Hot-phonon effects in photo-excited wide-bandgap semiconductors

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Abstract
Carrier and lattice relaxation after optical excitation is simulated for the prototypical wide-bandgap semiconductors CuI and ZnO. Transient temperature dynamics of electrons, holes as well as longitudinal-optic (LO), transverse-optic (TO) and acoustic phonons are distinguished. Carrier-LO-phonon interaction constitutes the dominant energy-loss channel as expected for polar semiconductors and hot-phonon effects are observed for strong optical excitation. Our results support the findings of recent time-resolved optical spectroscopy experiments.

Keywords: semiconductors, hot carriers, carrier relaxation, hot-phonon effect, time-resolved optical spectroscopy

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

1. Introduction

The investigation of charge carrier dynamics on ultrashort time scales in photo-excited semiconductors is often complicated due to several competing processes [1]. Then, numerical simulations can provide deeper insights in the underlying physical mechanisms and improve our understanding of time-resolved experiments. Various models describing the transient relaxation of charge carriers via different scattering processes to the lattice were reported in the last decades [2–9]. In general, above-bandgap optical excitation of semiconductors creates electron–hole pairs with excess energy according to their effective mass [10]. The excess energy is transferred via various scattering processes to the lattice (phonons) [11]. This transient relaxation is characterized by quasi-temperatures $T$ and chemical potentials $\mu$ that determine the corresponding Fermi–Dirac (carriers) and Bose–Einstein distributions (phonons), respectively [3, 12]. Often, only two temperatures (carriers and phonons) are employed which neglects their spectral dispersion, but consideration of different phonon branches is mandatory for a useful physical description [8, 9]. Modeling electrons and holes with a common temperature effectively underestimates (overestimates) the carrier type of the lower (higher) effective mass [13]. A physics-based, analytical description of the transient relaxation processes—in contrast to Monte-Carlo solutions of Boltzmann-transport equations [14, 15]—is provided by the non-equilibrium statistical operator approach (NSO) [5, 16].

In this work, we will employ an NSO-based relaxation model from the literature to simulate the transient carrier and lattice relaxation in the prototypical wide-bandgap semiconductors CuI [17] and ZnO [18] after pulsed optical excitation for various excitation conditions. We will compare our results to recent experimental findings of time-resolved photoluminescence spectroscopy and spectroscopic ellipsometry measurements on the aforementioned materials.

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2. Computational model

Description. The relaxation model reported by Maia et al [13] is an NSO-based method, which distinguishes between electrons and holes and contains longitudinal-optic (LO), transverse-optic (TO) and acoustic phonon branches. The greatest benefit of this model is its mathematical simplicity: only first-order ordinary differential equations (ODE) and no integrals are involved while still distinguishing between electrons and holes as well as three different phonon branches. The model equations are given below where we use SI units throughout the manuscript. We corrected a few typographical errors mostly found by dimensional analysis. The original model equations and the description of our corrections are described in the supplementary material (https://stacks.iop.org/JPCM/33/205701/mmedia). Chemical potentials are neglected such that changes of the carrier density by recombination and alike processes cannot be taken into account [19]. Carrier and phonons are coupled to a thermal bath at constant temperature $T_b$. All temperatures $T_i$ are connected to corresponding coldness functions $\beta_i = 1/(k_B T_i)$.

\[
\frac{d\beta}{dr} = -\frac{2}{3} \varepsilon_\text{sc}^\text{DP} \left[ E_{\text{e},\text{AC}}(t) + E_{\text{LO}}(t) + E_{\text{AC}}^\text{DP}(t) \right],
\]

\[
\frac{d\beta}{dr} = -\frac{2}{3} \varepsilon_\text{sc}^\text{PP} \left[ E_{\text{h},\text{AC}}(t) + E_{\text{LO}}(t) + E_{\text{AC}}^\text{PP}(t) \right]
+ E_{\text{h},\text{LO}}^\text{DP}(t) + E_{\text{h},\text{AC}}^\text{PP}(t),
\]

\[
\frac{d\beta_{\text{AC}}}{dr} = n V_c \varepsilon_\text{AC}^\text{DP} \left[ E_{\text{e},\text{AC}}(t) + E_{\text{h},\text{AC}}^\text{PP}(t) + E_{\text{AC}}^\text{DP}(t) \right]
+ E_{\text{AC},\text{LO}}^\text{AN}(t) + E_{\text{AC},\text{TO}}^\text{AN}(t)
- E_{\text{AC},\text{lat}}^\text{AN}(t),
\]

\[
\frac{d\beta_{\text{TO}}}{dr} = 2 n V_c \left[ \varepsilon_\text{TO} \left( E_{\text{TO}}(t) \right)^2 \right]^\frac{1}{2} \left[ E_{\text{TO}}(t) - E_{\text{AC},\text{TO}}^\text{AN}(t) \right].
\]

