Unusually Slow Temporal Evolution of Femtosecond Four-Wave-Mixing Signals in Intrinsic GaAs Quantum Wells: Direct Evidence for the Dominance of Interaction Effects

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Four-wave-mixing signals from excitons in high-quality GaAs quantum wells show an unusually slow temporal evolution, in stark contrast to the behavior expected for a noninteracting two-level system. We show that Coulomb interaction effects, generally neglected in the analyses of four-wave-mixing experiments, *dominate the signals by 2 orders of magnitude.* Numerical calculations based on extended optical Block equations for semiconductors provide good qualitative agreement with the data.

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Transient coherent spectroscopy has been increasingly used in investigating the properties of and the interactions among various elementary excitations in semiconductors. In the two-pulse, self-diffracted four-wave-mixing (FWM) experiment, the two pulses create a grating and the signal diffracted by this grating is measured in a background-free direction. In most experiments performed to date, the time-integrated FWM (TI-FWM) signal (or total diffracted energy) is measured as the delay between the two beams is varied. Considerable information about atoms, molecules, and solids has been obtained from such measurements [1–10]. Time resolving the diffracted signal has resulted in observation of photon echos from localized states in solids [3,11]. Most of these results have been interpreted in terms of a noninteracting two-level model [12].

In this Letter we show, using femtosecond time-resolved FWM (TR-FWM) experiments [13,14] on high-quality intrinsic GaAs quantum wells, that this *noninteracting picture is completely inadequate because interactions between the states strongly dominate the nonlinear response of semiconductors.* The noninteracting model for homogeneously broadened or moderately inhomogeneously broadened two-level systems predicts that the TR-FWM signal should peak close to the time of arrival of the second pulse. In stark contrast to this prediction, the measured diffracted signal at low temperatures exhibits an unusually slow rise, with the peak occurring as much as 1500 fs after the second pulse. From the temperature dependence of the peak position and the decay constants of TR-FWM, we deduce that the peak occurs close to T_2, the dephasing time. We show that this behavior is a consequence of Coulomb interaction between excitons.

Coulomb interactions between excitons [15] may be thought of as generating a local field that leads to diffraction of polarization in addition to the usual diffraction of fields [7,15]. This is expected to give TI-FWM signals at negative time delays; such signals have indeed been observed [7,16]. However, these experiments provided no information about the relative strengths of the normal (N) signal in the absence of interaction and the interaction-induced (II) signal. By temporally resolving the FWM signal, we demonstrate that *the generally neglected II signal dominates the nonlinear response by 2 orders of magnitude.* Furthermore, our data show interesting behavior as a function of time delay and polarization. We show that numerical calculations based on extended optical Bloch equations for semiconductors provide good qualitative agreement with the data. These conclusions provide new insights into the nonlinear response of semiconductors and will have significant implications for the interpretations of many coherent transient experiments in semiconductors.

Most of our experiments were performed on a high-quality, molecular-beam-epitaxy-grown intrinsic GaAs/$Al_{0.3}Ga_{0.7}As$ multiple quantum well sample (170-Å well width and 10 periods), with the substrate removed to allow transmission experiments. The excitonic absorption linewidth is 0.7 meV, and the Stokes shift between the absorption and luminescence is less than 0.1 meV. A tunable, passively mode-locked Ti-sapphire laser, with transform-limited 100-fs pulses, was used to perform FWM experiments at various lattice temperatures, laser wavelengths, and excitation densities. The sample is excited by two pulses propagating along $\mathbf{k}_1$ and $\mathbf{k}_2$ with collinear or cross-linear polarizations and the diffracted signal is measured in the phase-matched direction $\mathbf{k}_d$

