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Engineering Covalently Bonded 2D Layered Materials by Self-Intercalation

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Abstract:

Two-dimensional (2D) materials^{1–5} offer a unique platform for exploring the physics of topology and many-body phenomena. Filling the van der Waals (vdW) gap of 2D materials with intercalants is expected to create new properties^{6,7}, but post-growth intercalation is usually limited to alkali metals^{8–10}. Here, we show that self-intercalation of native atoms^{11,12} into bilayer transition metal

dichalcogenides (TMDs) during growth creates a whole new class of ultrathin, covalently bonded materials (named *ic*-2d). The stoichiometry of *ic*-2d is defined by periodic occupancy patterns of the octahedral vacancy sites in the vdW gap, and its properties can be tuned by varying the coverage and spatial arrangement of the filled sites^{7,13}. By performing growth under conditions of high metal chemical potential^{14,15}, we can grow a full spectrum of Ta-intercalated TaS(Se)_y, including 25% intercalated Ta₉S₁₆, 33.3% intercalated Ta₇S₁₂, 50% Ta₁₀S₁₆, 66.7% Ta₈Se₁₂ (Kagome lattice) and 100% Ta₉Se₁₂. Ferromagnetic order was detected for some of the intercalated phases. We have also verified that self-intercalated V₁₁S₁₆, In₁₁Se₁₆, and Fe_xTe_y, can be grown under metal-rich conditions. Our work establishes self-intercalation as a novel approach to grow a new class of *ic*-2d materials with stoichiometry or composition-dependent properties.

Introduction

The surge in 2D materials research has heralded a new branch of condensed-matter physics concerned with the description of electrons in atomically thin structures. Thus far, research efforts have primarily focused on 2D monolayers² and their hetero-stacked structures³, in which new properties can be engineered by generating superlattices of different Moiré wavelengths. However, these hetero-stacked structures are currently produced by bottom-up methods that have low yield and poor reproducibility¹⁶. An alternative way of compositional tuning is based on the intercalation of foreign atoms in the vdW gap sandwiched by the chalcogen atoms; this has been shown to induce pseudo-2D characteristics in bulk crystals and modify their electronic properties^{4,6,7}. Depending on the interlayer stacking registries, the vdW gaps in TMDs contain octahedral and tetrahedral vacancies or trigonal-prismatic vacancies¹³, which provide docking sites for a diverse range of intercalants. Examples of successful intercalants include alkali metals^{8–10} such as Li, Na, K; transition metals^{17–21} such as Cu, Co, Ni, Fe, Nb, Sn; noble metals^{22–24} such as Ag, Au, Pt; and various organic molecules^{25–27}. Charge transfer from the intercalants⁷, or increased spin-

orbit coupling owing to the presence of heavy atoms^{7,24,28}, can enhance superconductivity¹⁰, thermoelectricity²⁵, or spin polarization⁷. The intercalation process typically involves post-growth, diffusion-limited processes such as electrochemical or solid-state intercalation. A well-defined intercalated phase with long-range crystalline order is difficult to obtain by such methods and usually requires drastic treatment conditions²⁹. Moreover, an intercalation phase diagram that correlates the density and spatial distribution of intercalation atoms with mesoscopic properties of the intercalated compound is currently lacking. Compared with foreign atom intercalation, intercalation of a TMD by its native metal atoms has so far received scant attention^{11,29,30}. Such self-intercalated TMD compounds may exist as local energy minima in the part of the phase diagram where a metal-rich stoichiometry is promoted by growth conditions using high chemical potential of metal atoms. However, to date, growth windows of TMDs using high metal chemical potential remain relatively unexplored^{31,32}.

In this work, we studied the growth of 2D TMDs under conditions of high metal chemical potential using both molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). We discovered that independent of the employed growth method, a metal-rich chemical potential promotes the self-intercalation of M into MX, MX₂, or M₂X₃ layered 2D compounds to produce a covalently bonded *ic*-2d M_xX_y compound (M = metal, X = chalcogen). Using TaS₂ as an example, intercalated Ta atoms occupy the octahedral vacancies in the vdW gap to form distinct topographical patterns, as verified by the atomic resolution scanning transmission electron microscopy – annular dark field (STEM–ADF) imaging. By varying the ratio of intercalated atoms to the octahedral vacancies in the vdW gap, we were able to grow Ta_xS_y or Ta_xSe_y films with $\sigma\%$ of Ta-intercalation, where $\sigma\%$ refers to the ratio of occupied vacancy sites to the initial total vacancy sites. Our results indicate that self-intercalation is generic to a broad class of vdW crystals and it offers a powerful approach to transform layered 2D materials into ultrathin, covalently bonded *ic*-2d crystals with ferromagnetic properties.

