Quantum Kinetic Electron-Phonon Interaction in GaAs: Energy Nonconserving Scattering Events and Memory Effects

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Highly energetic electrons in GaAs emitting LO phonons are studied via femtosecond transmission spectroscopy. It is demonstrated for the first time that energy is not conserved on a time scale as short as a LO oscillation period: A replica of the initial distribution starts spectrally broadened before it sharpens into the excitation shape. This scenario is repeated for every step in the phonon cascade. Simulations combining an exact solution of quantum kinetics within a simplified model and a calculation of the polarization including Coulomb effects quantitatively agree with the data. [S0031-9007(97)03186-4]

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During the past decade, investigations of the femtosecond dynamics of photogenerated nonthermal carriers in semiconductors have become an important branch of solid state physics [1]. The research activities are triggered by both the fundamental questions arising in this field as well as its technological relevance. Most of the experiments have been explained theoretically on the basis of the semiclassical Boltzmann equation [2–4]. In this picture, the various mechanisms leading to the ultrafast carrier dynamics are calculated assuming that each collision strictly conserves energy and momentum. In high-purity semiconductors, carrier-carrier (CC) interactions via the Coulomb potential and carrier-phonon (CP) scattering provide the most relevant relaxation processes. Influences of the interband polarization [5] created, e.g., by a coherent laser pulse enter into an extension of the Boltzmann model, the semiconductor Bloch equations.

In any scattering process, energy conservation holds if the particle distributions vary slowly on the scale of the collision time. Under these conditions the individual interaction events become decoupled. The oscillation period of the energy quantum exchanged gives an estimate for the duration of a collision. In experiments with ultrahigh temporal resolution, this time interval can no longer be regarded as infinitely short. Consequently, typical quantum features such as energy nonconserving transitions and memory effects might show up. In theory, quantum kinetic phenomena are studied using models for the carrier dynamics derived within either the technique of the Keldysh nonequilibrium Green's functions [6] or the density matrix formalism [7]. The resulting non-Markovian equations contain memory kernels driving the distributions toward the Boltzmann limit as time proceeds. Unlike semiclassical physics, the temporal evolution is no longer determined by the status at a single point in time. Instead, the dynamics is connected to the history of a system via its memory.

It turns out that the emission of longitudinal optical (LO) phonons by energetic electrons in the Γ valley of bulk GaAs is an ideal example for the investigation of quantum kinetic effects: First, the long-wave LO phonons possess a well-defined energy of $\hbar\omega_{\mathrm{LO}} = 36$ meV. Second, the effective polar-optical coupling leads to a phonon emission time of the electrons of 240 ± 20 fs [8]. This time constant is longer but in the same order of magnitude as the LO oscillation period of 115 fs. Thus, a substantial part of the dynamics happens in a time regime where memory features are expected. This problem has attracted considerable interest, and a variety of theoretical papers has recently been published [9–13]. The details of the results strongly depend on the specific model used, e.g., on the form of the memory kernel or the inclusion of CC interaction. In the damped memory approach [11], for example, a pronounced initial broadening of the phonon replica is predicted. On the other side, the calculated distributions are very close to the semiclassical case if Coulomb renormalizations are taken into account [13]. Since the different theoretical treatments give conflicting results, experimental informations are highly desirable.

As a phenomenon which has to be described considering non-Markovian effects, ultrafast LO phonon quantum beats have been found in a four-wave mixing experiment investigating the decay of the excitonic interband polarization [14]. Very recently, quasi-instantaneous CC scattering reported at carrier concentrations above 10^{16} cm^{-3} has been attributed to non-Boltzmann kinetics [15].

In this Letter, we provide the first experimental evidence for memory effects and energy nonconserving transitions in the relaxation of hot carrier distributions. We work in a density regime where CP scattering predominates compared to CC interaction [16]. *For the present work, optimum temporal and energetic resolution at the uncertainty limit is required.* Additionally, *spin selectivity is*

exploited to suppress disturbing influences of the light-hole (lh) band.

