Subthreshold Carrier-LO Phonon Dynamics in Semiconductors with Intermediate Polaron Coupling: A Purely Quantum Kinetic Relaxation Channel

M. Betz,[1] G. Göger,[1] A. Laubereau,[1] P. Gartner,[2,3] L. Bányai,[2] H. Haug,[2]
K. Ortner,[4] C. R. Becker,[4] and A. Leitenstorfer[1]

[1]*Physik-Department E11, Technische Universität München, D-85748 Garching, Germany*
[2]*Institut für theoretische Physik, J. W. Goethe Universität, D-60054 Frankfurt am Main, Germany*
[3]*National Institute for Physics of Materials, Bucharest, Romania*
[4]*Physikalisches Institut, Universität Würzburg, D-97074 Würzburg, Germany*

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Femtosecond transmission spectra of highly polar CdTe are compared to more covalent GaAs contrasting semiclassical kinetics with two-time quantum kinetics based on the Dyson equation. Nonequilibrium heavy holes in CdTe show ultrafast energy redistribution via the Fröhlich mechanism even if photoexcited below the LO phonon energy. This subthreshold relaxation is a genuine quantum kinetic effect. It gains importance if the polaron self-energy is comparable to the phonon energy. Conservation of the free-particle energies is not required under these conditions.

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In recent years, several classes of semiconductors have obtained special attention as promising candidates for new applications: (i) The III-V nitrides have led to short-wavelength laser diodes [1] and bear large potential for high-speed electronics at elevated power levels and temperatures. (ii) II-VI compounds are currently receiving renewed interest due to their importance for future spintronics [2]. (iii) Organic semiconductors are opening up completely new perspectives such as superconducting field-effect transistors [3]. A common feature of these materials is their relatively high degree of ionicity compared to the well-established AlGaAs/InP family used in most high-frequency and optoelectronic devices. Accordingly, the polar-optical Fröhlich interaction of charge carriers with longitudinal-optical (LO) phonons is significantly stronger. This scattering mechanism is of central importance for the transport and optical properties of polar semiconductors. The coupling strength of LO phonon scattering for a carrier with effective mass m^* may be characterized by the dimensionless polaron coupling constant $\alpha = \frac{e^2}{\hbar}(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0})(\frac{m^*}{2\hbar\omega_{\mathrm{LO}}})^{1/2}$ which determines the ratio between the polaron self-energy and the LO phonon energy $\hbar\omega_{\mathrm{LO}}$. Electrons in the Γ valley of GaAs represent a typical example for weak Fröhlich interaction with $\alpha \ll 1$. In contrast, electrons at the bottom of the conduction band in GaN ($\alpha = 0.49$) or ZnS ($\alpha = 0.73$) fall into the so-called intermediate coupling regime where α is in the order of unity.

The most direct access to electron-phonon dynamics is provided by ultrafast optical spectroscopy [4]. Traditionally, the femtosecond kinetics of hot carriers has been treated theoretically relying on the semiclassical Boltzmann picture with instantaneous scattering events. In four-wave mixing experiments, a phenomenon which requires a quantum kinetic description [5] has been found: LO phonon quantum beats in the decay of the excitonic interband polarization [6–9]. Information on the time dependence of the energy distribution of nonequilibrium carriers interacting with phonons is gained in femtosecond transmission measurements [10]. In GaAs, scattering events without energy conservation and with memory effects have been observed for highly energetic electrons which emit LO phonons [11]. Quantum kinetic calculations agree with the experiment [12–15].

In this Letter, we demonstrate that the dynamics of nonequilibrium carriers for intermediate electron-phonon coupling exhibits qualitatively new and important features which are completely unexpected in semiclassical physics and may be understood only on the sophisticated level of quantum kinetic theories. The most striking result is that carriers injected below the one-LO phonon threshold still experience significant relaxation if the Fröhlich coupling is strong enough. The theoretical analysis of our experimental data in the intermediate coupling region is difficult since neither the perturbational approaches valid for $\alpha \ll 1$ nor the small polaron model ($\alpha \gg 1$) is expected to produce reliable results. In the equilibrium theory the intermediate-coupling polaron has been treated by unitary transformations and variational calculations [16]. We choose the direct II-VI material CdTe as a model substance for intermediate Fröhlich interaction: Electrons at the minimum of the conduction band ($m_e^* = 0.09m_0$) exhibit a polaron constant of $\alpha_e = 0.33$. Because of their larger effective mass (as in GaAs, $m_{hh}^*/m_e^* \approx 10$ in CdTe), the heavy holes are even more strongly coupled with $\alpha_{hh} \approx 1$. The band gap energy of CdTe is $E_g = 1.60$ eV at low temperatures and $\hbar\omega_{\mathrm{LO}} = 21$ meV. The results are directly compared to analogous investigations in GaAs where $E_g = 1.52$ eV, $m_e^* = 0.067m_0$, $\hbar\omega_{\mathrm{LO}} = 36$ meV, $\alpha_e = 0.06$, and $\alpha_{hh} \approx 0.15$.

