Exciton–KLO-Phonon Quantum Kinetics: Evidence of Memory Effects in Bulk GaAs

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Oscillations of the transient four-wave-mixing signal with a period of about 100 fs are observed in bulk GaAs using 14 fs pulses tuned to the exciton resonance at low temperatures. The measurements are explained in terms of the non-Markovian quantum kinetics for electron-hole pairs due to LO-phonon scattering. It is shown that the observed oscillations are evidence for memory effects. The experiments provide a first test of the central ideas of quantum kinetics, in which the effects of quantum coherence and of dissipation are intrinsically connected.

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Ultrafast relaxation in liquids and solids can directly be investigated in the time domain by femtosecond spectroscopy. The coupling of electronic excitations to a vibrational mode is a particularly interesting example. Semiconductor quantum dots, for which this coupling has recently been investigated [1,2], can be considered as an inhomogeneously broadened ensemble of two-level systems with a diagonal coupling to longitudinal optical (LO) phonons. This coupling through the Franck-Condon mechanism gives rise to quantum beats in the four-wave-mixing signal with exactly the phonon frequency [2], which are not related to non-Markovian relaxation. In bulk (polar) semiconductors, where the electronic excitations have a continuous band spectrum, the coupling to the optical phonons results in real intraband scattering transitions and provides the fastest relaxation and dephasing mechanism at low to moderate excitation densities. The ultrafast scattering kinetics in band states is thus distinctly different from the dynamics of discrete electronic states coupled to a lattice vibration mode. Particularly for time intervals, which are short compared to the period of an optical lattice oscillation period ($\simeq$ 115 fs in GaAs), the kinetics can no longer be described by the classical Boltzmann kinetics with its completed energy-conserving collisions. Instead, quantum kinetics has to be used in order to account for the partially coherent nature of electronic states in the band. *This quantum coherence gives rise to memory effects* [3–5]. Earlier solutions of the non-Markovian quantum kinetic equations for single-pulse excitation in spectral vicinity of the band edge indicated that the coupling to optical phonons gives rise to a periodic modulation superimposed on the polarization decay [6,7].

In order to test the theoretical prediction for bulk semiconductors we employ transient four-wave-mixing (FWM) experiments which are directly compared with solutions of the quantum kinetic equations under identical conditions. As usual, two pulses (of equal linear polarization) with wave vectors $\vec{q}_1$ and $\vec{q}_2$, respectively, are delayed in time and focused onto the sample. The self-diffracted signal in direction $2\vec{q}_2 - \vec{q}_1$ is detected as a function of time delay τ. The pulses are derived from a laser system similar to that of Ref. [8]. The sech^2-shaped pulses have a temporal full width at half maximum (FWHM) of 14.2 fs and a spectral FWHM of 87 meV, resulting in a bandwidth product of 0.30 close to the theoretical limit of 0.315. The autocorrelation has been taken under identical conditions as the FWM data. Every component introduced into the beams (like, e.g., neutral density filters) has been precompensated in a four-prism sequence. The sample is a high quality GaAs /$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ ($x = 0.3$) double heterostructure grown by metal-organic vapor phase epitaxy with a thickness of the bulk GaAs layer of 0.6 μm, resulting in a small optical density of 0.3 for continuum states at a lattice temperature of 77 K. The sample is glued to a sapphire substrate; its front side is antireflection coated. Electron-hole densities quoted are determined via the measured total incident flux and the spot radius of 35 μm, measured with a knife edge technique. For the effective absorption coefficient we have used half of the measured unsaturated continuum value of 1.1×10^4 cm^{-1}, since about half of the laser spectrum is below the band gap. Figure 1 exhibits typical signals as a function of time delay for three different excited electron-hole pair densities. The resonant excitation conditions can be seen from comparison of the laser spectrum with the FWM spectra in Fig. 2. The FWM signal (Fig. 1) exhibits a quantum beat [9] behavior, the period of which is density independent. For increasing density the modulation becomes less pronounced. We have fitted

