

Picosecond Quantum-Beat Spectroscopy of Bound Excitons in CdS

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We report the first observation of quantum beats in the resonance fluorescence of a bound exciton in a semiconductor, the ionized-donor exciton complex in CdS. Measurements of the polarization behavior and magnetic-field dependence of the beats permitted a detailed investigation of strain effects and magneto-optical parameters of the states. From the damping of the beats, coherence times of the order of several hundreds of picoseconds are deduced. For the neutral-donor and -acceptor bound exciton states, very rapid dephasing with coherence times of the order of 20 ps is found.

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Phase relaxation is of fundamental importance for the understanding of the dynamical behavior of electronic states. In solids, phase relaxation times in the picosecond and subpicosecond regime require high time resolution, and therefore only nonlinear optical techniques, like photon echo [1,2], transient absorption correlation [3], or four-wave mixing [4], hitherto allowed exploration of the dephasing of continuum electron-hole states and excitons in various semiconductor systems. However, an alternative, linear method to investigate dephasing of quantum states in solids is *quantum-beat spectroscopy*. This technique has widely been used in studies of atoms and molecules [5], but most recently, by studying the resonance fluorescence of free exciton states in AgBr [6], it was demonstrated to be applicable for solids too. In this technique, a set of nearly degenerate electronic states, e.g., split by a magnetic field, is excited coherently by a short laser pulse with a spectral width larger than the energy splitting of the levels. The beats show up as oscillations in the time-dependent resonance fluorescence from these states. From the damping of the beats, the coherence time τ_{coh} (also called dephasing time T_2) of the states can be deduced, which is defined through $1/\tau_{\text{coh}} = 2/T_1 + 1/T_2'$, where T_1 and T_2' denote the energy relaxation and pure dephasing times. The beating frequencies are directly related to the energy splitting of the states, which can be varied by the magnetic field, allowing a determination of important magneto-optical parameters like electron and hole g factors. A particular advantage of quantum beats in spontaneous fluorescence is that they are not affected at all by an inhomogeneous broadening of the states. Therefore, small splittings can be measured that are masked in the spectrum and not accessible to conventional spectroscopy. From a fundamental point of view, beats in spontaneous fluorescence originating from the superposition of wave functions have to be distinguished from beating phenomena observed in investigations of exciton states using nonlinear four-wave mixing [7,8], as these are due to interference of coherent polarizations oscillating at different frequencies.

In order to be able to use the full potential of quantum-beat spectroscopy, the coherence time of the states investigated should be long, corresponding to a

small homogeneous linewidth $\Gamma_{\text{hom}} = 2\hbar/\tau_{\text{coh}}$. In semiconductors, for bound-exciton transitions, in principle, long coherence times can be expected, as, due to localization, the number of relaxation channels for these states is greatly reduced. Indeed, indications of coherence times of the order of several hundreds of picoseconds have been found in previous studies of optical orientation of bound-exciton transitions in various II-VI compounds like CdS [9], and also for disorder-localized states in CdS/CdSe solid solutions at low temperature [2] by photon-echo experiments.

In this paper we report the first observation of quantum beats from bound exciton states in a semiconductor. As a model system, we have investigated the bound-exciton transitions I_1 , I_2 , and I_3 in CdS, the electronic configurations of which are well known from conventional spectroscopy [10]. These transitions are due to $\Gamma_9 \times \Gamma_7$ A -exciton complexes involving a neutral acceptor (A^0, X), a neutral donor (D^0, X), and a charged donor (D^+, X), respectively. In the case of the I_3 transition, in the presence of a magnetic field pronounced quantum beats are observed that decay with a coherence time of about 300 ps. By using fields up to 3.5 T, they can be exploited to determine electron and hole g factors of the (D^+, X) complex. For the other bound-exciton transitions, dephasing times are found to be extremely short, not permitting the observation of beats for these states within the available time resolution.

In our experimental setup (for details see [11]) excitation is accomplished by 5–8-ps pulses from a dye laser, operated with coumarin 102 and synchronously pumped by a mode-locked frequency-tripled Nd-doped yttrium lithium fluoride laser system. The scattered light is analyzed by means of a 1-m double monochromator having subtractive dispersion to compensate the light transit-time spread produced by a single grating (residual time broadening < 5 ps). This setup allowed us to achieve transform-limited performance down to this time range, the actual time resolution being limited by the time response of the photodetectors used (20 ps FWHM for a microchannel-plate photomultiplier and 10 ps for a synchroscan streak camera).