We define, $n$ the excited carrier density, $V_c$ the unit cell volume, $E_{\alpha}$ the phonon energies corresponding to $\gamma = \text{LO, TO, } E_{\text{ac},\text{AC}(t)}$ and $E_{\text{ac},\text{PP}(t)}$ are dissipation terms due to the scattering of carriers $\alpha$ ($\alpha$ = electron, hole, acoustic phonons (AC) via the deformation potential (DP) and the piezoelectric potential (PZ) [20] defined as

\[
E_{\text{AC},\text{AC}}^\text{PP}(t) = \theta_{\text{AC}} \left( \frac{2^{7/2}(C_{\text{AC}}^\text{DP})^2 m_{\text{ac}}^{3/2}}{\pi^3/2 \hbar^2 \rho} \right) \beta_{\alpha}^{3/2} \left[ \frac{\beta_{\alpha}}{\beta_{\text{AC}}} - 1 \right],
\]

\[
E_{\text{AC},\text{AC}}^\text{PP}(t) = \theta_{\text{AC}} \left( \frac{2^{1/2}(C_{\text{AC}}^\text{PZ})^2 m_{\text{ac}}^{3/2}}{\pi^3/2 \hbar^2 \varepsilon_\text{pp}^2 \rho} \right) \beta_{\alpha}^{1/2} \left[ \frac{\beta_{\alpha}}{\beta_{\text{AC}}} - 1 \right].
\]

$\theta_{\text{AC}}$ is the degeneracy of the AC-phonon mode, $C_{\text{AC}}^\text{DP}(C_{\text{AC}}^\text{PZ})$ are the DP (PZ) coupling constant, $\varepsilon_\text{pp}$ is the static dielectric constant, $e$ is the base unit of charge, $\rho$ mass density and $m_{\alpha}$ effective carrier mass.

The dissipation terms $E_{\text{LO}}^\text{AC,TO}(t)$ and $E_{\text{LO}}^\text{AC,TO}(t)$ result from carrier-longitudinal-optical-phonon (Fröhlich FR [21]) interaction and the electron–optical-phonon deformation-potential interaction (DP) [20] defined as

\[
E_{\text{LO}}^\text{AC,TO}(t) = \theta_{\text{LO}} \left( \frac{\varepsilon_\text{LO}^2 E_{\text{LO}}(t)^2}{(2\pi)^3/2 \hbar^2 \rho} \right) \left[ \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_1} \right]
\times \beta_{\alpha}^{1/2} \exp(-x_{\alpha,\text{LO}}) \left[ \frac{\nu_{\text{LO}}}{\nu_{\text{LO},\text{TO}}} - 1 \right] K_0(x_{\alpha,\text{LO}}),
\]

\[
E_{\text{LO}}^\text{AC,TO}(t) = \theta_{\text{LO,TO}} \left( \frac{\hbar \nu_{\text{LO,TO}} E_{\text{LO}}^\text{DP}(t)^2 m_{\alpha}^{3/2}}{2^{1/2}(2\pi)^3/2 \hbar^2 \rho} \right)
\times \beta_{\alpha}^{1/2} \exp(-x_{\alpha,\text{LO,TO}}) \left[ \frac{\nu_{\text{LO}}}{\nu_{\text{LO,TO}}} - 1 \right] K_1(x_{\alpha,\text{LO,TO}}).
\]

$\theta_{\text{LO,TO}}$ is the degeneracy of the longitudinal LO (transversal TO) optic phonon-mode whose energy $\hbar \omega_{\text{LO,TO}}$ is assumed to be constant. $C_{\text{LO,TO}}^\text{AC,TO}$ is the electron–optical-phonon deformation-potential coupling constant, $K_i$ are modified Bessel functions of second type and order $i$ [22] and $\varepsilon_\infty$ is the usual dielectric constant above phonon and below band-gap absorption.

