The colour of charge density wave order

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Like VSe$_2$, TaS$_2$, along with its doped variants, also belongs to the family of transition metal dichalcogenides (TMDCs). Not surprisingly, it holds CDW phases as many other TMDCs do. However, 1T-TaS$_2$ with its doped compound form a unique group of materials in the sense of its strongly correlating nature and the stronger-than-average inter-layer interaction. Besides, the commensurability of CDW phases plays an important role in its physics properties, while the transition of the CDW commensurability in VSe$_2$ is subtle [97]. As we shall see, the different commensurabilities in 1T-TaS$_{2-x}$Se$_x$ give distinct responses to the DC electric field as well as to light.

5.1. Research Background

The revival of the research interest of 1T-TaS$_2$ in the last decade is primarily concentrated in the debate of the Mottness of its low-temperature phase and its non-equilibrium phenomena.

Mott insulator or not, that is the question

Based on the fact of the insulating nature and the odd number of electrons in one unit cell in the commensurate phase, it was proposed that the commensurate CDW (CCDW) phase in pristine TaS$_2$ is an example of the Mott insulator [17]. Then the lower Hubbard band, which is barely dispersive, was identified in both tunnelling and APRES measurements with the Mott gap opened around Γ point in size of 300 ~ 400 meV [121–124]. One obvious splitting in the band structure is also found between Γ and M point in the reciprocal
space around 800 meV below the Fermi surface [122, 125, 126], which could be the consequence of the band folding in the commensurate phase [127]. Another gap which is already present in the ICCDW phase is observed between M and K point, and its size strongly depends on temperature, which evolves from 300 meV at 400 K to 800 meV at 130 K [125, 126]. The band structure reorganisation deep below the Fermi surface seems to suggest a strong electronic correlation as well. Furthermore, the doublon dynamics observed using the time-resolved ARPES supports the strong electronic correlation picture of TaS$_2$ [128]. Besides, a pseudogap is formed prior to the Mott transition, which is observed in the room temperature ARPES as well as the infrared spectroscopy [129–132]. In the case of doped TaS$_2$, the low-temperature phase could no longer be insulating but metallic and its pseudogap persists to the low temperature [133]. The theoretical calculations of the electronic structure of 1T-TaS$_2$ based on the strongly correlated scenario also give decent agreement with the experimental data [124, 134].

On the other hand, different from other TMDC materials, TaS$_2$ is shown to have an unusually strong inter-layer coupling. The symmetry of the star of David as the motif in the CCDW phase gives multiple possibilities of stacking. The stacking order strongly modifies the electronic structures. Ab initio calculations show that the electronic structures of TaS$_2$ strongly depend on the stacking orders [135, 136], and the DFT calculations of certain stackings, which enhances the interlayer hoping, could give a qualitative agreement with the ARPES data even without including the strong Coulomb repulsion U [127]. It was also shown that the seemingly flat band observed in ARPES could be reproduced by considering the hybridisation of rotational $t_{2g}$ orbitals [137].

Apart from the theoretical perspective, the effect of the stacking orders on the top layer electronic structure has been intensively studied using STM [138, 139], from which one learns that the gap size observed in STS could be strongly modified by different stacking orders or even closed near the stacking mismatch, i.e. the domain walls. The CCDW was therefore proposed as a normal band insulator as the result of the dimerisation in the c-axis [140].

The recent STM report on the surface adatom experiments shows the coexistence of the Mott insulating and the normal insulating regions depending on the stacking order of the top layer [141]. This result at least partially concludes the discussion of the Mottness in the past.