Results and discussion:

We first describe the self-intercalation of a TaS₂ bilayer by native atoms (*i.e.*, Ta) during MBE deposition on a silicon wafer, this is used as an example to demonstrate the transformation of a 2D bilayer film into an *ic*-2d film *via* octahedral vacancy filling. Wafer-scale Ta-intercalated TaS₂ bilayer films were grown on 2-inch 285 nm SiO₂/Si wafers in a dedicated MBE system¹⁴. Ultra-pure Ta and S molecular beams were evaporated from an e-beam evaporator and sulfur cracker cell equipped with a valve, respectively (Fig. 1a-b). We can routinely grow 2H-phase TaS₂ bilayer films using a high S chemical potential, *i.e.*, Ta to S flux ratio ~1:10 (Fig. 1a and Supplementary Fig. 1) for 3 hours, and a substrate temperature of 600 °C. When the Ta:S flux ratio was increased to 1:6 (Fig. 1c), the film became non-stoichiometric with respect to TaS₂ owing to the excess Ta atoms. A fingerprint of the Ta-rich environment is the presence of Ta adatoms (Fig. 1d) occupying the center of the honeycombs (highlighted in yellow) (Fig 1e) or atop of the Ta sites (highlighted in white) (Fig. 1f) in monolayer TaS₂ film, as observed by STEM when the growth was interrupted mid-way (Supplementary Fig. 2). By continually supplying Ta and S in the requisite ratio, the Ta adatoms become embedded and occupy the octahedral vacancies between two S layers (Fig. 1g). Therefore, the growth mechanism of *ic*-2d crystals follows a sequential TaS₂-Ta-TaS₂-Ta layer-by-layer growth, such that multilayer or bulk phase *ic*-2d crystals can be readily accessed by simply increasing the growth time. The thermodynamic stability of such intercalated phases is analyzed by the energy-composition phase diagram generated through our DFT calculations (Fig. 1h). It can be seen that stoichiometric H-phase TaS₂ is only formed under S rich conditions ($\mu_S > -5.3$ eV), whereas under low μ_S , various Ta-intercalated Ta_xS_y configurations, ranging from Ta₉S₁₆ (33.3% Ta intercalation) to Ta₉S₁₂ (100% Ta intercalation), entered a thermodynamically stable state.

Notably, a ~1:6 Ta:S ratio in the beam flux produced a $\sqrt{3}a \times \sqrt{3}a$ superlattice of Ta atoms (Fig. 2a) sandwiched between two TaS₂ monolayers. The coverage σ was 33.3%, and the overall stoichiometry of

the crystal thus became Ta_7S_{12} , as corroborated by both the real space STEM image (Fig. 2b) and the corresponding fast Fourier transform (FFT) pattern (Fig. 2c). Image simulation and sequential STEM images capturing the diffusion of intercalated atoms proved that the periodically arranged bright spots in the STEM image were induced by the Ta intercalation (see Fig. 2d, Supplementary Information section 1, and Supplementary Videos 1-2). We have also collected STEM cross-section image (Fig. 2e-f) to prove the existence of an intercalated Ta atomic layer in the vdW gap of *ic*-2d films grown by CVD.

The homogeneous Ta_7S_{12} phase was grown directly on a 2-inch silicon wafer (Supplementary Fig. 3). The Ta_7S_{12} film was formed by coalescence of nano-domain crystals (~50 nm) separated by mirror twin boundaries or tilted grain boundaries (Supplementary Information section 2). Amorphous islands and gaps seen in the STEM images were due to the poor stability of Ta_xS_y and sample damage during the sample transfer. Energy dispersive x-ray spectroscopy (EDS) and electron energy loss (EEL) spectroscopy (Supplementary Fig. 4) verified that the chemical composition comprised solely of Ta and S with no foreign elements. X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 5) confirmed that the chemical stoichiometry agrees very well with Ta_7S_{12} . The Raman spectra of the film exhibited two prominent E_g^3 and A_{1g}^3 peaks at 300 cm^{-1} and 400 cm^{-1} , respectively, matching those of H-phase TaS_2 films. The fingerprint of the intercalation came from a series of minor peaks in the 100 cm^{-1} to 170 cm^{-1} range (Supplementary Fig. 6), which were absent in pure H-phase TaS_2 ³³ attributed to the covalent bonds between the intercalated Ta atoms and their octahedrally coordinated S atoms (Supplementary Fig. 7).