Additional definitions comprise

\[
\nu_{\gamma} = \left[ \exp(\beta_{\gamma} \hbar \omega_{\gamma}) - 1 \right]^{-1},
\]

\[
\nu_{\gamma,\text{LO,TO}} = \left[ \exp(\beta_{\gamma} \hbar \omega_{\text{LO,TO}}) - 1 \right]^{-1},
\]

\[
\nu_{\text{AC,LO,TO}} = \left[ \exp(\beta_{\alpha} \hbar \omega_{\text{LO,TO}}) - 1 \right]^{-1},
\]

\[
x_{\alpha,\text{LO,TO}} = \frac{1}{2} \beta_{\alpha} \hbar \omega_{\text{LO,TO}},
\]

where $\eta$ stands for LO, TO and AC phonons. Anharmonic interactions (AN) of acoustic and optical phonons $E_{\text{AN,AN,TO}}^\text{AC,TO}$ and the final dissipation of energy to the thermal bath $E_{\text{AN,AN,TO}}^\text{AC,TO}$ are defined in the relaxation-time approximation

\[
E_{\text{AN,AN,TO}}^\text{AC,TO} = \frac{n V_c}{n V_c} \left( \frac{\nu_{\text{AC}} - \nu_{\text{AC,TO}}}{\tau_{\text{TO}}} \right),
\]

\[
E_{\text{AN,AN,TO}}^\text{AC,TO} = \frac{1}{n V_c} \left( \beta_{\text{AC}}^{-1} - \beta_{\text{AC}}^{-1} \right) .
\]

The phenomenological relaxation times $\tau_{\text{TO}}$ can be estimated from Raman linewidths, whereas $\tau_{\text{AC}}$ comprises ambipolar diffusion and the surface dimensions of the system. We set empirically $\tau_{\text{AC}} = 1$ ns for all simulations in accordance with the literature [1, 13].

This model assumes thermalization among electrons and holes individually, which means that previous scattering events led to Fermi–Dirac distribution of the carriers in the conduction and valence band, respectively [11]. This thermalization is completed after approximately few 100 fs after optical excitation [1, 11].
The system of coupled ODE is implemented and solved in ‘MATLAB®’ using the ode15s solver [23]. The initial conditions for the model validation are tabulated in table 1 and the material constants are provided in table 2. The relative error of each β, which is a constraint passed to the ODE solver, is 10⁻⁶.

**Validation.** The computer implementation of the relaxation model is validated using the simulation data of reference [13], which models hot-carrier relaxation experiments from the literature [24–26]. We digitize the plots with the reference simulation data and compare them to our model data. The initial conditions are provided in table 1, the material constants in table 2. We find excellent agreement with the data corresponding to the experiments of Shank et al [24, 25] shown in the top and middle row of figure 1 employing the modifications to the original formulas as discussed before. Only qualitative agreement is found with the experiment of Seymour et al [26] (figure 1 bottom row). Especially the transient hole temperature is not reproduced, which is likely related to the wrong initial LO-phonon temperature $T_{LO}^{AC} = 300$ K in reference [13]. It should rather be $T_{LO}^{AC} = 650$ K as given in references [3, 27]. Furthermore, we set the relaxation time $\tau_{AC}$ is 1 ps. However, such a small value for the final energy dissipation to the lattice is not expected [1]. We assume our model implementation to be still valid for our calculations for CuI and ZnO where the initial LO-phonon temperature is approximately equal to the thermal bath.

### Table 1. Initial conditions used in the model validation for the experiments on GaAs [24–26] for the solution of the system of coupled ODE (1) to (5).

| Parameter                        | Shank et al [24] | Shank et al [25] | Seymour et al [26] |
|----------------------------------|------------------|------------------|-------------------|
| Carrier density $n$ (m⁻³)        | $1 \times 10^{25}$ | $2 \times 10^{24}$ | $1 \times 10^{26}$ |
| Electron temperature $T_{el}$ (K) | 9800             | 6700             | 1300              |
| Hole temperature $T_{h}$ (K)     | 1333             | 911              | $300$ [13] $650$ [3, 27] |
| LO temperature $T_{LO}$ (K)      | 303              | 303              | 303               |
| TO temperature $T_{TO}$ (K)      | 303              | 303              | 303               |
| AC temperature $T_{AC}$ (K)      | 300              | 300              | 300               |
| Bath temperature $T_{bath}$ (K)  | 300              | 300              | 300               |
| Relaxation time $\tau_{AC}$ (ns) | 1                | 1                | $10^{-3}$         |
| Relaxation time $\tau_{LO,TO}$ (ps) | 10              | 10               | 7                 |