The CdS sample was of cylindrical shape with the crys-

tallographic c direction along the cylinder axis. The direction of the magnetic field and the c axis enclose an angle Θ , variable by rotating the sample, thus defining a plane of reference. The experiments were performed in Faraday geometry in a nearly backscattering configuration, whereby the resonance fluorescence was excited through the crystal surface with its normal parallel to the c axis. The excitation density was kept below 10 W/cm^2 to avoid any saturation effects. All measurements were performed with the sample immersed in superfluid helium ($T=2 \text{ K}$).

As depicted in Fig. 1, the electronic structure of the bound excitons and the magnetic-field splitting of the states are rather different for the cases considered here [10]. The (D^+, X) states closely resemble those of the free exciton with a Γ_1 ground state and a fourfold excited state with symmetries Γ_5 (optically dipole-allowed states Φ_1, Φ_2) and Γ_6 (dipole-forbidden states Φ_3, Φ_4). In contrast, due to a spin pairing of the two electrons, the molecular-type (D^0, X) complex has Kramer's degenerate ground and excited states with symmetry Γ_7 and Γ_9 , respectively. Compared with (D^0, X) , for the (A^0, X) complex the roles of electrons and holes are interchanged, giving rise to ground- and excited-state symmetries Γ_9 and Γ_7 .

The behavior of the transition energies and optical matrix elements in a magnetic field is governed by the Zeeman Hamiltonian which for all investigated cases has the form [10]

$$H_{\text{Zeeman}} = g_c \mu_B \mathbf{B} \cdot \mathbf{s} - g_v^{\parallel} B_z \sigma_z. \quad (1)$$

Here \mathbf{s} denotes the effective spin operator ($s = \frac{1}{2}$) of the electrons with an isotropic g value g_c , and σ the effective hole spin ($\sigma = \frac{1}{2}$). The g value of the Γ_9 hole is highly

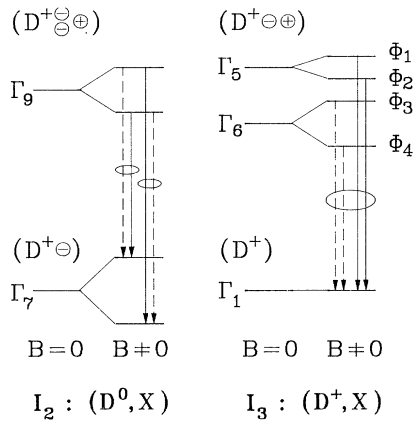


FIG. 1. Energy-level scheme and magnetic-field splitting for the exciton bound to a neutral donor (D^0, X) and to an ionized donor (D^+, X) . The optical transitions are represented by arrows, the dashed ones being only allowed for a magnetic field inclined to the c axis ($\Theta \neq 0^\circ$). The transitions for which quantum beats occur are grouped together by circles.

anisotropic with $g_c^{\perp} = 0$ [10]. Different from (D^0, X) and (A^0, X) , the I_3 -exciton states show an exchange splitting that is strain dependent and given by the effective Hamiltonian [12]

$$H_{\text{strain}} = 2\Delta s_z \sigma_z + c_1 [(\epsilon_{xx} - \epsilon_{yy}) s_x \sigma_x - 2\epsilon_{xy} s_y \sigma_x] + c_2 [(\epsilon_{xx} - \epsilon_{yy}) s_y \sigma_y + 2\epsilon_{xy} s_x \sigma_y] + c_3 [\epsilon_{xz} s_x \sigma_z + \epsilon_{yz} s_y \sigma_z]. \quad (2)$$

Here Δ is the exchange energy at zero strain, $\epsilon_{\alpha\beta}$ ($\alpha, \beta = x, y, z$) are the components of the strain tensors, and c_i ($i = 1, 2, 3$) are the appropriate deformation potential constants. As a result of this interaction, the exciton states show a zero-field splitting and a mixing of the eigenstates, causing a sensitive dependence of polarization selection rules on the strain in the sample.

