

Supplementary material: Charge transfer and spin-valley locking in 4Hb-TaS₂

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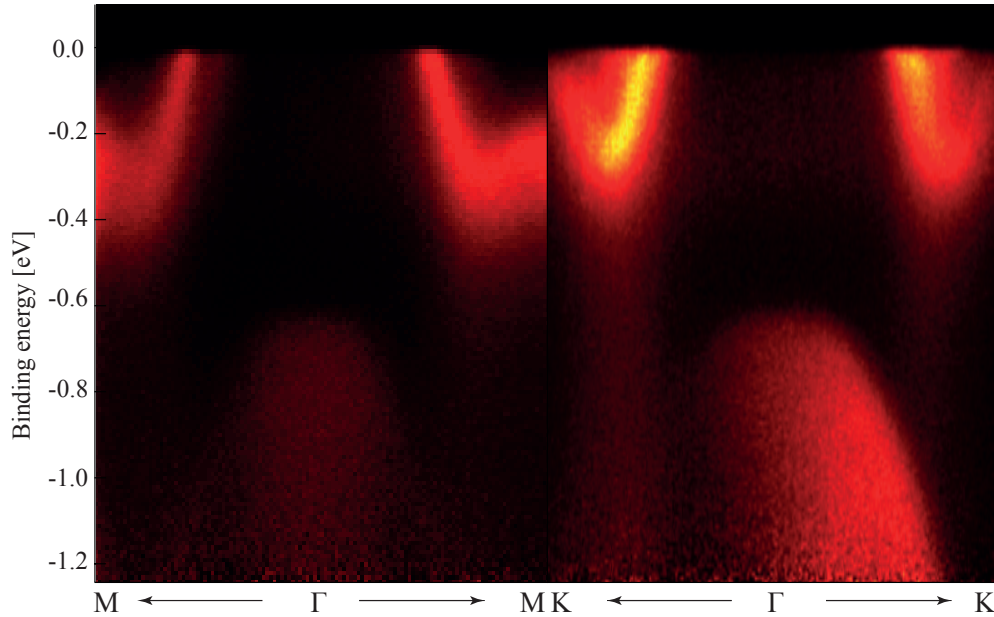
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Supplementary Note 1: 2H-TaS₂ comparison

As a comparison to the 4Hb-TaS₂ data shown in Figure 1 of the main text, we show ARPES spectra along the same high symmetry lines for 2H-TaS₂ in Supplementary Figure 1. Data was taken using $\hbar\nu=92$ eV photon energy.

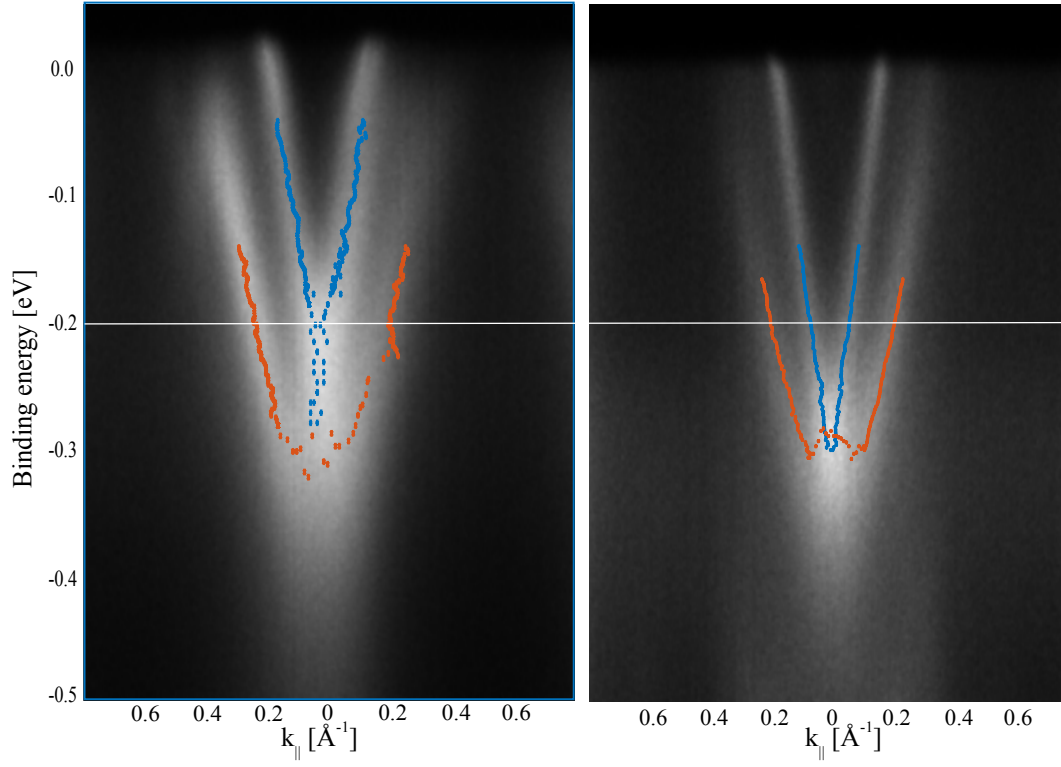
The new bands around the Γ point, which originates from the 1T-1H hybridization, are not present in the 2H-TaS₂ data.