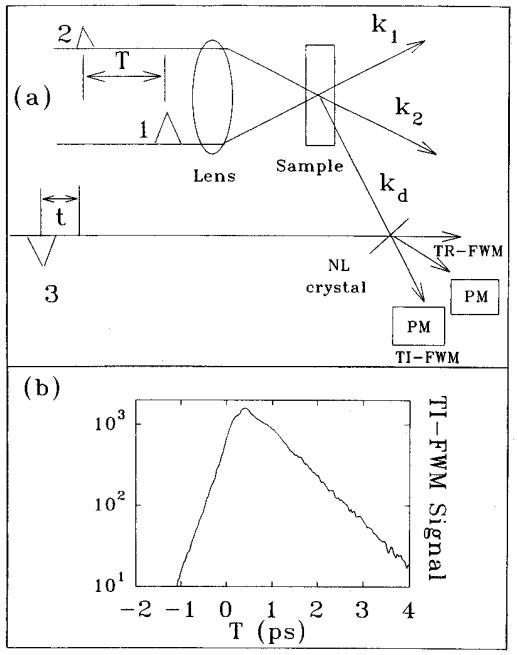

FIG. 1. (a) Schematic of the experimental configuration; PM denotes the photomultiplier tube. (b) TI-FWM at 10 K with linear co-polarized beams at an excitation density of 10^{10} cm^{-2}.

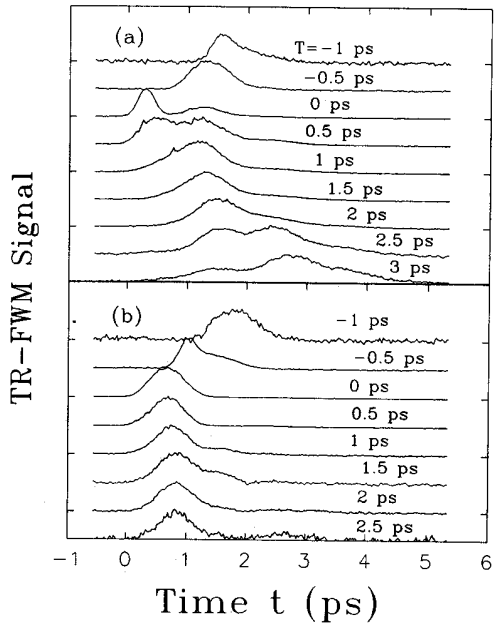

FIG. 2. TR-FWM spectra at various time delays T, (a) with linear co-polarized beams at 10 K, and (b) with linear cross-polarized beams. The time delays T are as indicated. All the curves are normalized to equal heights and displaced for clarity here and in Fig. 3.

$=2\mathbf{k}_2-\mathbf{k}_1$ [Fig. 1(a)]. We measure the usual TI-FWM signal as a function of time delay T (positive when pulse 1 precedes pulse 2), and the TR-FWM signal as a function of time t following the pulse along $\mathbf{k}_2$, by up-converting it with a part of the laser beam (beam 3) that did not go through the sample. $t=0$ is determined with an accuracy of <20 fs by up-converting the scattered light of the second beam into the direction of $\mathbf{k}_d$. We present here data for an excitation density of 1×10^{10} cm^{-2}, calculated from the measured spot diameter and total absorbed power.

Figure 1(b) shows a typical TI-FWM signal as a function of T. The nearly exponential decay is characterized by a decay constant τ. For the sample at 10 K, $\tau=0.65$ ps for the above excitation density and $=1$ ps at very low density. The low-density decay constant and the absorption linewidth can be self-consistently explained by a homogeneous linewidth of 0.66 meV ($T_2=2$ ps) and negligible inhomogeneous broadening. While we cannot rule out any inhomogeneous broadening on the basis of these measurements, they can be used to determine that the inhomogeneous broadening is <0.4 meV and the homogeneous broadening is >0.45 meV.

Figure 2(a) shows TR-FWM signals for collinearly polarized beams at various time delays T, with the laser centered 4 meV below the heavy-hole (HH) exciton absorption peak. Except for $T=0$ [17], *the dominant peak occurs at $t>1$ ps.* Thus the rise time of the signal is 10 times longer than the 100-fs pulse widths. The decay constant of TR-FWM is 0.65 ± 0.1 ps, in agreement with the decay constant in TI-FWM. A semilogarithmic plot of the temporal evolution shows an unresolved fast initial component that is about a factor of 100 smaller than the peak. The position of the peak is constant in t at small T but begins to shift at larger $T>1$ ps. Also, TR-FWM develops an additional peak at $t\approx T$ for larger T. Moving the excitation energy further below the HH excitons reduces the intensity of this additional peak. Figure 2(b) shows the TR-FWM signal at various time delays for cross-linear polarizations. The signal still peaks at long times, but the peak does not move with T and the additional peak is weak, in contrast to the data for collinearly polarized beams [Fig. 2(a)]. For negative time delays, the signal starts only after $t=|T|$ because there is no diffraction until both beams arrive at the sample.

