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Manifestation of exciton-amplitude fluctuations in the transient polarization state of four-wave-mixing signals

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The polarization state of the diffracted beam in degenerate four-wave mixing is experimentally and theoretically investigated, resolved in the time as well as in the frequency domain. The use of thin ZnSe quantum wells having large (bi)exciton binding energies makes it possible to restrict the optical excitation by broadband 110 fs pulses to quasi-two-dimensional heavy-hole excitons and biexcitons only. Despite these most simple experimental conditions, an extremely complex dynamics of the polarization state is observed when one circularly and one linearly polarized beam are used for excitation. The detailed behavior sensitively depends on the excitation density, showing the importance of nonlinearities of higher than third order even at exciton densities less than 0.01 times the Mott density. A comparison of the experimental data with theoretical results obtained by a microscopic density-matrix approach yields very close agreement. It turns out that a dynamical object describing fluctuations of the exciton amplitude has to be included in the theory in addition to biexcitonic contributions and correlated parts of the exciton-exciton scattering continuum. [S0163-1829(99)50112-4]

Recently, four-wave-mixing (FWM) experiments on semiconductors using ultrashort laser pulses have been extended by analyzing the transient polarization state of the diffracted beam.[1–4] Experiments have been performed in the time domain by ellipsometry and up-conversion techniques[1,2] as well as in the spectral domain by means of a method that has been called ''polarization labeled interference versus wavelength of only a glint.''[3,4] These investigations focus on the transient polarization in dependence on the angle between the linear polarizations of the exciting beams. It was found that the apparently unpolarized fraction of the signal observed in time-integrated data[5] was caused by temporarily averaging over a signal pulse having a perfect polarization state which, however, changes in time.[1] These data were recorded from GaAs multiple quantum wells (QW's) at quite strong excitation creating initial densities of heavy-hole (hh) excitons near one tenth of the Mott density. In this high-density regime, a qualitative understanding of the polarization transients has been obtained by solving the optical Bloch equations for the third-order polarization, extended by some phenomenological additives, such as a density-dependent dephasing, a bound biexciton level, and local-field corrections.[1]

The analysis of the dynamical polarization state of FWM signals provides new and interesting information on the dynamics of nonlinear processes in semiconductors. Data of this kind make it possible to test the predictions of modern many-particle theories that recently started to include two-exciton correlations[6–9] as well as exciton amplitude fluctuations[10,11] on a microscopic level (for a recent review, see Ref. 12). This is of particular interest for data taken at densities beyond the $\chi^{(3)}$ regime that is hard to attain in FWM experiments because of the weak intensity of the diffracted beam.[13,14] Detailed information about the origin of the complex dynamically changing polarization beyond phenomenological models has been missing up to now.

In the following, after a brief description of our experimental setup, we present both time and spectrally resolved experimental data yielding complementary information. The experimental results are discussed in terms of a microscopic density-matrix theory.

Experimental data were obtained from a 4.8 nm thin ZnSe single QW embedded in quaternary $Zn_{1-x}Mg_xS_ySe_{1-y}$ barriers grown lattice matched on a GaAs substrate by molecular-beam epitaxy. In order to perform experiments in transmission geometry the substrate was removed by wet-chemical etching. The sample exhibits an inhomogenous linewidth of 0.7 meV, large exciton and biexciton binding energies (about 21 and 6.2 meV, respectively), and a large hh-light-hole splitting (15 meV). Here the use of 110 fs pulses from a frequency-doubled Ti:sapphire laser with a spectral width of 15 meV allows for well defined conditions: Only hh excitons and the biexcitons composed of them are excited when the laser is tuned below the hh resonance.

