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# $\chi^{(5)}$ signature in the four-wave-mixing signal from a GaAs/$Al_{0.3}Ga_{0.7}As$ superlattice

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We analyze coherent beats with a period corresponding to the biexciton binding energy in time-integrated four-wave-mixing experiments in a GaAs/$Al_{0.3}Ga_{0.7}As$ superlattice at high excitation densities. Theoretical and experimental evidence is presented that the beating in the decay is a fifth-order process in the electric field, and therefore $\chi^{(5)}$ contributions to the four-wave-mixing signal in the $2\mathbf{k}_2-\mathbf{k}_1$ direction have to be considered for a qualitative interpretation of the measured data. In order to model the experiment we use a microscopic dynamic density-matrix theory in a real-space representation.

Four-wave-mixing (FWM) techniques have been used extensively to explore the dynamics of coherently excited exciton-biexciton systems in semiconductor heterostructures.[1–8] Biexcitons have been studied in various semiconductor materials,[9–11] in heterostructures,[12,13] and under the influence of magnetic fields.[5,14] A theoretical framework capable of describing the coherent dynamics of a transient exciton-biexciton excitation on a microscopic basis has recently been developed.[15–17] The demand for such a theory has frequently been pointed out.[2,6] In the measurements presented in Ref. 1 three-pulse experiments are applied to investigate coherent exciton-biexciton beats in the rising of a FWM signal in a third-order context. For higher intensities also beats in the decay have been observed and were suggested to be due to $\chi^{(5)}$ processes. Up to now, however, to the best of our knowledge, no thorough theoretical analysis of the corresponding contributions has been presented.

In the present paper we report on experiments that demonstrate that a beating phenomenon is also found in GaAs/$Al_{0.3}Ga_{0.7}As$ superlattices. Analyzing the strong dependencies on the excitation intensity within the theoretical frame of Ref. 17 we find evidence that the exciton-biexciton beating in the decay is indeed due to $\chi^{(5)}$ contributions to the nonlinear response.

Although a $\chi^{(5)}$ signal can be observed selectively in appropriate phase matching directions[18] like $3\mathbf{k}_2-2\mathbf{k}_1$, it must be stressed that these signals give information about different parts of the total $\chi^{(5)}$ response. In this paper we want to clarify that the signal detected in the $2\mathbf{k}_2-\mathbf{k}_1$ direction, which is usually interpreted considering only the leading $\chi^{(3)}$ contributions, is not only quantitatively but also qualitatively affected by $\chi^{(5)}$ effects for high excitation densities.

We use a standard two-pulse degenerated time-integrated FWM setup[19,20] to investigate the intensity and energy dependencies. The signal is detected in the direction of $2\mathbf{k}_2-\mathbf{k}_1$, with the two pulses separated by a delay time $\tau$, counted positive if pulse $\mathbf{k}_1$ arrives on the sample before pulse $\mathbf{k}_2$.

Our sample was a molecular beam epitaxy grown high quality GaAs/$Al_{0.3}Ga_{0.7}As$ superlattice on a $n$-type doped GaAs substrate. The intrinsic superlattice structure comprises 35 periods of 97 Å wells and 17 Å barriers. The sample was carefully characterized by c.w. photoluminescence[21] (PL) at 10 K. At low excitation density a slightly inhomogeneously broadened transition is observed (about 1 meV full width at half maximum) from the electron to heavy-hole (hh) exciton transition. This slightly inhomogeneous broadening is unavoidable in a 35 period superlattice. Nevertheless, clear evidence for the formation of biexcitons in the PL measurements at high excitation densities is observed.

The laser system is an $Ar^+$:ion pumped Kerr-lens modelocked Ti:sapphire system with a repetition rate of 76 MHz. The system is capable of delivering pulses from 1.7 to 2.5 ps with about 1 meV spectral width. This is small enough to spectrally resolve the resonances of interest.

We varied the excitation frequency in the range from 1.5415 eV to 1.5460 eV thus exciting first the hh biexciton and then the hh exciton resonance. The excitation density at the spectral position of the hh is about $4\times10^9$ cm$^{-2}$. The measured time-integrated FWM signal is shown for three different excitation frequencies in Fig. 1. Hereby the transient curves are normalized to the same amplitude at their maxima. The inset shows these amplitudes of the maxima as a function of the excitation frequency, with the unfilled circles symbolizing the three shown transients. Starting with 1.5420 eV the maximum of the signal is located at a delay time of $-1.5$ ps, after an increase of 0.5 meV to 1.5425 eV the whole curve shifts 1 ps to $-0.5$ ps. The third signal has been measured with an excitation frequency of 1.5435 eV and the signal shifts even more resulting in a positive value of 1.5 ps for the location of the maximum. Similar shifts have been observed in other experiments.[19] To interpret these shifts it has been pointed out in Ref. 19 that the resonant excitation of biexcitons leads to a signal at negative time delays in addition to the usual exciton-exciton contribu-

