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Accessing Chemically Ordered Phases in TaS_2 via High Temperature In-situ TEM

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TaS_2 is an exotic charge ordered van der Waals material that exhibits diverse correlated electron behavior such as superconductivity, metal–insulator transitions associated with charge density waves (CDWs), and a suggested quantum spin liquid host [1–3]. Intentional doping through chemical intercalation within the van der Waals (vdW) gap has also provided a route to engineering topological spin states and associated magnetic properties [4,5]. Here, we reveal the existence of inherent intercalates and chemical order in pristine 1T-TaS_2 using aberration-corrected scanning transmission electron microscopy (STEM) and selected area electron diffraction (SAED). Using in-situ high-temperature specimen holders, we show manipulation of the chemical order via high temperature thermal treatments (> 900°C) to form chemically ordered superlattices—distinct from previously reported CDW phases. SAED reveals these new phases have well defined commensurate superlattice peaks with real space superlattice constants $2a$ and $\sqrt{3}a$—suggesting a long-range order of chemical nature (a is real space lattice constant for TaS_2).

Figure 1a shows an in-situ SAED pattern of 1T-TaS_2 in the high-temperature incommensurate (IC) CDW phase (145°C). This well-known CDW phase is identifiable by azimuthally diffused superlattice peaks around each Bragg peak (Fig. 1a, yellow). However, there also exist overlooked sharp superlattice peaks appearing as a triplet group around each K-point (Fig. 1a, magenta) [1,6,7]. Across the diffraction pattern these triplet peak intensities decay similar to Bragg peaks—suggesting a chemical nature to the superlattice ordering (Fig. 1b). This contrasts with CDW superlattice peak intensity that increases pseudo-linearly in reciprocal (k-) space ($\propto k_r$) [1,8]. In Figure 1c, we visually confirm the presence of intercalates in pristine 1T-TaS_2 via atomic resolution cross-sectional STEM (a selenium doped sample was imaged to enhance the chalcogen visibility); intercalates in interlayer vdW gaps are highlighted with red circles. These intercalates could contribute to chemical ordering in pristine IC 1T-TaS_2 phase.

We also synthesized previously unreported chemically ordered phases of TaS_2 (Fig. 2a left) using high temperature in-situ processing. Controlled thermal treatment at > 900°C stabilized $\sqrt{3}\text{x}\sqrt{3}$ and 2x2 superlattices in TaS_2 (Fig. 2a). Exfoliated flakes of 1T-TaS_2 were heated well beyond reported octahedral (bulk 1T) to prismatic (bulk 2H, 3R) polytype transformation temperature (326°C [9]) and cooled slowly (~50°/min) to room temperature. Sharp, well-defined superlattice peaks emerge in SAED patterns of thermally treated samples (Fig. 2a, right). These superlattice peaks decay similarly with Bragg peaks, indicating chemical ordering (Fig. 2b). Notably, these superlattice peak locations match those of extrinsically intercalated TaS_2 [4,5].

In summary, we report strong evidence of intrinsic chemical order using in-situ SAED and directly imaged intercalates in pristine 1T-TaS_2 via cross-sectional aberration corrected STEM. In addition, we report two emergent chemically ordered superlattice phases obtained via high temperature in-situ thermal treatment. These findings suggest CDWs and chemical order coexist in TaS_2 without any extrinsic doping.

