3). We determine the binding energy from the beat energy according to $E_m^b = E^{\text{beat}}$ and $E_{mc}^b = 2E_{xc}^b - E_c^{\text{beat}}$, where E_{xc}^b just gives the binding energy of one exciton to the impurity centre. The termscheme also shows that the binding energy of the (A^0, M) -complex is defined with respect to the state formed by two free excitons. From the data given in Ref. [12] and our results in ZnSe [10] and CdS we may extract the binding energy E_{mc}^b for the neutral acceptor bound biexciton (A^0, M) (Table 1). The binding energies of the

Table 1

Beat- and binding energies of the (A^0, M) -complex and the free biexciton in various II–VI semiconductors; the nomenclature of the different energy is explained in Fig. 3

	CdSe	ZnSe	CdS
E_c^{beat} (meV)	5.4 [12]	7.7 ± 0.3	10.7 ± 0.3
E_{xc}^b (meV)	8.3 [12]	10.5	17.7
E_{mc}^b (meV)	11.2	13.3 ± 0.3	24.7 ± 0.3
$E_m^b - E_{xc}^b$ (meV)	2.9	2.8 ± 0.3	7.0 ± 0.3
E_m^b (meV)	?	3.5 ± 0.4	6.3 ± 0.3

(A^0, M) -complexes have been determined to $E_{mc}^b = 24.7$ meV and $E_{mc}^b = 13.3$ meV in CdS and ZnSe, respectively. Table 1 shows that in the investigated semiconductors the binding energy of the second exciton to the impurity complex is smaller than the binding energy of the first one. In indirect semiconductors like Ge the binding energy of the free biexcitons is larger than the binding energy of excitons to shallow impurity, leading to bound multiexciton luminescences energetically below the bound exciton recombinations [5,6]. In this case it is favourable to label those states ‘‘bound multiexciton’’. In the case of the direct II–VI compounds with their small biexciton binding energies one may rather label the (A^0, M) -state ‘‘exciton bound to an (A^0, X) -complex’’. Here, the bound biexciton is a complex with three holes associated with the $j = 3/2$ valence band. This three holes j – j couple to produce a singlet wavefunction and thus there is no splitting in this state due to hole–hole interactions. The (A^0, X) -complex has two holes in the valence band which j – j couple to produce states with $J = 0$ and $J = 2$. The radiative annihilation has as initial state the bound biexciton and as final states the bound exciton states from the $J = 0$ and $J = 2$ two hole state.

Since with broadband femtosecond-excitation two-step processes near the bandgap are rather likely, one expects to observe the X–M transition as DFWM-resonance. In forward geometry the strong scattering of polaritons close to the excitonic resonance leads to coherently excited excitons only in a small volume near the surface of the semiconductor facing the incoming beams. Therefore, we performed DFWM-experiments in backward geometry [13]. Here, the renormalisation of the polariton dispersion

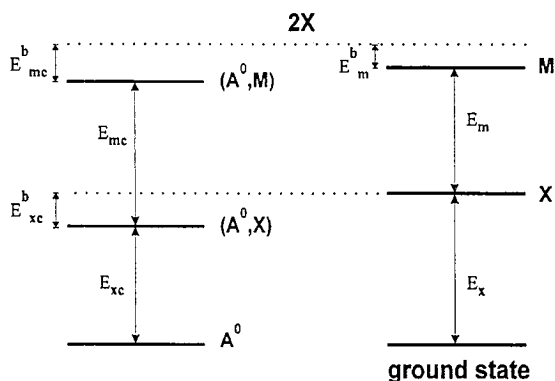


Fig. 3. Term scheme for the free biexciton (right part) and the biexciton bound to an impurity center A^0 (left part). E_x : transition energy between the biexciton state and the free exciton state; E_{xc} : transition energy of the exciton bound to the A^0 -center; E_{mc} : transition energy between the bound biexciton and the bound exciton; E_m^b : binding energy of the free biexciton; E_{mc}^b : binding energy of the biexciton bound to the A^0 -center; E_{xc}^b : binding energy of one exciton bound to the A^0 -center.

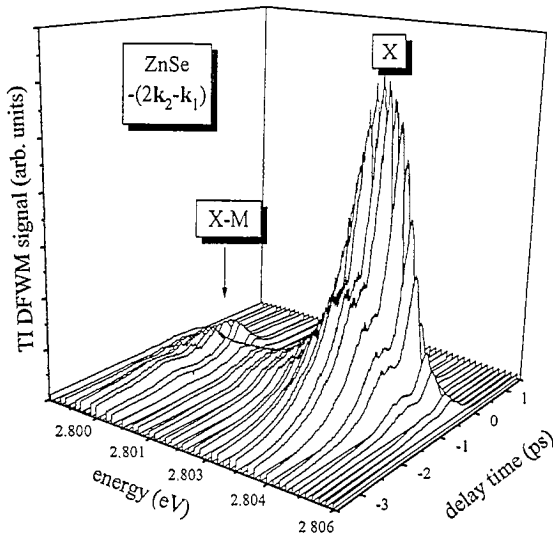


Fig. 4. Backward scattered DFWM signal in ZnSe in dependence on photon energy at 1.8 K.

near the two-step transition resonance to the free biexciton state should greatly enhance the DFWM signal. Fig. 4 shows spectrally resolved the backward scattered DFWM signal for ZnSe for different photon energies. The resonance labelled X–M exhibits quantum beats with the free exciton resonance. Therefore, we propose this resonance to be caused by the two-step transition from the free exciton to the free biexciton state. According to Fig. 3 the beat energy then gives the binding energy of the free biexciton which is compared with that for CdS, in Table 1. NQBS gives biexciton binding energies of 3.5 and 6.3 meV in strained ZnSe and CdS, respectively. These values are about 50% larger than those recently derived from two photon Raman scattering (TPRS) experiments [14,15]. However, high excitation density diffraction spectra of thin CdS platelets [4] show a renormalization of the polariton curve due to the formation of biexcitons yielding a biexciton binding energy of 5.9 meV. Additionally, calculations of the biexciton binding energies [3] support rather the NQBS than the TPRS values.

4. Conclusion

With broad band femtosecond-excitation, quantum beats in the three level system A^0 , (A^0, X) and (A^0, M) have been observed. The binding energies of the (A^0, M) -complexes have been determined to $E_{mc}^b = 24.7$ meV and $E_{mc}^b = 13.3$ meV in CdS and ZnSe, respectively. From the backward scattered DFWM signal the binding energies of the free biexciton state was found to amount to $E_m^b = 3.5$ meV in ZnSe and $E_m^b = 6.3$ meV in CdS.

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