Engineering Charge Density Waves using Interleaved Polytype Heterostructures

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$1T$-TaS_2 is a prototypical charge ordered van der Waals (vdW) material that hosts several charge density wave (CDW) phases that spontaneously break crystal symmetries, mediate metal–insulator transitions and compete with superconductivity [1–4]. CDWs in TaS_2 are two-dimensional (2D) and reside within each vdW layer. These low dimensional quantum states are promising candidates for novel devices [5–8], efficient ultrafast non-volatile switching [9,10], and suggest elusive chiral superconductivity [11,12]. Unfortunately, 2D charge ordering is fragile, and extrinsic and thermal disorder quickly degrades long-range order. Here, we show that fragile long-range ordered 2D-CDWs are stabilized at high temperature (~420 K) using endotaxial interleaved polytype heterostructures of TaS_2. Furthermore, we explore temperature vs disorder phase space of octahedrally coordinated TaS_2 using in-situ S/TEM to offer deeper understanding of the system.

Disorder—both extrinsic and thermal—significantly degrades CDWs. Nie, Tarjus, and Kivelson showed that 2D incommensurate (IC)-CDWs in cuprates are long-range ordered only at zero-disorder limit [13]. Here, we provide phase diagram of octahedrally coordinated (Oc)-TaS_2 as function of disorder and temperature (Fig. 1a). 1T (bulk Oc)-TaS_2 is mildly disordered; both the high-temperature IC phase and the room-temperature nearly-commensurate (NC) phase lack long-range order. Long-range ordering only emerges in the low-temperature (< 200 K) commensurate (C) phase. We can increase disorder (move right on the phase diagram) by substituting metal atoms. With 30% substitution ($1T$-$Ta_{0.7}Ti_{0.3}S_2$), room temperature NC phase gives way to hexatic-IC, and by 70% substitution ($1T$-$Ta_{0.3}Ti_{0.7}S_2$) the CDW completely vanishes.

Polytype engineering allows us to substantially decrease disorder to access new regions of the phase diagram (moving left, Fig 1a) where fragile low dimensional quantum states become stable. For example, we showed that for octahedrally coordinated TaS_2 long-range ordered C-CDW (stable < 200 K for 1T) is stable all the way up to ~350 K in interleaved polytype heterostructures [14]. Above ~350 K, polytype heterostructure recovers long-range order in IC phase. Also notably, hexatic-IC phase exists even above 620 K; in $1T$-TaS_2, CDWs completely vanishes at ~540 K [15]. Furthermore, we can control amount of disorder using *in-situ* electron microscopy by directly observing of layer-by-layer polytype transformations [14].

Figure 2b shows *in-situ* SAED pattern of $1T$-TaS_2 taken at 363 K. Notably, azimuthally diffused superlattice peaks are decorating each Bragg peak. By thermally treating the TaS_2 crystal above 600 K in oxygen-free inert conditions, most of layers convert to metallic prismatic layers (CDWs only at <

100K) and octahedral layers are sparsely interleaved as confirmed by cross-sectional HAADF-STEM micrographs of before (Fig. 2a) and after (Fig. 2d). Notably, metallic prismatic layers shield extrinsic disorder/defect potentials to provide a 'clean' environment for individual octahedral monolayers. *In-situ* SAED of the polytype heterostructure (Fig. 2c) taken at same 363 K shows superlattice peaks strikingly sharper and brighter by factor of 2 than pre-treatment. This is a surprising enhancement of charge order, especially considering the number of octahedral layers with CDWs has decreased.

In summary, we demonstrate that polytype engineering can stabilize the most fragile phases such as an ordered IC phase even at high temperatures. In addition, we now provide a schematic phase diagram of octahedrally coordinated TaS_2.
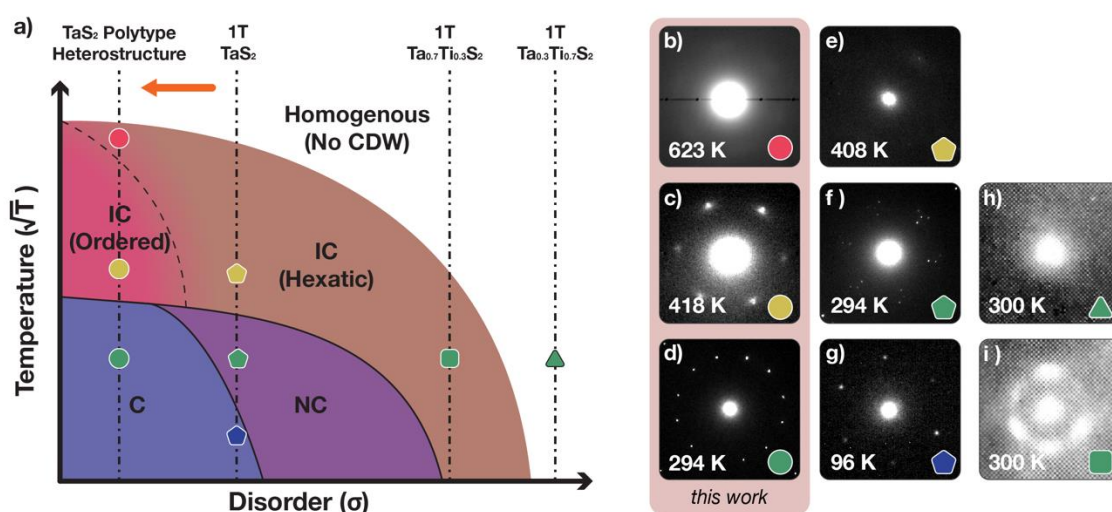