In the experiments, we create unbound electron-hole pairs with Gaussian light pulses (durations specified below) of a central photon energy above E_g. The samples are epitaxial layers of high-purity CdTe and GaAs of a

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thickness of $d = 370$ nm and 500 nm, respectively. They are antireflection coated on both sides, glued to transparent substrates, and mounted inside a He cryostate.

In order to gain insight into the dynamics of the photoexcited carrier distributions, we measure the pump induced transmission changes with a time delayed probe pulse of a duration of 15 fs and a bandwidth of 100 meV. The test pulse is spectrally dispersed with a double monochromator (spectral resolution set to 4 meV) after transmission through the sample.

Differential transmission spectra (DTS) for various delay times t_D were measured at a photoexcited electron-hole density of 4×10^{14} cm^{-3} with cross-linearly polarized pump and probe beams in GaAs (left column of Fig. 1) and CdTe (right column of Fig. 1). The excitation density is kept low to suppress carrier-carrier scattering [17]. A lattice temperature of 4.5 K ensures very slow scattering of carriers with acoustic phonons on a time scale of 10 ps. Consequently, the polar-optical interaction with LO phonons is by far the dominant relaxation mechanism in the subpicosecond regime. The kinetic energy of the excited carriers is determined by the excess energy of the photons and the ratio of the effective masses in the valence and conduction bands. Exciting GaAs with an 80 fs pulse at 1.65 eV results in a heavy-hole (hh) distribution centered at a kinetic energy of 18 meV which is smaller than $\hbar\omega_{\mathrm{LO}}$, i.e., no scattering with LO phonons is expected. In contrast, the electrons are created with an excess energy of 112 meV and allowed to transfer energy to the crystal lattice via rapid emission of LO phonons [10,11]. At $t_D = 50$ fs in GaAs, a signature of the nonthermal carrier distribution appears near the excitation energy. An additional transmission maximum at a probe photon energy of 1.59 eV is connected to electrons excited from the light hole (lh) band. For a delay of $t_D = 500$ fs, i.e., after twice the electron-LO phonon emission time of approximately 240 fs in GaAs [10,17], most of the electrons have relaxed towards the minimum of the Γ valley, inducing a transmission increase below a probe photon energy of 1.55 eV. A well-resolved bleaching peak due to the generated heavy holes remains at 1.63 eV (indicated by hh in Fig. 1). As late as 700 fs after excitation the increased transmission associated with the hh distribution is still clearly visible in GaAs.

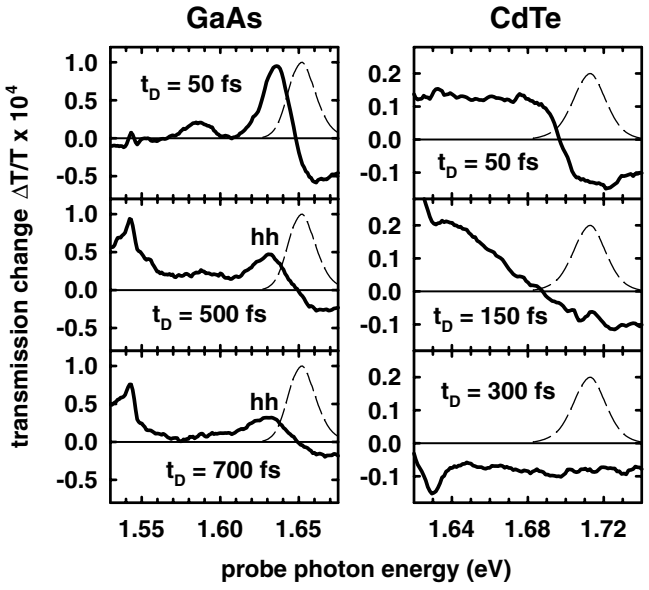

FIG. 1. Spectrally resolved transmission changes $\Delta T/T$ in GaAs (left) and CdTe (right) for various delay times t_D at a carrier density of 4×10^{14} cm^{-3} and $T_L = 4.5$ K. The excitation spectra are shown as dashed lines.