25% Ta-intercalated TaS_2 has a stoichiometry of Ta_9S_{16} and was produced at a slightly lowered Ta chemical potential, corresponding to a ~1:8 Ta:S ratio. The intercalated Ta atoms occupy the octahedral vacancies in every $2a \times \sqrt{3}$ a unit length, and this phase was distinguished by the square symmetry of the intercalated atomic lattice (Fig. 2g, 2k, and Supplementary Fig. 8). When the Ta:S flux ratio was further increased to 1:5, a $\text{Ta}_{10}\text{S}_{16}$ phase ($\sigma = 50\%$) was successfully grown (Fig. 2h). The intercalation

concentration was determined to be exactly 50% *via* atom counting (Supplementary Fig. 9). Interestingly, this phase is characterized by short-range interconnected atomic chains forming an overall glassy phase. Clear diffusive rings were observed in the proximity of the first order FFT spots (Fig. 2l and Supplementary Fig. 10), confirming the presence of this short-range ordered structure³⁴. When we further enhanced the Ta:S flux ratio, the glassy phase was retained, but the short Ta atomic chains became denser until it fully evolved into a complete atomic plane when σ reached $\sim 100\%$ (Supplementary Fig. 11). When the growth condition straddles between two high-symmetry phases, phase separations occur and atomically sharp domain boundaries separating two high-symmetry phases can be clearly seen (Supplementary Information section 3).

To verify that *ic*-2d films could be produced by methods other than MBE, we employed CVD to grow self-intercalated Ta_xSe_y crystals by using excess Ta precursors. The crystal domains of Ta-intercalated Ta_xSe_y films grown by CVD are in the micron-sized range, which are significantly larger than the nanosized domain grown by MBE (Supplementary Fig. 12). A typical $\text{Ta}_8\text{Se}_{12}$ crystal ($\sigma = 66.7\%$) is depicted in Fig. 2i. Interestingly, it reveals a signature Kagome lattice belonging to the P_6 wallpaper symmetry group. A well-defined $\sqrt{3}a \times \sqrt{3}a$ periodic lattice can be unambiguously identified in the atomic-resolution STEM image (Fig. 2m and the simulated image in Supplementary Fig. 13). At even higher Ta chemical potential, $\text{Ta}_9\text{Se}_{12}$ crystals ($\sigma = 100\%$) were successfully synthesized, arising from the full occupation of the prismatic vacant sites in AA-stacked $\text{Ta}_9\text{Se}_{12}$ (Fig. 2j), as seen in the STEM top view (Fig. 2n) and side view images (Fig. 2e & Supplementary Fig. 14). By precisely controlling the metal:chalcogen ratio during the growth, a full spectrum of Ta-intercalated Ta_xSe_y or Ta_xS_y compounds with intercalation ratio ranging from $\sigma = 25\%$ to over 100% can be grown, as further verified by EDS (Supplementary Fig. 15 & Supplementary Table 1).

In the above example, the intercalated Ta atoms were octahedrally coordinated to the S_6 cage as opposed to the trigonal prismatic coordination adopted by pristine TaS_2 . Charge transfer from the intercalated Ta

atoms to the TaS₂ host layers creates new electron ordering and modified its *d* band splitting. The tunability in this system stems from the fact that the amount of charge transfer is dependent on the intercalation concentration. To investigate if ferromagnetic order was present in the intercalated samples, magneto-transport measurements were carried out on MBE-grown Ta₇S₁₂ ($\sigma = 33.3\%$) with a predominantly 2H_a stacking registry (Fig. 3a and Supplementary Fig. 16) with bilayer thickness (Supplementary Fig. 17). Fig. 3c shows the temperature-dependent resistivity, where a non-saturating upturn is observed below 30 K, due to the disorder-induced metal-insulator transition in the polycrystalline sample³⁵. Linear magneto-resistance (MR) up to 9 T at low temperature is observed in Ta₇S₁₂ (Fig. 3d) due to the density and mobility fluctuations³⁶. The anomalous Hall effect (AHE) arises from the interplay of spin-orbit interactions and ferromagnetic order, and is a potentially useful probe of spin polarization. We observed AHE in Ta₇S₁₂ on top of the linear ordinary Hall effect (OHE). Fig. 3e shows the nonlinear Hall effect at the proximity of zero magnetic field and linear OHE at high field. While both multiband conduction and AHE contribute to nonlinear Hall effect, the observed linear OHE suggests single carrier conduction (hole) in Ta₇S₁₂ and thus excludes multiband transport as the origin of the nonlinear Hall effect^{37,38}. The nonlinear Hall effect is thus ascribed to AHE, which stems from ferromagnetism in conductors³⁹. After subtracting the linear OHE, anomalous hall resistance up to 0.75 Ω is observed at 1.5 K; it decreases with increasing temperature and vanishes at 10 K in line with Monte Carlo simulation based on Ising model (Supplementary Fig. 18).