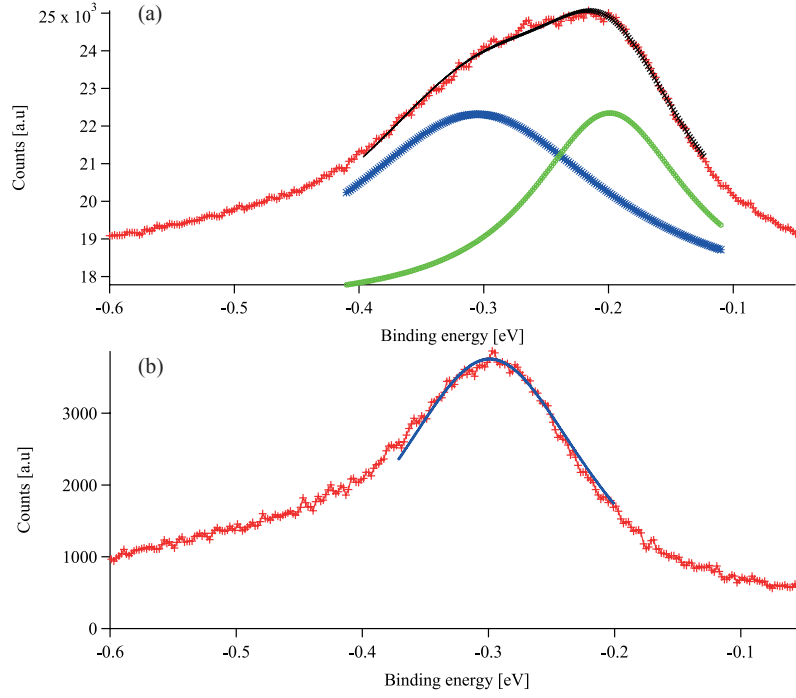
Supplementary Figure 1. 2H-TaS₂ ARPES data. ARPES spectra along the M- Γ -M, and K- Γ -K' lines.

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Supplementary Note 2: Extracting the gap from fits



Supplementary Figure 2. ARPES spectra in 2H-TaS₂ and 4Hb-TaS₂. ARPES spectra along the K-M-K' line in 2H-TaS₂ and 4Hb-TaS₂ (left and right respectively) with peaks extracted from fitting MDC's to Lorentzian functions. The inner pocket in 2H-TaS₂ ends at around 200 meV.



Supplementary Figure 3. Bands binding energy extracted from EDC fits. (a) EDC at the M point of a 2H-TaS₂ sample with a fit to two Lorentzians. (b) EDC at the M point of 4Hb-TaS₂ with a single Lorentzian fit. The Lorentzians are centered at -0.305 ± 5 and -0.199 ± 5 for 2H-TaS₂ and -0.3 ± 5 for 4Hb-TaS₂.

Supplementary Note 3: Calculating the charge transfer

In our paper we used the difference in Fermi-surfaces area to calculate the charge transfer between the 1T and 1H layer in 4Hb-TaS₂. We used the difference between the Fermi surface of 2H-TaS₂, and the Fermi pockets derived from the 1H layers in 4Hb-TaS₂.

The charge transfer is given by: $\Delta Q = \frac{\Delta S}{S_{BZ}}$ where ΔS is the difference in Fermi pockets area, and S_{BZ} is the Brillouin zone area.

