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Recovery of long-range order in two-dimensional charge density waves at high temperatures

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Charge density waves (CDW) are an emergent periodic modulation of the electron density that permeates a crystal with strong electron-lattice coupling [1, 2]. TaS_2 hosts several CDWs that spontaneously break crystal symmetries, mediate metal–insulator transitions [3, 4], and compete with superconductivity [5–7]. In low-dimensions, these quantum states are promising candidates for novel devices [8–11], efficient ultrafast non-volatile switching [12, 13], and suggest elusive chiral superconductivity [14, 15]. Unfortunately, extrinsic and thermal disorder in two-dimensions degrades correlation-driven quantum behavior [16, 17] and clean-limit 2D CDWs are absent. Here we realize incommensurate (IC) CDWs in clean limit 2D and show a distinct ordered phase emerges at high temperatures. Using in-situ heating with the transmission electron microscopy (TEM), we directly track discrete polytypic transitions in TaS_2 in plan-view, which we further confirm by cross-sectional scanning TEM (STEM) imaging [18]. The observation of the structural transformation not only provides insights into the formation of polytypes in layered materials but also leads to the formation of fragile 2D incommensurate CDW predicted to exist exclusively in the clean limit.

Bulk and thin-film 1T-TaS_2 hosts CDWs that melt into disordered IC-CDWs at 85°C with a metal–insulator transition. The IC-CDW is hexatically disordered—lacking long-range positional order while retaining rotational order. Figure 1a shows in-situ selected area electron diffraction (SAED) taken at 90°C, featuring azimuthally diffused CDW peaks. Six superlattice reflections (marked magenta) decorate bright Bragg peaks. In the inset, six third order Bragg peaks (Γ_3) are averaged to pronounce the diffused superlattice peaks, resembling the structure factor of hexatic glass [19].

Here we realize a novel ordered IC-CDW phase in 2D using a clean-limit confined polytype heterostructure. At high temperatures, the in-situ SAED pattern of the polytypic heterostructure (Fig. 1f) shows sharp CDW peaks (marked blue) decorating each Bragg peak—a signature of long-range ordered CDWs. This is dramatically different from the diffused CDW peaks expected (Fig. 1a). Averaged Γ_3 peaks better highlights the superlattice peak structure. The width of superlattice peaks in hexatic-CDW is about 10 times wider than in IC-CDW.

Our measurement of an ordered 2D IC-CDW is surprising. Nie, Tarjus and Kivelson has shown an ordered IC-CDW phase is unstable at finite temperature in 2D [17]. Long-range order in 2D only occurs in systems free of disorder [17]. We believe the long-range order of an IC-CDW is occurring in 2D under clean-limit conditions protected between metallic prismatic (Pr) polytypes—depicted in schematic Figure 2a. The metallic Pr-layers are hypothesized to screen out-of-plane interactions and impurity potentials to stabilize long-range ordered IC-CDWs [18]. As a result, the hexatic-CDW state no longer exists and a long-range ordered IC-CDW emerges as the stable phase. Under this interpretation observation of an ordered IC phase provides direct experimental evidence of Kivelson's description of correlated electron phases in 2D.

The polytypic heterostructure is synthesized by heat-treating 1T-TaS_2 at $\geq$ 400°C for several minutes in an inert environment. The metastable octahedral polytype gives way to stable prismatic coordination. In-situ TEM (200keV, Gatan OneView Camera) taken at 430°C reveals Oc to Pr transition is a slow layer-by-layer process (Fig. 1b–e) instead of rapid bulk transition. Each colored overlay denotes formation and growth of a prismatic domain. Domains nucleate and propagate independently, indicating layer-by-layer transition. We report that the rapid growth is along $\langle 10\bar{1}0 \rangle$ and propagates at ~10^2 nm/s, whereas the slow growth is along $\langle 11\bar{2}0 \rangle$ at ~10 nm/s. Atomic resolution cross-sectional high-angle annular dark-field (HAADF)-STEM images—taken at 300 keV, 22mrad—of 1T and heat-treated TaS_2 (Fig. 2c and d, respectively) reveals the polytypic heterostructure embeds a single Oc layer embedded within Pr layers.

In summary, we demonstrate that polytype engineering can achieve clean-limit 2D confinement and can stabilize the most fragile phases such as an ordered IC phase even at high temperatures. This work is enabled by advances in in-situ TEM where we can watch and count the Pr-layers as they form, and then take a cross-section to see the atomic structure at a single polytype heterojunction.

