Quasiparticle dispersion and dynamics temperature evolution in semimetallic 1T-TiTe$_2$

Shuang-Xing Zhu,¹ Chen Zhang,¹ Qi-Yi Wu,¹ Xiao-Fang Tang,¹ Hao Liu,¹ Zi-Teng Liu,¹ Yang Luo,¹ Jiao-Jiao Song,¹ Fan-Ying Wu,¹ Yin-Zou Zhao,¹ Shu-Yu Liu,¹ Tian Le,² Xin Lu,² He Ma,³ Kai-Hui Liu,³ Ya-Hua Yuan,¹ Han Huang,¹ Jun He,¹ H. Y. Liu,¹ Yu-Xia Duan,¹ and Jian-Qiao Meng¹,5

¹School of Physics and Electronics, Central South University, Changsha 410083, Hunan, China
²Center for Correlated Matter and Department of Physics, Zhejiang University, Hangzhou 310058, China
³State Key Laboratory for Mesoscopic Physics, Collaborative Innovation Center of Quantum Matter, School of Physics, Peking University, Beijing, 100871, China
⁴Beijing Academy of Quantum Information Sciences, Beijing 100085, China
⁵Synergetic Innovation Center for Quantum Effects and Applications (SICQEA), Hunan Normal University, Changsha 410081, China

(Dated: Friday 4th December, 2020)

Semimetallic 1T- TiTe$_2$ quasiparticle dispersion and dynamics were studied using high-resolution angle-resolved photoemission spectroscopy and ultrafast optical pump-probe spectroscopy. A kink and a flat band, having the same energy scale and temperature-dependent behaviors along the Γ-X direction, were detected. They both manifested at low temperature but blurred as temperature increased. The kink was formed by electron-phonon coupling. The localized flat band state might be due to a polaron effect associated with electron-phonon coupling. Ultrafast optical spectroscopy identified multiple distinct time scales in the 10 K to 300 K range. A quantitative analysis of the fastest component showed a significant lifetime temperature dependence at high temperature. While this starts to change slowly below 125 K where an anomalous Hall coefficient occurred. At low temperature, a coherent $A_{1g}$ phonon mode with a frequency of $\sim 4.36$ THz was extracted. Frequency temperature dependence suggests phonon-softening occurs as temperature increases and anharmonic effects can explain it. While Frequency fluence dependence indicates that the phonon mode is hard to tune by fluence.

PACS numbers: 74.25.Jb,71.18.+y,74.72.-h,79.60.-i

I. INTRODUCTION

Layered transition-metal dichalcogenides (TMDCs) with the chemical formula $TX_2$ ($T$: transition metal; $X$: chalcogen) are ideal platforms for experimentation due to their quasi-two-dimensional (2D) structures and rich physical properties [1-4]. They have a variety of structures, among which the 1T and 2H structures are the most widely studied. They consist of $X-T-X$ sandwiches held together by relatively weak “van der Waals” forces between layers [3]. Sample preparation technology has evolved them into valuable materials for studying thin films including monolayer materials [6,8]. The 2D TMDCs materials have several excellent qualities. They are widely used to construct high-performance field-effect and photodetector devices [9,13]. Metallic 2D TMDCs such as TaS$_2$, and TiSe$_2$ possess superconductive, charge density wave (CDW), and several other phases. These qualities provide an excellent research platform for studying various phenomena and laws of condensed matter physics [14,15].

1T-TiTe$_2$ is a model quasi-2D material. Its spectral lineshapes are consistent with a Fermi-Liquid scenario [16,22]. Electron-phonon ($e$-$ph$) coupling was considered when analyzing Ti 3d band spectral lineshapes [19,22]. Angle-resolved photoemission spectroscopy (ARPES) measurements have directly observed a weak $e$-$ph$ coupling induced kink with an energy of $\sim 18$ meV below the Fermi energy ($E_F$) [23]. Raman scattering has observed two phonon modes at $\sim$105 cm$^{-1}$ ($E_g$) and $\sim$143 cm$^{-1}$ ($A_{1g}$), respectively [24,25]. CDW phase transition has been found in many TMDCs [26,27], but not in bulk TiTe$_2$. It has previously been thought that weak $e$-$ph$ coupling cannot lead to superconductivity or CDW instability.