### Table 2. Material parameters for GaAs, CuI and ZnO. Furthermore, we used the basic unit of electric charge $e = 1.602 \times 10^{-19}$ As, Boltzmann constant $k_B = 1.38 \times 10^{-23}$ J K⁻¹, reduced Planck constant $\hbar = 1.054 \times 10^{-34}$ J s, electron rest mass $m_0 = 9.109 \times 10^{-31}$ kg and vacuum permittivity $\varepsilon_0 = 8.854 \times 10^{-12}$ As Vm⁻¹.

| Parameter                        | Unit | GaAs | CuI | ZnO |
|----------------------------------|------|------|-----|-----|
| Mass density $\rho$              | kg m⁻³ | 5310 | 5670 | 5606 |
| Volume unit cell $V_{cell}$       | 10⁻²⁸ m³ | 1.8 | 2.2 | 17 |
| Effective electron mass $m_e$     | μm   | 0.068 | 0.30 | 0.24 |
| Effective hole mass $m_h$         | μm   | 0.50 | 3.4a | 0.30 |
| High-frequency dielectric constant $\varepsilon_\infty$ | 12 | 5 | 31 | 3.70 |
| Static dielectric constant $\varepsilon_s$ | 11 | 7.8b | 7.77 | |
| LO-phonon energy $E_{LO}$         | meV  | 37   | 20  | 33  |
| TO-phonon energy $E_{TO}$         | meV  | 33   | 16c | 33  |
| Relaxation time to thermal bath $\tau_{AC}$ | ps | 1   | 13c | 18a |
| LO-phonon anharmonic-decay time $\tau_{LO}$ | ps | $10/10^{7}e$ | $10^{7}e$ | $10^{7}e$ |
| TO-phonon anharmonic-decay time $\tau_{TO}$ | ps | $10^{7}e$ | $10^{7}e$ | $10^{7}e$ |
| Electron–acoustic-phonon def. pot. $C_{DP,AC}^{\infty}$ | eV | 7 | 36 | 6 |
| Hole–acoustic-phonon def. pot. $C_{DP,bAC}^{\infty}$ | eV | 3.5 | 36 | 37 |
| Piezoelectric pot. $C_{DP}^{\infty}$ | C m⁻² | 0.16 | 0.127 | 0.85f |
| Hole–LO-phonon def. pot. $C_{DP,LO,TO}^{\infty}$ | 10¹⁰eV m⁻¹ | 0.6 | 40 | 10 |

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*We consider only the heavy hole here, because the ratio of the oscillator strengths between heavy hole and light hole is 3:1 [43].

*obtained via Lyddane–Sachs–Teller relation [20].

*Similar values where obtained from temperature-dependent Raman spectroscopy measurements on the CuI microwires, which will be part of a future publication.

*No literature values of $\tau_{AC}$ are available for CuI and ZnO. Therefore, we set it equal to the value of GaAs.

*Corresponding to the experiments [24][25][26].

*average of estimated values $\tilde{e}_{14} = -\sqrt{3}e_{14} = -\sqrt{3}e_{14}$ and $\tilde{e}_{14} = \sqrt{3}e_{14}$ [44] using $e_{15} = -0.37$, $e_{11} = -0.62$ and $e_{13} = 0.96$ (all values in C m⁻²) [45].
Figure 1. Validation of the implementation of the computational model by comparison to the results of Maia et al. [13] for the experiments of Shank et al. [24, 25] (top and middle row) and Seymour et al. [26] (bottom row). Effective carrier and phonon temperatures $T_i$ in linear (left column) and logarithmic (middle column) time scale are shown along with a zoomed-in view (right column). Reference data points taken from Maia et al. [13] are shown as symbols. [13] John Wiley & Sons. [Copyright © 1993 WILEY-VCH Verlag GmbH & Co. KGaA].

spectroscopy measurements on CuI microwires. For ZnO, we use the results of time-resolved spectroscopic ellipsometry measurements on a ZnO thin film [46].

