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### Suppression of the commensurate charge density wave phase in ultrathin 1T-TaS<sub>2</sub> evidenced by Raman hyperspectral analysis

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#### Abstract

Using temperature-dependent and low-frequency Raman spectroscopy, we address the question of how the transition from bulk to few atomic layers affects the charge density wave (CDW) phases in 1T-TaS<sub>2</sub>. We find that for crystals with thickness larger than  $\approx 10$  nm the transition temperatures between the different phases as well as the hysteresis that occurs in the thermal cycle correspond to the ones expected for a bulk sample. However, when the crystals become thinner than  $\approx 10$  nm, the low-temperature commensurate CDW phases can be suppressed down to the experimentally accessible temperatures (~80 K) upon cooling at moderate rates (~5 K min<sup>-1</sup>). In addition, even the near commensurate CDW phase is not accessible in few-layer flakes below  $\approx 4$  nm for even slower cooling rates (~1 K min<sup>-1</sup>). We employ Raman hyperspectral imaging to statistically confirm these findings and consider the interlayer coupling and its dynamics to play significant roles in determining the properties of CDW systems consisting of a few unit cells in the vertical direction.

#### **SECTION: Introduction**

In transition metal dichalcogenides, the competition of various effects such as dimensionality, electron-phonon coupling, electron-electron interactions, and disorder gives rise to a wealth of quantum phases [1]. The anisotropy of the crystal and the weak layer bonding are typically understood as responsible for their quasi 2D properties. However, attesting to the importance of the interlayer coupling, when thinned down from bulk to only a few atomic layers some material properties change [2]. Experimentally, exploring the questions of how thickness can tune material properties is possible due to advances in fabrication techniques following the demonstration of micromechanical cleavage of atomically thin materials [3]. In particular, the precise nature of the driving mechanisms and the many-body states such as charge density waves (CDW) in atomically thin layered materials is yet to be understood [4-9].

1T-TaS<sub>2</sub> has one of the richest phase diagrams[10]: metallic at higher temperatures, has at least three temperature-dependent CDW phases with different structures; under pressure and doping it becomes superconducting [11], it was suggested as Mott insulator [12] and quantum spin liquid [13]. In this letter we use variable-temperature and low-frequency Raman spectroscopy to show that by reducing the thickness *h* of 1T-TaS<sub>2</sub> to the range  $2 \gg h/nm \gg 4$ , the transition to a commensurate charge density wave (CCDW) is suppressed down to the experimentally accessed temperatures (~80 K) at moderately slow cooling rates (~1 K min<sup>-1</sup>). Furthermore, for crystals with thickness in the range  $\approx 5$  nm – 10 nm even the nearly commensurate (NC) CDW phase is suppressed.

In 1T-TaS<sub>2</sub> crystals (Figure 1(a)), different CDW phases arise upon cooling and warming (Figure 1(c)). Cooling from  $\approx 600$  K the system develops an incommensurate CDW (ICCDW) state and further cooling to  $\approx 350$  K takes it into a nearly commensurate CDW (NCCDW) arrangement. The term incommensurate implies that the CDW wavevector cannot be written as n/m times the reciprocal lattice wavevector, where n and m are integers. In the NCCDW phase, commensurate domains coexist with incommensurate ones. The transition below  $\approx 150$  K, is to a commensurate CDW (CCDW) when the Ta atoms participating in the associated periodic lattice distortion (PLD) are arranged in groups of 13 atoms (Star of David, Figure 1(b)). For details of the structure and resistivity characterization see Supplemental Material Figure S1 [14].

#### **SECTION: Raman results at different temperatures and number of layers**

Here we study the changes in the Raman spectra corresponding to crystal transitions into

different CDW phases, therefore probing the lattice vibrations for both few-layers crystals with different thicknesses as well as bulk. While bulk crystals were studied before [15-17], investigations for the thinnest of flakes are only recent [5-9]. Important differences emerged from these studies, leaving the field with an active debate regarding the nature and origin of the CDW phases in the atomically thin limit. Here, Raman hyperspectral imaging is employed as a novel approach in order to elucidate the distinctive properties of atomically thin samples by visualization of distribution and homogeneity of the spectral features.

