RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 8 15 AUGUST 1993-II

Nature of nonlinear four-wave-mixing beats in semiconductors

V. G. Lyssenko,* J. Erland, I. Balslev, K.-H. Pantke, B. S. Razbirin,† and J. M. Hvam‡
Fysisk Institut, Odense Universitet, Campusvej 55, DK-5230 Odense M, Denmark
(Received 26 April 1993; revised manuscript received 21 June 1993)

The nature of the beat modulations observed in nonlinear four-wave mixing in semiconductors is determined by spectral resolution of the time-integrated four-wave-mixing signals. Beats between close-lying bound-exciton resonances in CdSe are found to be described by macroscopic polarization interferences between two noninteracting two-level systems. Beats between heavy-hole excitons and light-hole excitons in GaAs quantum wells, on the other hand, are described by a three-level system, i.e., as a true quantum interference phenomenon.

Linear as well as nonlinear quantum beat spectroscopy has recently become an issue in the ultrafast laser spectroscopy of semiconducting materials and structures. The variety of more or less distinct excitonic resonances in semiconductors and the advent of ultrafast lasers with pulse lengths shorter than the typical dephasing times of excitons in semiconductors, have made it possible to observe quantum beats between close-lying excitonic transitions.[1–4] In particular, the beat phenomena have been observed in four-wave mixing (FWM) and/or photon-echo experiments on various exciton complexes in $GaAs/Al_xGa_{1-x}As$ multiple quantum wells,[5–11] as well as in bulk semiconductors.[4,12]

In these experiments, the laser beam with ultrafast pulses is split into two beams incident on the sample in the directions $\mathbf{k}_1$ and $\mathbf{k}_2$, and the nonlinear FWM signal is emitted in the direction $2\mathbf{k}_2-\mathbf{k}_1$, and usually detected time integrated as a function of the delay τ.[13] These correlation traces will, for delays much larger than the pulse length, and for systems that can reasonably well be described by a two-level system, show an exponential decay $I_{\mathrm{FWM}}(\tau)\propto I(0)e^{-c\gamma\tau}$, from which the dephasing time $T_2=1/\gamma$ can be determined if the coefficient c is known. For a purely homogeneously (inhomogeneously) broadened two-level system, $c=2$ ($c=4$).[13]

In nearly degenerate multilevel systems, which are simultaneously and coherently excited by the same ultrashort laser pulses, the correlation trace may additionally show modulations due to quantum interferences, e.g., in the simplest form[14]

$$I_{\mathrm{FWM}}(\tau)=I_{\mathrm{ave}}(\tau)[1+I_m(\tau)\sin(\Delta\omega\tau-\phi)]\ , \qquad (1)$$

where $\Delta\omega=\Delta E/\hbar$ is determined by the splitting $\Delta E=E_2-E_1$ of the nearly degenerate transition energies E_1 and E_2. The decays of the average signal $I_{\mathrm{ave}}(\tau)$ and of the modulation amplitude $I_m(\tau)$ are again determined by the dephasing times of the transitions involved. The phase of the modulation is specified by ϕ. Such modulations have been observed in GaAs quantum wells due to interference between heavy-hole excitons (hhx) and light-hole excitons (lhx),[5–7] between free and bound excitons,[8] between excitons and biexcitons,[9,10] and between Landau split magnetoexcitons.[11] They have also been observed due to interferences between different free and bound-exciton levels and complexes in bulk CdSe crystals.[4,12]

The question has been raised as to whether the observed modulations are due to true quantum beats between two or more transitions with one state in common, or they are due to polarization interferences between two or more independent, but coherently excited, two-level systems.[14,15] Göbel and co-workers[16,17] have recently suggested and performed an experiment to distinguish between the two cases in a specially prepared sample with GaAs multiple quantum wells. They time-resolve the FWM signal by cross correlation (up-conversion) with a third, delayed laser beam and observe the modulation in real time as a function of the delay between the two interfering incident beams. There is a simple alternative way, however, to retrieve the same information, i.e., to distinguish experimentally between true quantum beats and interferences between macroscopic polarizations, namely, by spectrally resolving the time-integrated FWM signal.[18] As we shall see, the information is embedded in the amplitude and the phase of the modulation in Eq. (1), which are functions of the detection frequency ω_d (photon energy $\hbar\omega_d$) of the nonlinear signal.

In the present paper, we present spectrally resolved FWM beats for two distinctly different cases: (1) polarization interferences between excitons bound to neutral donors (I_2) and acceptors (I_1) in CdSe, which are described as noninteracting two-level systems, and (2) quantum beats between hhx and lhx in GaAs quantum wells, which are described by a three-level system with a common ground state. In the two cases, we calculate the FWM signal from (1) two independent two-level systems, and (2) from a three-level system with a common ground state. In the calculations, we focus on the amplitude and phase of the modulations in the different cases.

