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Evidence of biexcitonic contributions to four-wave mixing in GaAs quantum wells

E.J. Mayer, G.O. Smith, V. Heuckeroth, and J. Kuhl
Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Federal Republic of Germany

K. Bott, A. Schulze, T. Meier, D. Bennhardt, S.W. Koch, and P. Thomas
Department of Physics and Materials Sciences Center, Philipps University, Renthof 5, D-35032 Marburg, Federal Republic of Germany

R. Hey and K. Ploog
Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, D-10177 Berlin, Federal Republic of Germany
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A three-pulse degenerate four-wave-mixing experiment and its theoretical analysis reveal contributions of local field and biexciton effects to the nonlinear optical response of the two-dimensional exciton. Quantum beats with a frequency equivalent to the biexciton binding energy appear only for specific polarizations. Polarization-dependent spectrally resolved four-wave mixing shows an additional peak that is separated from the $1s$ heavy-hole exciton line by the biexciton binding energy. These experimental results are in good agreement with the optical selection rules of the theoretical model, providing evidence for biexcitonic contributions to the four-wave mixing.

The strong nonlinear optical response of the two-dimensional (2D) exciton in GaAs quantum wells (QW's) at relatively low excitation densities has been observed in many experimental studies in accordance with theoretical predictions. Based on measurements on bulk GaAs, Wang *et al.*[1] showed that their experimental results can be explained by a density-dependent change of the dephasing rates [excitation-induced dephasing (EID)]. Wegener *et al.*[2] suggested that the polarization in a GaAs QW affects the external field [local field effects (LFE)]. In a previous paper dealing with the role of exciton-exciton interaction, we have suggested a model that phenomenologically includes a coupling between opposite spin excitons and that is able to describe biexciton formation (BIF).[3] At present, it is still an open question which of these mechanisms provides the dominant contributions to the nonlinearity. In particular, the role of biexcitons remains controversial.

Features observed in pump-probe studies,[4] the density dependence of the photoluminescence (PL) line shape,[5,6] and modulations detected in degenerate-four-wave-mixing (DFWM) experiments have been interpreted as evidence for the formation of biexcitons.[7,8] However, the interpretation was based on experiments using optical pulses that either were far away from the Fourier transform limit[7] or that had highly asymmetric pulse shapes.[8] These papers also did not address the possibility that biexcitonic features originate from fifth- and higher-order mixing processes rather than from a third-order polarization.

Here we present an interesting three-pulse DFWM configuration that is able to differentiate between local field effects and biexcitonic contributions to the time-integrated (TI) signal. Comparisons between experiment and theory demonstrate that LFE are able to explain the polarization dependence of the amplitude and temporal shapes of the DFWM signal. Evidence is presented showing that biexcitons are the source of pronounced modulation phenomena detected in four-wave mixing. The influence of EID is discussed, but this mechanism does not appear to be necessary in order to explain the present experimental data. Contributions due to biexcitons grow with excitation density and achieve a dominant influence when fifth-order processes become important. The presence of biexcitons is furthermore supported by the observation of two spectrally separated bands in the diffracted signal and the appearance of quantum beats,[9] assigned to quantum interference between bound (biexcitons) and unbound two-exciton states.

In the experiments, a single 20-nm $GaAs/Al_{0.3}Ga_{0.7}As$ QW (PL linewidth 0.3 meV, homogeneous linewidth 0.3 meV, no Stokes shift between PL excitation and PL) kept at 8 K is excited by three pulses of 1.0-ps duration from a mode-locked Ti:sapphire laser. These pulses have equal intensity, wave vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$, and delays τ_{12} and τ_{23}. The signal is monitored in the backward diffraction geometry in the direction $\mathbf{k}_s=\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3$ (see Fig. 1). The excitation density was less than 5×10^8 cm^{-2} in order to minimize fifth-order effects. Figures 1(a) and 1(b) depict the time-integrated signal measured for fixed $\tau_{12}=1.3$ ps and varying $\tau_{23}=\tau$ for seven different combinations of circularly or linearly polarized pulses, respectively. In both cases, identical polarization of all three pulses yields the strongest signal peak amplitude. The other signals are smaller by a factor of 2–3 with the exception of that observed for $\sigma^+\sigma^+\sigma^-$ configuration which is smaller by two orders of magnitude and is not shown in Fig. 1.