**Time-resolved photoluminescence spectroscopy on CuI microwires.** CuI microwires were prepared by vapor-phase transport growth as reported earlier [47, 48]. Single microwires were transferred onto a clean SiO$_2$/Si substrate using an acupuncture needle (dry-imprint technique). The substrate with the microwire samples was mounted in a helium-flow cryostat for micro-photoluminescence measurements at 10 K nominal temperature. A frequency-tripled titanium-sapphire (Ti:sapphire) laser (266 nm wavelength, 200 fs pulse duration, 76 MHz repetition rate) was used as excitation source. The laser beam was focused by a long-working-distance $\times 50$ NUV microscope objective (NA = 0.44) to a spot size of about 2 μm radius ($1/e^2$) for the non-resonant excitation of single microwires. The emitted photoluminescence was collected by the same objective, dispersed by a spectrometer (320 mm focal length, 600 grooves/mm grating) and guided to a streak camera (Hamamatsu C5680 with M5675 Synchroscan unit) with a timeresolution of about 10 ps in the time range of the measurements. Further details on the experimental setup can be found in reference [49]. The latter experiments were almost identical to our work, but they employed 364 nm/3.41 eV excitation energy. We choose a larger photon energy (266 nm/4.65 eV) for better comparison with our calculations for ZnO.

We show the transient photoluminescence spectra in figure 2(a) along with selected spectra in panel (b). The dashed line indicates the position of the free, longitudinal exciton resonance at around 3.06 eV [48]. The streak camera image was corrected for the temporal and spectral resolution given by the instrument [51]. We extract the transient carrier temperature $T$ from exponential fits $I(E) \propto \exp \left(-E/k_B T\right)$ (Eagles distribution [50]) to the line shape of the high-energy wing of the free, longitudinal exciton peak in the micro-photoluminescence spectrum of CuI microwires. Exemplary line shape fits are depicted in figure 2(b). The free-exciton emission is rather weak compared to the bound-exciton luminescence at lower energies due to trapping of free excitons by impurities [52, 53] as well as due to larger oscillator strength of bound excitons [54]. Thus, in order to get a meaningful line shape fit, we limit the fit range to 100 ps.

We find 35 K as the lowest carrier temperature after 100 ps which is still well above the nominal temperature of the helium cryostate. This seems to be a contradiction, however, a similar value is obtained from line-shape fits of time-integrated photoluminescence spectra of other CuI microwires. Furthermore, this value is in line with similar investigations on GaN nanowires [55]. We speculate that the insufficient thermal coupling of the SiO$_2$/Si substrate to the wires balances the heat input (laser excitation) and output (helium cryostate) above the cryostate temperature. Therefore, we set the temperature of the thermal bath $T_{\text{bath}} = 35$ K for the CuI simulations.

**Time-resolved spectroscopic ellipsometry on a ZnO thin film.** A 30 nm c-plane-oriented ZnO thin film was grown by means of pulsed laser deposition. Its transient optical properties, i.e. the complex dielectric function, after pulsed UV excitation were determined by means of femtosecond-time-resolved spectroscopic ellipsometry [56] at room temperature. The sample preparation, experimental details as well as the data analysis are detailed in reference [46]. The strong electron–phonon interaction present in ZnO has a drastic influence on the dielectric function [57, 58]. From the transient dielectric function, one can obtain an effective phonon energy $E_{\text{ph}}$ [46] which we correlate with our results of the transient carrier and lattice temperatures.
Figure 2. (a) Time-resolved photoluminescence (PL) of CuI microwires at 10 K nominal helium cryostate temperature for 266 nm fs-pulsed laser excitation measured with a streak camera. (b) Individual PL spectra at selected times in logarithmic scale (points) along with the line-shape analysis [50] (lines) that was conducted near the position of the free longitudinal exciton peak in CuI (dashed line). The spectra are successively multiplied by powers of ten for a clear separation on the logarithmic scale.