The effects of self-intercalation on the electrical properties of TMDCs are further tested on the Kagome lattice Ta₈Se₁₂ ($\sigma = 66.7\%$). It was observed that the intercalation of Ta atoms and formation of Kagome lattices stabilize the charge density wave (CDW) states. Temperature dependent Hall signal reveals AHE below 15 K and confirms the ferromagnetic order in Ta₈Se₁₂ (Supplementary Fig. 19-20).

We performed DFT calculations to gain an understanding of the origin of the magnetization in self-intercalated Ta₇S₁₂. Perfect bilayer 2H_a-stacked TaS₂ (Supplementary Fig. 21) possesses a non-magnetic ground state. Ferromagnetism can be induced by the double exchange mechanism⁴⁰ triggered by the charge transfer from intercalated Ta to pristine TaS₂ (Fig. 3f). When the intercalated Ta adopts a $\sqrt{3}a \times \sqrt{3}a$ superstructure, six S atoms bond with one intercalated Ta atom to form an octahedral unit in the vdW gap. In contrast, each S atom is shared by three Ta atoms in the pristine TaS₂ layer. This difference in local bonding arrangement induces charge transfer from the octahedral-coordinated intercalated Ta atom to the prismatic-coordinated Ta atom in the TaS₂ layer (Fig. 3f). In the pristine H-phase TaS₂, the Ta *d* and S *p* orbitals are well separated in terms of energy, with the states at the Fermi level having mainly Ta *d_{z²}* and Ta *d_{x²-y²}* characteristics (Supplementary Fig. 21). In Ta₇S₁₂ ($\sigma = 33.3\%$), the intercalated Ta atoms introduce additional spin-split bands across the Fermi level, and a magnetic ground state develops (Fig. 3g-h). The magnetic moments are localized on the *d* orbitals of the intercalated Ta atom, as evidenced by the calculated orbital-resolved spin up and spin down band structures in Fig. 3g and Fig. 3h, respectively. The states at the Fermi level comprise the prismatic-centred Ta *d_{z²}* orbitals hybridized with the spin-up band of the *d_{x²-y²}* orbital of the intercalated Ta. However, only the intercalated Ta atoms exhibit a net spin density, as illustrated in Fig. 3i, where the top view spin density isosurface matches the shape of the *d_{x²-y²}* orbital. In addition, the non-magnetic 3a x 3a CDW state of Ta₇S₁₂ can be ruled out owing to its relative instability compared to the ferromagnetic state⁴¹.

The existence of a magnetic moment correlates with a strong charge transfer between the intercalated Ta and the TaS₂ layers. Strong charge transfer occurs in the dilute Ta-intercalated compound, whereas the charge transfer becomes relatively weak in a heavily intercalated (Fig. 3j) compound in accordance with the calculated charge difference and the variation of Bader charge in the Ta atoms (Supplementary Table 2, & Supplementary Fig. 22).

190 To investigate whether the self-intercalation phenomenon occurred for other TMDs, we performed a
 191 high-throughput DFT study of 48 different intercalated TMD bilayers using a semi-automated workflow
 192 for maximal consistency and veracity⁴². Specifically, we considered TMDs of the transition metals Mo, W,
 193 Nb, Ta, Ti, Zr, Hf, V, Cr, Mn, Fe, Co, Ni, Pd, Pt, and Sn, and the chalcogens S, Se, and Te (highlighted in Fig.
 194 4a in blue and red, respectively) when σ equals 33.3% or 66.7%. Out of this set of TMDs, we observed that
 195 14 bilayer configurations, Ti_8S_{12} , $\text{Ti}_8\text{Se}_{12}$, $\text{Ti}_8\text{Te}_{12}$, Co_7S_{12} , $\text{Co}_7\text{Se}_{12}$, $\text{Co}_7\text{Te}_{12}$, Nb_7S_{12} , $\text{Nb}_7\text{Se}_{12}$, $\text{Nb}_7\text{Te}_{12}$, Mo_7S_{12} ,
 196 $\text{Mo}_7\text{Se}_{12}$, Ta_7S_{12} , $\text{Ta}_7\text{Se}_{12}$, and $\text{Ta}_7\text{Te}_{12}$, (highlighted in Fig. 4a and Supplementary Table 3 for magnetic
 197 moment) develop ferromagnetic order upon self-intercalation, whereas their parental MX_2 are
 198 nonferromagnetic. Notably, group V and VI TMDs, exhibit strong ferromagnetism after self-intercalation
 199 (Fig. 4b). Intrinsic ferromagnetic MX_2 (VX_2 , CrX_2 , MnX_2 , and FeX_2) retain ferromagnetism upon self-
 200 intercalation (highlighted in Fig. 4a in orange). Among the 14 types of self-intercalated 2D ferromagnets,
 201 the formation energies of 12 of them (the 2 exceptions being MoS_2 and MoSe_2) were lower than or similar
 202 to those of the non-intercalated materials (Supplementary Fig. 23-24), indicating that self-intercalation is
 203 energetically feasible.