For each selected area the Raman spectrum is recorded as a function of temperature. For a bulk crystal, Raman spectra were measured at temperatures from T = 403 K down to 80 K (Figure 2(a)). These spectra can be grouped according to their distinct spectral features corresponding to the different CDW states of the crystal. In Figure 2(b) we show characteristic spectra for the ICCDW, NCCDW and CCDW phases. The spectrum of the ICCDW phase has broad and weak peaks typical of incommensurate structures, where the translational symmetry is broken along the modulation direction. Rather than a finite number of peaks associated with zero-momentum phonons as in the case of a crystalline phase, the broad peaks of the ICCDW spectrum correspond to a convolution of an infinite number of modes within the interior of the Brillouin zone (BZ) of the high-temperature non-modulated phase, that are folded to the center of the BZ of the incommensurate phase. At lower temperatures, for the CCDW phase, we observe sharp peaks, typical of crystalline structures. In this state, the unit cell of the CCDW contains 39 atoms resulting in 117 phonon modes, from which  $19A_g + 19E_g$  are Raman active [17] [7] [18]. Using polarized Raman, we identified the majority of these phonon modes and tabulated their frequencies in the supplementary material. The spectrum of the NCCDW phase in Figure 2(b) has characteristics of both the ICCDW and CCDW.

To illustrate the changes in the Raman spectrum as the system goes through the different phase transitions, we plot Raman intensity charts as a function of temperature (left panel of Figure 2(c) - cooling cycle). Considerable changes occur at  $T \approx 150$  K corresponding to the NCCDW-CCDW transition. In the right panel of Figure 2(c) we exhibit the temperature dependence of the Raman spectrum, upon warming up. The abrupt change of the transition CCDW-NCCDW occurs at  $T \approx 215$  K. Its hysteretic nature (Figure 1(c)) can, therefore, be confirmed using a conventional Raman spectroscopy experiment (>100 cm<sup>-1</sup>). We observe, furthermore, that the low-frequency Raman A<sub>g</sub> mode at 78 cm<sup>-1</sup> (see Supplemental Material[19] ) of CCDW is significantly affected by the phase transition, weakening in intensity as one goes from the CCDW state to the NCCDW one (Figure 2(a)). This mode, thus, may be potentially used as an indicator for inferring the presence of long-range CCDW domains.

We will now explore the temperature dependent Raman spectra as a way to probe how the different CDW phases change when thinning down the system to a few atomic layers. Figure 3(a) shows a mechanically exfoliated flake with a thicker part (Area 1),  $h_1 \approx 160$  nm, and a thinner one (Area 2) with  $h_2 \approx (8 \pm 2)$  nm. Figure 3(b) presents the Raman spectra upon cooling for the two different areas. We observe the abrupt change at the NCCDW-CCDW as explained earlier. In contrast, the spectra of Area 2 below 200 K are different from the low temperature spectra of Area 1, especially in the 100-200 cm<sup>-1</sup> spectral range. In this case, the transition into a CCDW phase is not clearly observed, suggestive that it may remain in the NCCDW state at the lowest temperatures reached experimentally, i.e. ~ 80 K.

We now focus on samples with thicknesses below ~ 4 nm as shown in Figure 3(c), (e). In Figure 3(c) we plot the Raman spectra taken for the flake indicated as Area 3 at  $T \approx 273$  K, 136 K and 93 K and find them considerably similar. Whereas for the flake of Area 2 a clear and strong peak at 242 cm<sup>-1</sup> was observed, for that of Area 3, the absence of this peak and other spectral features is attributed to the ICCDW, as characterized in Figure 2(a), at any of the three temperatures investigated. This result implies that for such thin flakes the ICCDW-NCCDW transition may not even occur. When we measure flakes of intermediate thickness such as in Area 4, as seen in Figure 3(d), the spectrum develops a peak at  $\approx 242$  cm<sup>-1</sup>. Thus, these observations suggest that, depending on the thickness, the system may or may not undergo transitions into the respective CDW phases.