CDW order was recently observed in single-layer TiTe$_2$ with a transition temperature of 92±3 K [28], and also in epitaxial strained TiTe$_2$ multilayer films with a room temperature transition temperature [29]. In prior ARPES experiments 1T-TiTe$_2$ has been found to exhibit typical semimetallic characteristics with a negative indirect bandgap of $\sim 0.8$ eV [18]. Theoretical studies have suggested that both doping [30], and strain [31], can lead to a topological phase transition. Experimental results suggest that pressure can cause both topological phase and structural transitions [32]. It may even lead to superconductivity [33].

The complex and numerous physical properties of solid materials are known to be closely related to the many-body interactions among charge, lattice, spin, and orbit. When phase transitions occur specific changes occur in many-body interactions. For example, energy and evolution of $e$-$ph$ coupling trends may change with temperature. Exploring the many-body interaction modes and their evolutions with temperature provides a better channel for understanding the situation.
ARPES and ultrafast optical pump-probe spectroscopy were combined to study single crystalline $1T$-TiTe$_2$ quasiparticle dispersion and dynamics. ARPES is a powerful tool for studying many-body interactions as it provides direct information on single-particle spectral functions. Ultrafast optical pump-probe spectroscopy is also very useful for studying ultrafast quasiparticle dynamics of in the time-domain, since the transmission/reflectivity changes of the optical probe have been inferred to result from the photoexcited quasiparticles and collective excitations [34, 35].

II. SAMPLES AND EXPERIMENTAL MEASUREMENT

High-quality $1T$-TiTe$_2$ single crystals were grown via chemical vapor transport method with iodine as the transport agent. Platelike single crystals with shiny surfaces as large as $10 \text{ mm} \times 10 \text{ mm} \times 0.5 \text{ mm}$ were obtained.

High-resolution temperature dependent ARPES measurements were performed at beamline 5-4 of the Stanford Synchrotron Radiation Lightsource (SSRL), using a Scienta R4000 electron energy analyzer. All samples were cleaved in situ and measured in an ultrahigh vacuum with base pressure better than $3 \times 10^{-11} \text{ mbar}$. A 20 eV photon energy beam with an overall energy resolution of $\sim 7 \text{ meV}$ was selected to probe the temperature evolution of $\epsilon$-$\text{ph}$ coupling in Ti 3 $d$ band along the high-symmetry $\Gamma$-$M$ direction. This photon energy can achieve a very narrow quasiparticle bandwidth and a clear $\epsilon$-$\text{ph}$ coupling-induced kink structure [23]. Angular resolution was kept at $0.2^\circ$ for all measurements.

Ultrafast optical pump-probe measurements were carried out with a pulse laser produced by a Ti: sapphire femtosecond (fs) laser oscillator. The pulses had a center wavelength of 800 nm (1.55 eV), a pulse width of $\sim 35 \text{ fs}$, and a repetition rate of 1 MHz. Pump and probe beams spot sizes on the sample were 160 and 40 µm in diameter, respectively. The pump-probe was cross-polarized. Data were collected from 10 K up to 300 K on freshly cleaved surfaces. All measurements were taken in vacuum ($10^{-6}$ Torr).

III. ARPES EXPERIMENTAL

Figures 1(a1-a8) show the $1T$-TiTe$_2$ temperature-dependent energy-momentum images. As temperature rose, quasiparticle dispersion intensity weakened. No CDW evidence observed here like that in monolayer TiTe$_2$ [28], in which a replica of Te 5$p$ bands shifted from $\Gamma$ to $M$ at low temperatures. Shallow Ti 3$d$ band dispersion is not easily extracted using fitting momentum distribution curves (MDCs) or energy distribution curves (EDCs) [16, 23]. Figures 1(b1-b8) present the quasiparticle dispersion reduced by a second-derivative along the energy direction to sharpen the band structures while maintaining the main band structure. As temperature rose, the kink structure shown by the red arrow was detected readily at around 18 meV below the $E_F$ at low temperatures. Our prior work has well discussed and attributed the kink structure to $\epsilon$-$\text{ph}$ coupling [23]. As the temperature rose, the kink blurred until becoming indistinguishable at around 70 K.

A flat band near the $E_F$ marked by the green arrow is well resolved in the second-derivative figures at low temperatures. This flat band was not predicted by theoretical calculations in this material. Flat bands are com-
monly found in TMDCs: TiTe$_2$ [29, 30], TaS$_2$ [37], TaSe$_2$ [37], and VSe$_2$ [38]. The flat band has been considered to be due to emission from a narrow impurity band or polaron effect associated with CDW order [29, 30]. A CDW caused polaron effect is unlikely as no CDW order was observed in the bulk TiTe$_2$. The flat band has the same energy as the kink. Their temperature-dependent behavior is identical and is readily detected at low temperatures. The flat band also weakens as temperature increases until becoming indistinguishable around 70 K. The flat band is suspected to be due to a polaron effect associated with the $e$-$ph$ interaction. However, one cannot rule out the possibility of an emission from a narrow impurity band as prior studies of Ti 3$d$ on spectral lineshapes have detected impurity contributions at around 14 or 17 meV [19] [21], which is similar to the location of the flat band.