In strong contrast to GaAs, no analogous signature of a hh distribution is found in CdTe (right column of Fig. 1): Excitation with an 80 fs pulse centered at 1.71 eV generates heavy holes with an average kinetic energy of 12 meV. In the semiclassical picture of carrier relaxation the hh distribution should therefore behave similarly as in GaAs. However, at a delay time of $t_D = 150$ fs, approximately twice the electron-LO phonon emission time of 70 fs in CdTe [17], no bleaching peak is observed close to the excitation energy. 300 fs after excitation, the spectrum high in the absorption continuum is essentially flat. The negative background is related to the renormalization of the fundamental band-gap energy by the pump generated carriers. Apparently, the distribution of heavy holes in CdTe relaxes on a time scale comparable to the electrons even though real emission of LO phonons should be energetically impossible. Nevertheless, the surprisingly fast dynamics can be related only to the increased polaron coupling in CdTe since all other parameters are very similar in GaAs.

To analyze our observation of the missing bleaching signature due to heavy holes in CdTe and to illuminate the physical origin of this phenomenon, we have performed extensive theoretical studies. Since the simulations are based on a two-band model taking into account the hh and conduction bands, the calculations are compared to DTS recorded with cocircularly polarized pump and probe pulses. In this geometry the influence of the lh band on the measured transmission changes is minimized [11]. Interband transitions are excited in CdTe with a pump pulse of a duration of 100 fs at 1.72 eV. As a result, we expect an initial electron distribution at 107 meV and a hh distribution around 13 meV. The excitation bandwidth of 16 meV is smaller than $\hbar\omega_{\mathrm{LO}}$. Energy resolved transmission changes $\Delta T/T$ measured after excitation of 1.3×10^{15} electron-hole pairs per cm^3 are shown in Fig. 2(a).

In the theoretical treatment we consider a quantum kinetic approach based on the Keldysh Green functions (GF's) with two time arguments. The photoexcited electrons and holes interact with LO phonons. Coulomb collisions between carriers are neglected in this low density regime, but the exciton and excitonic enhancement are included through the Hartree-Fock (HF) approximation. The Dyson equation for the nonequilibrium GF's (see Ref. [5] for a detailed presentation) in general matrix notation

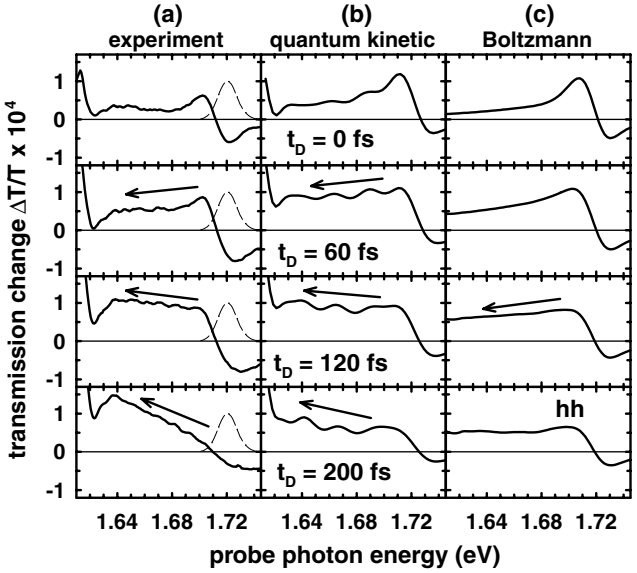

FIG. 2. Differential transmission spectra in CdTe for various delay times t_D at a carrier density of 1.3×10^{15} cm^{-3} (a) as measured at $T_L = 3$ K, (b) calculated in a fully two-time dependent quantum kinetic theory, and (c) obtained via the semiclassical kinetics.

including band-index, momentum, and time indices as well as Keldysh time-contour integrations is $G = G_0 + G_0 \Sigma G$, where G_0 is the free-particle propagator. The self-energy Σ contains instantaneous HF and optical field terms as well as a phonon interaction part, $\Sigma_{\vec{k}}(t,t') = \imath\hbar \sum_{\vec{q}} g_{\vec{q}}^2 D_{\vec{q}}(t - t') G_{\vec{k}-\vec{q}}(t,t')$.

