# Effects of Coherent Polarization Interactions on Time-Resolved Degenerate Four-Wave Mixing

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(Received 13 April 1990)

We report the first observation of coherent polarization interactions in dense media in time-resolved degenerate four-wave mixing in semiconductors. For near-resonant ultrashort-optical-pulse excitation, these interactions lead to a diffracted signal at negative delay times, with a slope half that for positive delay times. At higher intensities, *two temporal maxima* appear in the diffracted signal, in agreement with many-body theory.

PACS numbers: 42.50.Md, 42.65.Re, 71.35.+z

Time-resolved degenerate four-wave mixing (DFWM) is a very powerful technique to study the nonlinear response and the loss of coherence of optically excited states in atoms, molecules, and solids. In the so-called two-pulse self-diffraction geometry sketched in the inset of Fig. 1, two perpendicularly polarized laser pulses propagating in the directions $\mathbf{k}_1$ and $\mathbf{k}_2$ interfere in the sample and generate an orientational grating, as long as their time delay $T=t_2-t_1$ is of the order of the polarization dephasing time $T_2$. Photons of beam 2 are diffracted by this grating, giving rise to a nonlinear signal in the direction $\mathbf{k}_3=2\mathbf{k}_2-\mathbf{k}_1$. For an ensemble of homogeneously broadened two-level systems and ultrashort optical pulses, the third-order theory of Yajima and Taira[1] predicts that this diffracted signal is identical to zero for $T<0$ and decays as $\sim\exp(-2T/T_2)$ for $T>0$. Measurements of the temporal evolution of the DFWM signal thus yield information about the phase-relaxation processes and the nature of the excited states. In fact, in previous experiments on semiconductors, time-resolved DFWM has been used to determine the dephasing of excitons[2] and free electrons and holes[3] due to scattering with phonons or other excitons and free electrons and holes. These studies have concentrated on the decay of the diffracted signal at positive time delays.

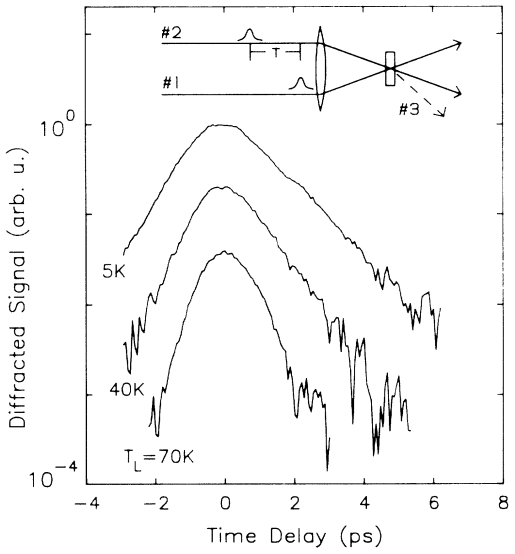


FIG. 1. DFWM signals in GaAs/AlGaAs vs time delay for different lattice temperatures and low excitation intensity. Inset: Experimental configuration.

In this Letter, we report the observation of a diffracted signal at negative time delays, for which the two-level theory predicts no signal at all. For near-resonant ultrashort-optical-pulse excitation of semiconductors, this signal due to coherent polarization interactions rises as $\sim\exp(4T/T_2)$, as predicted theoretically in Ref. 4. At higher excitation intensities, the coherent polarization interaction manifests itself in the form of two temporal maxima that evolve continuously out of the rising signal at negative time delays. We analyze these novel experimental results in two different material systems with a microscopic theory based on the solution of the quantum kinetic equations for interacting excitons in semiconductors.[4,5] We discuss the importance of polarization interaction effects for four-wave-mixing experiments in all dense media.

In a first set of experiments, we have studied the dynamics of DFWM at low excitation intensities in a 170-Å GaAs/AlGaAs multiple-quantum-well structure. The GaAs substrate of the sample was removed by etching, thereby allowing transmission experiments. The inset of Fig. 2 shows the transmission spectrum at 5 K in the spectral vicinity of the heavy-hole (hh) and light-hole (lh) excitons. The linewidth of the hh exciton is about

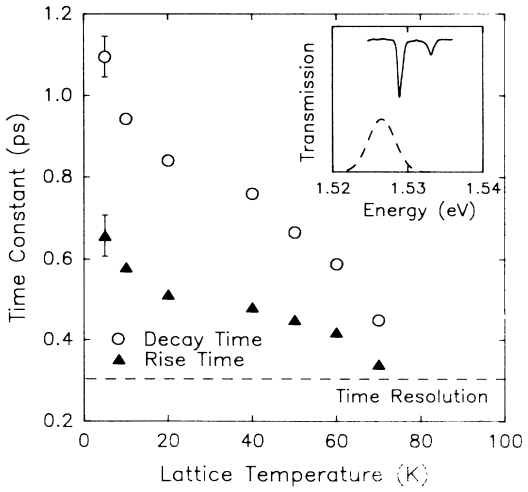


FIG. 2. Rise (triangles) and decay (circles) times of the DFWM signals of Fig. 1 vs lattice temperature. The time resolution of the experiment (~300 fs) is indicated by the dashed line. Inset: Sample transmission (solid curve) at 5 K and the pulse spectrum (dashed curve).