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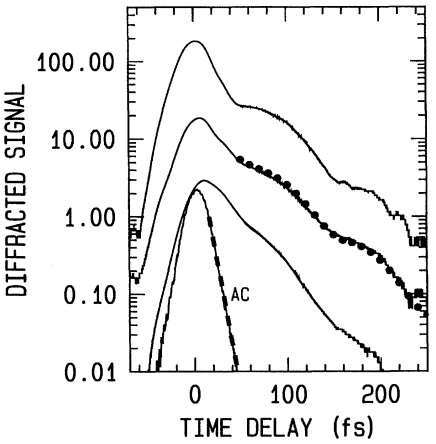

FIG. 1. Experiment: transient four-wave mixing on GaAs at 77 K. The diffracted signal is shown as a function of time delay for three different carrier densities (from top to bottom: 1.2×10^{16}, 1.9×10^{16}, and 6.3×10^{16} cm^{-3}). The curves are vertically displaced for clarity. The dots are the result of the quantum kinetic theory. The curve labeled *AC* is the autocorrelation of the laser pulses, the exponential wings of which are well fitted by a 6.5 fs time constant (dashed line).

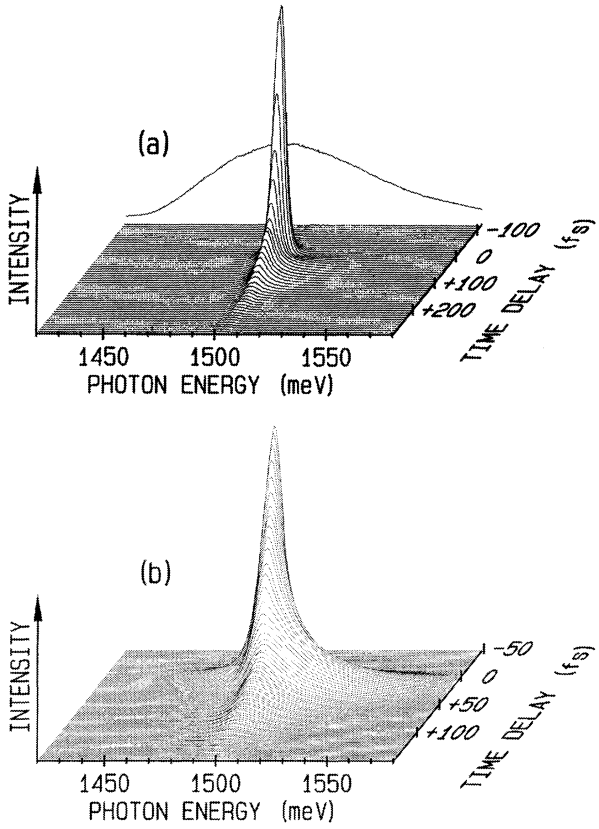

FIG. 2. Experiment: spectrally resolved four-wave-mixing signal as a function of time delay for a density of (a) 1.9×10^{16} and (b) 6.3×10^{16} cm^{-3}; other parameters as in Fig. 1. The resonant excitation condition can be seen from the laser spectrum depicted in the background of (a).

the decays in Fig. 1 with a function of the form $\sim [1 + a \sin(\omega_{\rm osc}\tau - \alpha)]\exp(-\tau/T_{\rm eff})$, obtaining best fits with periods $T_{\rm osc} = 2\pi/\omega_{\rm osc}$ of 100, 98, and 98 fs for the densities 1.2×10^{16}, 1.9×10^{16}, and 6.3×10^{16} cm^{-3}. The decay time constants $T_{\rm eff}$ are 44.1, 46.7, and 32.5 fs and the modulation amplitudes a 0.26, 0.17, and 0.17, respectively. For yet higher densities the modulation is less pronounced; for lower densities the worse signal-to-noise ratio inhibits detailed analysis. Interestingly, we observe only one peak in the FWM spectra as a function of time delay (Fig. 2) and no satellite related to the LO-phonon energy. Via the Fourier theorem this is equivalent to the absence of oscillatory structures in the signal as a function of time for any given time delay. From the density-independent modulation period we can clearly exclude any interpretation along the lines of Rabi or plasmon oscillations. Furthermore, the magnitude of the expected period is completely off for either mechanism. Propagation effects would also lead to a much longer oscillation period. *Surprisingly, the observed period of about* 100 *fs is smaller than expected from the well-established LO-phonon energy in GaAs of* $\hbar\omega_{\rm LO} = 36$ *meV equivalent to an oscillation period of* 115 *fs*.

