Ultrafast hot carrier dynamics of ZrTe$_5$ from time-resolved optical reflectivity

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We investigate the hot carrier dynamics of ZrTe$_5$ by ultrafast time-resolved optical reflectivity. Our results reveal a phonon-mediated across-gap recombination, consistent with its temperature-dependent gap nature as observed previously by photoemission. In addition, two distinct relaxations with a kink feature right after initial photoexcitation are well resolved, suggesting the complexity of the electron thermalization process. Our findings indicate that correlated many-body effects play important role for the transient dynamics of ZrTe$_5$.

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I. INTRODUCTION

Transition metal pentatellurid ZrTe$_5$ has recently triggered considerable interests for its unique electronic properties. It is predicted to be on the boundary between strong and weak topological insulators depending on its lattice parameter$^{12}$. Angle-resolved photoemission spectroscopy (ARPES) measurements have evidenced its temperature-dependent electronic structure from a p-type semimetal to a semiconductor and to a n-type semimetal, associated with a bandgap variation from 30 to $\sim$ 20 meV$^{13,14}$, providing clear interpretation for the strong resistivity peak and the sign reversal of Hall effect near 135 K$^{5,6}$. ZrTe$_5$ hosts both 1D chain and 2D layer structures$^{3,5}$ with weak interlayer coupling comparable to that of graphite$^1$. In addition, it has high in-plane carrier mobility comparable to that of graphene$^7$ and strong electron-electron (e-e) interaction$^{10}$. These remind us with some low-dimensional quantum-confined systems with enhanced Coulomb interaction and carrier-carrier scattering, such as graphene$^{8,11}$ and semiconductor nanocrystals$^{12,13}$. At this stage, comprehensive ultrafast time-resolved studies are required to unveil many-body interactions in ZrTe$_5$.

Time-resolved optical spectroscopy is an effective way of tracking photoexcited hot carrier dynamics in ultrafast timescales from few femtoseconds (fs) to nanoseconds (ns). In general, for gapped systems under weak excitation (too weak to break the ordered state), hot carriers after initial photoexcitation (at $t_1$) relax to equilibrium in two steps as shown in Fig. 1a: (i) $t_1 < t < t_2$, hot carriers rapidly lose energy by fast e-e scattering and electron-phonon (e-ph) scattering, and accumulate above the gap around the Fermi level ($E_F$), referring to the thermalization process; (ii) $t > t_2$, across-gap recombination occurs by the emission of gap-frequency phonons, resulting in the gap- and phonon-sensitive equilibriation process. In Fig. 1a we use the sketch of band structure at $\Gamma$ in ZrTe$_5$, where most of the electronic spectral weight was found around $E_F$ by ARPES$^3$, corresponding to the highest excitation probability. The optical probe is dedicated to measure the relaxation of the dielectric constant resulting from the transient electronic distribution, for example, in the equilibration process (ii) the density of hot carriers is proportional to spectroscopy changes in transmission/reflectivity (Fig. 1b)$^{16,17}$. Therefore time-resolved optical spectroscopy allows direct investigation of carrier dynamics, gap properties and many-body effects in many materials, such as graphene$^{18}$, superconductors$^{19–22}$, semiconductors$^{23}$ and charge density wave materials$^{24–26}$. In most materials, the thermalization process (i) has a very short time constant within few tens of fs$^{16}$, resulting in a sharp signal rising edge that is comparable to the duration of pump and probe pulses. However, in some low-dimensional quantum-confined systems with enhanced Coulomb coupling such as graphene$^{18}$ and semiconductor nanocrystals$^{12,13}$, e-e scattering has a time constant up to 200 fs, offering a opportunity to directly study related effects such as quasiparticle multiplication and impact excitation.