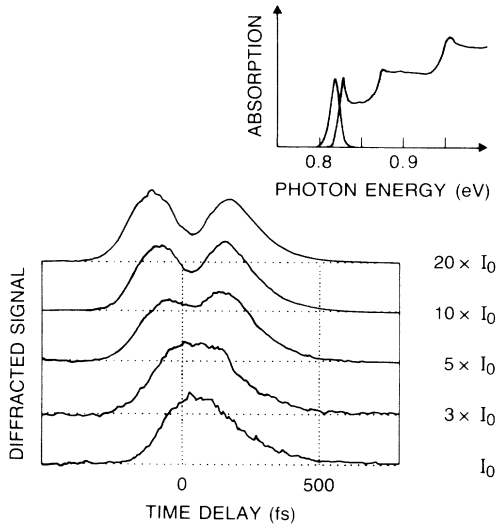


FIG. 3. DFWM signals in InGaAs/InAlAs vs time delay for a lattice temperature of 5 K, 10-meV laser detuning, and different excitation intensities. Inset: Sample absorption at 5 K and the pulse spectrum.

0.7 meV. The results for the dephasing time $T_2$ (see below) and the very small Stokes shift between photoluminescence and photoluminescence-excitation spectra of less than 0.2 meV demonstrate the high quality of the sample and show that the inhomogeneous contribution to the linewidth is small. The laser source is a tandem, synchronously pumped, dye (LDS 751) laser system that produces 500-fs pulses tunable between 700 and 815 nm. The pulse spectrum is also shown in the inset of Fig. 2. The excitation wavelength was chosen to be 3 meV below the hh exciton to avoid direct generation of energetically higher states like the lh exciton.

Figure 1 shows the time-integrated diffracted signal versus time delay $T$ for three different lattice temperatures, 5, 40, and 70 K, and low excitation intensity ($\sim 160$ kW cm$^{-2}$). The signals are asymmetric in time and consist of exponentially rising and decaying wings. It is immediately visible that they cannot be described by the simple two-level theory: With increasing lattice temperature, both the decay and the rise time get shorter, ruling out the pulse profile as determining either of them.

This is shown in more detail in Fig. 2, in which the rise and decay times of Fig. 1 are plotted versus the lattice temperature. At low temperatures, where the thermal phonon contribution to the dephasing is small, the decay time is found to be about 1150 fs, in reasonable agreement with earlier measurements on GaAs/AlGaAs.[2] The corresponding rise time is about 650 fs, i.e., about a factor of 2 smaller, as predicted theoretically in Ref. 4. With increasing lattice temperature, both time constants decrease and the time resolution of the experiment (~300 fs, indicated by the dashed line) causes an increasing deviation from the 2:1 ratio. Similar behavior is observed if $T_2$ is decreased by increasing the excitation intensity.

In a second set of experiments, we have studied the dynamics of DFWM at high excitation intensities in a high-quality 200-Å InGaAs/InAlAs multiple-quantum-well structure grown on InP (a 200-Å InGaAs/InP structure gave identical results). The laser source is an additive-pulse mode-locked color-center laser that produces pulses of about 140 fs duration tunable around 1500 nm. The absorption spectrum of the sample at 5 K and the pulse spectrum are shown in the inset of Fig. 3. The excitation wavelength is again slightly tuned below the exciton resonance to avoid direct generation of free electrons and holes.

Figure 3 shows the time-integrated diffracted signal versus time dealy $T$ for five different excitation intensities, $I_0$ (~3 MW cm$^{-2}$), $3I_0$, $5I_0$, $10I_0$, and $20I_0$, 10-meV laser detuning, and a lattice temperature of 5 K. At low excitation intensities ($I_0$), an asymmetric signal is observed, similar to the ones shown in Fig. 1. The decay time is about 140 fs which is an order of magnitude shorter than in GaAs/AlGaAs. The additional dephasing is most likely due to scattering off local band-gap variations in the ternary alloy InGaAs.[6]

With increasing excitation intensity, the DFWM signal exhibits striking changes. The top of the asymmetric signal flattens ($3I_0$) and finally develops two distinct temporal maxima ($20I_0$), with a "temporal hole" near zero time delay. At the same time, the decay constant decreases to about 80 fs, due to exciton-exciton scattering. With decreasing laser detuning, these dramatic changes become less pronounced and one observes only a shoulder at negative time delays as the intensity is in-

creased. In the intensity range accessible to us, the GaAs/AlGaAs sample also shows the latter behavior.