There are three Fermi pockets in 2H-TaS₂ a single hole pocket around the Γ point (S_Γ), 6 halves of the "dog-bone" shaped pockets ($S_{Dog-Bone}$) and 6 thirds of the circular pockets around the K point (S_K). Using these definitions we can write:

$$\Delta Q = \frac{\Delta S}{S_{BZ}} = \frac{\Delta S_\Gamma + \Delta S_K + \Delta S_{Dog-Bone}}{S_{BZ}} \quad (1)$$

ARPES results and ARPES resolution give the next results:

$$S_{BZ} = 4.16 \text{ \AA}^{-2} \quad (2)$$

$$\Delta S_\Gamma = 0.11 \pm 0.03 \text{ \AA}^{-2} \quad (3)$$

$$\Delta S_K = 0.055 \pm 0.01 \text{ \AA}^{-2} \quad (4)$$

$$\Delta S_{Dog-Bone} = 0.13 \pm 0.015 \text{ \AA}^{-2} \quad (5)$$

$$\Delta Q = \frac{0.295}{4.16} \pm \frac{0.035}{4.16} = (0.0709 \pm 0.008)e \text{ per unit cell (Ta atom)}. \quad (6)$$

DFT of 2H-TaS₂, finds a corrugated Fermi surface along k_z . For 2H-TaS₂ the corrugation of the cylindrical hole pocket around the Γ -point is at most 3% (based on DFT results), with the largest diameter near the Z point. As for the "dog-bone" shaped pockets the corrugation is about 1%, based on DFT and ARPES data. Both of this corrugation values gives errors of $0.009 \text{ \AA}^{-1}$ ($\pm 1.5\%$) for the hole pocket k_f and $0.0001 \text{ \AA}^{-1}$ for the M point inner pocket. These corresponds to an error of 10% and 1% in the area-difference and are taken into account in the errors estimates shown above.

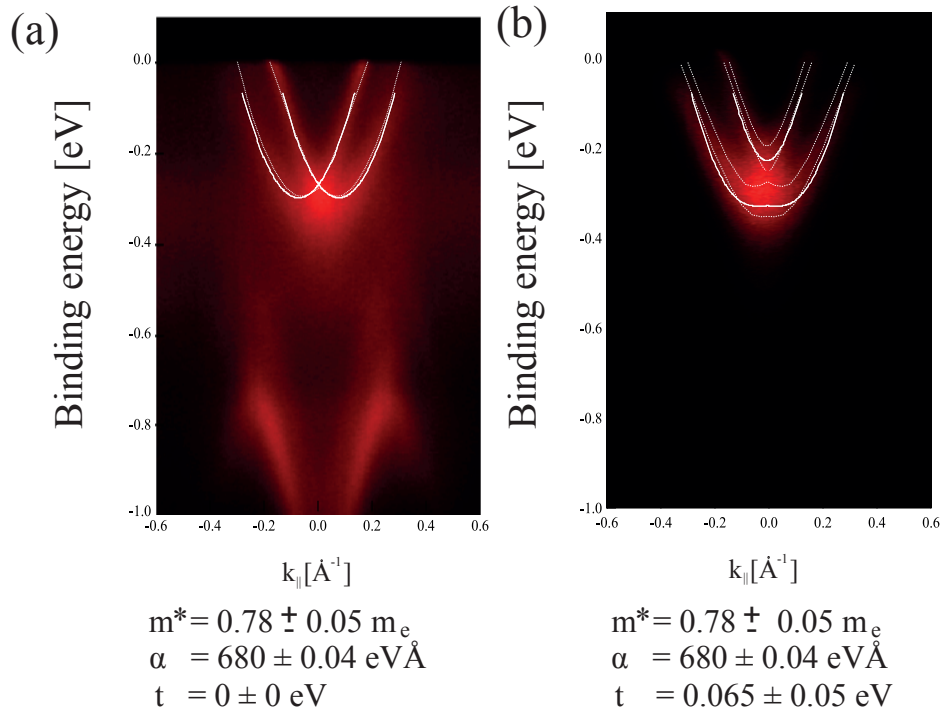
Supplementary Note 4: Tight Binding Model

For fitting the ARPES data around the M point a simple tight-binding model with inter-layer coupling and spin-orbit coupling was used. The tight binding model is given by:

$$H = \frac{\hbar^2}{2m^*} \sigma_0 \tau_0 k^2 + \alpha \sigma_z \tau_z k + \sigma_0 \tau_x t \quad (7)$$

where σ are the Pauli matrices for the spin and τ are the Pauli matrices representing the layer, α is the spin-orbit coupling (SOC) and t is the inter-layer coupling (ILC).