204 To validate the theoretical predictions, we attempted to grow a wide variety of *ic*-2d, as highlighted by
 205 the triangle in the top left corner in Fig. 4a. Blue triangles indicate that the self-intercalation can be
 206 experimentally realized^{11,12}, whereas gray triangles indicate that intercalation was not be successful under
 207 our experimental conditions. We had succeeded to grow several *ic*-2d crystals, namely $\text{V}_{11}\text{S}_{16}$ (Fig. 4c and
 208 Supplementary Fig. 25), $\text{In}_{11}\text{Se}_{16}$ (Fig. 4d and Supplementary Fig. 26), and Fe_xTe_y (Fig. 4e and
 209 Supplementary Fig. 27) by CVD or MBE. Their clear topological features and corresponding FFT patterns
 210 are depicted in Fig. 4f-h. The intercalated $\text{V}_{11}\text{S}_{16}$ revealed a $2a \times 2a$ superstructure, and the intercalation
 211 ratio was estimated at 75% (Fig. 4f). $\text{In}_{11}\text{Se}_{16}$ also showed a $2a \times 2a$ superstructure, but in this case, the
 212 intercalated In atoms reveal a signature honeycomb structure (Fig. 4g). The crystal structure of self-
 213 intercalated Fe_xTe_y was rather complicated with additional Fe intercalated into the atomic network of the

pristine FeTe matrix as interstitials because telluride based TMDs offer the largest spacing between the host atoms⁴³. Upon intercalation, the novel Fe_xTe_y phase reveals new symmetries as confirmed by the emergence of superspots in the FFT pattern (Fig. 4h). Similar complex intercalation network has also been observed in V_xTe_y (Supplementary Fig. 28).

Conclusion

We have discovered a robust way to perform composition engineering of a broad class of TMD by self-intercalation with native metal atoms during growth. The main principle is to apply a high chemical potential of metal atoms to provide the driving force for intercalation during growth, thus it should work for most growth methods. The metal intercalants occupy octahedral vacant sites in the vdW gap, and depending on the coverage patterns, distinct stoichiometric phases are produced. High throughput DFT simulations, supported by growth experiments, show that the self-intercalation method is applicable to a large class of 2D layered materials, thus allowing a whole new library of materials with potentially new properties to be created from existing layered materials. Owing to the versatility in composition control, it is possible to tune in one class of materials, properties that can vary from ferromagnetic to non-ferromagnetic, and spin-frustrated Kagome lattices. In particular, ferromagnetic order can be introduced into non-magnetic layered materials *via* the self-intercalation approach, giving rise to a unique topological phase such as ferromagnetic Kagome lattices. The implication of this work is that bilayer TMD (or thicker) can be transformed into ultrathin covalent bonded 3D material, with a stoichiometry that is tuneable by the concentration of the intercalants over a broad range.

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Author contributions

X. Z., S. J. P., and K. P. L. conceived the idea. S. J. P., and K. P. L. supervised the execution of the whole work. X. Z. performed the electron microscopy experiments and data analysis. X. L., A. C. R. and C. C. W. did the DFT calculation and data analysis. A. C. R-J. and K. S. T. performed the high-throughput DFT calculations. W. F., Y. D., and L. K. grew the samples. D. W. measured the magnetism. P. S. did device fabrication and measurement. J. D., and S. N. developed the python scripts for data analysis. All the authors discussed the results. All authors participated in writing the manuscripts. X. Z., and P. S. contributed equally to this work.

Competing interests

The authors declare no conflict of interest.

