Coexistence of the Charge-Density-Wave Phase in the Photo-Induced Metallic Phase in 1T-TaS₂

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We investigate the nonequilibrium electronic structure of 1T-TaS₂ by time- and angle-resolved photoemission spectroscopy. We observe that strong photo excitation induces collapse of the Mott gap, leading to the photo-induced metallic phase. It is also found that the oscillation of photoemission intensity occurs as a result of the excitations of coherent phonons corresponding to the amplitude mode of the charge density wave (CDW). To study the dynamical change of the band dispersions modulated by the CDW amplitude mode, we perform analyses by using frequency-domain angle-resolved photoemission spectroscopy. We find that two different peak structures exhibit anti-phase oscillation with respect to each other. They are attributed to the minimum and maximum band positions in energy, where the single band is oscillating between them synchronizing with the CDW amplitude mode. We further find that the flat band constructed as a result of CDW band folding survive with the collapse of Mott gap. Our results strongly suggest the CDW phase is more robust than the Mott insulating phase, and the lattice modulation corresponding to the CDW amplitude mode dynamically modulate the Mott gap.

Transition-metal dichalcogenide (TMD) is a large class of widely studied layered two-dimensional materials. Many of TMDs show a metal-insulator transition (MIT) and some kind of an ordered ground state. Among them, 1T-TaS₂ is a typical example and shows successive charge-density-wave (CDW) phase transitions [1] [2]. As temperature decreases, it undergoes incommensurate CDW (ICCW), nearly-commensurate CDW (NCCDW), and commensurate CDW (CCDW) phases below 550, 350, and 180 K, respectively, as schematically shown in Fig. 1(a)-(c) for the band evolution. In the CCDW phase, the 13 Ta atoms are modulated to form a Star of David cluster as schematically shown in Fig. 1(d). Besides, angle-resolved photoemission spectra suggest that there exists the Mott insulating phase coexistent with the CDW phase as schematically shown in Fig. 1(e) [3] [4] [5]. Furthermore, it also shows superconductivity by applying pressure [6] or chemical doping [7]. These intriguing features such as the coexistence of CDW and Mott-insulating phases or the emergence of superconductivity have motivated intensive studies of 1T-TaS₂ for understanding the roles of electron-electron and electron-phonon interactions for a long time.

While many experimental methods have been employed to investigate physical properties in equilibrium conditions for 1T-TaS₂ [4], ultrafast spectroscopies have provided an alternative route to investigate the nature underlying above phases via a non-equilibrium state [8]. Furthermore, strong photo-excitation can be found to alter this system to photo-induced metastable metallic phase, which suggested the possibility of opto-electronic devices and triggered

![Fig. 1 (a)-(c) Schematic illustration of the band evolution crossing the different phases [5]. (d) Schematic illustration for the in-plane lattice modulations in the commensurate CDW phase (CCDW).](attachment:image.png)
intensive works [9] [10] [11]. Apart from the quest for such a hidden state, many ultrafast methods have been performed to investigate the interplay between electrons and phonons by perturbing or melting the charge order and analyzing the temporal response [12]. In this regards, time- and angle-resolved photoemission spectroscopy (TARPES) is very powerful method because it can track the temporal band structure and gain direct information of nonequilibrium electronic states [13] [14] [15]. Especially in 1T-TaS$_2$, where the Fermi surface (FS) is located around the M point in the high temperature metallic phase, TARPES using the large photon energy obtained by high harmonic generation (HHG) using noble gas to reach the entire 1st Brillouin zone is very ideal [16] [17] [18] [19].

While many previous works using HHG TARPES successfully revealed the striking and fundamental electronic properties in 1T-TaS$_2$, selective observation of melting dynamics of the Mott and CDW phases associated with the Mott gap and the flat band structure, respectively, is still missing. The reason might be lied in the difficulty to distinguish them in time-domain spectra. Recently we developed a new analysis method, which we call frequency-domain ARPES (FDARPES) [20]. This method allows us to distinguish the coexisting bands by selectively detecting band dispersions in the frequency-domain even during the photo-induced phase transition.

In this work, we applied TARPES and FDARPES method to 1T-TaS$_2$ to investigate the dynamical properties of the Mott and CDW phases associated with the Mott gap and the flat band structure. We directly observe photo-induced melting of the Mott gap in the momentum space and the oscillating behavior as a result of the A$_{1g}$ coherent-phonon excitations in the TARPES image. Strikingly, further FDARPES analysis allows us to find out the flat band structure survives even during the photo-induced insulator-to-metal transition (IMT). Besides, the phase of FDARPES revealed the antiphase behavior between different two bands, which indicate the opposite sign of electron-phonon couplings between them.

TARPES measurements were performed with a commercial extremely stable Ti:sapphire regenerative amplifier system (Spectra-Physics, Solstice Ace) with the center wavelength of 800 nm, the repetition rate of 10 kHz, and the pulse duration of ~35 fs [21], which was used for the pump light. After taking a second harmonic (SH) via 0.2-mm-thick $\beta$-BaB$_2$O$_4$ (BBO), the SH light is focused to the static gas cell filled with Ar.
and the high harmonics are generated. We selected the seventh harmonic of the SH (hv = 21.7 eV) for the probe light using a set of SiC/Mg multilayer mirrors. Photoelectrons are collected by a hemispherical electron analyzer (Scienta Omicron, R4000). The temporal resolution was evaluated to be ~70 fs from the TARPES intensity far above the Fermi level corresponding to the cross correlation between pump and probe pulses. The total energy resolution was set to ~250 meV. All the spectra for the TARPES measurements were taken at 15 K.