Table 3. Excitation energies in eV used for the simulation. TH stands for the third harmonic of the fundamental mode of the laser.

|             | CuI                     | ZnO                     |
|-------------|-------------------------|-------------------------|
| 3.12        | Fundamental band gap    | 3.37                    |
| 3.50        | TH of Nd:YAG laser      | 3.45                    |
| 3.76        | Split-off band gap      | 4.00                    |
| 4.65        | TH of Ti:sapphire laser | 4.65                    |

*We set the excitation energy 10 meV above the band gap to simulate quasi-resonant excitation with negligible excess energy $\Delta E_a$.

4. Results

We apply the relaxation model reported by Maia et al [13] to calculate the carrier and lattice cooling after optical excitation in the prototypical wide-gap semiconductors CuI [17] and ZnO [18]. The initial carrier excess energies $\Delta E_a$ and thus carrier temperatures $\Delta T_a = 3/2k_B T_a$ depend on the energy of the initial excitation $h\omega_0$, the band gap $E_g$ as well as the carrier effective masses $m_a$ and is calculated via [59]

$$\Delta E_a = \frac{h\omega_0 - E_g}{1 + \frac{m_e}{m_h}},$$

$$\Delta E_b = \frac{h\omega_0 - E_g}{1 + \frac{m_h}{m_e}} = (h\omega_0 - E_g) - \Delta E_a.

We choose representative excitation energies $h\omega_0$ provided in table 3 to determine the initial temperatures of the carriers $T_a$ and the lattice $T_r$ [60]. The initial phonon temperatures $T_{LO,TO}$ are estimated from an energy conservation argument [3] and are typically close to $T_{bath}$.

The transient carrier and phonon temperatures after optical excitation of CuI (left column) and ZnO (right column) are depicted in figure 3. The colored curves correspond to the different excitation energies (table 3) and the corresponding transient dissipation terms $\dot{E}_i$ are provided in the supplementary material. The case of the maximal excitation energy (266 nm/4.65 eV) is shown in figure 4. In general, carrier and lattice relaxation in CuI and ZnO proceeds similarly. The phonon systems remain initially in equilibrium with the bath (see supplementary material). For quasi-resonant optical excitation ($E_g + 10$ meV), carriers heat up to the bath temperature for ZnO at $T_{bath} = 300$ K ($\equiv 25$ meV) within less than 100 fs while they cool down on the same time scale for CuI at $T_{bath} = 35$ K ($\equiv 3$ meV). For non-negligible excess energies, electrons are heated up to several thousand Kelvin while the initial hole temperature is lower because of their higher effective mass. Electrons cool down faster to the phonon temperatures for ZnO, because of their stronger Fröhlich interaction related to the larger LO-phonon energy and the larger LO–TO mode-splitting in ZnO [18, 33]. Cooling of holes to the phonon temperatures appears even quicker for both materials, because of the stronger interaction with the lattice. In particular, holes are additionally subject to electron–optical-phonon deformation-potential interaction $\dot{E}_{i,LO,TO} \equiv DP$ (equation (2)) in this model and thus have more energy-loss channels compared to electrons [62].
Carrier relaxation is mainly dominated by the Fröhlich interaction (figure 4 and supplementary material) for high carrier temperature in accordance with earlier results \[13, 64\] and as generally expected for polar semiconductors \[10, 65\]. Most of the other dissipation source defined in equations (1)–(5) can be neglected for our chosen initial conditions. Thus, most energy is transferred to the LO phonons which heat up to 45 K in the calculation for CuI (370 K for ZnO) after about 3 ps (100 fs) for the largest excitation energy (figure 4). We find the maximal transient phonon temperature is proportional to the excess energy \(\Delta E\). In turn, the LO phonons re-heat both electrons and holes as well as AC and TO phonons by about 5 K for CuI (50 K for ZnO) on the time scale 1 ps...1 ns. In particular, as seen in figure 4 the carrier temperatures (blue and red curves) would decrease directly to \(T_{\text{bath}}\) following the initial temperature loss-rate, but scattering with phonons keeps their temperature above \(T_{\text{bath}}\). On this time scale, optical-phonon deformation-potential interaction of holes is of the same order of magnitude as the Fröhlich interaction. Thus, re-absorption of phonons delays the carrier relaxation by a few picoseconds, which is a manifestation of ‘hot-phonon effects’ \[10, 11, 59\]. This emphasizes once more the importance of the phonon properties for the carrier relaxation of wide-bandgap semiconductors. Thermal equilibrium with the bath is only reached after about 10 ns for both ZnO and CuI, which is mainly determined by the relaxation time \(\tau_{\text{AC}}\).