We performed experiments in the impurity–bound-exciton region in CdSe as previously described in detail.[4,12] The laser pulses, with a coherence time less than 500 fs, excite coherently the I_1 and I_2 levels. Spectrally resolving the nonlinear signal with photon energies $\hbar\omega_d$ around the I_2 resonance, modulations with a period of 900 fs are observed [see Fig. 1(a)] corresponding to the I_2-I_1 splitting of 4.8 meV. The nonlinear signal was observed on a time scale beyond 10 ps, revealing the dephasing time of the I_2 impurity–bound-excitons in CdSe.

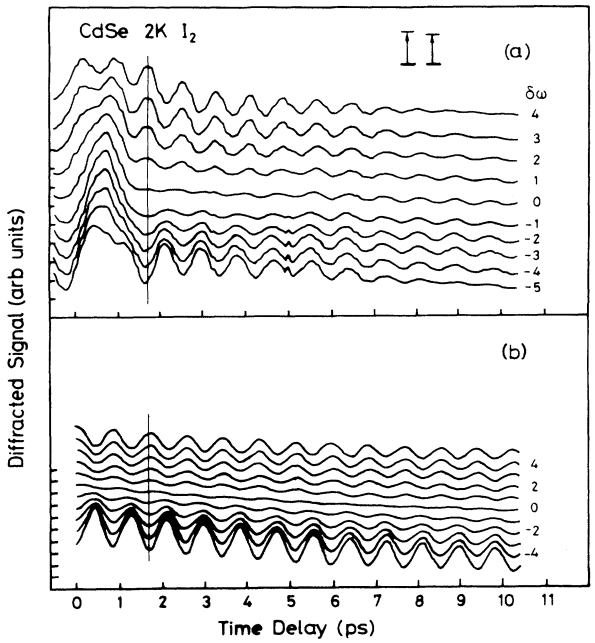

FIG. 1. Diffracted FWM signal for different detunings $\delta\omega=(\omega_d-\omega_2)/0.08$ meV around the I_2 bound-exciton resonance in CdSe. The exciting laser is centered near the I_1 bound-exciton resonance, but coherently exciting both resonances. All the curves are normalized to their maximum value, and they are shifted along the ordinate axis as indicated by the zero-level marks. The upper curves (a) are experimental with an excitation level of 0.8 kW/cm^2. The lower curves (b) are calculated from Eq. (2) with $\hbar(\omega_2-\omega_1)=4.8$ meV, $\gamma_1=0$, $\hbar\gamma_2=0.03$ meV, and $R_1/R_2=1.6$.

The dephasing time of the I_1 exciton in CdSe has previously been found to be much larger.[19] The experimental signals are normalized to their maximum values, giving the possibility to compare, directly, the modulation amplitudes I_m and the phases ϕ for different detunings $\delta\omega=\omega_d-\omega_2$, as shown in Fig. 1(a). Moving through the I_2 resonance, both the modulation amplitude I_m and the phase ϕ are strongly dependent on the detuning $\delta\omega$. In resonance ($\delta\omega=0$), the modulation amplitude is minimum, but finite, and the phase undergoes a shift of about π (see vertical line in Fig. 1).

For low concentrations of donor and acceptor impurities, there is negligible spatial overlap between I_1 and I_2 bound excitons, and the nonlinear signal is expected to arise from two noninteracting two-level systems. We have calculated the third-order polarization for such a system from simple Bloch-type equations, using the density-matrix formalism and Green's-function techniques as employed by Yajima and Taira.[13] Let ω_1 and ω_2 be the frequencies of the two allowed transitions. Assuming Fourier-limited pulses having a spectral width, which is much smaller than ω_1,ω_2 and much larger than $|\omega_1-\omega_2|$, the third-order nonlinear polarization is expressed by[20]

$$P^{(3)}(\omega_d,\tau)=\frac{R_1 e^{i\omega_1\tau}}{\omega_1-\omega_d-i\gamma_1}+\frac{R_2 e^{i\omega_2\tau}}{\omega_2-\omega_d-i\gamma_2}+\text{c.c.}\ , \qquad (2)$$

where $R_i=2N_iM_i^4\exp\{-\gamma_i\tau\}$ is a slowly varying function containing the dipole matrix element M_i, and the dephasing rate γ_i of the excitons of type i. N_i is in itself a complicated function of the time-integrated pulse amplitude, its spectral overlap with the resonance number i, and the concentration of two-level centers of this type. The polarization in Eq. (2) is propagating in the direction $2\mathbf{k}_2-\mathbf{k}_1$ and it is assumed that pulse 1 arrives before pulse 2 ($\tau>0$).[13] We have also neglected contributions from pulse overlap, i.e., we consider only delays τ larger than the pulse width.

