Quantum beats of exciton polaritons in hexagonal CdS crystals

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We have investigated the coherent dynamics of excitons in hexagonal CdS single crystals using femtosecond transient and spectrally resolved four-wave mixing. When the *A*- and *B*-exciton transitions are simultaneously excited, we find a pronounced beating of the signal with two distinct beat periods of 275 fs and 4 ps. We attribute the short beat period to quantum beats between the *A* and *B* excitons, whereas the long beat period arises from the quantum-mechanical interference between the lower and intermediate *B*-polariton branches caused by the $\vec{k}$-linear term in the *B* valence band. For the *A*-exciton transition we have determined a dephasing time of 1.2 ps corresponding to a homogeneous linewidth of 1.1 meV. The homogeneous linewidth is of the same order as the longitudinal-transverse splitting, which confirms the importance of the polariton or strong-coupling picture for the quantitative interpretation of the data. [S0163-1829(97)06316-9]

The coherence properties of excitons in wide-gap II-VI semiconductors have attracted considerable interest since they allow insight into fundamental interaction processes within the crystal.[1,2] Transient four-wave mixing (FWM) has been used to determine the homogeneous linewidth of the exciton transitions and to investigate the dynamics of coherently excited excitons.[3] Recently, strong nonlinearities[4] and peculiar propagation effects have been reported for the free and bound exciton resonances in wide-gap II-VI semiconductors.[5–7] The FWM experiments were mostly focused either on bound excitons complexes[2,8,9] or on free exciton resonances of cubic ZnSe bulk and heterostructures.[4,10,11] The intrinsic exciton transitions in hexagonal crystals show interesting properties, which are not present in cubic crystals. In particular, the optical properties near the band gap are determined by *three* exciton series, caused by a threefold splitting of the highest valence band, which results from the spin-orbit coupling and the internal hexagonal crystal field.[12] In addition, two of these valence bands have Γ_7 symmetry, which gives rise to a term linear in $\vec{k}$ in the dispersion relation for wave vectors $\vec{k}$ perpendicular to the crystal axis $\vec{c}$, $\vec{k} \perp \vec{c}$ (see Fig. 1). The observation of this $\vec{k}$-linear term is very difficult in conventional linear optical spectroscopy because of the small energy splitting of the optical transitions. This splitting has been observed only in high-quality samples, e.g., by linear reflection experiments.[12–14] FWM experiments are much more sensitive to energy splittings since they measure the homogeneous linewidth even in the presence of inhomogeneous broadening. Thus we are able to study the coherent interaction of the intrinsic *A*- and *B*-exciton transitions under simultaneous excitation by a short, i.e., spectrally broad, laser pulse. In particular, we are able to investigate the influence of the $\vec{k}$-linear term on the coherent exciton dynamics.

First we will present the results of the transient and spectrally resolved FWM experiments obtained for a light field polarized perpendicular to the crystal axis, where we find a strong modulation of the FWM signal with two distinct time periods. Then we discuss the results obtained for a light field

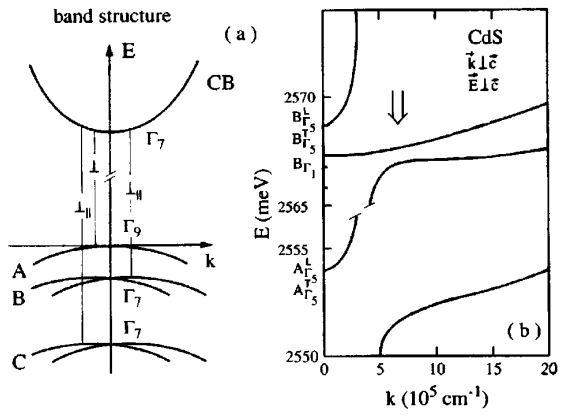

FIG. 1. Band structure of (a) hexagonal CdS and (b) the resulting exciton-polariton dispersion. The arrow indicates the region in *k* space where the density of states is especially high and from where the quantum beats arise.