In atomically thin samples, the presence of disorder can hamper the more metastable NCCDW-CCDW transition [9]. To minimize the effect of the environment on our samples, we prepared and measured PMMA-encapsulated 1T-TaS<sub>2</sub> flakes, as shown in Figure 3(e). The Raman spectra of Areas 5 and 6 ( $h_5 \approx (3 \pm 1)$  nm,  $h_6 \approx (6 \pm 2)$  nm) and an arbitrary bulk one were collected at 80 K and presented in Figure 3(f). They are qualitatively similar to those previously shown, many of the spectral features characteristic to the CCDW and/or NCCDW weaken with decreasing flake thickness. Nevertheless, owing to a higher signal-to-noise ratio of the hyperspectral measurements, a better definition of the spectral features, such as a weak peak at  $\approx 242 \text{ cm}^{-1}$ , could be identified for the flake of Area 5.

#### **SECTION: Hyperspectral Raman imaging results**

In order to explore the homogeneity and morphology of the 1T-TaS2, we used 2D hyperspectral Raman imaging. Examining the variation of a single parameter for a specific Raman band, such as peak intensity, position or width, within a scanned area provides insight into the distribution of properties [20]. To characterize all the three CDW phases, we consider the spectra of the ICCDW and CCDW to be the basis spectral components and analyze their distributions. In Figure 4(a), these are shown against the Raman spectra taken within Areas 5 and 6. In our analysis, we focus on the frequency regions with the three most prominent CCDW bands in the low-frequency regime – same as the peak top region of the broad Raman band for the ICCDW phase (Figure 4(a)). The result presented in Figure 4(b) is the weight distribution map for each basis component obtained from the fitting of the hyperspectra acquired at 80 K for the flakes of Figure 3(e). They indicate where a given basis spectrum fit the hyperspectra, the intensity providing the weight of the spectrum used. The IC-component is only present within Areas 5 and 6, while the C-component is absent from Area 5 and present within Area 6 and other areas occupied by thicker flakes. Thus, we classify the flakes into: (1) Raman spectrum is exactly matched with only component C (flakes thicker than Areas 5 and 6); (2) Raman spectrum is well represented by a mixing of components C and IC (Area 6); and (3) Raman spectrum is achieved only by component IC (Area 5). This further supports that few-layer flakes, with thicknesses below ~ 4 nm, do not undergo phase transitions into the CCDW state, nor into the NCCDW one, when cooled down to 80 K; the flake being within a state which is predominantly close to the ICCDW one in terms of the vibrational properties. Similarly, the thicker flakes with thicknesses h within the regime 4 < h/nm < 10 are not observed to be within the CCDW state at 80 K, but instead reside within a state similar to NCCDW.

#### **SECTION: Discussion**

The results above indicate the suppression of the CCDW phase for the ultrathin samples, which, together with the variation of spectral characters with flake thickness can be connected to interlayer coupling and periodicity of the vertical stacking. For the NCCDW, X-ray and TEM experiments have determined a 3-layer period [21-23]. For the CCDW phase, some reports propose a disordered stacking [24], while others suggest periods of 13 layers [23].