Figure 3 shows the temperature dependence of the TR-FWM at $T=1$ ps. The rise time of the TR-FWM signal decreases with increasing temperature and the peak occurs at shorter t, leading to the conclusion that the rise time is not related to the pulse width or T. A comparison of the peak position and the decay constant τ shows that the signal peaks roughly at 2τ or close to T_2. The fact that the signal in Fig. 2(b) peaks at an earlier time than in Fig. 2(a) is consistent with the results in Fig. 3, and our observation that TI-FWM for cross-polarized beams decays faster ($\tau=0.45$ ps) than for co-polarized beams, a result that is in agreement with previous reports [18].

Several important qualitative conclusions can be drawn immediately from the data. Most of the FWM data in the past have been successfully explained on the basis of a noninteracting two-level model [12]. For an inhomogene-

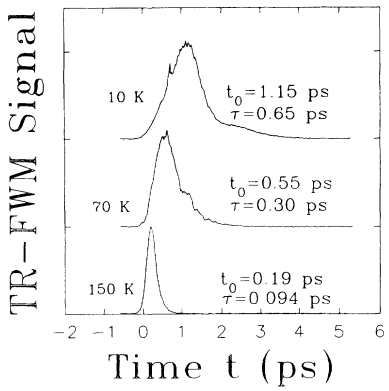

FIG. 3. Temperature dependence of TR-FWM spectra for co-polarized beams. $T=1$ ps, and the temperatures from top to bottom are 10, 70, and 150 K. t_0 is the peak position and τ is the decay constant determined from the TR- and TI-FWM, which are nearly the same.

ously broadened system, this model predicts that the TR-FWM is a Gaussian peaking at $t=T$ (the well-known photon echo) [19]. For a homogeneously broadened system, or for a weakly inhomogeneously broadened system like ours [20], the model predicts that the TR-FWM signal peaks within one or two pulse widths of the second pulse exciting the sample and then decays with a time related to the dephasing time T_2. In stark contrast to this model, we observe that TR-FWM peaks at 10–15 times the pulse width at 10 K and that the peak position is not related to the pulse width or the delay, but to the dephasing time. Furthermore, we also observe a fairly strong signal for negative T not predicted by this model. *We, therefore, conclude that the generally accepted noninteracting two-level model is completely inadequate for describing our results in semiconductors.*

As discussed above, the Coulomb interaction between excitons leads to the diffraction of polarization [7,15]. For a nearly homogeneous system, the induced polarization decays with T_2. Therefore, when $T_2 > t_p$ (pulse width), the II signal is expected to rise after the second pulse, and peak close to T_2. This is precisely what we observe. Our TR-FWM results show directly that the delayed signal is 100 times stronger than the fast initial component; i.e., *the interaction-induced signal is 2 orders of magnitude stronger than the noninteracting signal.* Thus, the II signal completely dominates both the TR- and TI-FWM signals. The dominance of the interaction effect was not realized earlier because the TI-FWM signal varies as $\exp(-2T/T_2)$ for positive T for both the N and II signals [7]. Our femtosecond-time-resolved studies have thus provided new insight into coherent interactions in semiconductors.

If the strength of the local field effect is represented by a phenomenological potential energy V, the ratio of the II versus N signal varies as $(VT_2/\hbar)^2$. In our experiments, $T_2 \approx 1.3$ ps and the measured ratio ≈ 100, so that V is a few meV, of the order of the binding energy of the excitons, as one might expect in a simplified case. With increasing temperature, T_2 decreases and the exciton homogeneous linewidth becomes comparable to V. This diminishes the relative contribution from the interaction effects, as evidenced by the shift of the peak in Fig. 3. We emphasize that although the discussions are cast in terms of excitons, the ideas discussed here have general validity and should be applicable to a variety of systems.