The phonons are taken to be in equilibrium and the coupling constant is related to the Fröhlich constant α of electrons or holes via $g_{\vec{q}}^2 = \alpha \frac{4\pi\hbar(\hbar\omega_{\mathrm{LO}})^{3/2}}{(2m^*)^{1/2} q^2 V}$. In a previous publication [18] we have developed a straightforward procedure to solve these equations numerically. Our solution for $0.1 < \alpha < 1$ predicted important deviations from the earlier one-time approximations. Vertex corrections are not included, because they are reduced by extra time integrations over short time intervals. For equilibrium this was checked numerically to hold in the relevant time range for intermediate couplings [19]. We take into account delayed optical test and pump pulses where the coordinate dependence is implemented parametrically through the abstract phases $\phi_P = \vec{k}_P \vec{x}$ and $\phi_T = \vec{k}_T \vec{x}$ in order to distinguish the fields (as in Refs. [6,13]). The interband polarization is related to the Green functions by $p(t) = \sum_{\vec{k}} G^<_{\vec{k},cv}(t,t)$ and its part propagating in the test direction is defined by $p(t)_T = \frac{1}{2\pi} \int_0^{2\pi} d\phi_T \, e^{-\imath\phi_T} p(t;\phi_T)$. The absorption coefficient of the test pulse is $\alpha(\omega) = \frac{4\pi\omega_T}{c} \mathrm{Im} \frac{p_T(\omega)}{\mathcal{E}_T(\omega)}$ with $p_T(\omega) = \int dt \, e^{\imath\omega t} p_T(t)$. The electron and hole populations may also be expressed through the Green functions by $f_{\vec{k}}^e(t) = -\imath\hbar G^<_{\vec{k},cc}(t,t)$ and $f_{\vec{k}}^h(t) = 1 + \imath\hbar G^<_{\vec{k},vv}(t,t)$.

Numerical calculations are performed for the parameters of CdTe and GaAs at $T_L = 3$ K. The bare band gap used in the theory was deduced from the experimental gap by taking into account the calculated equilibrium polaron shift. This correction is important in CdTe.

As may be seen from Figs. 2(a) and 2(b) the most important common feature of the experimental and the quantum kinetic results is a reversal of the slope of the DTS between $t_D = 60$ and 200 fs, as indicated by the arrows. This is a new feature absent for low LO phonon coupling as in GaAs, which is dominated by the phonon replicas in the electron distribution and a stationary bleaching peak due to the hole population [11,13].

To demonstrate the quantum kinetic origin of our findings in CdTe a comparison is made with a simplified, semiclassical theory based on the semiconductor Bloch equation (with HF effects). Conventional Boltzmann collision terms are assumed for LO phonon assisted transitions of the populations, according to Fermi's golden rule. For the polarization a phenomenological dephasing time of $T_2 = 120$ fs is adopted. Because of the strict energy conservation the heavy holes cannot relax. The results are shown in Fig. 2(c): In contrast to the experiment and the quantum kinetic simulation [Figs. 2(a) and 2(b)], the semiclassically calculated DTS spectra never reverse slope and a transmission maximum induced by the heavy holes [see Fig. 2(c)] remains prominent at $t_D = 200$ fs.

The hh energy distributions computed with the two-time quantum kinetics (thick lines) and the semiclassical Boltzmann kinetics (thin lines) are depicted in Fig. 3 for GaAs (left column) and CdTe (right column). In GaAs, both models result in practically identical hh populations for all delay times. A strongly peaked distribution is conserved on a subpicosecond time scale. In contrast, the populations obtained with the Dyson equation for CdTe show a significant relaxation of the holes, resulting in a broad background already after a time delay t_D as short as 60 fs. Even at a delay time of $t_D = 200$ fs the background component in CdTe experiences further relaxation indicating that the phenomenon is not linked exclusively to the energy uncertainty during the ultrafast carrier generation process. These effects are purely quantum kinetic in nature: If the subthreshold hole dynamics in CdTe is simulated semiclassically (thin lines in the right column of Fig. 3), the distribution functions undergo no relaxation.