For the theoretical analysis we use the semiconductor Bloch equations [10] combined with the retarded collision integrals for the LO-phonon scattering. This accounts for the important fact that the lattice cannot react on a time scale shorter than a lattice vibration period. The scattering rates of this delayed, partially coherent early time regime can be derived either with nonequilibrium Green functions (GF's) [3–6,11,12] or, alternatively, in a density matrix theory [13–15]. We use the nonequilibrium GF theory which allows the inclusion of nonperturbative effects by partial summations. It results in coupled nonlinear integrodifferential equations for the density matrix $\rho_{\mu\nu,k}(t) = \langle a^\dagger_{\nu,k}(t) a_{\mu,k}(t)\rangle$ (μ, ν are band indices, k is the momentum), which is just the equal time limit of the two-time particle propagator $G^<_{\mu\nu,k}(t,t') = i\langle a^\dagger_{\nu,k}(t) a_{\mu,k}(t')\rangle$ with $\hbar = 1$. The resulting collision rates for the equal time density matrix contain integrals over the history of the system. A typical term has the form $\sum_\sigma \int_{-\infty}^t dt' \Sigma^>_{\mu\sigma,k}(t,t') G^<_{\sigma\nu,k}(t',t)$, where $\Sigma^{\lessgtr}_{\mu\nu,k}(t,t')$ are the scattering self-energies. These self-energies are taken in the simple loop approximation $\Sigma^{\lessgtr}_{\mu\nu,k}(t,t') = i\sum_q g_q^2 D^{\lessgtr}_q(t,t') G^{\lessgtr}_{\mu\nu,k-q}(t,t')$, where for simplicity the phonons are considered as a thermal bath, and their propagators $D^{\lessgtr}$ are taken in the free-particle approximation. g_q is the Fröhlich interaction matrix element. The quantum kinetic equation is finally closed by the generalized Kadanoff-Baym ansatz (GKBA)