Free electron-hole pairs are generated, exciting the sample [17] with Gaussian light pulses of a duration of 120 fs and an energetic width of 15 meV. The central photon energy of 1.67 eV is substantially higher than the band-gap energy of 1.52 eV. As a consequence, the carriers initially possess large kinetic energies: Excitation out of the heavy-hole (hh) band yields an electron distribution centered at an excess energy of 135 meV and a hh distribution about 15 meV. For the transition from the lh to the conduction band more similar effective masses lead to initial energies of 90 and 60 meV, respectively. The carrier dynamics is probed with weak pulses of a duration of 25 fs, a spectral width of 70 meV, and a central photon energy of 1.64 eV. Both pump and probe pulses are circularly polarized with a photon spin of $+1$ (σ^+). In GaAs, the hh band belongs to projections of the total angular momentum of $j_z = \pm\frac{3}{2}$, the lh band to $j_z = \pm\frac{1}{2}$, and the conduction band to $s_z = \pm\frac{1}{2}$ [18]. Exciting with σ^+, we generate spin-polarized electrons with opposite projections of s_z for the transitions out of the two valence bands. This spin alignment persists on time scales substantially longer than the range of the present study [19]. Because of the selection rules, the absorption changes seen by the probe essentially originate from the carriers generated involving the hh band. The probe pulses are analyzed in a double monochromator after having passed through the sample. The spectral resolution is set to 6 meV. A two-color Ti:sapphire laser provides perfectly synchronized pulse trains for excitation and probing. Employing a differential lock-in technique for the detection of the transmission changes, the sensitivity of our setup is limited only by the shot noise of the photon current of the probe pulses.

In Fig. 1 we present energy resolved transmission changes $\Delta T/T$ measured at delay times t_D ranging from 0 to 500 fs. The excitation density of 8×10^{14} electron-hole pairs per cm^3 is held low to keep CC scattering inefficient. At $t_D = 0$ fs, a well-pronounced peak (no LO) of increased transmission is seen at a probe photon energy of 1.66 eV. The spectral hole is slightly redshifted with respect to the excitation spectrum (dashed) and an induced absorption appears around a probing energy of 1.68 eV. This phenomenon is related to the excitonic enhancement of the absorption continuum and will be discussed below. At time delays of 40 and 80 fs, a shoulder belonging to the electrons which have emitted one LO phonon arises in the energy range from 1.59 to 1.64 eV. This feature is energetically much broader than the initial bleaching peak, clearly demonstrating that energy does not have to be conserved in the scattering events on such an early time scale. It has to be stressed that *in the Boltzmann limit a distinct minimum between the initial distribution and the phonon satellite should exist at any delay time*. In fact, experimentally this minimum

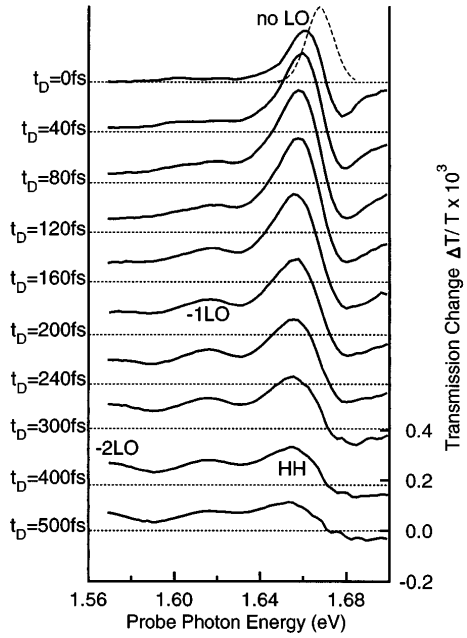

FIG. 1. Spectrally resolved transmission changes $\Delta T/T$ in GaAs (lattice temperature $T_L = 15$ K) measured for different time delays t_D at a carrier density of 8×10^{14} cm^{-3}. The excitation spectrum is shown as a dashed line.

appears beyond $t_D = 100$ fs at an energy of 1.63 eV. Interestingly, the start of this process coincides roughly with the end of the first LO phonon cycle 115 fs after the maximum of the pump pulse. After 200 fs the first replica (-1 LO) at 1.62 eV exhibits a width equal to the original maximum: The system has "remembered" its history. The electrons which initially had experienced collisions without energy conservation have now been transferred to the peak. The driving force of this memory effect is quantum interference working constructively in the center of each replica and destructively outside. However, there is still no well-defined separation between the first and second phonon satellite. At a probing energy of 1.59 eV, a minimum between these two maxima cuts in after approximately 300 fs. This delay corresponds to the formation time of the first replica extended by an additional LO oscillation period. For $t_D = 400$ fs, the second satellite (-2 LO) has also narrowed. Obviously, *the total time elapsed since the original excitation is not the true criterion for memory effects to be observed*: In a cascading process, e.g., the subsequent emission of phonons, *the quantum phenomena repeat themselves*. As a result of the system memory, quantum kinetic features are important on much longer time scales than expected from the uncertainty principle simply by taking into account the energies exchanged.