Calculations based on a model of independent two-level systems are unable to simulate the shape of the measured TI-DFWM signal; in particular, no signal is predicted for all mixed circular polarizations [Fig. 2(a)]. However, we achieve a very good agreement between experiment and theory by solving the optical Bloch equations for a five-level system (5LS) which takes into account single-exciton as well as two-exciton states. This 5LS is an extension of the previously discussed four-level system (4LS),[3] wherein an additional two-exciton state is introduced phenomenologically

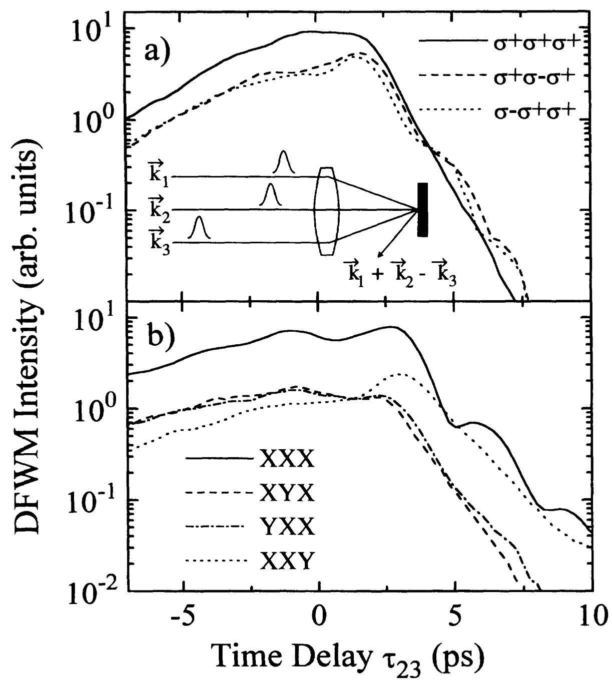

FIG. 1. The measured TI-DFWM signal as a function of the delay time τ_{23} for various combinations of circular (a) and linear (b) polarization. The inset in part (a) displays the excitation geometry for three-pulse TI-DFWM.

[see Fig. 2(f)]. The two-exciton states consisting of σ^+ and σ^- excitons describe the biexcitons and scattering states of two excitons and are separated from each other by the biexciton binding energy Δ. Detailed information about the optical Bloch equations and their solution can be found in Refs. 3, 10, and 11.

The influence of LFE, EID, and BIF on the TI-DFWM signal shape diffracted into the direction $\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3$ is shown in Fig. 2 for different configurations with circularly polarized pulses. The curve in Fig. 2(a) is calculated for two noninteracting two-level systems. Figures 2(b) and 2(c) are obtained if LFE and EID are introduced into the calculations, respectively. Figure 2(d) shows the contribution of the formation of biexcitons to the signal in the 4LS, whereas in Fig. 2(e) the results are depicted for the above-mentioned 5LS. The most important results of these model calculations are the following.

The signal for the $\sigma^+\sigma^+\sigma^-$ geometry is zero in the third-order approximation for all models investigated.

The 2LS, without assuming LFE, EID, and BIF [Fig. 2(a)], shows no signal for mixed polarizations as well as no signal for $\tau_{23}>0$ beyond the duration of the exciting pulses in the $\sigma^+\sigma^+\sigma^+$ geometry.

The LFE [Fig. 2(b)] lead to a slower decay of the signal for $\tau_{23}>0$ as observed previously,[2,12] but still give no signal for different polarizations.

The EID coupling of the two noninteracting 2LS [Fig. 2(c)] gives signals for mixed polarized configurations which are smaller than that for copolarized excitation.

The curves plotted in Fig. 2(d) are calculated including BIF within the 4LS by assuming a biexciton binding energy

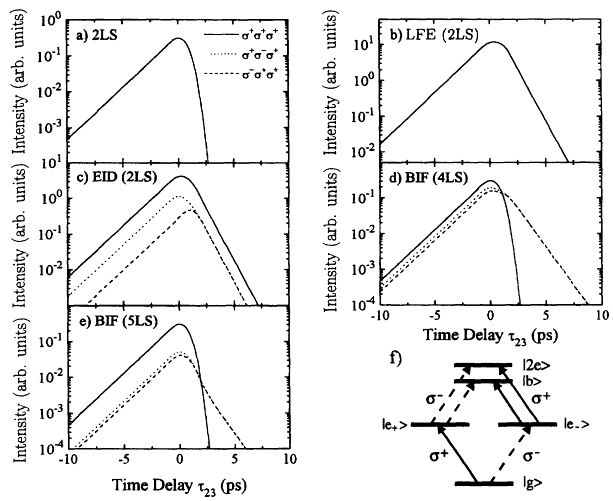

FIG. 2. Calculated curves of the TI-DFWM signal vs delay time τ_{23} for (a) 2LS without interactions, (b) 2LS with LFE $=1.2$ meV, (c) 2LS with EID $=1.2$ meV, (d) 4LS with biexciton ($\Delta=1.2$ meV), (e) same as (d) including a two-exciton scattering state, (f) the 5LS including the ground state $|g\rangle$, the hh exciton states $|e_+\rangle$ and $|e_-\rangle$, and the noninteracting two-exciton scattering states $|2e\rangle$ and the biexciton $|b\rangle$ built by two single hh excitons. The polarization for the optical excitation is denoted by σ^+ and σ^-. Other parameters are $\tau_{12}=1.3$ ps, $\Delta t_{\text{laser}}=1.0$ ps.