[3,4] which relates the two-time particle propagator to the density matrix: $G^{<}_{\mu\nu,k}(t,t') = -\sum_{\sigma} G^{r}_{\mu\sigma,k}(t,t')\rho_{\sigma\nu,k}(t')$ for $t > t'$. For $t < t'$ the advanced GF G^{a} enters in this relation. The GKBA is exact for a mean-field Hamiltonian [7] because the correction term to the GKBA is proportional to a scattering self-energy. With the GKBA one typical term of the scattering rates becomes, e.g., $\sum_{\sigma,q}\int_{-\infty}^{t} dt'\ \mathrm{K}(t,t')\rho_{\mu\sigma,k-q}(t')[1-\rho_{\sigma\nu,k}(t')]$, where the memory kernel is given by $\mathrm{K}(t,t') = g_q^2 e^{i\omega_{\mathrm{LO}}(t-t')} G^{r}_{\mu\sigma,k-q}(t,t') G^{a}_{\sigma\mu,k}(t',t) n_q$, with the phonon distribution n_q. Previously [3,4,6], diagonal free-particle Wigner-Weisskopf approximations for the spectral functions have been used. For long times the scattering rate approaches asymptotically the Boltzmann limit with a broadened energy-conserving delta function. With the diagonal approximation Thoai and Haug [16] showed that oscillations with the LO-phonon frequency [contained in $D^{\lessgtr}(t,t')$] are superimposed on the decay of the interband polarization induced by a short laser pulse. These oscillations are due to interference of the various LO-phonon sideband polarizations and can therefore be interpreted as LO-phonon quantum beats. Here, we have improved the description of the spectral functions by a mean-field approximation [7] for which the GKBA is still exact. In this description—combined again with a Wigner-Weisskopf collision damping—the spectral functions are calculated under the influence of the coherent light pulses and the Coulomb Hartree-Fock interaction consistently with the density matrix equations. Thus all optical band mixing effects and the important excitonic effects are now contained consistently in both the semiconductor Bloch equations and the spectral functions. We solve the quantum kinetic equations for two delayed excitation pulses $E_0(t)e^{i\vec{q}_1\cdot\vec{x}}$ and $E_0(t-\tau)e^{i\vec{q}_2\cdot\vec{x}}$, with $E_0(t) = E_0\, e^{-i\omega_0 t}/\cosh(t/\Delta t)$ and a FWHM of the intensity of 15 fs, corresponding to the experiment. The diffracted signal in direction $2\vec{q}_2 - \vec{q}_1$ is calculated in the following manner. The interference pattern with wave vector $\Delta\vec{q} = \vec{q}_2 - \vec{q}_1$ can transfer multiples of $\Delta\vec{q}$ to the two beams. We therefore calculate the time dependence of the total polarization $P(t,\tau,\phi)$ as a function of the phase $\phi = \vec{x}\cdot\Delta\vec{q}$ and time delay τ. The various diffracted orders $P_n(t,\tau)$ can then be projected out of the calculated function $P(t,\tau,\phi)$. As in the experiment, we choose the direction $2\vec{q}_2 - \vec{q}_1$ corresponding to $n = 2$. This sequential procedure is essential for the iteration of the huge set of coupled equations. Furthermore, we neglect propagation effects which are of minor importance at low optical densities. In Fig. 3 we show the calculated time-integrated diffracted signal $\int_{-\infty}^{+\infty} dt|P_2(t,\tau)|^2$ as a function of time delay for GaAs parameters at 77 K: heavy-hole-electron mass ratio $m_h/m_e = 6.67$, exciton Rydberg $R_y = 4.15$ meV, and Bohr radius $a_B = 12.5$ nm. The collisional damping is taken to be $\gamma_c = \gamma_v = 1$ meV. The excited electron-hole density is $n = 1.6\times 10^{16}$ cm^{-3}, comparable to the experiment. In order to model the experiment at 77 K we have added an additional, phenomenological dephasing mechanism with $T_2 = 143$ fs. This additional dephasing mechanism is most likely the Coulomb scattering among carriers, consistent with the fact that the oscillations vanish at higher excitation densities. Except for very short delay times, the agreement between theory and experiment is very good. From the same fitting procedure as in the experiment we obtain $T_{\mathrm{osc}} = 98$ fs, $T_{\mathrm{eff}} = 45$ fs, and $a = 0.17$. The oscillation period of about 100 fs can be interpreted as a simple beating of interband-polarization components with frequencies ω and ω' which are connected by coherent LO-phonon scattering. These frequency components are resonant with the band states k and k': $\hbar\omega = \hbar^2k^2/2\mu + E_g'$ and $\hbar\omega' = \hbar^2k'^2/2\mu + E_g'$, where μ is the reduced electron-heavy-hole mass $\mu = m_e m_h/(m_e + m_h)$ and E_g' is the Hartree-Fock renormalized band gap. The two interfering momentum states are coupled by an LO-phonon scattering event in the conduction band $\hbar^2(k'^2 - k^2)/2m_e = \hbar\omega_{\mathrm{LO}}$, from which one gets $\omega_{\mathrm{osc}} = \omega' - \omega = (1 + m_e/m_h)\,\omega_{\mathrm{LO}}$, which yields a period of 100 fs, close to the experiment. We have checked that this interpretation holds indeed for various mass ratios up to $m_h/m_e = 1$. The contribution of the scattering in the flat valence band is much smaller because the Fröhlich coupling is weak for large momentum transfer. This interpretation clearly shows that the observed effect is connected to band-to-band transitions; however, excitonic effects are important because they increase the necessary coherence considerably. In fact, the oscillation amplitude becomes very small if the

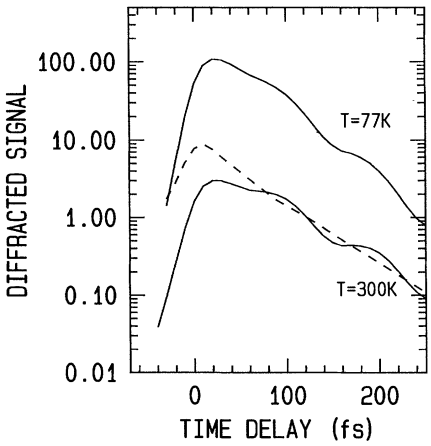

FIG. 3. Quantum kinetic theory: time-integrated four-wave-mixing signal as a function of time delay for GaAs at two different temperatures. $T = 77$ K, full line: theory with an additional dephasing mechanism with $T_2 = 143$ fs (same as dots in Fig. 1); $T = 300$ K, full line: quantum kinetic theory for phonon scattering only; dashed line: Markovian limit.