In this paper, we investigate the hot carrier dynamics in ZrTe$_5$ by ultrafast time-resolved optical reflectivity, by inter-band photoexcitation using two pump photon energies: 1.55 eV (800 nm) and 3.10 eV (400 nm). Our results reveal a relaxation bottleneck in the equilibration process where a phonon-mediated across-gap recombination occurs, consistent with the gap nature and phase transitions. In the thermalization process, we find a resolvable rising edge for the buildup dynamics of the bottom of the conduction band (BCB buildup) with a constant kink feature at 500 fs, allowing us to investigate the complexity in the transient dynamics.
in our experimental setup, the infrared pulses were generated by a mode-locked Ti:sapphire regenerative amplifier system working at 1 KHz repetition rate, centered at 800 nm. Both the pump and probe beam were focused onto the a-c plane of a freshly cleaved sample surface in vacuum (Fig. 1b), with spot sizes at ~ 0.4 mm (pump) and ~ 0.2 mm (probe) in diameter. The 400 nm pump was obtained by second harmonic generation using a nonlinear phase-matched barium borate (BBO) crystal (thickness 0.5 mm). The reflected probe signal was collected by a Si-based detector and a lock-in amplifier. The time delay was realized by scanning the delay time between pump and probe pulses, using a motorized delay line. The sample was mounted on a cryostat with a temperature sensor embedded nearby, allowing a precise control of temperatures from 6 to 300 K. High quality ZrTe₅ single crystal was grown by chemical vapor transport technique with iodine methods. The crystal structure consists of ZrTe₅ sheets extend along the b axis (perpendicular to the a-c plane) forming a layered structure (Fig. 1c), and the adjacent two sheets is quite large and held together by weak interlayer van der Waals force.

II. METHOD

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III. RESULTS AND DISCUSSION

Figure 1d shows representative reflectivity changes |ΔR/R| at 6, 135 and 300 K, for the cases of n-type semimetal, semiconductor and p-type semimetal, pumped by 3.10 and 1.55 eV optical pulses. In all |ΔR/R| curves, a wide rising edge immediately appears after the initial photoexcitation (t₁), pointing to resolvable relaxation channels in the BCB buildup dynamics. The BCB buildup time t₂ is reached at ~ 1 ps (1.55 eV) and ~ 1.5 ps (3.10 eV), respectively. These suggest that tuning the pump to higher photon energy triggers more scattering events in the thermalization process. We also note that t₂ agrees with the population time of holes in the valence band and electrons in the conduction band observed by time-resolved photoemission. In the inset of Fig. 1d, the linear increase of [ΔR/R] max as a function of pump fluence F, implies that the maximum of the reflectivity changes is proportional to the density of photoexcited hot carriers at t₂ when the BCB buildup forms.

Systematic measurement results are mapped out in Fig. 2a, in which the intensity and relaxation time in |ΔR/R| significantly increases with temperature decreasing. Let’s first focus on the across-gap recombination (t > t₂), by using a single exponential function |ΔR/R| = Aₑ exp(−t/τₑ) + A₀, where Aₑ and A₀ correspond to the across-gap recombination and long-lived heating diffusion. In Fig. 2b and 2c, both τₑ and Aₑ show two transition temperatures at around 165 and 105 K, indicating that the transient dynamics after t₂ is closely related to the gap property. The linear relation between Aₑ and F in Fig. 4c suggests that Aₑ is proportional to the number of hot carrier accumulated above the energy gap.

For a gapped system with e-ph coupling, the hot carrier across-gap recombination occurs by the emission of gap-frequency phonons. As phenomenologically described by the Rothwarf-Taylor mode, gap-frequency phonons/bosons play a dominate role in the reformation dynamics of Cooper pairs in both cuprates and iron-based superconductors and electron-hole pairs in CDW materials. Smaller gap allows low frequency phonons to be involved in the across-gap recombination process, resulting in a longer lifetime, or even a divergence if the gap is completely closed. In this case, for simplicity, the relaxation time can be inversely proportional to the gap size τₑ ∝ 1/Eₑ₂. In Fig. 2b, the τₑ(T) curves agree well with 1/Eₑ(T), where Eₑ(T) is
FIG. 2: Across-gap relaxation of the BCB buildup after \( t_2 \).
(a) Comprehensive \( \Delta R/R \) results with pump fluence \( F = 18 \mu J/cm^2 \) by 3.10 and 1.55 eV. (b) Relaxation time \( \tau_r \) as a function of temperature, extracted from (a). The error bars are obtained from fits. The pink circles in (b) are the inverse of \( T \)-dependent gap, confirming \( \tau_r \propto 1/E_g \) (\( E_g \) taken from Ref.\textsuperscript{2} with authors’ permission). (c) Normalized amplitude \( A_r \) as a function of temperature. The gray thick curves in (b) and (c) are used to guide the eye for the slope changes at 105 and 165 K.