It can also be seen from the figures that with the decrease of temperature, the Fermi momentum shifts to the left, which means that the hole pocket volume formed by the Ti 3$d$ band increases with as temperatures fell. This is consistent with the Hall coefficient anomaly found in TiTe$_2$ [36], in which the Hall effect is believed to be composed of nearly offsetting electron and hole contributions. As it is well-known the Hall effect is sensitive to small changes of carrier concentration in a simple two-carrier model. The band shift in our study provides a possible explanation for the long-standing uncertainty about the Hall coefficient anomalies.

IV. ULTRAFAST OPTICAL PUMP-PROBE MEASUREMENT

Carrier dynamics in solid are sensitive to many-body interactions among the charge, lattice, spin, and orbital. Ultrafast optical spectroscopy is a potent tool for investigating carrier dynamics. It has been used to study heavy fermions [40, 41], high-temperature superconductivity [42, 44], semiconductors [15], topological materials [35, 46, 47], and CDW materials [38]. Ultrafast optical pump-probe measurements were performed on single-crystal 1T-TiTe$_2$ to investigate quasiparticle dynamics and phonon modes.

Figure 2(a) shows $\Delta R/R$ signals for 1T-TiTe$_2$ at various temperatures at a pump fluence of $\sim 25 \mu J/cm^2$. Upon photoexcitation, $\Delta R/R$ signal changes instantaneously. It is then followed by a long recovery process. Reflectivity signal peak intensity increases gradually as temperature decreases. $\Delta R/R$ signal oscillates significantly at all measured temperatures becoming more pronounced as temperature drops. Figure 2(b) is a 2D pseudo-colour $\Delta R/R$ mapping image and is shown as a function of pump-probe delay ($x$-axis) and temperature ($y$-axis).

The nonoscillatory background decay does not change significantly with temperature. Relaxation can be roughly divided into four stages (inset of Figure 2(c) and Figure A1 of the Appendix [48]). A fast recovery process ($\tau_1$) occurs within 0.7 ps, followed by a second slower
component is observed ($\tau_2$). A pervasive second rising ($\tau_3$) shows up within a few ps, which is usually found in strongly correlated materials [48] and topological insulators [49]. The final relatively slow relaxation ($\tau_1 > 20$ ps) is usually considered as phonon-acoustic-phonon interaction.

Quantitative analysis of quasiparticle dynamics was conducted to study its temperature and fluence dependence behavior. The relaxation process fitted well with four exponential decays convoluted with a Gaussian laser pulse [Figure 2(c)]. The obtained decay times $\tau_1$, $\tau_2$, and $\tau_3$ were plotted in red in Figure 2(d) and (e) as a function of temperature. The figures also show the change of lifetimes with temperature at a pump fluence of $\sim 50$ $\mu$J/cm$^2$ (green marks).

For both fluence, $\tau_1$ shows significant temperature-dependent behavior at high temperature. And it starts to change slowly around $\sim 100$ K, just below the temperature when the thermoelectric power $\alpha$ changes sign and the anomalous Hall coefficient occurs [36]. Also, by precise temperature-dependent resistivity measurements, it can be found that its derivative $\frac{d\rho}{dT}$ has a broad hump at the same temperature scale, starting $\sim 125$ K and centered $\sim 100$K (see Figure. S2 of the Supplemental Material [48] for details). The time scales of the initial decay, $\tau_1$, is plotted as a function of pump fluence in the inset of Figure 2(d). Within our experimental resolution, the change of $\tau_1$ can be negligible in the wide range of pump fluence used here. This universal lifetime $\tau_1$ with pump fluence indicates a table ground state.

In determining the possible physical origins for these relaxation processes the following is to be considered. By analyzing the electronic band structure of 1T-TiTe$_2$, we can uncovered the origin of the decays. Typical semimetallic electronic structures had been observed in 1T-TiTe$_2$, including multiple hole pockets around $\Gamma$ points and electron pockets around $M$($M'$) point [23]. This means that pairs of electron and hole pockets dominantly the feature of Fermi surface structure.