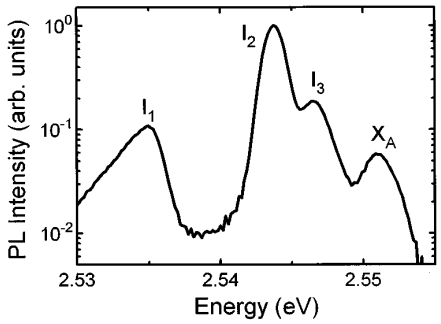

FIG. 2. Semilogarithmic plot of the PL spectrum of the CdS sample at 8 K under mercury lamp band-to-band exitation. I_1, I_2, and I_3 stand for luminescence of excitons bound to neutral donors, acceptors, and charged donors and X_A is the free $A\Gamma_5$ exciton polariton emission.

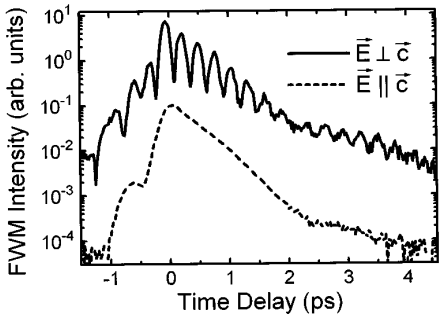

FIG. 3. Semilogarithmic plot of the measured transient FWM signal as a function of time delay τ for $\vec{E} \perp \vec{c} \perp \vec{k}$ (full line) and for $\vec{E} \| \vec{c} \perp \vec{k}$ (dashed line) at 8 K and an exciton density of about 5×10^{14} cm^{-3}. The intensities are normalized and the transients are shifted by a factor of 100 in the y direction for clarity.

polarized parallel to the crystal axis and finally we determine the homogeneous linewidth of the A-exciton transition, which will be compared to its longitudinal-transverse splitting Δ_{LT}.

We have studied crystal platelets of different thickness ($1-20$ μm) and with an in-plane crystal axis ($\vec{k} \perp \vec{c}$). The experiments are performed at 8 K in a He-flow cryostat. Here we present the results obtained from a 20-μm-thick sample. We have verified that the results obtained in reflection geometry are independent of sample thickness. The photoluminescence (PL) spectrum of this sample obtained under mercury lamp band-to-band excitation is plotted on a logarithmic scale in Fig. 2. The PL spectrum contains the well-known recombination lines due to free and bound exciton recombination.[15] The emission is dominated by the I_2 line (2.544 eV), which corresponds to the radiative recombination of an exciton bound to a neutral donor. In addition, the low-energy peak (2.535 eV) corresponds to the acceptor bound exciton, whereas the high-energy peak (2.547 eV) can be attributed to an exciton bound to an ionized donor. The PL peak at 2.551 eV corresponds to the free $A\Gamma_5$ exciton polariton transition and indicates the high quality of the sample under investigation.

The FWM experiments are performed using the second harmonic of a passively mode-locked Ti:sapphire laser as the excitation source. This laser system provides 110-fs pulses (equivalent to a spectral width of 20 meV) at a repetition rate of 76 MHz. The spectral maximum of the excitation pulse is tuned to an energy position between the $n=1$ A-exciton and $n=1$ B-exciton transitions in order to excite both transitions simultaneously. The nonlinear signal is measured in the two-beam self-diffraction configuration in reflection geometry. The reflection geometry is used in order to avoid effects resulting from the propagation of the signal through the optically thick sample. The nonlinear signal is monitored either spectrally integrated by a slow photomultiplier as a function of the time delay τ between the two incoming pulses or spectrally resolved by a 0.25 m spectrometer with an optical multichannel analyzer having a spectral resolution of 0.5 meV.