Theoretically, arrangements of energetically favorable stacking were explored [25-30] and configurations such as on-top and displaced stacking (See Supplemental Material Figure S4[31]), were observed [6,23,32-35]. Reference [23] finds two types of repetitive stacking patterns, sliding and screw stacking (Figure S4(c)). In these scenarios, the CCDW stacking is only partially disordered and the commensurate domains are organized within bilayer sub-units characterized by on-top stacking. Interestingly, investigations of monolayer 1T-TaS<sub>2</sub> indicates a CCDW phase with the same Raman spectrum as the bulk [7]. This, along with our results, suggest that although the monolayer can undergo intralayer charge ordering as to produce the long-ranged commensurate domains at low temperatures, the same process may become hampered by the interlayer interactions when the number of layers is decreased to the bi- or tri-layer limit.

Although the flake with thickness below ~ 4 nm was deduced to be within an ICCDW state, the existence of weak spectral features (broad peaks) attributable to the CCDW/NCCDW state are well identifiable within the Raman spectrum, as shown in Figure 4(a). We speculate that such features can originate from the dynamical manifestation of unstable CCDW domains within a predominantly ICCDW matrix. Recent work strongly suggests the manifestation of the CCDW state in very thin flakes of  $1T-TaS_2$  to be dependent on the cooling rate [8], proposing the presence of CCDW domains even within CCDW-suppressed samples, where the time for stabilization of such domains increases with decreasing thickness. By comparison, here we observe CCDW suppression to commence below ~ 10 nm.

#### **SECTION: Conclusion**

In conclusion, using temperature-dependent and low-frequency Raman spectroscopy we address the question of how the transition from bulk to few atomic layers affects the charge density wave (CDW) phases in 1T-TaS<sub>2</sub>. We find two thickness regimes where the CDW phases of the crystals are significantly altered. Both the CCDW and NCCDW are suppressed in samples with thickness below ~ 4 nm, and only the CCDW is suppressed for thickness in the range ~ 4 to 10 nm. We argue that the critical thickness regimes we experimentally found to influence the formation of the CDW structures are related to the loss of long-range stacking order as the thickness is decreased. Consequently, our results support the notion of some type of periodicity in the stacking organization involving ~7 to 14 layers and are consistent with the previously reported c-axis periods for the two phases [27]. These experimental results attest to the

importance of the interlayer coupling in determining the properties of ultrathin van der Waals materials and open up possibilities for tuning their phase diagram by varying thickness.

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FIG. 1. (a) Schematic of 1T-TaS<sub>2</sub> crystal. (b) The structure of the CCDW phase; Ta atoms in a Star of David pattern. (c) Different phases in 1T-TaS<sub>2</sub> as a function of temperature.



FIG. 2. (a) Raman spectra taken at the indicated temperatures with a 532nm laser on a bulk sample. (b) Enlarged view of the Raman spectra for the different CDW phases (black - CCDW, blue - NCCDW, red - ICCDW). (c) Raman intensity charts measured as a function of temperature with a 514nm laser for a bulk sample in a cooling and warming cycle respectively at rates of 1 K min<sup>-1</sup>.



FIG. 3. (a) Optical micrograph of Area 1 and Area 2. (b) Comparison at the indicated temperatures between the Raman spectra taken for Areas 1 and 2 with a 514nm laser. (c) Raman spectrum taken at different temperatures at the position indicated in the optical image of the flake as Area 3. Inset: optical micrograph of Area 3 and Area 4. (d) Raman spectra for the indicated areas. (e) Optical micrograph of the flake with Areas 5 and 6. (f) Averaged Raman spectra of indicated areas as extracted from a hyperspectra collected by scanning the sample with a 532nm laser.



FIG. 4. (a) Low-frequency Raman spectra of Area 5 and Area 6 taken at 80 K with a 532nm laser. For comparison, CCDW (black) and ICCDW (orange) are spectra for the bulk, collected respectively at 80 K and 403 K. The colored strips highlight the Raman bands and frequency ranges analyzed for the spectral deconvolution. (b) Weight distribution maps of the deconvoluted spectral components for Areas 5 and 6 as extracted from a hyperspectra collected at 80 K with a 532nm laser. Top: incommensurate (IC) component. Bottom: commensurate (C) component.