Figure 3 shows the illustration of the band structure of 1T-TiTe$_2$ near the Fermi level ($E_F$) along the $\Gamma$-$M$ direction. $\tau_1$, $\tau_2$, and $\tau_3$ represents the $e$-$ph$ thermalization, phonon-assisted interband $e$-$h$ recombination, and re-excite $e$-$h$ pairs processes, respectively.

![FIG. 3. (Color online) Schematic band structure of semimetal 1T-TiTe$_2$ near the Fermi level ($E_F$) along the $\Gamma$-$M$ direction. $\tau_1$, $\tau_2$, and $\tau_3$ represents the $e$-$ph$ thermalization, phonon-assisted interband $e$-$h$ recombination, and re-excite $e$-$h$ pairs processes, respectively.](image-url)
4(c) as a function of temperature. The frequency extracted with a pump fluence of $\sim 50 \mu J/cm^2$ is added and represented by green circles. The $\omega/2\pi$ becomes nearly constant at low temperature. For both pump fluence, the $A_{1g}$ phonon mode hardens monotonically, blue shift, as temperature falls from $\sim 4.26$ THz at 300 K to $\sim 4.36$ at 10 K. An $A_{1g}$ phonon blue shift below $\sim 8$ GPa has been observed when high hydrostatic pressure was applied $[25]$. This was suggested to be due to state densities near the $E_F$, which decreases dramatically with hydrostatic pressure $[53]$. However, this is not the case here. It can be seen from ARPES data in Figure 1, the density of states near the $E_F$ increases significantly with the decrease of temperature. Here, its temperature dependence can be well explained by anharmonic effects of optical phonon $[54][55]$. Figure 4(d) displays the derived frequency $\omega/2\pi$ at 10 K as a function of pump fluence, while the blue line serve as guide for the eyes. Within the pump fluence used here, the frequency decrease linearly and slowly with increasing fluence. This may be due to the non-negligible thermal effect caused by the high fluence.

VI. CONCLUSIONS

High-resolution ARPES and ultrafast transient reflectivity measurements have been performed on bulk 1T-TiTe$_2$. Along the $\overline{T-M}$ direction, a kink and a flat band are revealed at 18 meV by ARPES. The kink and flat band have the same energy scale and temperature-dependent behavior, which is readily observable at low temperature and blurs as temperature increases. The formation of these two is closely related to the $e$-$ph$ interaction. The kink is formed by $e$-$ph$ coupling. The localized flat band state is likely due to a polaron effect associated with the $e$-$ph$ interaction. In the 10 K to 300 K range, multiple decay processes have been revealed by ultrafast optical spectroscopy. The $\tau_1$, $\tau_2$, and $\tau_3$ are ascribed to carrier cooling through $e$-$ph$ thermalization, phonon-assisted $e$-$h$ recombination and re-excitation, respectively. And $\tau_4$ is considered as phonon-acoustic-phonon interaction. At 10 K, a coherent $A_{1g}$ phonon mode with a frequency of $\sim 4.36$ THz was extracted. It was consistent with ARPES and Raman measurements. The temperature dependence of $A_{1g}$ mode frequency can be well explained using an anharmonic phonon model.

VII. ACKNOWLEDGEMENT

We thank Gey-Hong Gweon for his unreserved support. This work was supported by the Innovation-driven Plan in Central South University (2016CXS032). X. Lu was supported by National Natural Science Foundation of China (NSFC, Grants No. 11674279).

* Corresponding author: jqmeng@csu.edu.cn

[1] B. Sipos, A. F. Kusmartseva, A. Akrap, H. Berger, L. Forro, and E. Tutis, nature materials 7, 960 (2008).
[2] K. F. Mak, K. He, J. Shan, and T. F. Heinz, Nature Nanotech 7, 494-498(2012).
[3] M. N. Ali, J. Xiong, S. Flynn, J. Tao, Q. D. Gibson, L. M. Schoop, T. Liang, N. Haldolaarachchige, M. Hirschberger, N. P. Ong, and R. J. Cava, Nature 514, 205-208(2014).
[4] M. Bonilla, S. Kolekar, Y. Ma, H. C. Diaz, V. Kalapattil, R. Das, T. Eggers, H. R. Gutierrez, M. Phan, and M. Batzill, Nature Nanotechnology 13, 289-293(2018).
[54] M. Balkanski, R. F. Wallis, and E. Haro, Phys. Rev. B 28, 1928 (1983).
[55] J. Menendez and M. Cardona, Phys. Rev. B 29, 2051 (1984).