To work out more clearly the basic physics seen in the experiment, we adopt results from a simplified model which allows, however, an *analytical* solution. Based on the Tomonaga-Luttinger model, Meden *et al.* [20]

recently derived an exact expression for the electron-phonon quantum kinetics in a one-dimensional band structure with linear dispersion. After putting an electron with energy ϵ_0 at time $t = 0$ into the empty system, the distribution f_k evolves according to

$$f_k(t) = \Theta(t)e^{-gt}\delta(\Delta) + \Theta(t)\,e^{-gt}\frac{1}{\pi} \times \int_0^t dz\,\mathrm{Re}\,e^{i\Delta z}(e^{g(t-z)\exp(i\omega_{\mathrm{LO}}z)} - 1) \quad (1)$$

with $\hbar\Delta = \epsilon_k - \epsilon_0$. The excitation peak at $\epsilon_k = \epsilon_0$ decreases exponentially (the CP coupling strength g will be taken as $4\ \mathrm{ps}^{-1}$), and the integral gives the time evolution of the replicas. Initially, a very broad distribution appears, even at energies above the input energy ϵ_0, underlining the lack of energy conservation. At least one LO cycle of integration time is necessary for the double exponent to sharpen into a maximum at $\epsilon_0 - \hbar\omega_{\mathrm{LO}}$, and even longer times are needed for the subsequent replicas to be formed. Compared with approximate calculations in more realistic band structures [21], *we find the 1D linear model to be well justified as long as the carriers do not reach the bottom of the band*. To model the experimental conditions, we convolute Eq. (1) with the spectral and temporal width of the excitation pulse.

We now discuss the phenomena involved in the ultrafast probing process: In a first approximation, carrier distributions can be extracted directly from the spectrally resolved transmission $T(\omega)$ of a probe pulse,

$$T(\omega) \sim \exp[\alpha_0(1 - f_{ke} - f_{kh})d], \qquad \epsilon_{ke} + \epsilon_{kh} = \hbar\omega\,. \quad (2)$$

A peak in the distribution function would give rise to a similar peak in the differential transmission spectrum. However, a dispersive feature is seen at the excitation frequency in the experiment, Fig. 1. This difference comes from the Coulomb interaction left out in the free-particle absorption of Eq. (2). The transmission change induced by nonthermal carriers has two components: phase space occupation of the free electron-hole transitions and many-body corrections due to the Coulomb interaction [22,23].

For a time-resolved experiment, it is appropriate to calculate the interband polarization $P_k(t)$ driven by the probe field $E_p(t)$ from

$$i\hbar\partial_t P_k(t) = \Big(\epsilon_{ke} + \epsilon_{kh} - i\gamma - \sum_{k'} v_{k-k'}F_{k'}(t)\Big)P_k(t) - [1 - F_k(t)]\Big\{\mu E_p(t) + \sum_{k'} v_{k-k'}P_{k'}(t)\Big\} \quad (3)$$

with $F_k = f_{ke} + f_{kh}$ and the interband dipole μ. This equation has been derived from the semiconductor Bloch equations [24] which include the Coulomb interaction $v_{k-k'}$. The coherent coupling between pump and probe is neglected, and the CP effect on the polarization is simplified as a homogeneous dephasing $\gamma = g/2$. We integrate Eq. (3) by inserting a Gaussian probe pulse with time delay t_D and the time-dependent distribution function for the electrons, Eq. (1). The transmitted spectrum follows from a Fourier transform of $\sum_{\mathbf{k}} P_{\mathbf{k}}(t)$. The numerical method in [25] has been refined for a reliable description of the excitonic continuum high in the band.