**Non-equilibrium phenomena**

The stacking-order-sensitive nature of TaS$_2$ also gives rise to more complicated physics as the inter-layer van der Waals bond can be easily rearranged with external excitations. DFT calculations show that many of the stacking orders are not the ground state [127, 136], thus one could imagine that different stacking orders lead to many local minima in the free energy landscape [9, 23, 29, 30], though the relation between the stacking order and the meta-stable state was realised long after the finding of the meta-stable states.
The meta-stable states, found in the low-temperature region, are typical signs of the non-equilibrium physics in 1T-TaS$_2$ and are named the hidden phase. The hidden phase was discovered as the insulating CCDW phase jumps to a much less insulating phase after being excited by the laser pulse [21, 22] or the electric pulse [23, 24]. The ultra-fast transition from the stable CCDW phase to the hidden phase involves the large reduction of in-plane and out-of-plane resistivity in the order of 100 times smaller [21, 24]. Combined with the STM, it was proved that such drastic change in the resistivity is due to the formation of the in-plane domains and rearrangement of the out-of-plane stacking orders [24–26]. The hidden phase also features with the amorphous packing of the stars of David and a glass-like relaxation rate, which is introduced as an example of the quantum jamming transition [25, 142]. From the perspective of the application, such hidden phase can be fast switched on and off using lasers or electric pulses, which could be used as a potential memristive device working at low-temperature [21, 23, 27].

For such a jamming transition, the relaxation time scale of this system could be comparable with the cooling rate achieved in the experiments. As expected, it was found that the NCCDW phase in the nano-thick TaS$_2$ can be super-cooled if the cooling rate is high (1 K/min sim 10 K/min depending on the thickness of the sample). Then the CCDW phase is absent, and the super-cooled NCCDW phase is much less insulating than the CCDW phase as the hidden phase [8, 9]. However, the bulk TaS$_2$ can only be super-cooled once the cooling rate is at least higher than 30 K/min [28]. In general, the critical cooling rate which leads to the super-cooled state is lower as the TaS$_2$ sample is thinner [8]. One STM paper reports that both the voltage-excited hidden phase and the super-cooled NCCDW have similar mosaic-like domain distribution.

The real space image of the hidden phase is obtained via STM. Applying voltage pulses in the CCDW phase forms the mosaic-like domains, where the 'Mott' gap in the CCDW phase is closed[28, 143–145]. Each domain has a certain phase shift between adjacent layers, i.e. the stacking order [28, 144]. The domain walls are regions where the in-plane commensurability changes or the stacking order changes [144]. Such a mosaic pattern can be stabilised due to strain [145]. Recently it was even claimed to be found in equilibrium, which could be due to the existence of a high density of defects [146]. Doping could also help stabilise such mosaic phase as the CCDW phase is then suppressed which is demonstrated in the Ti-doped samples [147] or Se-doped samples [148].

The theory work on the hidden phase also brings new insight. DFT calculation shows that the CCDW phase is stable upon electron doping while could be suppressed by hole doping [149]. In the case of light or in-plane field-induced hole doping, the energy of CCDW increases. One Monte Carlo simulation points out that the stacking order could be frozen during the fast cooling so that the system will end up with some kind of meta-stable state other than the CCDW phase [136]. As for the theoretical description of the hidden phase, it
was proposed that one should consider the interacting polaronic Wigner crystal as the minimal model [150], where each polaron is the single layer star of David with the odd number of electrons and surrounded by the lattice distortion. The following up Monte Carlo work reproduces the mosaic pattern in the hidden phase using this polaronic model by introducing random defects which eventually coalesce into the domain walls [151]. Further expanded work based on this polaronic model suggests that the mosaic phase might be the result of the frustration of the commensurability between the polaron distribution and the lattice [152].

Se doping could be a powerful tool to study the possible Mott physics and the non-equilibrium physics in TaS$_2$ since it gradually suppresses the CCDW phase [7, 124, 153] and stabilises the mosaic phase [124, 148]. The cooling down and warming up phase diagram was obtained using transport [7, 154] and the specific heat measurement [155] respectively. For TaS$_{2-x}$Se$_x$, one critical doping level is around $x = 0.8$ where the CCDW is fully suppressed and the superconductivity is induced in the phase diagram [7]. Moreover, the thermal electric power curve changes sign around $x = 0.8$, where the majority carrier changes from electron (S rich) to (Se rich). Besides, the DFT+U shows that the band structure changes from a Mott insulator at low doping to a charge transfer insulator around $x = 0.8$ [124]. One paper studied the hidden phase in Se-doped samples, where multiple meta-stable states could be reached by tuning the fluence of the excitation light [156].