As already alluded to, these experimental observations cannot be understood on the basis of the isolated two-level model, but require a theory taking into account the interaction of the nonlinear species probed by DFWM. In our case, one needs a microscopic theory of the coherent nonlinear optical response of excitons. Such a theory has been developed some time ago[5] and has recently been applied to time-resolved DFWM.[4] The most important feature of the theory is that it treats on an equal footing the applied electric field $E$ and the Coulomb potential $V_{k,k'}$ which is responsible for the formation of excitons as well as their interaction. In particular, it accounts for the fact that the optically coupled electron-hole pair amplitudes $\psi_k$, corresponding to vertical transitions at wave vector $k$, do not only experience the applied Rabi frequency $\mu_k E$ ($\mu_k$ is the interband dipole matrix element), but also the potential of all the other pairs at $k'$. Hence the total coupling is $\Delta_k = \mu_k E + \sum_{k'} V_{k,k'} \psi_{k'}$. For ultrashort laser pulses $E \sim \delta(t)$, the first term in $\Delta_k$ varies like $\sim\delta(t)$ and produces a DFWM signal with a time dependence that follows the two-level model of Yajima and Taira.[1] The induced pair amplitude $\psi_k$ and thus the second term in $\Delta_k$, however, exhibit a steplike rise and a $\sim\exp(-t/T_2)$ decay. The associated polarization ($P = \sum_k \mu_k^* \psi_k$) can and does interact with the polarization grating for both $T<0$ and $T>0$. This interaction involves two polarizations propagating in the direction $\mathbf{k}_2$ and one propagating in the direction $\mathbf{k}_1$ and hence produces a $\sim\exp(4T/T_2)$ DFWM signal for negative time delays. (For positive time delays, the resulting DFWM signal decays as the signal arising from the first term in $\Delta_k$, with a similar magnitude.) The free induction decay itself does not produce a signal in the direction $\mathbf{k}_3$.

Although we have observed and discussed this effect for the particular case of Wannier-exciton interactions, it is clear that it should be observable in other systems as well. Its generality can be inferred by considering an (symbolic) expansion of the free energy in powers of the electric field and the polarization, as is often performed in nonlinear optics.[7] Besides a two-level-like nonlinear $P^3E$ term, one obtains a nonlinear (anharmonic oscillator) $P^4$ term, describing, e.g., an exciton wave function and energy renormalization due to exciton-exciton interactions, as observed previously in nonlinear frequency-domain (transmission) experiments.[2,8,9] In the context of DFWM, the $P^4$ term can be directly thought of as describing the scattering of the polarization $P$ off a polarization grating (while the $P^3E$ term describes the scattering of the electric field $E$); it should be present in many other dense media for which strong nonlinear couplings of the macroscopic polarization occur.[10]

For finite pulse duration and higher excitation intensities, calculations can only be performed numerically. Figure 4 shows theoretical DFWM signals for 110-fs

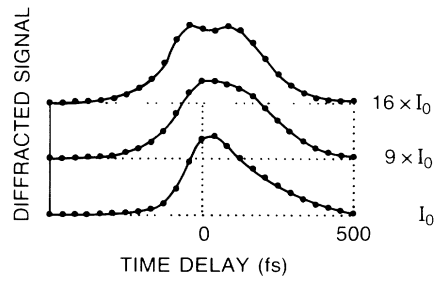


FIG. 4. Calculated DFWM signals vs time delay for different excitation intensities.

Gaussian pulses with peak Rabi frequencies of 0.2, 0.6, and 0.8 excitonic rydbergs ($\mathcal{R}_{ex}$) tuned $3\mathcal{R}_{ex}$ below the exciton resonance. The material parameters are those of bulk GaAs and a dephasing time of $T_2 = 0.4\mathcal{R}_{ex}^{-1}$ was assumed. $T_1$ (here the carrier lifetime) is much larger than $T_2$ and is therefore neglected in the analysis. In qualitative agreement with the experimental data of Fig. 3, the low-intensity signal ($I_0$) first flattens ($9I_0$) and then evolves into a signal with two distinct temporal maxima ($16I_0$). This is due to a subtle interference between the third-order response discussed above and higher-order processes which manifests itself at the maximum intensity, i.e., when the two pulses overlap in time at $T \sim 0$. The theory also reproduces the shoulder observed at small detuning; we note, however, that the details are quite sensitive to the different time and energy scales in the problem.[10]

In conclusion, we have demonstrated that coherent exciton-exciton interactions give rise to novel effects in time-resolved degenerate four-wave mixing in semiconductors. The unusual signals observed in GaAs/AlGaAs and InGaAs/InAlAs quantum-well structures are in qualitative agreement with theoretical results based on the solution of the quantum kinetic equations for interacting electrons and holes. The results show that the theory based on isolated two-level systems,[1] which has been used up to now to analyze DFWM experiments,[2,3] is insufficient. The polarization interaction effects, which we have studied here for excitons in quantum wells, are much more general and should be important in all dense media.

We thank G. Sucha for his expert assistance in experiments with color-center lasers. We are indebted to K. Köhler and P. Ganser for growing the GaAs/AlGaAs sample, and N. Sauer, T. Chang, U. Koren, B. Miller, A. Cho, and D. Sivco for providing the InGaAs samples. The work of K.L. was supported by the Max-Planck-Gesellschaft zur Förderung der Wissenschaten EV.

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