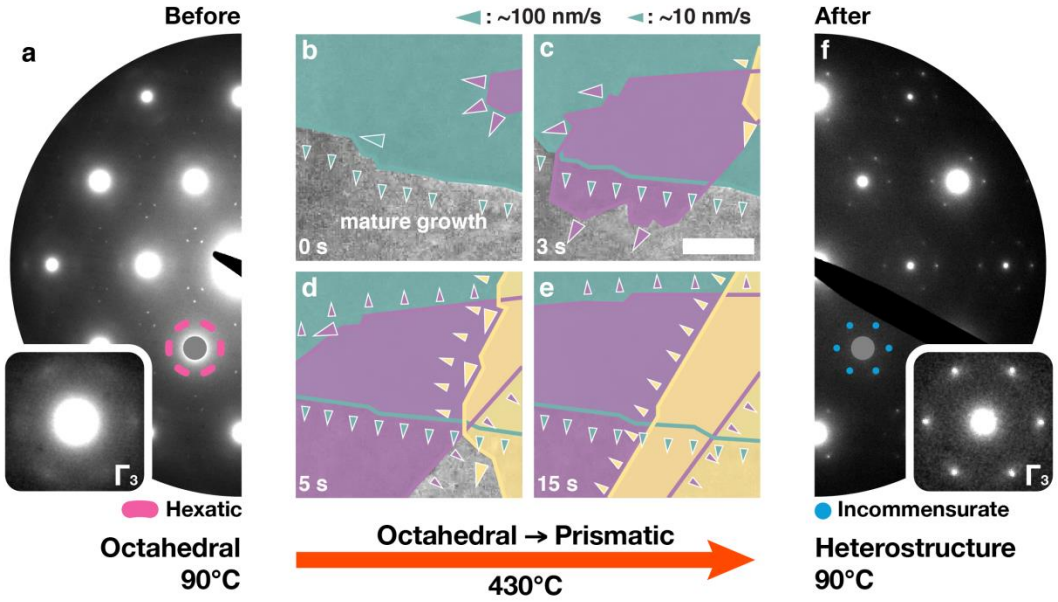

Figure 1. Figure 1 | Recovery of Long-range order in 2D IC-CDW a) In-situ SAED pattern of 1T-TaS2 taken at 90°C. Six azimuthally diffused superlattice peaks (marked magenta) decorates bright Bragg peaks; CDW is hexatically disordered. Diffusion of superlattice peak is clearly visible. b–e) In-situ TEM reveals layer-by-layer Oc to Pr polytypic transformations during heat treatment. Multiple polytype domains (denoted green, purple, and yellow) nucleate and glow simultaneously without interaction. Scale bar is 350 nm. f) In-situ SAED pattern of TaS2 polytypic heterostructure post heat-treatment, taken at 90°C. Six superlattice peaks are sharp: evidence of long-range order in CDW. Insets in a,b shows superlattice peaks surrounding Bragg peak as averaged from six Γ3 peaks.

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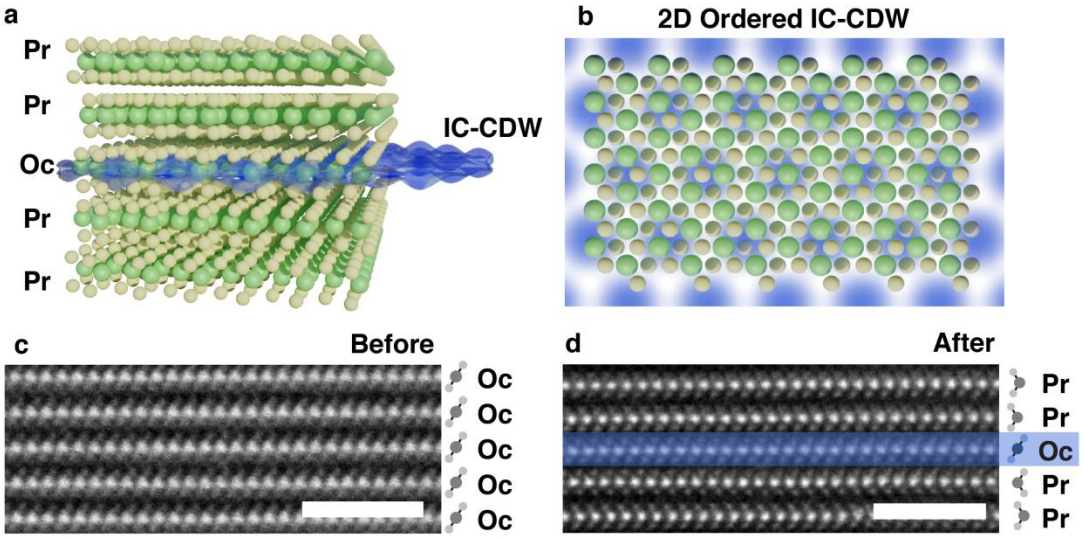

Figure 2. Figure 2 | Interdigitated Polytypic Heterostructure a) Schematic illustration of long-range ordered 2D IC-CDW in TaS2. Blue overlay represents IC-CDW embedded within Oc coordinated TaS2. Metallic Pr polytypes isolate Oc layers to retain long-range order. b) Schematic representation of long-range ordered 2D IC-CDW overlayed on Oc coordinated TaS2. c–d) Atomic resolution cross-sectional HAADF-STEM of c) pristine and d) heat-treated TaSxSe2-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.

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