First we will discuss the results obtained for the polarization $\vec{E} \perp \vec{c}$. The upper trace in Fig. 3 shows the transient FWM signal as a function of the time delay for $\vec{E} \perp \vec{c}$ (full line) at an exciton density of about 5×10^{14} cm^{-3}. We find a pronounced beating of the transient FWM signal with a period of $T_{B1} = 275 \pm 30$ fs for positive and negative delays. By a detailed analysis of the temporal behavior of this signal, we observe that the fast beating vanishes at $\tau = 2 \pm 0.1$ ps and reappears again, giving evidence for a superimposed long beat period with a period of $T_{B2} \approx 4$ ps. The energy spacing of the excited transitions can be determined from the observed beat period using the relation $\Delta E = h/T_B$. Thus the fast beating corresponds to an energy spacing of about $\Delta E_{B1} = 15 \pm 1.5$ meV and the long period beating corresponds to $\Delta E_{B2} = 1 \pm 0.05$ meV. In order to determine the absolute spectral position of the involved transitions, we have resolved the FWM signal spectrally. In Fig. 4 the spectrum is depicted as a function of the time delay τ. The dif-

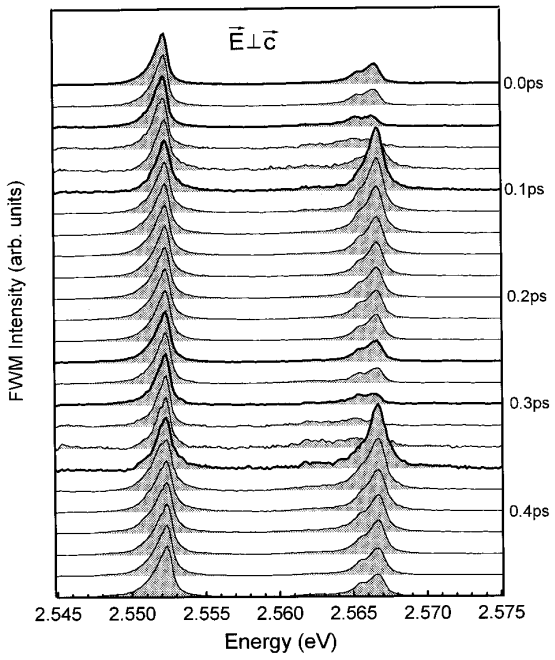

FIG. 4. Measured FWM spectra as a function of time delay between the two incoming pulses for $\vec{E} \perp \vec{c}$ at 8 K. The spectra are normalized to the intensity of the A-exciton resonance. For the explanation of the thick solid traces see the text.

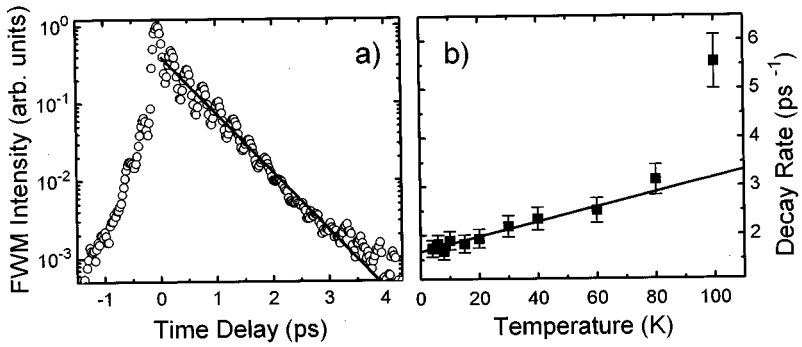

FIG. 5. (a) Measured transient FWM signal as a function of time delay τ for $\vec{E}\perp\vec{c}$ (open circles) and a fit according to a single exponential decay (full line). (b) Decay rate of the FWM signal as a function of the temperature. The laser energy is centered on the A exciton.