For the occurrence of *quantum beats* from the split states, the exciting laser pulse has to be sufficiently short to accomplish coherent excitation. In addition, optical transitions connecting at least two of the excited states

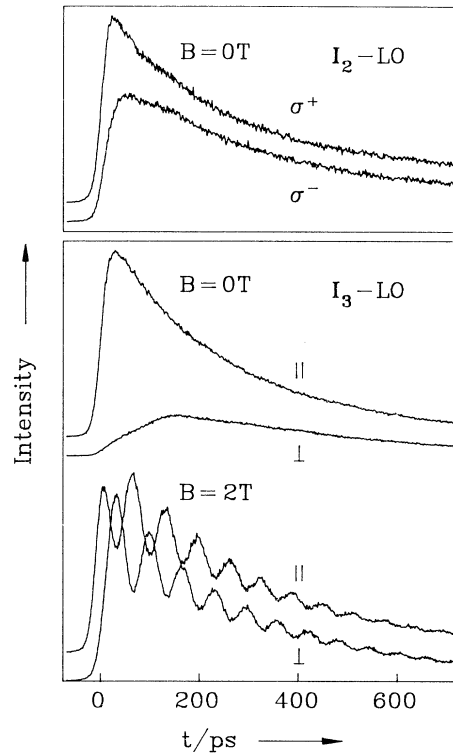


FIG. 2. Time dependence of polarized I_2 and I_3 resonance fluorescence at zero magnetic field and at $B=2 \text{ T}$ for $\Theta=0^\circ$. The signals are detected in the 1-LO replica of each line. For the I_2 -LO transition the excitation is left-circularly (σ^+) polarized, while detection is with left (σ^+) and right (σ^-) circular polarization. The I_3 -LO line is excited with light linearly polarized at 45° to the plane of reference (see text). The fluorescence light is linearly polarized at 45° (\parallel) and -45° (\perp). Zero of time scale is given by the system response to the laser pulse (not shown).

with the same ground-state level have to be allowed. Working out the selection rules, it follows that for I_1 and I_2 , quantum beats are only possible for an inclined magnetic field ($\Theta \neq 0^\circ$). In the case of I_3 , for $\Theta = 0^\circ$ beats occur only between the Γ_5 sublevels, while for $\Theta \neq 0^\circ$ all four transitions may interfere.

Figure 2 shows examples for the observed time dependence of the I_2 and I_3 intensities at different magnetic fields. Here, and in all figures shown later, excitation was accomplished in resonance with the exciton transition, while the scattered light was detected in the corresponding 1-LO replica of the line to avoid any disturbing effect of elastically scattered light at the exciting laser frequency.

According to the quantum-mechanical theory of light scattering [13,14], it follows from the selection rules at $B=0$ T for the (D^+, X) exciton states in the scattered light that there is a fast Raman-like component for detection with polarization parallel to that of the exciting laser and a slow luminescencelike component in the orthogonal polarization state, irrespective of excitation polarization. Different from that, we found for most polarization directions temporal oscillations of the scattered intensity in the two orthogonal detection polarizations, indicating that already at zero field the (D^+, X) exciton states are split by residual strain in the sample. As implied by the absence of any beating for an excitation polarization at 45° to the plane of reference (decay curves for $B=0$ T displayed in the lower part of Fig. 2), only one of the excitonic eigenstates is excited for this case. This proves that, according to the Hamiltonian [Eq. (2)], the dominant strain in the sample is of type ϵ_{xy} . The magnitude of the strain splitting $\Delta_{12} = c_1 \epsilon_{xy}$ between exciton states Φ_1 and Φ_2 is obtained from the observed beat frequency for excitation polarization parallel to the plane of reference as 0.02 meV (compare upper curve in Fig. 3). Since dephasing effects are small, by applying a magnetic field $\mathbf{B} \parallel c$ beat patterns are observable, extending over the whole lifetime of the states. In this geometry, the beating involves only transitions to the states Φ_1 and Φ_2 and, as shown in Fig. 2 (bottom), occurs in both parallel and perpendicular polarization, being phase shifted by 180° as is expected from theory [14]. Both the energy relaxation time of 220 ps and the coherence time of about 300 ps, which were obtained from the damping of the beats and found independent of magnetic field, are consistent with the depolarization behavior at zero magnetic field.

For the (A^0, X) and (D^0, X) states the dephasing can be observed for excitation with circularly polarized light. As exemplified for the I_2 transition (upper part of Fig. 2) the depolarization for these transitions is rather fast. From a quantitative analysis a dephasing time of about 20 ps can be deduced. This fast dephasing then damps out completely the beats expected in the scattered light for $B \neq 0$ which therefore could not be investigated further.