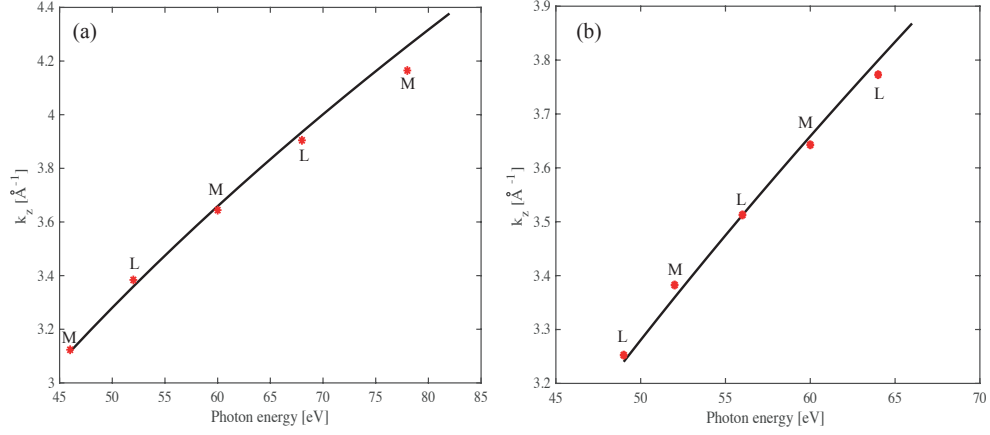
The tight binding model fits the data very well around the band minimum as can be seen in Supplementary Figure 4. The values extracted from the best fits are given in the figure. In 4Hb-TaS₂ There is no gap between the two bands indicating that the ILC is negligible.



Supplementary Figure 4. Tight binding and DFT calculations overlying ARPES spectra around the M point. ARPES spectra around the M point in (a) 4H-TaS₂ and (b) 2H-TaS₂ with overlying DFT calculations (dashed lines) and our simple tight binding model (solid line). The values of the couplings and effective mass, extracted from the fits, are shown below each spectrum. In 2H-TaS₂ the two sets of dashed lines represents the k_z span of the bands. The white solid line represents the tight binding model best fit to the data. DFT results are from a 10 unit cells slab calculation.

Supplementary Note 5: k_z Extraction

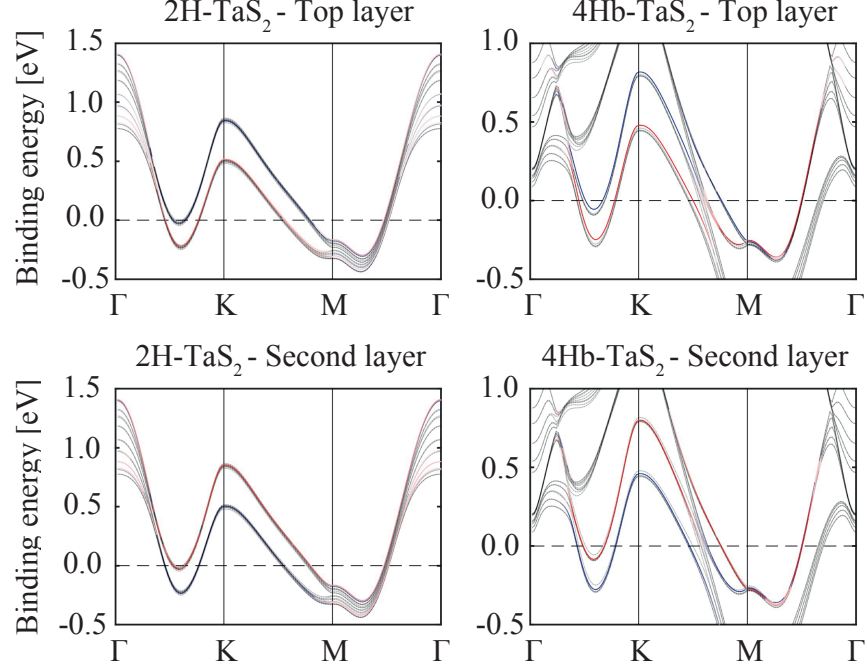
In Supplementary Figure 5 we show the k_z versus the photon energy for both 4Hb-TaS₂ and 2H-TaS₂.



Supplementary Figure 5. Fit of k_z . The fits used to extract k_z values for each photon energy. The value used for the inner potential is 9 eV. We extract the inner potential from the 2H-TaS₂ data (a) where we see a clear k_z dispersion, and used it also for the 4Hb-TaS₂ data (b).