electron-hole attraction is switched off in our calculations. Note that we have treated the LO phonons as a thermal bath. In reality a certain number of phonons is generated by the hot carriers excited by the spectrally rather broad 15 fs pulse. It is known for the numerically much simpler diagonal approximation for the spectral functions that the combined quantum kinetics of the electronic excitations and the LO phonons [15,16] provide both a faster relaxation and a larger amplitude of the quantum beats. Therefore we also present calculations at 300 K with no additional dephasing time and damping constants which are determined self-consistently using Fermi's golden rule. The actual phonon populations in the experiment are somewhere in between these two curves which, however, exhibit no qualitative difference. We also show *that the observed oscillations as a function of time delay are absent in the Markovian limit of the theory* (dashed curve in Fig. 3). Figure 4 finally depicts the calculated FWM spectra at 77 K versus delay time. They are in good qualitative agreement with the corresponding experimental FWM spectra (Fig. 2), even though the theoretical spectra tend to be somewhat broader. In particular, the FWM signal exhibits no sign of oscillations in real time t, showing that the dynamics in the delay time τ and in real time are not simply connected.

Because of the good agreement between theory and experiment, the reported measurements provide a first direct experimental verification of the basic ideas of quantum kinetics. According to quantum kinetics, quantum coherence—here observed in the form of LO-phonon related quantum beats—cannot be separated from dephasing and relaxation on time scales which are shorter or comparable to the inverse frequency of characteristic resonances in the system.

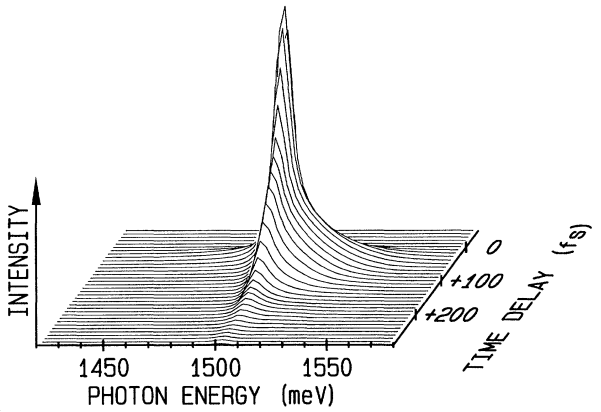

FIG. 4. Quantum kinetic theory: spectrally resolved diffracted signal versus time delay. Parameters as in Fig. 3 for $T = 77$ K.

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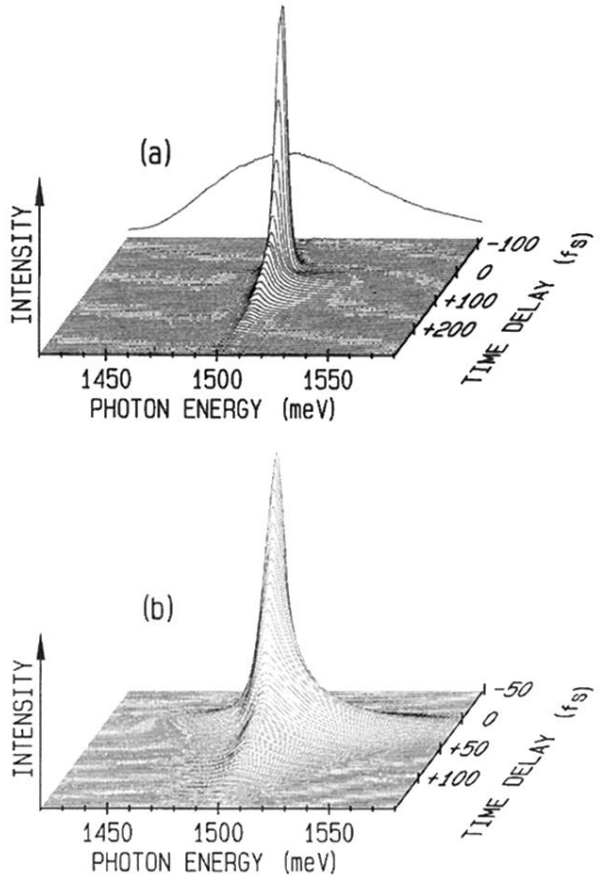

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