Our calculations show that the band-gap renormalization [sum in the first line of Eq. (3)] gives rise to a small and unstructured decrease in transmission. The fingerprint of the distribution function comes in through the Pauli blocking term $1 - F_k(t)$. If only the probe field were present, this component could be observed with the temporal resolution given by the pulse duration. However, the polarization enters via the Coulomb interaction, and it is the effective field P_{eff} [curly bracket in Eq. (3)] which sets the time window for probing. The inset of Fig. 2 displays P_{eff} for k corresponding to the transition at 1.67 eV: Compared to $E_p(t)$, the effective field exhibits only a small tail extending to later times. Although the individual polarization components $P_{k'}$ persist longer (of the order of $1/\gamma$), destructive interference works when summing over k', resulting in a shape of $P_{\mathrm{eff}}(t)$ similar to the probe field (nearly adiabatic following). Therefore, the Coulomb effects do not spoil the resolution of the probing process.

The transmission changes simulated via Eqs. (1) and (3) are depicted in Figs. 2(a)–2(c) for three selected time delays (thick lines). In excellent agreement with the experiment, no minimum between the unrelaxed maximum

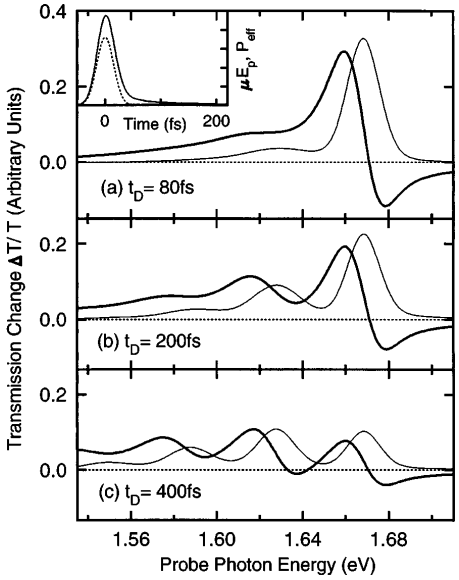

FIG. 2. (a)–(c) Calculated transmission changes $\Delta T/T$ for three delay times t_D. The thick lines are obtained including Coulomb effects, whereas the results for a noninteracting model are drawn thin. Inset: effective field amplitude (full line) compared with the driving probe field (dotted line).

and the first phonon replica is seen at a delay time of 80 fs [Fig. 2(a)]. After 200 fs [Fig. 2(b)], the first satellite has narrowed substantially giving rise to a dip at a probing energy of 1.63 eV. As seen in the experiment, the first and second phonon replica are not yet separated. For a time delay of 400 fs [Fig. 2(c)], a minimum is obtained at 1.59 eV. The astonishing success of the 1D linear calculation with its exact treatment of the memory features has important consequences: Since the present day 3D parabolic models seem to either underestimate or overestimate the quantum kinetic effects we see experimentally, an improved treatment of the system memory appears to be the crucial point in future simulations. The Coulomb contributions to the transmission changes are also reproduced quantitatively: The bleaching peaks are redshifted by approximately 10 meV with respect to the position expected in a noninteracting system and an induced absorption around 1.68 eV is calculated. The spectra obtained neglecting Coulomb effects are shown as thin lines. These curves reflect the underlying electron distributions. We note that the distance of the peaks in Figs. 1 and 2 is larger than $\hbar\omega_{\mathrm{LO}}$: The hh dispersion results in a stretching factor of $1 + m_e/m_{\mathrm{hh}}$ since the interband transition is probed.

Slight differences between experiment and simulation are explained by two points missing in our present model: (i) For the probing process the decay of the interband polarization is taken into account phenomenologically, and coherent effects during the excitation pulse are neglected. Together, these details lead to an underestimation of the widths of the bleaching maxima by our calculation [5]. (ii) Even at the late delay times of 400 and 500 fs in Fig. 1, the initial peak (HH) remains the most prominent maximum in the spectra: The heavy holes generated in our experiment are below the threshold for LO emission. They provide an almost constant, slowly broadening contribution to the bleaching at 1.66 eV [26].

In conclusion, we have presented experimental proof of influences of quantum kinetic effects in the relaxation of hot carriers scattering with the crystal lattice. Strict energy conservation is seen to be violated and memory features are found. Generally, we expect such effects to play a dominant role in many dynamical systems whenever *transition rates* are of the same order of magnitude or even faster than the *oscillation frequencies* of the energy quanta involved.

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