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Main figure legends:

Figure 1. Self-intercalation in TaS₂ crystals. Schematic illustration showing the MBE growth of (a) pristine TaS₂ and (b) self-intercalated Ta₇S₁₂ under a low and high Ta-flux environment, respectively. The lower Ta flux produces stoichiometric TaS₂, whereas higher Ta flux leads to a self-intercalated phase. (c) Photographs of MBE-grown 1L-TaS₂ and 2L-Ta₇S₁₂ on 2-inch SiO₂/Si wafer. (d) Atomic-resolution STEM-ADF image of monolayer TaS₂ under Ta rich conditions with abundant Ta interstitials locating at the (e) center of honeycomb or (f) on top of the Ta site. Corresponding atomic models were depicted in the right panels. (g) Schematic illustration depicting the layer-by-layer growth of *ic*-2d crystals. (h) Calculated formation energies of various self-intercalated Ta_xS_y phases where the intercalation concentrations are

25%, 33.3%, 50%, 66.7%, and 100%, respectively, as a function of sulfur chemical potential. Scale bars: 2
nm in (d); 0.5 nm in (e-f).

Figure 2. Compositional engineering of self-intercalated Ta_xS_y (Ta_xSe_y) with different intercalated Ta concentrations. (a) Atomic-resolution STEM-ADF image of the MBE grown self-intercalated Ta_7S_{12} showing well defined $\sqrt{3}a \times \sqrt{3}a$ superstructure and (b) the enlarged image overlaid with the atomic model. (c) corresponding FFT pattern of (a) with $\sqrt{3}a$ superspots highlighted by the orange circles. (d) Atomic model of self-intercalated Ta_7S_{12} . (e) STEM cross-section view of 100% Ta-intercalated Ta_9Se_{12} , and

382 (f) its corresponding simulated image derived from the DFT optimized atomic model. Atomic-resolution
 383 STEM images of (g) 25% self-intercalated Ta_9S_{16} , (h) 50% self-intercalated $\text{Ta}_{10}\text{S}_{16}$, (i) 66.7% self-
 384 intercalated $\text{Ta}_8\text{Se}_{12}$, and (j) 100% self-intercalated $\text{Ta}_9\text{Se}_{12}$ *ic*-2d crystals. (k-n) Enlarged white box regions
 385 from (g-j), respectively, and their corresponding FFT patterns and atomic models are depicted in the right,
 386 and lower panels, respectively. Scale bars: 2 nm in (a, g-j); 0.5 nm in (b, e, k-n).

388 **Figure 3. Ferromagnetism in self-intercalated Ta₇S₁₂ *ic*-2d crystals.** (a) Atomic-resolution STEM-ADF
 389 image of a typical self-intercalated Ta₇S₁₂ film. (b) Optical microscopy image of Ta₇S₁₂ Hall bar device
 390 encapsulated with *h*-BN. (c) Resistivity as a function of temperature. Temperature dependent (d)
 391 longitudinal resistance (R_{xx}) and (e) Hall resistance (R_{xy}) under the out-of-plane magnetic field. (f) Contour
 392 plot of charge density difference in Ta-intercalated Ta₇S₁₂. Orbital-resolved (g) spin up and (h) spin down
 393 band structures of Ta₇S₁₂. (i) Top view and the side view spin density isosurface of Ta-intercalated Ta₇S₁₂.
 394 (j) Calculated magnetic moments as a function of Ta intercalation concentration in nonstoichiometric Ta_xS_y.
 395 The STEM-ADF image shown in Fig. 3a was collected using a half-angle range from ~30 to 110 mrad to
 396 enhance the contrast of S. Scale bar: 0.5 nm in (a); 20 μ m in (b).

Figure 4. A library of *ic*-2d crystals. (a) Periodic table showing metal (highlighted blue) and chalcogen (highlighted red) combinations that form *ic*-2d crystals according to our DFT calculation; the list is non-exhaustive. Blue triangles indicate that the self-intercalation can be experimentally realized, whereas gray triangles indicate that intercalation was not successful under our experimental conditions. Intrinsic ferromagnetic MX_2 are highlighted by orange triangles. (b) DFT calculated *ic*-2d atomic models showing ferromagnetism. STEM-ADF images of self-intercalated (c) $V_{11}S_{16}$, (d) $In_{11}Se_{16}$, and (e) Fe_xTe_y . Their

enlarged images and corresponding FFT patterns are depicted in (f-h), respectively. 2 nm in (c-e); 0.5 nm in (f-h); 5 nm⁻¹ for all FFT patterns in (f-h).