The nonlinear signal is proportional to the square of the polarization in Eq. (2) yielding an expression as in Eq. (1), where the beat originates from the product involving both resonance denominators. This explains the observed variation in modulation amplitude and phase when ω_d passes through one of the transition frequencies, as shown in Fig. 1(b) for a representative set of parameters. The qualitative agreement between the experiments and the calculations verifies that the beating bound excitons can be considered as noninteracting.

To observe a substantial modulation of the nonlinear signal, the two terms in Eq. (2) have to be of the same order of magnitude. For comparable matrix elements of the two transitions, $M_1\approx M_2$, this can be obtained by exciting near one resonance, $N_1\gg N_2$, and detecting near

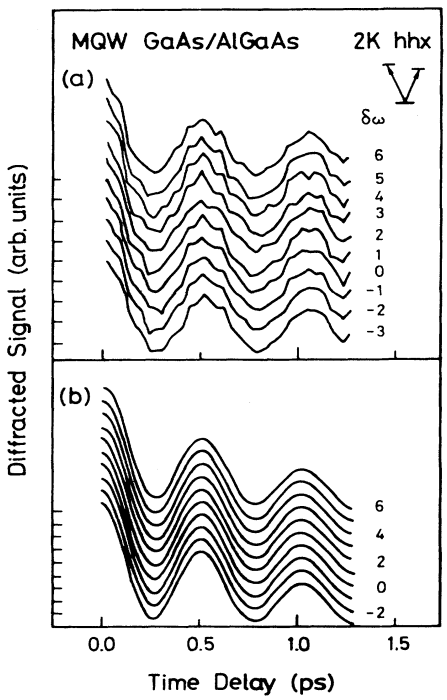

FIG. 2. Diffracted FWM signal for different detunings $\delta\omega=(\omega_d-\omega_1)/0.08$ meV around the hhx resonance (ω_1) in a GaAs MQW. All the curves are normalized to their maximum value, and they are shifted along the ordinate axis as indicated by the zero-level marks. The upper curves (a) are experimental with an excitation level of 0.2 kW/cm^2, and the laser is centered between the hhx and lhx resonances. The lower curves (b) are calculated from Eq. (3) with $\hbar(\omega_2-\omega_1)=7.7$ meV, $\hbar\gamma_1=\hbar\gamma_2=0.3$ meV, and $R_1/Q_{12}=2$.

the other resonance $\omega_d \approx \omega_2$, as in Fig. 1.

A similar experiment was performed in a 20-period 116-Å-wide GaAs multiple quantum well (MQW).[7] Exciting coherently the hhx and lhx excitons with laser pulses having a coherence time less than 190 fs and detecting the nonlinear signal around the hhx resonance (ω_1), we observe modulations with a period of 530 fs, in agreement with the hhx-lhx splitting of 7.7 meV. As seen in the normalized plot in Fig. 2(a), the modulation amplitude I_m and phase ϕ are now behaving differently as compared to the previous case, being independent of the detected frequency ω_d. The nonlinear signal is detected on a shorter time scale due to a shorter dephasing time of the lhx in the MQW structure (2–4 ps).

Assuming that the observed modulations are due to quantum beats in the three-level system formed by the hhx and lhx resonances with a common ground state, we have calculated the third-order polarization from such a three-level system in the same approximation as above for the two-level systems. The result can be expressed as[20]

$$P^{(3)}(\omega_d,\tau)=\frac{R_1 e^{i\omega_1\tau}+Q_{12}e^{i\omega_2\tau}}{\omega_1-\omega_d-i\gamma_1}+\frac{R_2 e^{i\omega_2\tau}+Q_{21}e^{i\omega_1\tau}}{\omega_2-\omega_d-i\gamma_2}+\text{c.c.}\ , \tag{3}$$

where $Q_{ij}=N_i M_i^2 M_j^2 \exp\{-\gamma_j\tau\}$ and the other symbols are as in Eq. (2).

Again, the nonlinear intensity is proportional to the square of the polarization in Eq. (3), where for $\omega_d \approx \omega_1$ the resonant term will dominate. For comparable matrix elements of the two transitions, $M_1 \approx M_2$, a strong modulation of the signal as in Eq. (1) will appear, now as a real quantum beat. In this case, the amplitude and phase of the modulation are nearly constant when going through the resonance as shown in Fig. 2(b), again with a representative set of parameters. The agreement between the spectral dependence of the experimentally observed and calculated quantum beats is rather convincing, revealing the simple nature of the observed modulations. It should be mentioned that in the calculations only homogeneous broadening of the system is considered.