Figure 1. Phase Diagram of Octahedrally Coordinated TaS_2 a) Schematic temperature vs disorder phase diagram of octahedrally coordinated TaS_2. As extrinsic disorder (σ) decreases, more ordered CDW phases are stabilized. At room temperature, polytype heterostructures with low disorder stabilizes C-CDW(d) instead of NC-CDW(f), and long-range ordered IC-CDW(c) phase instead of hexatically disordered IC-CDW(e). Furthermore, it stabilizes CDWs(b) at higher temperatures then bulk 1T-TaS_2 can ($T_{CDW} \cong 540K$ [15]). Substitutional disorder, on the other hand, destroys long-range order and hexatic IC-CDW is stable at room temperature(i) and leads to complete destruction of CDW eventually(h). b–i) electron diffraction patterns showing superlattice peaks around a single Bragg peak reveals the charge ordering states. h,i) are adapted from [1].
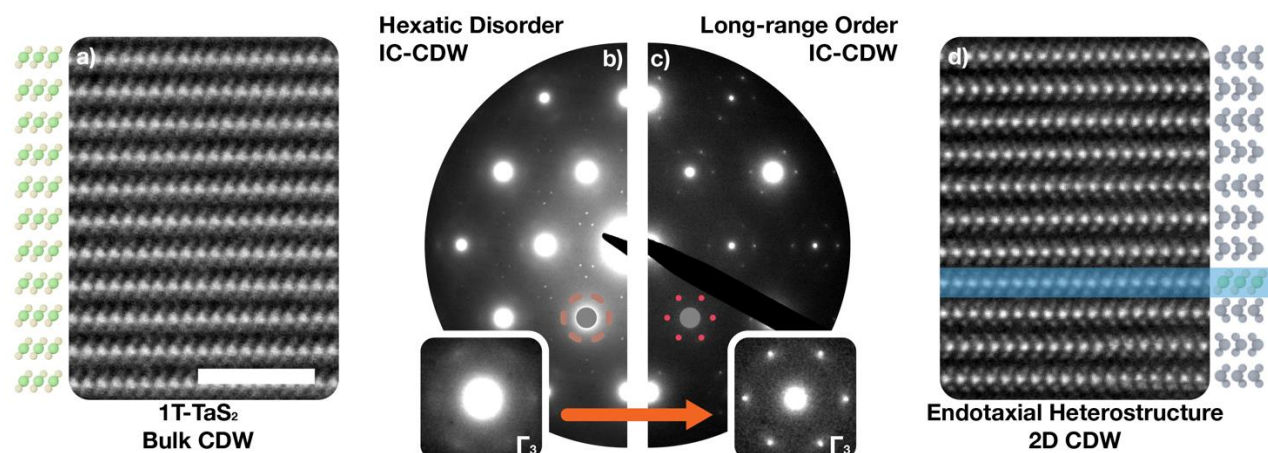
Figure 2. Interleaved Polytypic Heterostructure of TaS$_2$. Atomic resolution cross-sectional HAADF-STEM of a) pristine and d) heat-treated TaS$_x$Se$_{2-x}$ confirms polytypic transformation. After treatment, Pr layers encapsulate monolayers of Oc layers. Scale bar is 2 nm. A selenium doped sample was imaged to enhance chalcogen visibility. b) In pristine TaS$_2$, hexatic-IC phase emerges above 350 K, with characteristic azimuthally blurred superlattice peaks. c) IC-CDW in endotaxial polytype heterostructure has enhanced long-range order and amplitude. Superlattice peaks are well-defined and brighter.

References:

[1] J Wilson et al., Adv. Phys. **24** (1975), p.117.
[2] E Navarro-Moratalla et al., Nat. Commun. **7** (2016), p. 11043.
[3] R Ang et al., Nat. Commun. **6** (2015), p. 60981.
[4] L Li et al., npj Quantum Mater. **2** (2017), p. 11.
[5] DN Basov et al., Nat. Mater. **16** (2017), p. 1077.
[6] Y Tokura et al., Nat. Phys. **13** (2017), p.1056.
[7] MJ Hollander et al., Nano Lett. **15** (2015), p.1861.
[8] G Liu et al., Nat. Nanotechnol. **11** (2016), p. 845.
[9] I Vaskivsky et al., Nat. Commun. **7** (2016), p. 11442.
[10] AW Tsen et al., Proc. Natl. Acad. Sci. **112**: (2015), p. 15054.
[11] A Ribak et al., Sci. Adv. **6** (2020), p. aax9480.
[12] R Ganesh et al., Phys. Rev. Lett. **113** (2014), p. 177001.
[13] L Nie, G Tarjus and SA Kivelson, Proc. Natl. Acad. Sci. **111** (2014), p.7980.
[14] SH. Sung et al., Nat. Commun. **13** (2022), p. 413.
[15] SC Bayliss, A Clarke and WY Liang, J. Phys. C: Solid State Phys. **16** (1983), p. L831.