The polarizations of the incident pulses with wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ are set independently by use of longitudinal KD*P Pockels cells. Linear polarizations are designated $x(y)$ for the electrical field vector being perpendicular (parallel) to the

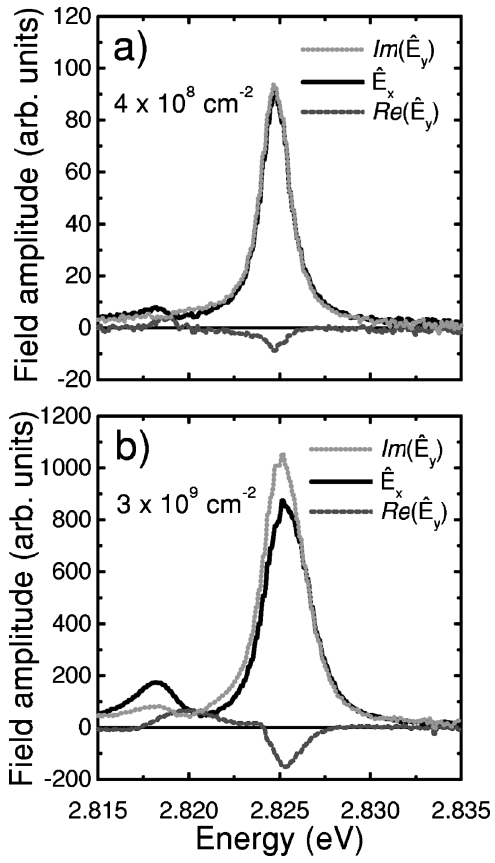

FIG. 1. Experimental FWM spectra of the different polarization components for two different exciton densities after excitation with two beams having (x,σ^+) polarization, respectively. The pulse delay amounts to $\tau=0$.

scattering plane, respectively. The polarization of the diffracted beam in direction $(2\boldsymbol{k}_2-\boldsymbol{k}_1)$ is projected on different polarization states (x, y, σ^+, σ^-, and linear polarization at $\pm 45°$ with respect to x) by means of a sequence of two Pockels cells and a polarizer. All extinction ratios exceed 2000:1. For time-resolved measurements, frequency summation of the FWM signal and pulses of the residual red beam of the Ti:sapphire laser is performed. The resulting ultraviolet light is detected by a photomultiplier tube. For spectrally resolved measurements the light is directed from the polarizer directly into a monochromator and detected by a nitrogen-cooled charge coupled device camera. Samples are kept at 2 K in superfluid helium.

The measurements fully determine the FWM polarization except for an overall phase factor. The polarization state $\hat{\mathbf{E}}$ displayed in the figures is connected to the complex FWM polarization $\mathbf{E}$ by

$$\hat{\mathbf{E}}=\exp(-i\phi)\mathbf{E}, \tag{1}$$

$$\phi=\arctan\left[\frac{\mathrm{Im}(\mathbf{E_x})}{\mathrm{Re}(\mathbf{E_x})}\right], \tag{2}$$

where ϕ is defined such that the x component of $\hat{\mathbf{E}}$ is real and positive. While the component $\mathrm{Re}(\hat{\mathbf{E}}_\mathbf{y})$ determines the sign and magnitude of the tilt angle of the long axis of the polarization ellipse, the sign of the imaginary part $\mathrm{Im}(\hat{\mathbf{E}}_\mathbf{y})$ determines the sense of rotation of the field amplitude.

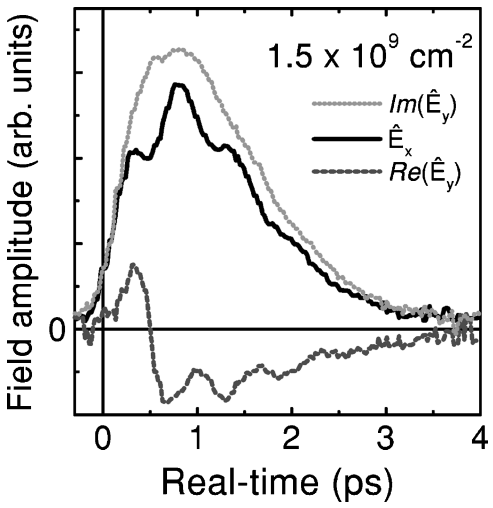

FIG. 2. Measured transients of the polarization components for an exciton density of 1.5×10^9 cm^{-2} at $\tau=0$.