In order to confirm the cleaved surfaces of the sample and temperature-induced phase transitions, we perform the static ARPES measurements with a He discharge lamp (hv = 21.2 eV). Figures 2(a) shows the Fermi surface (FS) mapping of 17'TaS2 measured at 240 K. The FS is clearly observed around the M point, which is indicated as a red oval. The photoemission intensity around the Γ point is ascribed to the flat band associated with the NCCDW phase [5]. Figures 2(b)-2(i) show the temperature-dependent ARPES images along the (b)-(e) Γ-M-Γ and (f)-(i) Γ-K-M directions. With decreasing temperature, the flat band structure is more pronounced at the Γ point as a result of the enhancement of CDW phase. It is also of notice that a small gap below the Fermi level (E_F) corresponds to the Mott gap denoted as Δ_{Mott}, which is consistent with the previous ARPES report [4]. Regarding the CDW phases, the ICCDW gap denoted as Δ_{ICCDW} around the M point increases with decreasing temperature. Besides, the two gaps associated with the CDDW phase denoted as Δ_{CDDW1/2} are observed at the band dispersion around the Γ point. These findings are consistent with the previous report [4].

Now we discuss the TARPES results. Figure 3(a) shows the TARPES image before the arrival of the pump pulse around the Γ point along the M-Γ-M direction. While either the CDDW gap or the flat band is clearly seen due to the lack of energy resolution, which is typical for the HHG TARPES measurements, we can identify them by comparing static ARPES images shown in Fig. 2. After the strong pump pulse excitation of 4.2 mJ/cm², the system turns into metallic phase [18]. Figure 3(b) shows the differential TARPES image at the delay time (Δt) of 240 fs. The increase and decrease of photoemission intensity are indicated as red and blue colors, respectively. It is noticed that the band dispersion crosses E_F as the red region around E_F increases. This demonstrates the photo-induced IMT with a collapse of the Mott gap as previously reported [18]. The transient electron temperature at 160 fs is estimated to be higher than 600 K [22], which is above the NCCDW phase (350 K).

To study the dynamics in more detail, Fig. 3(c) shows the time-dependent photoemission intensity integrated at the energy-momentum region denoted as I and II in Figs. 3(a) and 3(b). Overall, the immediate increase (decrease) at Δt = 0 ps followed by the fast decrease (increase) and slow relaxation is observed for the region I (II). Besides, significant oscillations are confirmed to be superimposed onto both data. Moreover, these oscillations have anti-phase character with respect to each other. For highlighting the

![Fig. 3: (a) TARPES image before the arrival of the pump pulse. (b) Differential TARPES image at the delay time of 240 fs. (c) Time-dependent photoemission intensity integrated at the energy-momentum region denoted as I and II in (a) and (b). (d) Amplitudes of the Fourier transform of the oscillatory components deduced from I and II in (c).](image-url)
oscillatory components, we first subtract overall dynamics by fitting to a double-exponential function convoluted with a Gaussian, shown as the black solid lines in Fig. 3(c). Fourier transformations are performed for the subtracted data, and amplitudes for each frequency component are shown in Fig. 3(d). One can see the strong single peak at 2.5 THz, which corresponds to the breathing $A_{1g}$ mode and is also called the CDW amplitude mode, confirmed by Raman spectroscopy [23], and the oscillation is as a result of coherent-phonon excitations based on the displacive excitation mechanism [24]. It should also be mentioned that the oscillation appeared in the TARPES image is due to the electron-phonon coupling, which connect the modulations between the lattice structure and electronic wave functions [25].

To further investigate the dynamical change of the electronic band dispersions modulated by the CDW amplitude mode, we proceed to FDARPES analysis. Figures 4(a) and 4(b) show the FDARPES images for amplitude and phase, respectively, at the frequency of 2.5 THz around the $\Gamma$ point. FDARPES images at the different momentum cuts are shown in Fig. S2 [22]. One can notice that there exist two distinctive peak structures near and below $E_F$ shown as black squares and circles, respectively, in Fig. 4(a). Interestingly, their phases shown in Fig. 4(b) are different by nearly $\pi$, which was already seen as an anti-phase behavior in the time-dependent photoemission intensity in Fig. 3(c). This anti-phase character clearly shows that the single band oscillates between these two peak structures, synchronizing with the lattice modulation corresponding to the CDW amplitude mode, which is schematically shown in Fig. 5. Strikingly, the shape of the band drastically change between these two peak positions, and the flat band structure with a smaller

![Amplitude and Phase Images](image)

**Fig. 4:** Frequency-domain ARPES images for (a) amplitude and (b) phase at the frequency of 2.5 THz. Black markers show the peak positions for the amplitude (a).

Mott gap is clearly seen near $E_F$ shown as black circles in Fig. 4. This strongly suggests that CDW phase survives even though the Mott phase is strongly suppressed seen as a collapse of the Mott gap. Furthermore, it is unveiled that the CDW amplitude mode can dynamically modulate the Mott gap. It is also of notice that these clear peaks are only elucidated in the frequency domain, never extracted in the time domain analysis. The FDARPES technique relying on the lock-in amplification can greatly improve the signal-to-noise ratio by selecting only the relevant frequency component.

In summary, we have conducted TARPES measurements on 1T-TaS$_2$ and proceed to perform FDARPES analysis to understand the underlying nature of the photo-induced metallic phase. While the Mott-insulating gap is closed confirmed by TARPES, the flat band dispersion is clearly seen in the FDARPES image, which strongly indicates survival of the CDW phase even during the photo-induced IMT. Our results shed new light in the electron-electron and electron-phonon interactions in this system.

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