Our collaborators recently discovered more specialties about the $x = 0.8$ doping [157]. First, the low-temperature meta-stable state can be reached even at a relatively low cooling rate ($\sim 1$ K/min). Second, the meta-stable state can only be reached if the cooling process starts from the ICCDW phase. Therefore, if we warm up the sample from the meta-stable state only back to room temperature, the next cooling down will end up with the normal CCDW phase with high resistivity. Thus the relaxation time in $x = 0.8$ samples should be much larger than pristine TaS$_2$, and it shows some kind of thermal path-dependent memory effect.

In summary, the Se-doped samples not only provide the playground for the evolution of many interesting physical phenomena, such as the collapse of the Mottness [124] and emerging of the superconductivity [7] but also give rise to novel non-equilibrium phenomena. And the doping level around $x = 0.8$ requires particular attention.

### 5.2. The Fundamentals of CDW in 1T-TaS$_2$

From high temperature to low temperature, four CDW phases in 1T-TaS$_2$ with different commensurabilities have been observed and fully characterised with various techniques. Each phase transition between different in-plane commensurabilities is accompanied by a sharp jump of the electric resistivity [140, 158] and the change of the out-of-plane stacking order [159, 160]. At low temperatures, the CDW order becomes commensurate, where the star of David
structure made of 13 Ta atoms is the unit motif in-plane and occupies the whole system. When the temperature increases, the CDW order partially loses commensurability. The charge order modulation and the lattice have a small angle difference, then the two periodicities form a Moiré pattern so that the commensurate CDW motifs cluster together and it appears to have a long-range modulation with 10~20 lattice constant [161]. The high-temperature phase is incommensurate. In the warming-up process, an extra CDW order: triclinic phase is found between the CCDW and NCCDW phase, where the commensurate region is arranged in the stripe pattern [159, 162].

As shown in Fig. 5.1 does not consider the effect of the cooling rate on the phase transitions. Thus it does not contain any information on the meta-stable state. Our optics data show that the hysteresis of the phase transitions is quite sensitive to the cooling rate as well\(^1\)

We, therefore, make a modified phase diagram based on our optical data which will be discussed later. The integrated \(\sigma_1(\omega)\) as the function of temperature is accompanied by a significant signal jump as shown in Fig. 5.2. The temperature changing rate is set to be 1.7 K/min. The new phase diagram is shown in Fig. 5.3. Compared with Fig. 5.1, the cooling down phase diagram is only slightly modified from the previous reports [7, 154]. The warming-up phase diagram is compatible with the specific heat measurements in the sense that we determine the similar boundary between the T-phase and the CCDW

\[^1\text{For example, according to Fig. 5.2 the } T_c \text{ of the phase transitions shifts } \sim 10 \text{ K when the cooling rate changes from 1.7 K/min to 2 K/min. The reflectivity of the meta-stable state also changes a lot.}\]
5.3. Experimental details

Samples are grown using chemical vapour deposition [157]. Infrared reflectivity spectra are collected over the energy range from 6 meV to 4 eV and between 16 K and 400 K for two samples with Se contents $x = 0.8$ and $x = 1.0$. In order to study the hysteresis in this system, a temperature loop is designed to start cooling from 400 K down to 16 K. At base temperature data is collected for 20 minutes and then the sample is heated to 400 K. Both cooling and warming experiments are carried out with a constant temperature change of 1.7 K/min. Each cycle is repeated several times to verify the reproducibility and reduce the noise in the data. The experiment is repeated right after the in situ evaporation of silver or gold on the samples to obtain reference spectra. These allow us to determine the absolute reflectivity of our samples. To obtain the optical conductivity, we use the variational dielectric function method proposed in Ref. [81].