In Fig. 1 the spectrally resolved polarization analysis of the FWM signal is displayed. The polarization of the incident beams $(\boldsymbol{k}_1,\boldsymbol{k}_2)$ is (x,σ^+), respectively. The main contribution to the FWM signal is observed at the spectral position of the hh exciton at 2.825 meV. In third order no signal is expected for this configuration on the exciton-biexciton resonance (EBR) located one biexciton binding energy E_B^{XX} below the hh exciton, since the two σ^+ photons of wave vector $\boldsymbol{k}_2$ needed for the generation of the FWM signal cannot excite a ground-state biexciton with zero angular momentum. For a basic FWM characterization of this specific sample and selection rules, see Ref. 14. In the more sensitive spectrally resolved measurements we observe an almost cubic intensity dependence,[14] showing that the $\chi^{(3)}$ regime is nearly attained. Correspondingly, virtually no signal is observed on the EBR (2.818 eV) at low density [Fig. 1(a)]. Moreover, it follows from the vanishing unpolarized contributions (not shown), the almost vanishing real part in y direction, and the equal magnitudes of $\hat{\mathbf{E}}_x$ and $\mathrm{Im}(\hat{\mathbf{E}}_y)$ that the signal is nearly perfectly σ^+ polarized as is the $\boldsymbol{k}_2$ beam. This directly implies that the polarization does not change in real time as well. In contrast to that, for increased excitation density bound-biexciton contributions appear at the EBR [Fig. 1(b)]. The signal now exhibits an energy-dependent ellipticity.

We now turn to time-resolved data measured at higher excitation density. In Fig. 2 transients of the three polarization components are displayed. In correspondence to the spectra of Fig. 1(b) a considerable strength of $\mathrm{Re}(\hat{\mathbf{E}}_y)$ is observed. All transients exhibit modulations [rather weak for $\mathrm{Im}(\hat{\mathbf{E}}_\mathbf{y})$] the period of which roughly fits the biexciton binding energy of 6.2 meV determined from spectrally resolved data. These beat phenomena in the real-time domain show up simultaneously with the spectral contribution at the EBR in Fig. 1(b), which itself exhibits beating behavior also in the delay-time domain.[15]

Our theoretical analysis is based on a microscopic density-matrix model taking into account higher-order

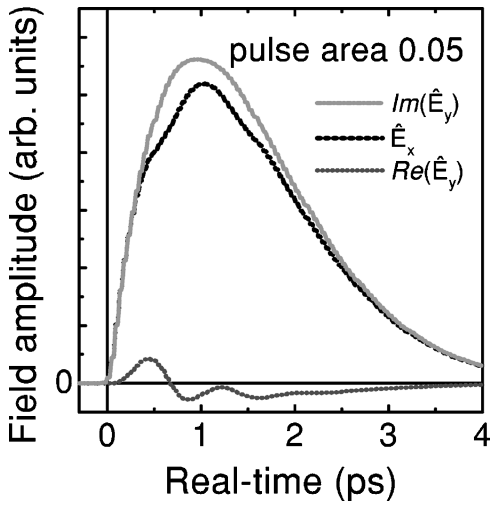

FIG. 3. Calculated transients of the components of the polarization state for a pulse area of 0.05 at $\tau=0$. An inhomogeneous broadening of the band gap of 0.7 meV has been phenomenologically included by convoluting the homogeneous result with a Gaussian.