We compare our results for the highest excitation energy (266 nm/4.65 eV) to experimental results in figure 4 along with the dissipation terms. For CuI, we extract the transient exciton temperature from exponential fits \[50\] to the line shape of the free, longitudinal exciton peak in the microphotoluminescence spectrum of CuI microwires. We find the onset of the temperature decay and the final temperature in very good agreement with our simulated values in the time range 5 ps–100 ps when carriers and phonons equilibrate with each other. Earlier time-resolved photoluminescence measurements employed picosecond pulses on CuI single crystals \[66\]. They fitted the line shape of the first LO-phonon replica of the free exciton with the relation \(I(E) \propto E^{3/2} \exp \left(-E/k_{\text{B}}T\right)\) assuming parabolic and isotropic excitonic dispersion relation as well as low excited carrier density (ca 10\(^{18}\) m\(^{-3}\)) \[67\]. Their temperature dynamics show the same qualitative behavior. However, the relaxation model does not account for various different scattering processes. Similar measurements on CuI thin films suggest also the Fröhlich interaction as the dominant energy-loss channel \[68\]. More recent investigations \[64, 69\] for higher excitation densities on CuI thin films by the optical-Kerr-gating method are focused on the excitation-energy dependence of the photoluminescence originating from...
Figure 4. Effective carrier and phonon temperatures $T_i$ of CuI (left column) and ZnO (right column) for 266 nm (4.65 eV) optical excitation along with the corresponding dissipation terms $E_i$. Dissipation terms that are negligible small on this scale are not shown. Black symbols represent experimental data: for CuI, we show the transient carrier temperature extracted from exponential fits [50] to the line shape of the free, longitudinal exciton peak in the micro-photoluminescence spectrum of CuI microwires. For ZnO, we show the transient effective phonon energy $E_{\text{Ph}}$ obtained by femtosecond-time-resolved spectroscopic ellipsometry taken from [46].

Exciton–exciton scattering (P-band [70]). The relaxation of excitons can take longer, because their bosonic nature and the vanishing total electric charge leads to smaller interaction strengths with defects and phonons compared to electrons and holes [71]. An empirical bi-exponential relaxation model was applied to transient photoluminescence curves reported by Das et al [72]. Note that for extremely pure samples, line-shape fits of the second LO-phonon replica of the free exciton yield the temperature of the entire exciton population and not only the subset which recombines at the center of the Brillouin zone [73].

In the case of ZnO, we correlate the calculated kinetics with the transient effective phonon energy $E_{\text{Ph}}$ taken from femtosecond spectroscopic ellipsometry measurements [46]. The effective phonon energy increases upon optical excitation, because of the creation of (high-energy) LO phonons as the most efficient energy-loss channel [74]. Furthermore, it seems that $E_{\text{Ph}}$ is correlated with the simulated phonon temperatures. This can be explained by the increased optical-phonon temperature after about 100 fs that leads to higher occupation of the LO and TO phonon modes assuming Bose–Einstein distribution of the phonon subsystems. Hence, the effective phonon energy of the crystal increases. The acoustic phonon subsystem equilibrates with the carriers and optical phonons until about 10 ps thereby increasing the occupation of AC phonons and consequently decreasing $E_{\text{Ph}}$ again. Generally, we find good agreement between the transient recovery of $E_{\text{Ph}}$ and the equilibrated carrier and lattice temperatures between 10 ps and 10 ns. As in the case of CuI, re-absorption of phonons delays the carrier relaxation by a few ps in agreement with the findings of Richter et al [46].

In summary, we employed the model reported by Maia et al to describe carrier and lattice relaxation after optical excitation to the prototypical wide-gap semiconductors CuI and ZnO. The computer implementation of the model was validated against the results of the original report. This model is useful because of its mathematical simplicity while still distinguishing electrons and holes as well as LO, TO and acoustic phonon branches. Thereby, our calculations yield additional physical understanding to recent time-resolved optical spectroscopy experiments. We find the relaxation dominated by carrier-LO-phonon (Fröhlich) interaction while re-absorption of phonons with temperatures larger than the thermal bath (hot-phonon effect) delays the relaxation process by few picoseconds. We expect this model to be adaptable to other wide-bandgap semiconductors such as oxides, nitrides and alike.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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