Methods

MBE growth of self-intercalated TMD films. *Ta-intercalated Ta_xS_y* films were grown in a dedicated MBE chamber (base pressure < 6×10⁻¹⁰ torr). Prior to the growth, the 2-inch SiO₂ substrates were degassed in the same chamber at 500 °C for 2 h. Ultrapure Ta (99.995%, Goodfellow) and S powders (99.5% Alfa Aesar) were evaporated from a mini electron-beam evaporator and a standard sulphur valved cracker, respectively. The flux density of Ta was precisely controlled by adjusting the flux current. The S cracker cell temperature was maintained at 110 °C, and the flux density was controlled by the shutter of the cracker valve. The substrate temperature was maintained at 600 to 650 °C and the growth time is about 3 hours for all thin films. 25% Ta-intercalated Ta₉S₁₆, 33.3% Ta₇S₁₂, and 50% Ta₁₀S₁₆ films were controlled grown when the Ta/S ratio is set as ~1:8, ~1:6, and ~1:5, respectively. A slightly higher growth temperature will facilitate the self-intercalation process. After growth, both sources were turned off and the sample was further annealed for another 30 mins before cooling down to the room temperature. *In-intercalated In_xSe_y* were grown in a customized MBE chamber (base pressure < 6×10⁻¹⁰ torr). Prior to growth, the 1 cm × 1 cm SiO₂ substrate was degassed in the chamber at 600 °C for 1 h. Ultrapure In₂Se₃ powder (99.99%) and Se pellets (99.999%) were evaporated from a mini electron-beam evaporator and an effusion cell, respectively. The Se effusion-cell temperature was set at 150 °C with a hot-lip at 220 °C. The substrate temperature was maintained at 400 °C and the growth time is about 2 hours. In₁₁Se₁₆ films were controlled grown when the In₂Se₃/Se ratio is set as ~1:3.

CVD growth of self-intercalated TMD films. *Ta-intercalated Ta_xSe_y* crystals were grown by CVD. Prior to the growth, the SiO₂ substrate was sequentially cleaned by water and acetone, followed by 5 min of O₂

plasma. The furnace was purged by 300 sccm Ar gas for 5 mins. Se powders and mixed Ta/TaCl₅ powders were applied as precursors that were located upstream in a one-inch quartz tube. 40 sccm Ar and 10 sccm H₂ were used as a carrier gas. The samples were grown at 800 °C for 30 mins. After growth, the sample was cooled down quickly in a continuous stream of Ar. 66.7% Ta-intercalated Ta₈Se₁₂, and 100% Ta-intercalated Ta₉Se₁₂ were controlled grown when the Se powders and mixed Ta/TaCl₅ powders are 1 g/15 mg/1.5 mg, and 1 g/30 mg/3 mg, respectively. ***V-intercalated V_xS_y*** crystals were grown by CVD. Prior to the growth, the SiO₂ substrates were treated by the same method as indicated in growing Ta_xSe_y. Two quartz boats containing 0.5 g S, and 0.3 g VCl₃ were loaded in the upstream of the one-inch quartz tube serving as precursors. Carrier gases were 40 sccm Ar together with 10 sccm H₂. The sample was grown at 680 °C for 30 mins. After growth, the sample was cooled down quickly under the protection of 100 sccm Ar. ***Fe-intercalated Fe_xTe_y*** crystals were grown by CVD. Prior to the growth, the SiO₂ substrates were treated by the same method as indicated in growing Ta_xSe_y. Two quartz boats containing Te (>99.997%) and FeCl₂ (>99.9%) were placed in the upstream in sequence of the one-inch quartz tube serving as precursors. The sample was grown at 600 °C for 30 mins. After growth, the sample was cooled down quickly under the protection of 100 sccm Ar.

Sample characterization. XPS was performed using SPECS XR 50 X-ray Al K α (1486.6eV) source with a pass energy of 30 eV. The chamber base pressure is lower than 8×10^{-10} mbar. Raman spectra were collected at room temperature using the confocal WiTec Alpha 300R Raman Microscope (laser excitation: 532 nm).