 

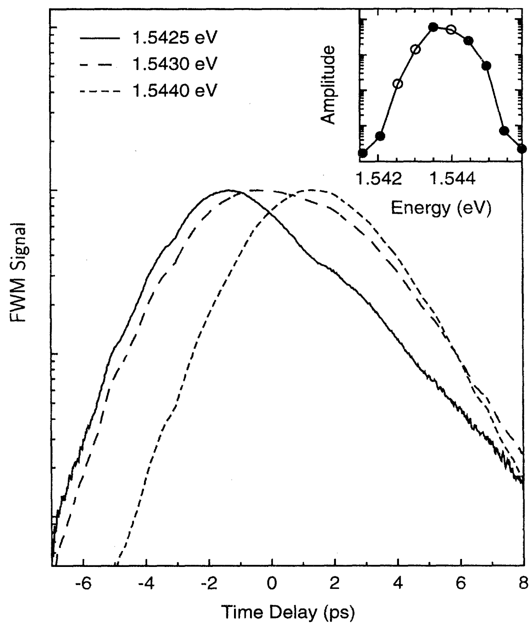


FIG. 1. Semilogarithmic plot of the FWM signal traces at three different excitation energies 1.5425 eV, 1.5430 eV, and 1.5440 eV normalized to the same amplitude. The corresponding amplitudes at the maximum are shown in the inset from 1.5415 eV to 1.546 eV; the positions corresponding to the time-resolved data are symbolized by unfilled circles.

tions.[22] Therefore close to the biexciton resonance a shift of the maximum to negative delay times can be expected.

In Fig. 2 the FWM amplitude is plotted for two different carrier densities per superlattice period: $a$, $4\times10^9$ cm$^{-2}$ (solid line) and $b$, $10^9$ cm$^{-2}$ (dashed line). Curve $b$ does not show any beating at all, while curve $a$ is clearly modulated for positive delays. The beating period corresponds to a binding energy of 1.2 meV for the biexciton in our 7.3 nm well width superlattice, which is about the same as in a 20 nm

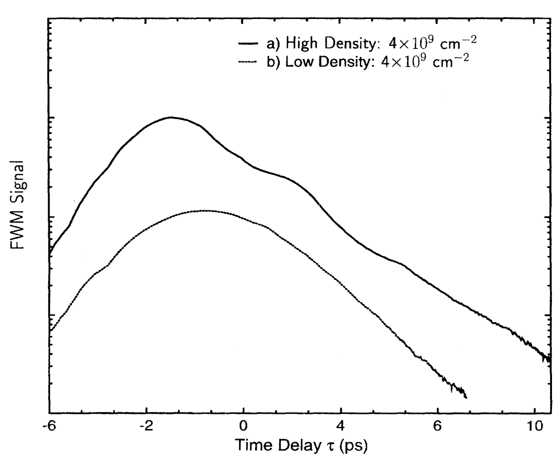


FIG. 2. Semilogarithmic plot of the FWM signal traces for two different excitation densities: $a$, $4\times10^9$ cm$^{-2}$ and $b$, $10^9$ cm$^{-2}$ per superlattice period.

single quantum well structure.[1,21] This beating is only observable at higher intensities and vanishes continuously for lower ones, corresponding to the behavior one expects for contributions of fifth and higher order in the electric field. Additionally the laser energy has to be tuned to 1.5434 eV to observe the beating; a small detuning of about 0.5 meV suffices to destroy the beating. This proves the biexcitonic origin of the beat and rules out a hypothetic explanation due to propagation effects.[23] Also excitons bound to impurities cannot be the cause of the beating, since then the amplitude of the beating should decrease with increasing fields due to saturation effects.[24] For negative delays a slight modulation is also visible, but not as distinct as for single quantum well structures reported in Ref. 1. This is due to the different internal structure of envelope functions in superlattices as well as to the unavoidable inhomogeneous broadening in these structures.[25]

To get a first understanding of the origin of this beating it is useful to consider the five-level model introduced in Ref. 26, consisting of the ground state, two of the lowest exciton states, the lowest biexciton state, and one state representing the exciton-exciton scattering continuum. In analogy to the well known hh-lh beating one might be tempted to think that also a beating between the biexciton and the scattering level should occur for both a positive and a negative delay time $\tau$, for an ideal sample without, e.g., inhomogeneous broadening. The low intensity experiments show a different behavior which can be attributed to the fact that the biexciton cannot be excited by a single photon but requires a two-photon process. Therefore coherent beats are only possible if the biexciton is activated by two photons of the pulse arriving first at the sample. Thus in a $\chi^{(3)}$ experiment detected in $2\mathbf{k}_2-\mathbf{k}_1$ direction the beating occurs only in the rising part where the temporally first pulse ($\mathbf{k}_2$) contributes twice. To observe a beating in the decay the pulse with wave vector $\mathbf{k}_1$ has to activate the biexciton which is possible in the $\chi^{(5)}$ but not in the $\chi^{(3)}$ regime. These fifth-order processes are actually not four- but six-wave-mixing contributions, characterized by $\mathbf{k}_{\rm out}=2\mathbf{k}_2+(\mathbf{k}_1-\mathbf{k}_1)-\mathbf{k}_1$. A theoretical model for the description of such effects has to consider these fifth-order contributions.