ferent traces in Fig. 4 are normalized to the FWM intensity of the A exciton. For $\tau=0$ ps we find three peaks contributing to the FWM signal. By comparing the spectral positions of the peak with the exciton polariton dispersion in Fig. 1(b), the strong signal at 2.5525 eV can be assigned to the lower A-polariton branch of the A exciton.[16] The two peaks around 2.566 eV result from the B excitons. The polariton dispersion of the B exciton consists of three optically allowed branches as depicted in Fig. 1(b). In addition to the upper and lower branches, the $\vec{k}$-linear term in the dispersion relation of the B valence band gives rise to an intermediate polariton branch. We attribute the peak at 2.5655 eV to the lower polariton branch of the B exciton. This value is about 1.5 meV smaller than that one published earlier.[13,14] This difference is probably caused by different strain in the platelets. The interpretation of the second peak of the B-exciton transition at 2.5665 meV is more subtile and we assign it to the intermediate polariton branch. The upper polariton branches of the A and B excitons are not found in the spectra, which is probably due to their smaller density of states in comparison to the lower branches.

In the following we will discuss the temporal evolution of the spectrum as a function of the time delay between the two excitation pulses, which allows one to distinguish between quantum beats and polarization interference.[17,18] For $\tau=0$ ps the intensity of the two peaks of the B excitons roughly reflects the relative excitation strength in comparison to the A excitons. Figure 4 shows evidence for an oscillation of the signal corresponding to B excitons relative to the normalized signal corresponding to the A exciton as a function of the time delay, which indicates the quantum-beat nature of the oscillations. Obviously, the lower A-polariton branch and the lower and intermediate B-polariton branches represent a quantum-mechanically coupled system. The coupling results from the common conduction-band states, which contribute to all of these three polariton branches. The quantum beats arising from the three polariton branches can be described by two beat frequencies: $\omega_1=\Delta E_1/\hbar$, stemming from the interference between the lower A and the lower B branch, and $\omega_2=\Delta E_2/\hbar$, steming from the interference between the lower A- and the intermediate B branch. The slight difference in the beat frequencies can be directly seen in the spectra. For $\tau=0$ ps the peak corresponding to the intermediate B-polariton branch is stronger than the peak corresponding to the lower B-polariton branch. For increasing time delay both become equal. Furthermore, they become weaker due to the destructive interference with the A exciton. By further increasing the time delay, first the signal of the intermediate branch arises again, then the signal of the lower branch appears at the low-energy side, both become equal again, and so on. The different steps are marked by the thick solid lines in Fig. 4. The difference frequency $\omega_3=(\Delta E_2-\Delta E_1)/\hbar$ can be explained by a beating between the two frequencies ω_1 and ω_2 and corresponds directly to the long beat period observed in the transient FWM signal in Fig. 3. Consequently, we conclude that the splitting of the B exciton, which has been observed in the spectra, is related to the long beat period in the transient FWM signal. It is caused by a quantum-mechanical interference between the lower and intermediate polariton branches, resulting from the $\vec{k}$-linear term in the B valence band. To give further evidence of this interpretation, we have measured the FWM signal with the light field polarized parallel to the crystal axis ($\vec{E}\|\vec{c}$). See Fig. 3, lower trace. Due to the optical selection rules, only the B exciton is then dipole allowed, whereas the A exciton is dipole forbidden. Thus we expect that the fast beat period that we have attributed to the A- and B-exciton splitting should vanish, whereas the long beat period arising from the lower and intermediate $B\Gamma_5$ polariton branches should remain. This is in agreement with the experimental findings.

It is well known that the polaritons are the eigenstates of light in matter.[12] Consequently, we used the polariton or strong-coupling concept throughout. The almost constant splitting of the lower and intermediate $B\Gamma_5$ polariton branch of about 1 meV over a certain range of k vectors [see Fig. 1(b)] can be understood only in the polariton picture.