of $\Delta=1.2$ meV and a variation of the dephasing times of the upper state. The trailing edges for mixed polarization show a longer decay time than that for copolarized excitation. This slower decay can be attributed to the biexciton dephasing time, which is assumed to be significantly longer than the dephasing time of the corresponding two-exciton scattering state.

Figure 2(e) shows calculations performed within the extended 5LS where the two-exciton scattering state has been introduced in addition to the 4LS calculations. This level is responsible for the intensity difference between the copolarized and the mixed polarized signals, which is greater than in the case of the 4LS. The mixed polarized signals still show an increase in the dephasing time for $\tau_{23}>0$. The oscillator strengths for the transitions from the single-exciton states to the two-exciton scattering state and biexciton are assumed to be equal.

A combination of both BIF within the 5LS and LFE leads to beats for mixed polarizations and $\tau_{23}>0$. Their frequency is given by the biexciton binding energy, and their modulation depth depends on the strength of LFE. In the case of circular (linear) polarization, comparison of the curves in Fig. 3(a) [3(b)] with the experimental data in Fig. 1 demonstrates excellent agreement between experiment and theory with respect to relative signal amplitudes, as well as slope of the rising and trailing edges. Even the appearance of quantum beats at positive delays τ_{23} for the mixed circular and copolarized linear polarization configurations are reproduced correctly. As the theory predicts a vanishing signal for the $\sigma^+\sigma^+\sigma^-$ case, the two orders of magnitude smaller signal observed in the experiment is mostly due to a fifth-order process.

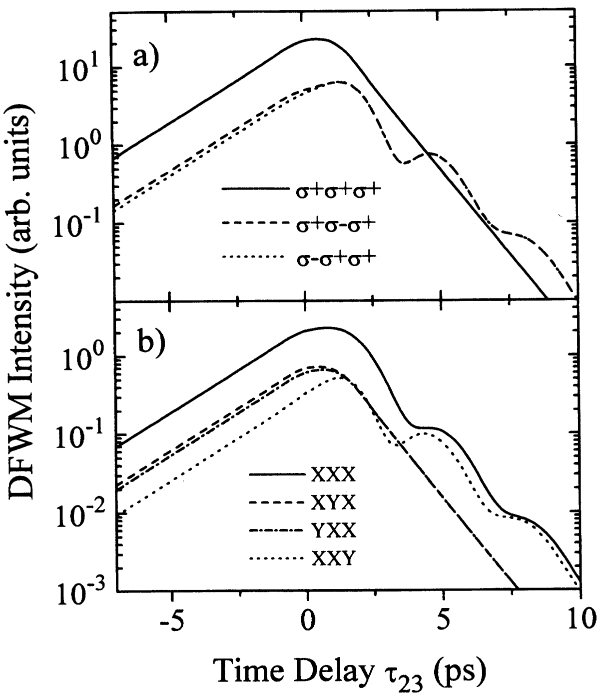

FIG. 3. Calculated curves of the TI-DFWM signal as a function of the delay time τ_{23} for (a) circular and (b) linear polarization including contributions from LFE [see Fig. 2(b)] and BIF within the 5LS [see Fig. 2(e)].

In order to obtain an estimate for the biexciton contribution to the third-order nonlinear response, we have performed a spectral analysis of the DFWM signal. The dashed curve in Fig. 4, recorded for the case of $\sigma^+\sigma^-\sigma^+$ excitation at 12 296 cm^{-1}, reveals a second spectral line on the low-energy side which is separated from the main peak by 10.5 ± 0.5 cm^{-1}. This separation is in good agreement with