In contrast to this qualitative few-level picture our numerical analysis is based on the microscopic model described in Refs. 15–17 and 27. As justified by the experimental setup the resonant hh exciton and hh biexciton bound states were taken into account for the calculations.

In a coherent $\chi^{(5)}$ process besides the typical $\chi^{(3)}$ variables one has to consider also a transition density involving the annihilation of three electron hole pairs[17] $W_{246}^{135}\equiv\langle\hat{d}_1\hat{c}_2\hat{d}_3\hat{c}_4\hat{d}_5\hat{c}_6\rangle$. All indices summarize band and site information, as described in Ref. 17. In analogy to the biexciton transition density $B_{24}^{13}\equiv\langle\hat{d}_1\hat{c}_2\hat{d}_3\hat{c}_4\rangle$ one could call $W$ the triexciton transition density. The existence of bound triexcitonic molecules, however, is not likely. We therefore assume that $W_{246}^{135}$ mainly contains information on the exciton-biexciton scattering. To the best of our knowledge, up to now no attempt has been made in order to account for such contributions in a few-level model.

Our calculation is based on the hierachy of density matrices presented in Refs. 15–17. The main result of this theory is that for a coherent $\chi^{(n)}$ calculation only $[\frac{n+1}{2}]$ density matrices have to be calculated.[17] Here we are interested in a $\chi^{(5)}$ calculation and thus have to account for the three transition densities connecting the ground state with states containing one, two, or three pairs, respectively. In the actual calculation of the $\chi^{(5)}$ response we have used a slightly modified version of the equations of motion presented in Ref. 17. In order to avoid artificial divergences we have introduced a cumulant representation[28,29] and derived differential equations for the irreducible parts of the four- and six-point functions. Thus we transformed our equations using the following definitions:

$$B_{24}^{13}=Y_2^1Y_4^3-Y_4^1Y_2^3+\bar{B}_{24}^{13}$$

and

$$\begin{aligned}W_{246}^{135}=&Y_2^1\bar{B}_{46}^{35}-Y_4^1\bar{B}_{26}^{35}-Y_6^1\bar{B}_{42}^{35}-Y_2^3\bar{B}_{46}^{15}+Y_4^3\bar{B}_{26}^{15}+Y_6^3\bar{B}_{42}^{15}\\&-Y_2^5\bar{B}_{46}^{31}+Y_4^5\bar{B}_{26}^{31}+Y_6^5\bar{B}_{42}^{31}+Y_2^1Y_4^3Y_6^5-Y_4^1Y_2^3Y_6^5\\&-Y_6^1Y_4^3Y_2^5-Y_2^1Y_4^5Y_6^3+Y_4^5Y_2^3Y_6^1+Y_6^3Y_4^1Y_2^5+\bar{W}_{246}^{135}.\end{aligned}$$

Here the quantities marked with an overbar symbolize the irreducible part of these correlations. While we took into account the equation of motion for $\bar{B}_{24}^{13}$ because bound biexcitons play an important role in the nonlinear system response, we neglected the irreducible rest on the six-point level $\bar{W}_{246}^{135}$ which is expected to lead to an enhancement caused by exciton-biexciton interaction.

The resulting set of differential equations has been solved by an eigenfunction expansion keeping only bound states and an additional state with zero biexcitonic binding energy accounting for the biexciton continuum as explained in detail in Ref. 27. The shape of the exciting pulses has been approximated by $\delta$ functions.

We believe that for the problem at hand our method is the most appropriate one. To make this clear let us briefly consider possible alternatives like the semiconductor Bloch equations[30] (SBE) or phenomenological few-level models[26,31] (FLM). The SBE are not able to account for biexcitonic effects, even when corrections to the random-phase approximation (RPA) are taken into account in the usual way as scattering contributions. FLM, on the other hand, provide a phenomenological way to deal with biexcitons. Besides the biexciton also other many-particle effects, as, e.g., band gap renormalization and the effect of the internal field, in these models have to be introduced by hand. Although FLM calculations including contributions higher than third order have been performed,[18,32] we know of no results which account for the biexciton in a fifth order context. Furthermore the effects of the exciton-biexciton interaction contained in the transition density $W$ have been completely neglected so far.