In conclusion, we have described the origin of the observed oscillations in a time-integrated four-wave-mixing experiment in different systems, which have two resonances coherently excited. In the impurity–bound-exciton system in CdSe, we observe a phase shift of the beat signal, when we move through one of the resonances. This phase shift is a distinct signature of polarization interference between two independent two-level systems. In GaAs quantum wells, where the hhx and lhx share a common ground state, no phase shift is observed when we move through one of the resonances. Theoretically, this is predicted for quantum beats in a three-level system. In view of the general nature of the calculations, spectral resolution of the time-integrated FWM signal thus seems to provide distinct and unambiguous information about the nature of the observed beats in systems where level schemes and system interactions are not known in advance. We are presently investigating more complicated multilevel systems, such as cascaded three-level systems and four-level systems,[20] that should describe the FWM beats observed from coherent mixtures of excitons and biexcitons in GaAs/Al_xGa_{1-x}As MQW systems.[9,10]

The authors want to thank D. Oberhauser for providing the GaAs/Ga_xAl_{1-x}As sample, grown by G. Weimann. The work was supported by the Danish Natural Science Research Council.

*Permanent address: Institute of Microelectronics Technology and Superpure Materials, Chernogolovka, Moscow District 142432, Russia.

†Permanent address: A. F. Ioffe Physical-Technical Institute, 194021 St. Petersburg, Politekhnicheskaya 26, Russia.

‡Present address: Mikroelektronik Centret, Technical University of Denmark, DK-2800 Lyngby, Denmark.

[1]V. Langer, H. Stolz, and W. von der Osten, Phys. Rev. Lett. **64**, 854 (1990).

[2]W. A. J. A. van der Poel, A. L. G. J. Severens, and C. T. Foxon, Opt. Commun. **76**, 116 (1990).

[3]H. Stolz, in *Festkörperprobleme/Advances in Solid State Physics*, edited by U. Rössler (Vieweg, Braunsweig, 1991), Vol. 31, p. 219.

[4]K.-H. Pantke, V. G. Lyssenko, B. S. Razbirin, J. Erland, and J. M. Hvam, in *Proceedings of the 21st International Conference on the Physics of Semiconductors, Beijing, 1992,* edited by P. Jiang and H.-Z. Zheng (World Scientific, Singapore, 1992), p. 129.

[5]K. Leo, T. C. Damen, J. Shah, E. O. Göbel, and K. Köhler, Appl. Phys. Lett. **57**, 19 (1990).

[6]B. F. Feuerbacher, J. Kuhl, R. Eccleston, and K. Ploog, Solid State Commun. **74**, 1279 (1990).

[7]D. Oberhauser, K.-H. Pantke, J. M. Hvam, K.-H. Schlaad, G. Weimann, and C. Klingshirn, *Proceedings of the International Conference Laser '91, San Diego, 1991* (STS, McLean, VA, 1992), p. 368.

[8]K. Leo, T. C. Damen, J. Shah, and K. Köhler, Phys. Rev. B **42**, 11 359 (1990).

[9]D. J. Lovering, R. T. Phillips, G. J. Denton, and G. W. Smith, Phys. Rev. Lett. **68**, 1880 (1992).

[10]K.-H. Pantke, D. Oberhauser, V. G. Lyssenko, and J. M. Hvam, Phys. Rev. B **47**, 2413 (1993).

[11]S. Bar-Ad and I. Bar-Joseph, Phys. Rev. Lett. **66**, 2491 (1991).

[12]K.-H. Pantke, P. Schillak, J. Erland, V. G. Lyssenko, B. S. Razbirin, and J. M. Hvam, Phys. Status Solidi B **173**, 91 (1992).

[13]T. Yajima and Y. Taira, J. Phys. Soc. Jpn. **47**, 1620 (1979).

[14]L. Q. Lampert, A. Compaan, and I. D. Abella, Phys. Rev. A **4**, 2022 (1971).

[15]H. Stolz, V. Langer, E. Schreiber, S. Permogorov, and W. von der Osten, Phys. Rev. Lett. **67**, 679 (1991).

[16]E. O. Göbel, M. Koch, J. Feldmann, G. von Plessen, T. Meier, A. Schultze, P. Thomas, S. Schmitt-Rink, K. Köhler, and K.

Ploog, Phys. Status Solidi B **173**, 21 (1992).
[17]M. Koch, J. Feldmann, G. von Plessen, E. O. Göbel, and P. Thomas, Phys. Rev. Lett. **69**, 3631 (1993).
[18]T. Tokizaki, A. Nakamura, Y. Ishida, T. Yajima, I. Akai, and T. Karasawa, in *Ultrafast Phenomena VII,* edited by C. B. Harris, E. P. Ippen, G. A. Mourou, and A. H. Zewail, Springer Series in Chemical Physics Vol. 53 (Springer-Verlag, Berlin, 1990), p. 253.
[19]H. Schwab, V. G. Lyssenko, and J. M. Hvam, Phys. Rev. B **44**, 3999 (1991).
[20]J. Erland and I. Balslev, Phys. Rev. A (to be published).