correlations.[16] Within this model the FWM signal can be calculated from the exciton transition amplitude $Y_j^i = \langle \hat{d}^i \hat{c}_j \rangle$, the expectation value of the operator which annihilates an electron (hole) at site $j(i)$. The equation of motion for the two-point correlation Y_j^i is coupled by the Coulomb interaction to four-point correlations that are in turn coupled to six-point correlation functions and so on. In order to obtain a closed set of equations of motion we have applied the so-called dynamics-controlled truncation scheme.[17] This scheme relies on a classification of higher-order density matrices according to their leading order in the laser field. Here, we have set the truncation such that the $\chi^{(3)}$ response is fully accounted for in the coherent limit. This way $\chi^{(5)}$ contributions involving correlations between three or more electron hole pairs such as triexcitons or exciton strings have been neglected. In addition to the contributions present in the coherent limit we have accounted for fluctuations of the exciton transition amplitude described by the four-point function $\overline{N}_{jj'}^{ii'} \equiv \langle (\hat{d}^i \hat{c}_j - \langle \hat{d}^i \hat{c}_j \rangle)^\dagger (\hat{d}^{i'} \hat{c}_{j'} - \langle \hat{d}^{i'} \hat{c}_{j'} \rangle) \rangle$. $\overline{N}_{jj'}^{ii'}$ can also be interpreted as an exciton density comprising incoherent as well as intraband coherent parts. The physical meaning of this dualism is exactly the same as in the more commonly known case of the optical field, where fluctuations of the field amplitude are by definition identified as the incoherent part of the intensity. The dynamics is described by a coupled set of nonlinear equations for the single-pair transition amplitude Y_j^i, the correlated part of the biexciton transition amplitude $B_{jj'}^{ii'} \equiv \langle \hat{d}^i \hat{c}_j \hat{d}^{i'} \hat{c}_{j'} \rangle - \langle \hat{d}^i \hat{c}_j \rangle \langle \hat{d}^{i'} \hat{c}_{j'} \rangle + \langle \hat{d}^i \hat{c}_{j'} \rangle \langle \hat{d}^{i'} \hat{c}_j \rangle$, and the amplitude fluctuation $\overline{N}_{jj'}^{ii'}$.[11] For the calculation of the FWM signals, these equations have been projected onto the lowest hh-exciton states. The biexcitonic correlations are incorporated using the memory-kernel representation presented in Refs. 8 and 9. Here, however, the kernel is determined for a two-dimensional model. The set of equations is solved self-consistently in order to include the remaining contributions beyond the $\chi^{(3)}$ level.

For low densities the calculations yield no contribution of

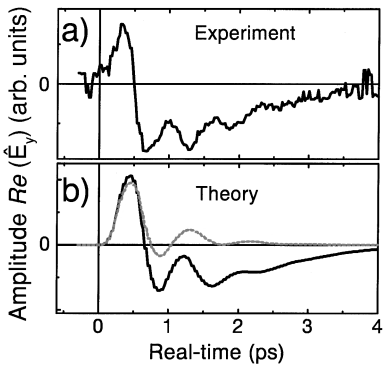

FIG. 4. Time dependence of the polarization component $\mathrm{Re}(\hat{\mathbf{E}}_\mathbf{y})$. Calculations have been performed with (solid line) and without (dashed line) incorporation of exciton amplitude fluctuations.

$\mathrm{Re}(\hat{\mathbf{E}}_\mathbf{y})$ and equal field strengths of $\hat{\mathbf{E}}_\mathbf{x}$ and $\mathrm{Im}(\hat{\mathbf{E}}_\mathbf{y})$. This corresponds to a time-independent circular (σ^+) polarization of the signal beam and, thus, fits to the spectrally resolved experimental result depicted in Fig. 1(a). For moderately increased densities (pulse area of 0.05), a considerable contribution of $\mathrm{Re}(\hat{\mathbf{E}}_\mathbf{y})$ appears (see Fig. 3). All essential features of the calculated transients match the experimental results shown in Fig. 2. The transient of $\mathrm{Im}(\hat{\mathbf{E}}_\mathbf{y})$ dominates but remains nearly unstructured. Beating appears on the two other transients. However, the modulation period does not exactly match the experimental result, since the calculation underestimates the biexciton binding energy (4.5 meV as compared to 6.2 meV).

In order to analyze the results in more detail, we now focus on the polarization component $\mathrm{Re}(\hat{\mathbf{E}}_\mathbf{y})$. Since this quantity vanishes in $\chi^{(3)}$ it is most sensitive to higher-order nonlinear contributions. Figures 4 and 5 show, in direct comparison of experiment and calculation, real-time transients and spectra, respectively, for increased excitation densities (parameters are those used in Figs. 2 and 3). In addition to the full theory (solid lines), results of a calculation neglecting the exciton amplitude fluctuations $\overline{N}_{jj'}^{ii'}$ are depicted (dotted lines). The full theory correctly reproduces all the quali-

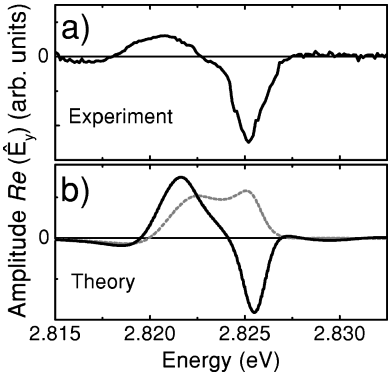

FIG. 5. Spectral dependence of the polarization component $\mathrm{Re}(\hat{\mathbf{E}}_\mathbf{y})$. Calculations have been performed with (solid line) and without (dashed line) incorporation of exciton amplitude fluctuations.