The complicated dependence of TR-FWM on T [Fig. 2(a)] cannot be explained by the simple local-field model discussed above. A more realistic calculation, which can account for such intensity-dependent effects as band-gap renormalization and reduction in binding energy, is done using the semiconductor Bloch equation including the Coulomb interaction matrix $V_{k,k'}$ coupling electron-hole pair states k and k', and exchange self-energy Σ_k so that the Hamiltonian can be written as $H_{k,k'}=E_k+2\Sigma_k-(1-2f_k)V_{k,k'}$. Here, E_k is the energy without the Coulomb correction and $1-2f_k$ is the Pauli-blocking factor. The calculation is done for bulk GaAs but should yield similar results for GaAs quantum wells. If we neglect the self-energy correction, the semiconductor Bloch equation yields results very similar to those using the local-field model when the signal is dominated by the occupation of $1s$ excitons. The results of such calculations for equal intensities of both pulses at various time delays (Fig. 4, dashed lines) show *a delayed peak close to T_2, in agreement with our observations discussed above.* When the self-energy corrections such as the band-gap renormalization are included, the peak position of the delayed signal is no longer simply determined by T_2, but also by such parameters as the excitation density [21–23] and time delay T. The results of including the self-energy corrections are represented by solid lines. Between $T=0.6$ and 1.2 ps, the peak position changes with time delay T in *an echolike fashion due to the admixture of continuum states.* In comparison with this model calculation, our data of Fig. 2(a) show little change in the

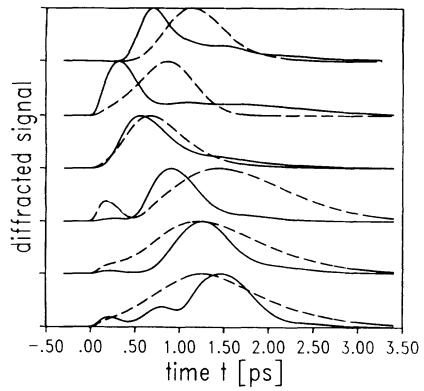

FIG. 4. Theoretical calculation of TR-FWM using the semiconductor Bloch equation for GaAs. Dashed lines ignore the self-energy correction whereas solid lines includes all contributions. Time delays from top to bottom are −0.3, 0, 0.3, 0.6, 0.9, and 1.2 ps.

peak position of the delayed signal between $T=0$ and 1 ps but show echolike behavior between $T=1$ and 3 ps. This might be because the relative strength of the self-energy correction to the Coulomb potential is larger for bulk GaAs than GaAs quantum wells where the Coulomb interaction is enhanced. As a result, the solid curves overemphasize the echolike behavior. The TR-FWM at $T=3$ ps is the most complicated, which might indicate the manifestation of the self-energy correction. The calculation including the self-energy corrections yields all the essential features of the experiments [Fig. 2(a)] such as dominance of the delayed signal, the complicated dependence on T, and the existence of the prompt signal at $T=0$. Furthermore, it also predicts that the self-energy effects are not expected in the cross-polarization geometry [24], in agreement with the data shown in Fig. 2(b) that show no change in the peak position throughout the time delays used. Thus, the additional peak in Fig. 2(a) for large T is consistent with the intrinsic photon-echo-like behavior resulting from the self-energy effects discussed above.

In conclusion, we have demonstrated the unexpected, complete dominance of the coherent interaction effect on the four-wave-mixing signal of the excitons. This conclusion was drawn by noticing that the FWM signal of our experiments continued to rise long after both pulses were gone. We have shown that the often-used noninteracting two-level system description of excitons is completely inadequate, and that the local-field model is also inadequate. We show that a realistic calculation using the semiconductor Bloch equation including Coulomb coupling between different k states and exchange self-energy provides a good qualitative understanding of the most important results. Our results that nonlinear response of semiconductors is dominated by Coulomb interaction effects between excitons have implications for any coherently interacting system as well as other experiments involving nonlinearities of excitons.

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[19] Our TR-FWM results on a sample with strongly inhomogeneously broadened exciton (FWHM ≈ 2.5 meV) show clear evidence of this extrinsic photon echo and different decay constants of TR- and TI-FWM, unlike the sample discussed in the text.

[20] An inhomogeneous broadening of 0.4 meV will introduce a photon-echo term $\exp[-(t-T)^2/T^{*2}]$ with FWHM ≈ 7 ps which multiplies the free-induction-decay terms arising from diffraction of fields or polarizations. Because the time delays ($T \leq 3$ ps) and T_2 (1.3 ps) of our experiments are small compared to this FWHM, the effects of this possible inhomogeneous broadening on the interpretation of our data are minimal.

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