In order to check that the quantum kinetic features in the DTS originate alone from the modification of the hole distribution, we introduced the pump generated populations obtained with the Dyson equation directly into the simplified Bloch equation for the polarization. As in the fully quantum kinetic treatment, the DTS reverses its slope at the same delay time as in the experiment.

To understand the unexpected dynamics of the heavy holes, one has to take into account the fact that within the two-time quantum kinetics with a stronger coupling constant the energy of the free particles is no longer conserved. The interaction energy plays an important role and allows transitions that are forbidden in the Boltzmann picture. This nonconservation is related to the finite lifetime of the

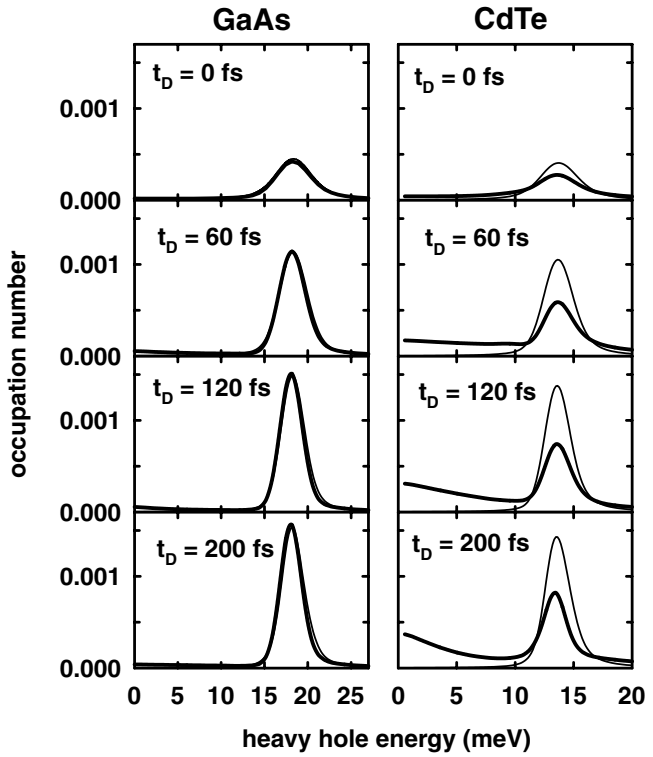

FIG. 3. Heavy-hole energy distributions in GaAs (left) and CdTe (right), as calculated in the two-time quantum kinetic simulation based on the Dyson equation (thick lines) and with the semiconductor Bloch equations including Boltzmann scattering terms (thin lines) for various delay times t_D.

states and increases with the strength of the interaction. The unusual broadening of the hole distribution may also be interpreted as the buildup of a polaronic state [20].

In the measured DTS [Fig. 2(a)] a sharp maximum at 1.609 eV (one LO energy above a strong exciton bleaching at 1.588 eV) and a transmission minimum at 1.615 eV are found. These features result from a combination of excitonic nonlinearities and polaron effects. Their position and shape is reproduced by the quantum kinetics [Fig. 2(b)]. In contrast, only a shift of the band edge and the exciton (not shown) appears in the DTS calculated via the Boltzmann equation while the structure in the absorption continuum is absent [Fig. 2(c)].

At intermediate electron-phonon coupling, the phonon replicas of the electron distribution in the DTS are smeared out [Fig. 2(a)]. This effect is well understood as a result of time-energy uncertainty in the generation process [21] and is reproduced also in the framework of the simplified Boltzmann kinetics [Fig. 2(c)]. In the full quantum kinetic calculations [Fig. 2(b)] one still sees a trace of the phonon satellite structure which is not resolved in the experiment. Possible explanations for this slight discrepancy are spurious contributions due to the light holes as well as the anisotropy of the hh band which are not included in the simulations.

In conclusion, we have found an ultrafast dynamics of low-energy heavy holes interacting with unoccupied polar-optical modes in CdTe. A theoretical description of the subthreshold scattering calls for a sophisticated quantum kinetic treatment beyond the Kadanoff-Baym ansatz. This phenomenon represents a typical many-body effect: The free-particle energy ceases to be a constant of motion in systems where the coupling between electronic and lattice degrees of freedom can no longer be regarded as a weak perturbation.

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