tative features of the time-resolved measurements (Fig. 4): After an initially positive value, $\mathrm{Re}(\hat{\mathbf{E}}_y)$ exhibits a single sign change at about 0.5 ps, and an oscillation is superimposed to the subsequent decay to zero. The theoretical result also shows excellent agreement with the spectrally resolved data (Fig. 5): The full theory even accounts for tiny details, as, e.g., the observed negative sign at energies far on the low-energy side of the hh exciton. In contrast to that, strong discrepancies appear between the experimental data and theoretical results when the coherent limit is assumed (dotted lines in Figs. 4 and 5). It is worth stressing that the permanent negative sign for late times in Fig. 4 is not due to a simple density-induced decrease of the dephasing time. Instead, the inclusion of the exciton-amplitude fluctuation results in a new type of contribution to the nonlinear response.

In conclusion, our investigation shows the distinct influence of different higher-order correlations on the time-resolved polarization state of the FWM signal. For the combination of linearly and circularly polarized excitation beams, the polarization state of FWM signals is only fixed in the strict $\chi^{(3)}$ limit. For slightly increased excitation densities it becomes dynamically dependent on real time and detection energy. Our analysis shows that the time evolution of the polarization state cannot satisfactorily be described by taking into account only the interband coherent contributions corresponding to two-pair correlations, namely biexcitonic transitions and the exciton-exciton scattering continuum. Instead, our experiments reveal a decisive influence of the fluctuations of the exciton amplitude, as seen most clearly in the observable $\mathrm{Re}(\hat{\mathbf{E}}_y)$ determining the tilt angle of the polarization ellipse. In our opinion, this result sheds new light on the transient coherent response of semiconductors. Even at density levels quite common in FWM experiments this response is determined also by excitations that already have lost their interband coherence.

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[1] A. E. Paul, J. A. Bolger, A. L. Smirl, and J. G. Pellegrino, J. Opt. Soc. Am. B **13**, 1016 (1996).

[2] J. A. Bolger, A. E. Paul, and A. L. Smirl, Phys. Rev. B **54**, 11 666 (1996).

[3] O. Buccafusca, X. Chen, W. J. Walecki, and A. L. Smirl, J. Opt. Soc. Am. B **15**, 1218 (1998).

[4] X. Chen, O. Buccafusca, and A. L. Smirl, in *Proceedings of the International Quantum Electronics Conference, San Francisco, 1998*, OSA Technical Digest Series (Optical Society of America, Washington D.C., 1998), Vol. 7, p. 211.

[5] S. Patkar *et al.*, Phys. Rev. B **51**, 10 789 (1995).

[6] W. Schäfer *et al.*, Phys. Rev. B **53**, 16 429 (1996).

[7] P. Kner *et al.*, Phys. Rev. Lett. **78**, 1319 (1997).

[8] K. Victor and A. Stahl, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors, Berlin, 1996*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), p. 709.

[9] V. M. Axt, K. Victor, and T. Kuhn, Phys. Status Solidi B **206**, 189 (1998).

[10] G. Bartels *et al.*, Phys. Rev. B **55**, 16 404 (1997).

[11] G. Bartels and A. Stahl, Phys. Status Solidi B **206**, 325 (1998).

[12] V. M. Axt and S. Mukamel, Rev. Mod. Phys. **70**, 145 (1998).

[13] M. U. Wehner, J. Hetzler, and M. Wegener, Phys. Rev. B **55**, 4031 (1997).

[14] B. Haase *et al.*, Phys. Status Solidi B **206**, 363 (1998).

[15] B. Haase *et al.*, in Proceedings of the 24th International Conference on the Physics of Semiconductors, Jerusalem, 1998, (World Scientific, Singapore, in press).

[16] K. Victor, V. M. Axt, and A. Stahl, Phys. Rev. B **51**, 14 164 (1995).

[17] V. M. Axt and A. Stahl, Z. Phys. B **93**, 195 (1994).