5.4. Results

The real part of the optical conductivity, $\sigma_1(\omega, T)$, is shown in Fig. 5.4 for both the $x = 0.8$ (top row) and $x = 1.0$ crystals (bottom row). Data are presented separately for cooling and heating to highlight the distinct behaviour of the optical response. The optical conductivity of the incommensurate charge
5.4. Results

Figure 5.3: The phase diagram of Se doped 1T-TaS\(_2\) in the cooling down and warming up process with fast temperature changing rate (~1.7 K/min). The cooling down phase diagram is slightly modified based on \([7]\), The \(T_c\) of the meta-stable state is determined in the optics measurement. The critical temperatures of pristine TaS\(_2\) in the warming up phase diagram are from \([140]\), and the boundary of the T-phase in dashed lines was verified in the specific heat measurements seen in \([155]\).

density wave phase (ICCDW; \(T \sim 400\) K) is characterized by a nearly frequency-independent free charge response. Compared to the optical conductivity of pristine 1T-TaS\(_2\), reported in Ref.\([132]\) and Ref.\([163]\), the extrapolated DC conductivity of Se doped crystals is similar. The interband conductivity above 1 eV is significantly larger, although the three interband transitions at 1 eV, 1.66 eV and 2.2 eV are also observed in previous measurements.

At the transition to the nearly commensurate state (NCCDW; \(T_{NCCDW} \approx 370\) K), we observe a sudden depletion of spectral weight below 1 eV (visible as a step in the temperature-dependent conductivity in Fig. 5.4(c),(d),(g) and (h)). This depletion evolves similarly for both crystals with decreasing temperature. The \(x = 0.8\) crystal undergoes a second transition at 130 K where another sudden removal of spectral weight takes place. For 1T-TaS\(_2\), this transition has been identified as the formation of the commensurate CDW phase (CCDW). As we will discuss below, the \(x = 0.8\) crystal first enters an intermediate meta-stable phase.

As the screening from free charge carriers is reduced, a series of phonon modes becomes visible. A group theoretical analysis predicts 40 infrared active phonon modes in the CCDW phase of 1T-TaS\(_2\) \([132]\). This number can be expected to become even larger for Se-doped crystals since the substitution of some of the S atoms with Se atoms will lead to mode splitting and frequency shifts. This is indeed what we observe: there are two additional phonon modes at 18 meV and 19.6 meV that are not present in the earlier infrared data\([132, 163]\). As was pointed out in Ref. \([163]\), the frequency splitting between the phonon modes can be very small. Our experimental resolution of 0.25 meV
5. Non-equilibrium phenomena in CDW phases of $\text{TaS}_2-\text{Se}_x$

Figure 5.4: Optical conductivity of Se doped $\text{TaS}_2-\text{Se}_x$. The top row shows the data for $x=0.8$ and the bottom row for $x=1.0$. (a): $\sigma_1(\omega,T)$ for selected temperatures, measured during cooling. As temperature decreases a series of IR active phonon modes become visible. (b): $\sigma_1(\omega,T)$ for selected temperatures, measured during heating. The data shows clear spectral differences compared to the cooling data. (c,d): the temperature dependence at two selected frequencies clearly shows distinct cooling and heating transitions that are not simply different due to the hysteresis of the transitions. Notably, panel (d) shows two distinct transitions while cooling and 4 transitions while heating. Panels (e-g) show the same results as (a-d) except that in the $x=1.0$ sample the mosaic and CCDW phase is suppressed.

is certainly not sufficient to observe all possible infrared active modes. Apart from the extra phonon modes, we observe a similar number of modes although they are all shifted in frequency. Most modes appear broader and we attribute this to unresolved mode splitting due to Se substitution.

We now return to the second transition of the $x=0.8$ crystal at 130 K. In 1T-$\text{TaS}_2$ a transition from the NCCDW to CCDW phase takes place at 180 K. Angle-resolved photoemission spectroscopy (ARPES) and scanning tunnelling microscopy (STM) experiments have shown that this transition is accompanied by the opening of a large gap at the Fermi level and the formation of bands below and above the Fermi level [138, 140, 164, 165]. Regardless of the nature of this transition, it has been shown that the resistivity below this transition becomes insulating with an exponential enhancement of the resistivity, $\rho(T) \propto \exp(-A/k_B T)$ [166].