The theoretical results for the FWM signal are shown in Fig. 3 as a function of the delay time $\tau$. In calculations based on $\delta$-shaped pulses the frequency selection is modeled by keeping only the relevant resonances of the system response, while the excitation frequency does not show up explicitly in the calculated signal. Therefore features depending on the excitation frequency as the shifts observed in Fig. 1 cannot be modeled without taking into account finite pulse lengths. A calculation with finite pulses, however, is up to now not feasible because the signal is composed of many contributing terms, involving 54 different five-dimensional integrations in time regime.

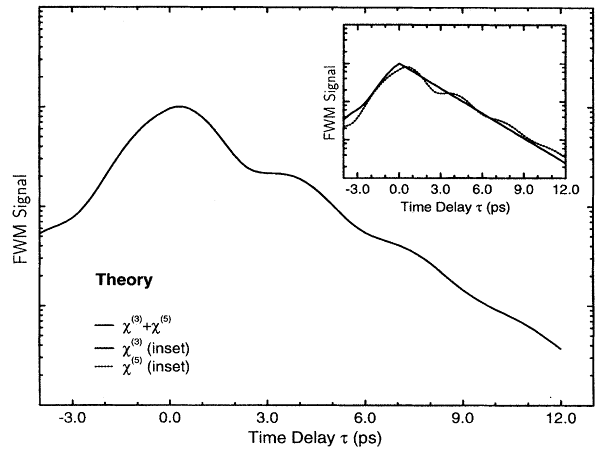


FIG. 3. Semilogarithmic plot of the calculated FWM signal, in $\chi^{(5)}$ regime, with real-space matrix elements used as fit factors to the experimental curve. Further parameters are exciton dephasing $\gamma_Y=0.23$ ps$^{-1}$; dephasing of the irreducible parts of the biexcitonic contributions $\gamma_{\bar{B}}=0.18$ ps$^{-1}$; exciton energy $E_Y=1528$ meV; biexciton binding energy $E_B=1.2$ meV; the exciting field was modeled using $\delta$-shaped pulses. Inset: $\chi^{(3)}$ (solid line) and pure $\chi^{(5)}$ (dashed line) contributions in the $2\mathbf{k}_2-\mathbf{k}_1$ direction.

Obviously the curve marked "$\chi^{(3)}$" shown in the inset, which comprises only $\chi^{(3)}$ contributions, does not exhibit any beating for positive delays. A slight modulation is found at negative delays. This demonstrates that the exciton-biexciton beating in the decay of a time-integrated FWM signal is not a $\chi^{(3)}$ effect which is in accordance with our measurements as well as with calculations based on more simplified models.[1] The kink in the calculated curve at delay zero is due to the short pulse limit.

The curve marked "$\chi^{(3)}+\chi^{(5)}$" results from third- and fifth-order contributions and their respective interferences. The decay of the corresponding calculated curve is still dominated by the $\chi^{(3)}$ contributions, but it is modulated by the $\chi^{(5)}$ contributions to give quantum beats reflecting the biexciton binding energy in good qualitative agreement with the experimental data.

Also in Refs. 18 and 22 a pulse reshaping for excitation in the transparent region with high densities has been reported. In contrast to our experimental findings this reshaping manifests itself in a dip at delay zero for extremely high intensities, and has been interpreted as an interference between $\chi^{(3)}$ and higher-order contributions of excitonic origin. The biexciton has not been considered. In the inset of Fig. 3 the pure $\chi^{(5)}$ contributions to the signal in $2\mathbf{k}_2-\mathbf{k}_1$ are shown. They are modulated by quantum beats even stronger than the signal including the $\chi^{(3)}$ contributions. Therefore the beat structure in our case is inherent to the $\chi^{(5)}$ contribution and cannot be explained only by interference of excitonic contributions of different orders. To our opinion a quantitative description of the experimental data would require besides the use of realistic pulse shapes a detailed evaluation of the biexciton continuum.

To conclude we found theoretical and experimental evidence for the existence of bound biexcitons in superlattices by identifying beats in the FWM signal as coherent exciton-biexciton beats with a period corresponding to the biexciton binding energy. We modeled the FWM signal using a microscopic density-matrix theory in real space representation taking fifth-order contributions into account. A third-order calculation is not able to reproduce the observed coherent beats for positive time delays $\tau$. We showed that the beating in the decay is a fifth-order process in the electric field of the laser pulses, as proposed in Ref. 1. This beating is demonstrated to be an inherent feature of the $\chi^{(5)}$ contribution and is not due to interference between third and fifth order. Our results reveal that for the excitation densities considered in this paper RPA-based models like the semiconductor Bloch equations are not even qualitatively able to explain the observed features.

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