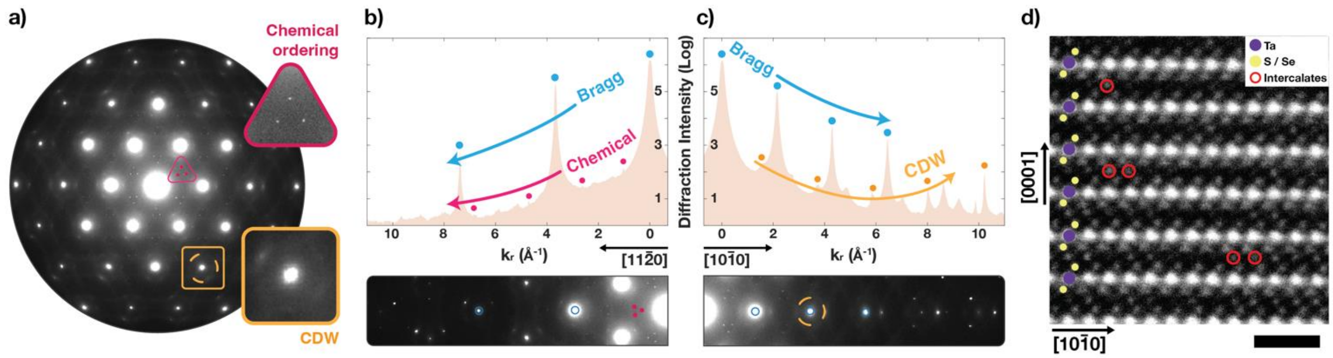

Figure 1| Intrinsic Chemical Order in 1T-TaS$_2$ | a) In-situ SAED pattern of incommensurate (IC) 1T-TaS$_2$ taken at (145°C) shows characteristic azimuthally diffused CDW peaks (yellow). There also exists triplet superlattice peaks around K-points (magenta). b,c) Line profile (log-scaled) along [11$\bar{2}$0] and [10$\bar{1}$0], respectively. Bragg peaks, triplet peaks and CDW peaks are annotated with blue, magenta and yellow. b) Triplet peaks decay similar to Bragg peaks as expected for chemically ordered superlattice peaks. c) CDW superlattice peak intensities increase at high k_r. d) Atomic resolution cross-sectional STEM of 1T-TaS$_2$ clearly shows individual intercalates (circled red) in between vdW gaps. The scale bar is 1 nm.

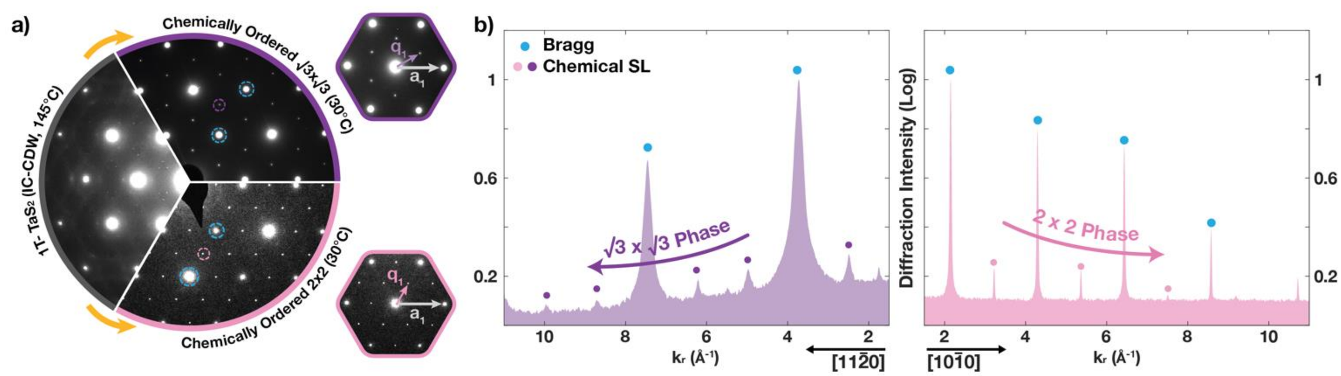

Figure 2 | High temperature in-situ TEM processing creates superlattice order | a) High temperature (> 900°C) thermal treatment manipulates the intrinsic chemical order to form 2x2 (bottom right) and √3x√3 (top right) superlattice structure. b) Line profile (log-scaled) across the superlattice peaks shows intensity decay similar to Bragg peaks.

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