Our optical conductivity data indeed shows the formation of a gap, but still has a significant background conductivity at 16 K. Resistivity measurements on our crystals show that the low-temperature resistivity does not show the expected exponential enhancement, but instead only shows a minor increase. A significant enhancement of the resistivity only occurs when the temperature is
increased to above 130 K. This is reflected in our experiments by another sudden depletion of spectral weight as the crystal is heated to above approximately 130 K (Fig. 5.4(c,d); red curve).

This behaviour is reminiscent of the 'hidden' or 'mosaic' phase that has previously been observed in 1T-TaS$_2$. Here a photo-induced [21] or voltage-induced [9, 24] meta-stable phase can be obtained that is accompanied by a significant reduction of the resistivity. More recently, this phase was also observed in Ti substituted TaS$_2$[147] and at the surface of 1T-TaS$_2$[146]. The temperature dependence of the optical conductivity provides another clue that this phase is indeed meta-stable. During our experiment, we stabilize the temperature after cooling to 16 K for 20 minutes. We observe a small but significant change in the optical response that is most prominently visible in Fig. 5.4(d). As we start increasing the temperature back to 400 K, we note a small difference between the cooling and heating curves between 16 K and 130 K. This difference is most prominent in the energy range around 60 meV. Based on these observations, we thus identify the 16 K optical conductivity as representative of the electronic spectrum of the mosaic phase. The lowest temperature optical conductivity spectrum of the CCDW phase in our experiment is only obtained above 130 K after heating the sample (Fig. 5.4(b); green curve). We can exclude that this transition is to one of the other CDW phases that have been observed in 1T-TaS$_2$ [155, 162, 167]: as temperature increases further, three more transitions are visible in our data. These then correspond to the T-phase (305 K), NCCDW phase (340 K) and ICCDW phase (385 K). We can therefore use the 157 K data in Fig. 5.4b to estimate the size of the CCDW gap, $\Delta_{CCDW} \approx 60$ meV. This is smaller than observed for 1T-TaS$_2$ where a value of $\Delta_{CCDW} \approx 100$ meV was extracted [132]. The gap to $T_c$ ratio for TaS$_{1.2}$Se$_{0.8}$ is reduced to $2\Delta/k_BT_c \approx 8.5$ from $2\Delta/k_BT_c \approx 13$ for 1T-TaS$_2$.

The question that now emerges is whether there is a difference in the nature of the transitions between the NCCDW and mosaic phases and between the mosaic and CCDW phases. These questions are often approached by making use of spectral weight analysis. However, in many TMDCs, it has been observed that the temperature dependence of the optical spectra is significant even in the visible and UV parts of the optical spectrum [168]. It has been speculated that this is a consequence of changes in the interlayer coupling that emerge when lattice expansion or contraction takes place [167, 169]. The temperature dependence of 1T-TaS$_2$ appears to follow this trend. Our optical conductivity data shows significant temperature dependence over the entire spectral range, up to 2 eV. A significant portion of this spectral weight enhancement appears to be unrelated to the various charge density wave transitions and so we have no way to disentangle 'trivial' spectral weight changes from re-distributions due to the opening of new charge density wave related gaps.

We, therefore, turn to the normalised difference of the optical conductivity to highlight differences in the formation of the mosaic and CCDW phases. In Fig. 5.5, we calculate the difference between the optical conductivity and
a reference temperature, normalised to the conductivity at the same reference temperature, $\Delta \sigma_1(\omega, T, T_0)/\sigma_1(\omega, T_0)$. Having identified the transition temperature of the NCCDW to the mosaic phase around $T_0 \approx 145$ K from Fig. 5.4(c), we plot in Fig. 5.5(a) $\Delta \sigma_1(\omega, T, 145$ K$)/\sigma_1(\omega, 145$ K$)$. With decreasing temperature, the spectral weight at low energy is depleted, with the largest changes happening at the lowest photon energy. As the photon energy increases, the changes become gradually smaller, as can be more clearly seen from Fig. 5.5b.