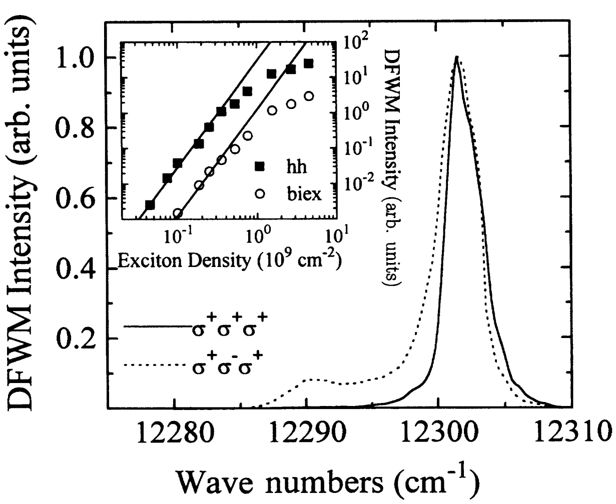

FIG. 4. The spectrally resolved DFWM signal for $\sigma^+\sigma^-\sigma^+$ (dashed line) and $\sigma^+\sigma^+\sigma^+$ (solid line) circular polarization. Inset: Nonlinear growth of the TI-DFWM signal amplitude measured at the hh and biexciton transition frequencies. The line indicates third-order signal response ($I_{\rm DFWM} \propto I_L^3$).

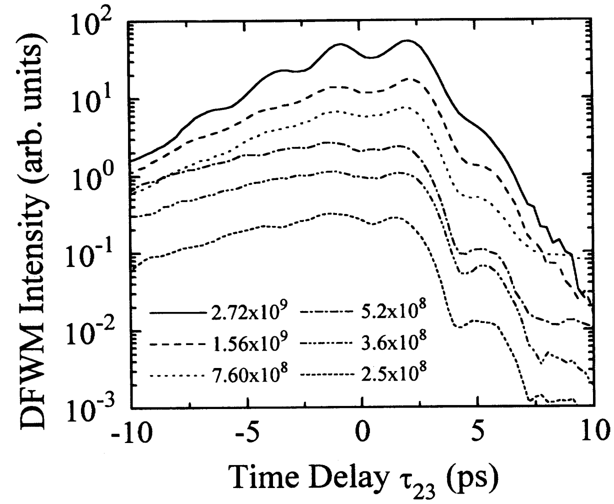

FIG. 5. Experimental TI-DFWM signal using parallel polarization at $\tau_{12} = 1$ ps for various excitation intensities. The values given in the figure are the densities expressed in cm^{-2}.

the beat frequency observed on the DFWM signal suggesting that this second spectral peak is a biexcitonic feature. It also agrees with the splitting found in PL spectra at higher excitation densities. It should be noted that we observe no shift of the biexciton PL peak to lower energies as has been previously reported.[5,6]

The interpretation that this additional peak is a biexcitonic feature is confirmed by its disappearance in the case of $\sigma^+\sigma^+\sigma^+$ polarization. This geometry excites only σ^+ excitons and thus population of the bound two-exciton state is excluded. The inset of Fig. 4 depicts the density dependence of the diffracted signal observed at the spectral position of the heavy-hole (hh) (dark squares) and biexciton transition (open circles) for the $\sigma^+\sigma^-\sigma^+$ configuration and $\tau_{12} = \tau_{23} = 0$ ps. The solid lines represent the increase of the signals with the third power of the intensity. This graph demonstrates that modeling of the diffracted signal by pure third-order effects is correct only at very low excitation levels. For an average power level as low as 200 μW for each of the three incident beams (corresponding to an exciton density of 10^9 cm^{-2} in the focal spot with a 200 μm diameter), fifth- and higher-order mixing processes can no longer be neglected. These fifth-order processes manifest themselves in the time-integrated signal by the occurrence of increasingly pronounced beating for $\tau < 0$ at higher intensities (see Fig. 5). Analysis of the spectrally[13] and time-resolved DFWM measurements[14] shows that the observed modulation results from quantum beating between bound and unbound two-exciton states and is not due to polarization interference.[9] The presence of fifth-order processes at these excitation intensities has been further confirmed by the detection of a small signal diffracted into the direction $3\mathbf{k}_1 - 2\mathbf{k}_2$ in a two-pulse self-diffraction experiment.

In summary, the results presented in this paper provide strong evidence of biexcitonic contributions to the nonlinear optical response of the 2D exciton in GaAs QW's. In particular, (1) the spectrally resolved DFWM signal clearly shows an additional contribution at the biexciton energy whose polarization dependence is in agreement with the selection rules; (2) the presence of biexcitons manifests itself by the appearance of beating with a frequency equivalent to the biexciton binding energy for $\tau_{23}>0$ in selected polarization configurations (the beating is due to the simultaneous coherent excitation of bound and unbound two-exciton states); (3) pronounced variations of the signal amplitude with polarization geometry are observed and can be explained by local field effects and biexciton formation. Furthermore, at excitation levels as low as 10^9 cm^{-2}, fifth-order processes achieve an important influence on the signal shape as confirmed by the intensity dependence of the signal amplitude and the occurrence of strong exciton-biexciton beating on the time-integrated signal for $\tau<0$.

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