STEM sample preparation, image characterization, and image simulation. The as-grown TMD films were transferred *via* a PMMA method under the protection of graphene. Continuous graphene film was coated on fresh Ta₇S₁₂ film to protect the surface oxidation *via* conventional PMMA method. Subsequently, graphene/Ta₇S₁₂ composites were immersed in 1 M KOH solution to detach the PMMA/ Ta₇S₁₂ composite from the SiO₂ substrate, followed by rinsing in DI water. The PMMA/graphene/Ta₇S₁₂ film was then placed

onto Cu quantifoil TEM grid which was precoated with continuous graphene film⁴⁴. The TEM grid was then immersed in acetone to remove the PMMA films. Atomic-resolution STEM-ADF imaging was performed on an aberration-corrected ARM200F, equipped with a cold field-emission gun and an ASCOR corrector operating at 60 kV. The STEM-ADF images were collected using a half-angle range from ~ 81 to 280 mrad unless indicated elsewhere. The convergence semiangle of the probe was ~ 30 mrad. Image simulations were done with the QSTEM package assuming an aberration-free probe with a probe size of ~ 1 Å. The convergence semiangle of the probe was set as ~ 30 mrad, and the accelerating voltage is 60 kV in line with the experiments. The collection angle for HAADF and MAADF images were from 81 to 280 mrad and 30 to 110 mrad, respectively. The thermal diffuse scattering (TDS) was set as 30 with defocus value 0 . The STEM-EDS were collected and processed in an Oxford Aztec EDS system

Device fabrication and measurements. MBE-grown Ta_7S_{12} and CVD-grown $\text{Ta}_8\text{Se}_{12}$ were selected to fabricate Hall-bar devices using e-beam lithography and e-beam evaporation of Ti/Au ($2/60$ nm). The MBE-grown Ta_7S_{12} film was then etched into Hall-bar geometry using deep reactive ion etching. The final devices were encapsulated with *h*-BN flakes using a dry-transfer method in the glovebox (both O_2 and H_2O less than 1 ppm), to avoid degradation of Ta_7S_{12} and $\text{Ta}_8\text{Se}_{12}$ under ambient conditions. Low-temperature Transport measurements were carried out in Oxford Teslatron system. All resistances were derived from four-terminal measurements using SR830 lock-in amplifier, with constant excitation current of 1 μA .

DFT calculations. First-principles calculations based on Density Functional Theory (DFT) were implemented in the plane wave code VASP using the projector-augmented wave (PAW) potential approach. For the exchange and correlation functional, both the local density approximation (LDA) and the PBE flavor of the generalized gradient approximation are used and found no significant differences in the results. A kinetic energy cutoff of 500 eV is used for the TaS_2 . A Monkhorst Pack k-grid samplings with a k-point density of 6.0 Å⁻¹ were used for geometry optimization. For thin-film calculations, a vacuum

thickness of 20 Å is added in the slab to minimize the interaction between adjacent image cells. Geometry optimization was performed with the maximum force convergence criterion of 0.005 eV/Å. To treat the strong on-site Coulomb interaction of localized Ta-d orbitals, we use Dudarev's approach with an effective U parameter of $U_{\text{eff}}=3.0$ eV. The zone center phonon modes were calculated by using the density functional perturbation theory (DFPT) with the local density approximation functionals. **High-throughput DFT calculations** were carried out with the electronic structure code GPAW⁴⁵ following a semi-automated workflow for maximal consistency and accuracy⁴². The relaxations of the self-intercalated bilayers are done on a Monkhorst-Pack⁴⁶ grid with a k-point density of 6.0 Å⁻¹ using the PBE⁴⁷ and BEEF-vdW functionals⁴⁸ for describing exchange-correlation effects. 15 Å vacuum is used in the out-of-plane direction to avoid non-physical periodic interactions. The plane-wave expansion is cut-off at 800 eV. All systems are relaxed until the maximum force on any atom is 0.01 eV/Å and the maximum stress on the unit cell is 0.002 eV/Å³. All systems are calculated in the intercalated structure with both a spin-paired calculation and a spin-polarized calculation. If the total energy of the spin-polarized structure is found to be over 0.01 eV/atom lower than the spin-paired structure, the structure is concluded to be magnetically more stable than its non-magnetic counterpart. The atomic structures of calculated self-intercalated TMDs (33.3% and 66.7% intercalation concentration) were presented in Supplementary Fig. 29, in which the polymorphism of single layer MoX₂, WX₂, NbX₂, and TaX₂ (X = S, Se, and Te) reveals an H-phase, whereas the rest TMDs are T-phase taking an AA stacking polytype. MoX₂, and WX₂ comply the AA' stacking order whereas NbX₂, and TaX₂ take the AB' stacking registry. All intercalants occupy the octahedral vacancies in the vdW gap.

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503 development with Bayesian error estimation. *Phys. Rev. B* **85**, 235149 (2012).
- 504 **Data availability.** The main data supporting the findings of this study are available within the paper and
505 its Supplementary Information. Extra data are available from the corresponding authors upon request.