The transition from the mosaic to the CCDW state during heating follows a different behaviour. To highlight this, we take $T_0 \approx 124$ K as reference.
Fig. 5.5c shows that a pronounced minimum develops around 0.1 eV and possibly a second minimum around 0.2 eV. Fig. 5.5(d) shows that the largest change in the optical response now takes place at finite photon energy between 50-100 meV. This difference in temperature dependence between cooling and heating points to different gap formation mechanisms as we will discuss next.

The two likely scenarios along which a gap opens at the Fermi level are a depletion (Fig. 5.5i) or gradual opening of a gap (Fig. 5.5k) of the density of states around the Fermi level. The later case is often associated with spontaneous symmetry-breaking phases that are accompanied by the formation of a temperature-dependent gap and associated Goldstone modes (sliding modes in this case). The temperature-dependent optical response of such a BCS type phase transition was numerically evaluated by Zimmerman et al. in Ref. [48] and has been implemented in the software package RefFit [78]. We model the temperature-dependent response of $\Delta \sigma (\omega, T, T_c)$ using this numerical code and plot the result in Fig. 5.5g. The temperature dependence at selected energies is shown in Fig. 5.5h. A comparison between these panels and corresponding experimental panels (Fig. 5.5c and d respectively), shows qualitatively similar behavior.

The impact of a depletion in the density of states on the optical response is harder to model: it requires a concrete theoretical backing of the phenomenon or one has to resort to approximate estimates making use of the joint density of states (JDOS). The advantage of the JDOS is that an approximate estimation of the optical response can be used for both gap opening and gap closing scenarios. However, since we have an exact method available for the BCS case, we use a similar approach to model the pseudogap formation. This is achieved by taking a sum of a Drude term and the $T=0$ BCS optical conductivity:

$$\sigma (\omega, T) = \left( \frac{T}{T_c} \right)^2 \sigma_{Dr} (\omega, T) + \left( 1 - \frac{T}{T_c} \right)^2 \sigma_{BCS} (\omega, 0)$$  \hspace{1cm} (5.1)

We have verified that this gives the same qualitative result as the JDOS approximation. Eq. 5.1 allows us to introduce a small temperature dependence in the Drude response, in particular in the Drude width $\Gamma (T)$. The result of these simulations is shown in Fig. 5.5e,f. The results qualitatively reproduce the experimental results in Fig. 5.5a,b. The depletion of $\Delta \sigma_1 (\omega, T, 145 K)/\sigma_1 (\omega, 145 K)$ above 0.1 eV is reproduced in panel 5.5e for energies $\omega/\Delta > 1$. This requires us to assume a temperature-dependent Drude component for which the $\Gamma (T)$ decreases. The temperature dependence in the experimental data (Fig. 5.5b) is much faster, but we can qualitatively reproduce the observation that the depletion is largest at the lowest energy.

We now turn to the possible interpretation of our experimental results. The key observation is that the low-temperature optical conductivity features a residual metallic contribution as observed previously in non-equilibrium experiments [21, 170, 171] etc. The metallic has previously been attributed to stacking faults in the CCDW order that leads to the formation of small domains with ‘charged’ domain walls [146]. As temperature increases, thermal
fluctuations lead to the removal of these stacking faults, and the long-range CCDW order can set in.

The analysis of our optical data shows that there is a distinct difference between the formation of the mosaic and the long-range ordered CCDW state. The former is accompanied by the formation of a depleted density of states around the Fermi level. Such a gradual depletion is often referred to as a 'pseudogap' in the context of the cuprate superconductors. Its origin in the cuprate case is unknown, but some form of pair formation without long-range coherence [172] has been suggested as a possible source. In TaS$_2$, this scenario may hold true in the mosaic phase where the onset of long-range CCDW order is suppressed. The interplay between the metallic domain boundaries and short-range CCDW order could be analogous to incoherent fluctuations of the pairing field, thus providing a route to the formation of 'preformed density fluctuations'.

At elevated temperatures, or if the cooling rate is significantly decreased [157], stacking faults can be annealed away, allowing the CCDW state to emerge in full. In our optical data, this is accompanied by the opening of a gap that we estimated to be of order 60 meV.