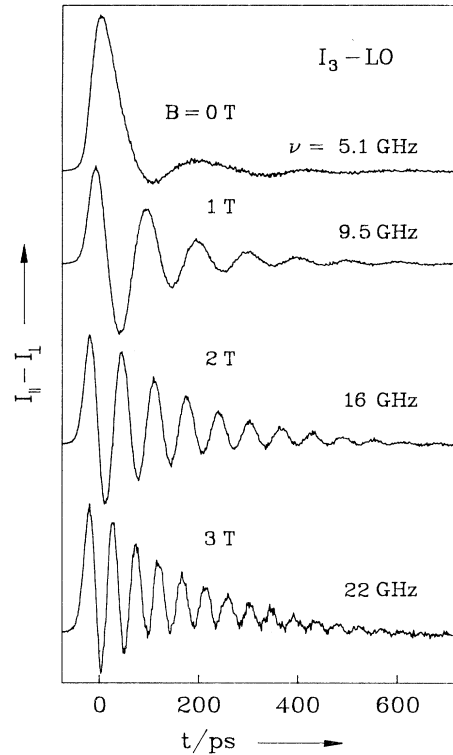


FIG. 3. Quantum beats observed at different magnetic fields ($\Theta = 0^\circ$) for the I_3 -LO transition. Plotted is the difference of fluorescence intensities with polarization parallel (I_{\parallel}) and perpendicular (I_{\perp}) to that of the exciting laser, which is linearly polarized in the plane of reference.

Beat patterns obtained as the difference between parallel and perpendicular polarized fluorescence intensities are displayed in Fig. 3 for magnetic fields $\mathbf{B} \parallel c$ and up to $B=3$ T, showing the expected increase in oscillation frequency with B . The beat frequencies and hence the energy splitting between the states Φ_1 and Φ_2 can be directly obtained by Fourier transformation of the data. The results are shown in Fig. 4, together with a fit obtained by numerical diagonalization of Eqs. (1) and (2). The maximum splitting at $B=3.5$ T corresponds to about 27 GHz, the highest frequency observed so far for quantum beats in fluorescence.

For the chosen excitation and detection geometry, the only parameter (besides the strain splitting) which determines the magnetic-field dependence of the splitting of the exciton states is the difference between electron and hole g factors. The solid line was obtained assuming $|g_e - g_h^{\parallel}| = 0.5$ and $\Delta_{12} = 0.02$ meV. This shows that for the I_3 state the electron and hole g factors are quite different, a result which could not be obtained by conventional magneto-optics [10] because of the large inhomogeneous broadening masking the splitting of the states. As the difference in g factors is almost equal to that

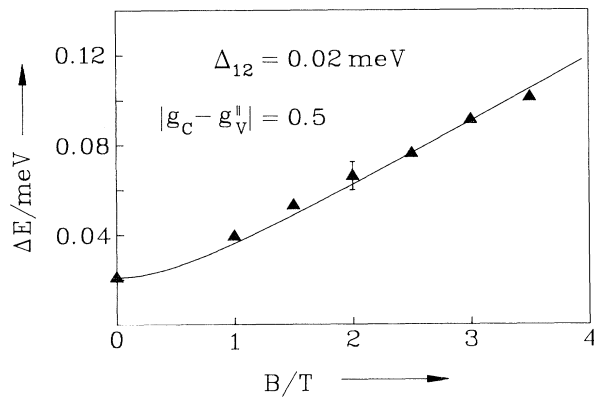


FIG. 4. Magnetic-field dependence of the energy splitting between exciton states Φ_1, Φ_2 of the (D^+, X) complex for $\Theta = 0^\circ$ as obtained from analyzing the quantum-beat signals. Triangles: experimental data. Solid line: fit obtained by numerical diagonalization of the Zeeman and strain Hamiltonian using the parameters given in the figure.

found for the free A -exciton state [15], we conclude that the binding of the exciton to the ionized donor does not change the electronic wave functions very much. To substantiate this conclusion, measurements of the other magneto-optical parameters are under way.

The fast dephasing observed for I_1 and I_2 may be related to the much higher concentration of the neutral donor and acceptor species compared with that of the ionized donors in our sample. From the strength of the I_1 and I_2 LO replica relative to that of I_3 under resonant excitation a corresponding concentration ratio of at least 10^3 is suggested. At this rather high doping level, one expects fast energy-transfer processes to occur between the centers by which the coherence may be effectively destroyed. This is supported by the time dependence of the I_2 resonance fluorescence, where a pronounced nonexponential behavior is found, characteristic for such processes. To clarify this point, experiments are planned in which the neutral-donor concentration will be varied either by different dop-

ing levels or by additional sub-band-gap light irradiation. The authors are indebted to the Deutsche Forschungsgemeinschaft for support of this project.

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