The specific signatures of the polariton concept will be increasingly washed out when the damping Γ gets larger than the longitudinal-transvers splitting Δ_{LT}.[12,19] For the Γ_5 exciton the latter quantity is, in CdS, 2 meV.[12–16] The homogeneous linewidth of the A exciton can be determined from the decay of the FWM signal. In order to reduce the influence of the B excitons we have centered the spectrum of the laser on the A-exciton transition. In Fig. 5(a) the transient FWM signal (circles) is plotted as a function of time delay for $\vec{E}\perp\vec{c}$ at $T=8$ K. The full line represents a single exponential fit to the transient with a time constant of 575 ± 50 fs. This implies a dephasing time of about $T_2=1.15\pm0.1$ ps, corresponding to a damping or homogeneous linewidth of $\Gamma_{\mathrm{hom}}(T=8\ \mathrm{K})=1.14\pm0.12$ meV for the A excitons if we assume a homogeneous broadening of the transition.[21] This assumption is supported by the fact that we observe a FWM signal at negative time delays, which should disappear if the broadening of the optical transition is predominantly inhomogeneous.[22] The appearance of this signal is an indi-

cation of coherent exciton-exciton interaction[22] or polariton effects.[23] From the experimental results presented here we cannot distinguish between these two effects. Also biexcitons can lead to a signal at negative time delay, but we do not see contributions from the biexcitonic transition in the spectrally resolved FWM experiments even at negative time delay. Therefore, it is unlikely that their contribution is the most dominant for this FWM signal. The homogeneous linewidth involves contributions from intrinsic scattering processes, such as exciton-exciton and exciton-phonon scattering, and extrinsic ones, namely, impurity, and defect scattering. The intrinsic scattering processes can be studied by temperature- and density-dependent FWM experiments. In Fig. 5(b) the decay rate $1/\tau_{dec}$ of the FWM signal is plotted as a function of temperature. The linear increase of the decay rate with temperature between 5 K and 60 K implies that acoustic-phonon scattering is the dominant temperature-dependent dephasing mechanism in this temperature range. For higher temperatures the scattering with optical phonons becomes relevant, resulting in an increase of the decay rate. From the slope of the linear regression in Fig. 5(b) for 5 K $<T<60$ K we obtain the exciton–acoustic-phonon coupling strength $\gamma_{ac}=0.015\pm0.003$ ps^{-1} K^{-1} and the intercept of $1/\tau_{dec}(T=0\ \mathrm{K})=1.7\pm0.1$ ps^{-1} for the A-exciton transition accounts for temperature-independent processes. These values are comparable to those reported recently for ZnSe.[4] We find no significant variation of the decay time with the exciton density in the range between 5×10^{14} and 10^{16} cm^{-2}. Therefore, we conclude that in this low-density regime the exciton-exciton scattering is weak and its contribution to the homogeneous linewidth can be neglected. We attribute the obtained intercept $1/\tau_{dec}(T=0\ \mathrm{K})$, which corresponds to a temperature-independent homogeneous linewidth of $\Gamma_{hom}(T=0\ \mathrm{K})=1.1\pm0.1$ meV, to extrinsic scattering processes, which depend on the quality of the sample. The above data clearly show that at low temperature $\Delta_{LT}>\Gamma_{hom}$ and that polariton effects must be included for a quantitative description of the data.

Finally, it should be noted that we have also performed the FWM experiment in transmission geometry. The results we obtained look significantly different from those in reflection geometry.[24] This is probably caused by the fact that in transmission geometry the propagation effects of the polaritons come additionally into play.

In summary, we have investigated the coherent dynamics of the excitons in hexagonal CdS platelets using subpicosecond transient and spectrally resolved FWM experiments in reflection geometry. The observed quantum beats with two distinct beat periods are attributed to the interaction between the lower polariton branch of the A exciton and the lower and intermediate branches of the B excitons. The appearance of the intermediate branch is caused by the $\vec{k}$-linear term in the B valence band and is a peculiarity of the Γ_7 symmetry in the hexagonal crystal structure of CdS.

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