The temperature-dependent gap at \( E_F \) from ARPES\textsuperscript{3}. In addition, \( \tau_r \) is independent of pump photon energy and pump fluence (Fig. 4), confirming that the relaxation bottleneck is dominated by the gap and phonon properties. Simultaneously, from an energy conservation relation \( n_{pc}E_g = \epsilon_l \), where \( n_{pc} \propto A_r \) is the number of photoexcited hot electrons that relax through the across-gap channel and \( \epsilon_l \) is the energy absorption proportional to \( F \). Again we obtain a simple relation \( A_r \propto 1/E_g \). In Fig. 2c, the \( A_r(T) \) curve slightly decrease below \( \sim 105 \) K and deviates from \( 1/E_g(T) \). We speculate that here the across-gap probability reduces since few electrons start to occupy the bottom of the conduction band in the n-type semimetal case in equilibrium state.

A deeper inspection of the BCB buildup dynamics, i.e., the zoom-in of the rising edge, is shown in Fig. 3a. As discussed above, the wide rising edge between \( t_1 \) and \( t_2 \) refers to the immediate hot carrier redistribution/thermalization after pump light off through e-e and e-\( \hbar \) scattering channels. An universal kink feature in terms of a slope change is clearly observed at a time constant \( \tau_{Kink} \equiv 500 \) fs, suggesting coexistence of two scattering channels. We fit the \( \Delta R/R \) curves from \( t_1 \) to \( t_2 \), using a two-component exponential function convolved with a temporal resolution

\[
\frac{\Delta R}{R}(t) = [A_{\text{max}} - A_{\text{fast}} \exp(\frac{t}{\tau_{\text{fast}}})] - A_{\text{slow}} \exp(\frac{t}{\tau_{\text{slow}}}) \times R(\delta t)
\]  

(1)

where \( R(\delta t) \) is a Gassian curve with FWHM obtained from the cross-correlation measurement.

Figure 3b shows that the slow relaxation, which increases at higher pump photon energy, suggesting more intra/inter-band e-\( \hbar \) scattering events occur in the BCB buildup process. More interestingly, \( \tau_{\text{slow}} \) increases linearly with lattice temperature increasing and is \( F \)-independent (Fig. 4d). Obviously the e-\( \hbar \) decay channel here is unable to be described by the effective temperature model, which predicts e-\( \hbar \) scattering rate \( \tau_{e-\hbar} \propto T_e \propto F^{31,32} \), since this model requires high excitation density with electron temperature \( T_e \) much higher than lattice temperature. Our results rather agree with the non-equilibrium model, with e-\( \hbar \) scattering written as\textsuperscript{31}

\[
\tau_{e-\hbar} = \frac{2\pi k_B T_l}{\hbar \lambda (\omega^2)}
\]  

(2)

where \( \lambda \) is the coupling strength, and \( T_l \) is the lattice/sample temperature.

On the other hand, in Fig. 3c and 4d, we find \( \tau_{\text{fast}} = 250 \pm 70 \) fs, is weakly dependent of temperature, pump photon energy and \( F \). One possibility for the origin of \( \tau_{\text{fast}} \) is the e-e scattering channel, which is more likely a instantaneous process, analogous to that in graphene\textsuperscript{33} and semiconductor nanocrystals\textsuperscript{11}. Here we consider the impact excitation process in which a low energy electron on the top of the valence band gets excited over the bandgap by absorbing the energy loss.
from a high-energy hot electron, resulting in an additional electron-hole pair, as depicted in Fig. 1a. The efficiency of the impact excitation relies on the energy and momentum conservation in e-e scattering. In addition, the impact excitation can be very efficient because of high density of carriers as it has been found in graphene. In ZrTe$_2$, these conditions are possibly to be satisfied owing to its multi-band electronic structure with a bunch of conduction band valleys and high electron density at Γ. The two-dimensional crystal structure and in-layer carrier density in ZrTe$_2$ ($10^{12} \sim 10^{13}$ cm$^{-2}$), comparable to that of doped graphene, might enable analogous enhancement of e-e scattering as that in quantum-confined systems. However, we cannot exclude the frequency-dependence of $\Delta R/R$, since the transient dielectric constant varies when hot carriers relax between high-lying conduction bands. Yet more theoretical work and frequency-dependent studies are required to further pin down this behavior.

IV. CONCLUSION

In summary, we have studied the hot carrier dynamics by ultrafast time-resolved optical spectroscopy. We have clearly evidenced temperature-dependent across-gap recombination dynamics, confirming its gap nature. Further analysis of its electron thermalization dynamics resolves a e-ph scattering channel ruled by the non-equilibrium model. A possible e-e scattering channel is proposed for the fast relaxation, which asks for further investigations. Our results show the importance of many-body effects in ZrTe$_2$ and may further help the understanding of light-matter interaction for its application as photoelectric devices.

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