Supplementary Note 6: DFT calculation of the spin polarization in different 1H layers

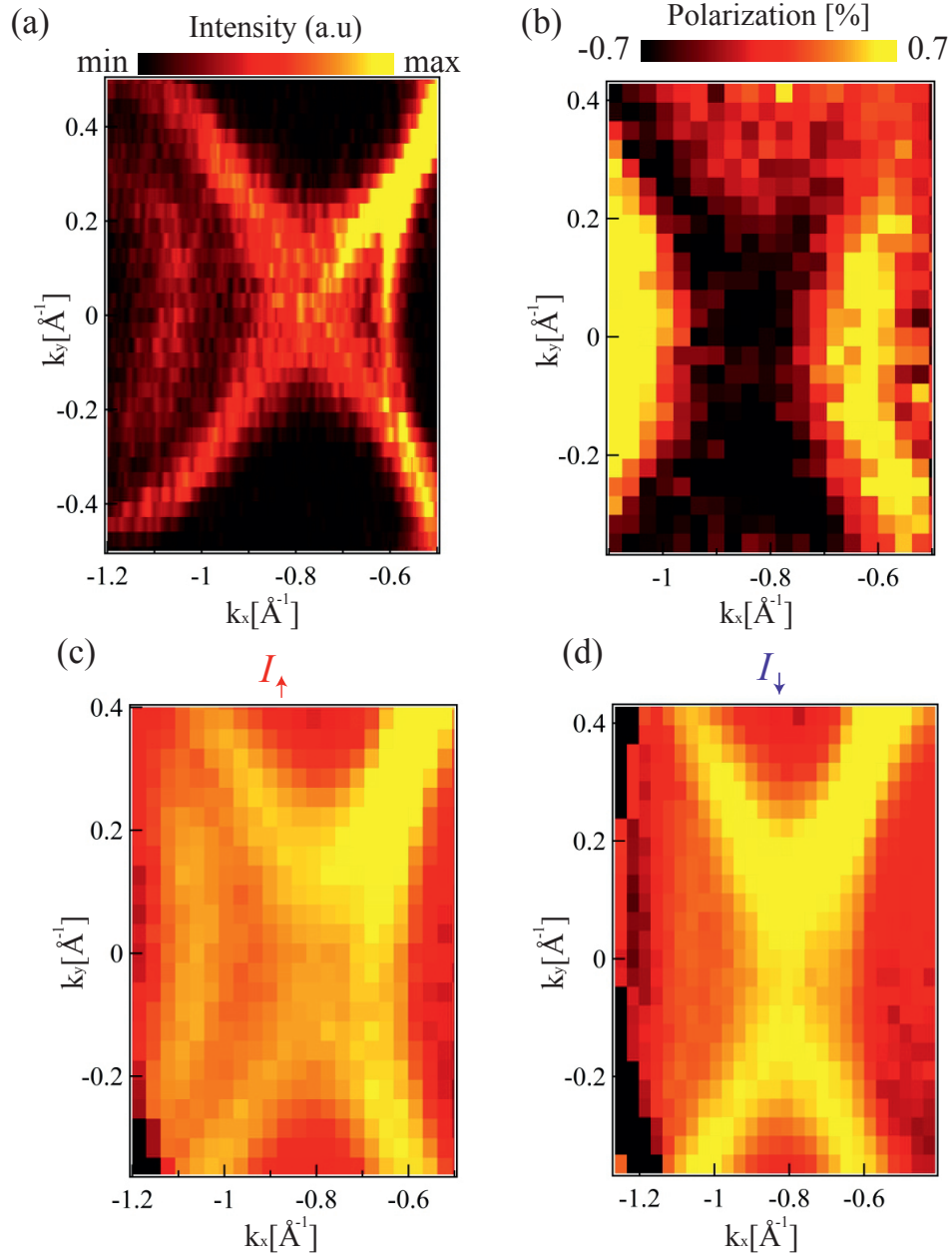
In Supplementary Figure 6 we show a DFT calculation of a 10-layers slab. We show the spin resolved dispersion for both the top-most 1H layer and the one beneath it for 2H-TaS₂ and 4Hb-TaS₂. The red (blue) lines represent spin-up (spin-down). As expected we find a large degree of spin polarization and the opposite spin on the two 1H layers.



Supplementary Figure 6. DFT results of the different layers in 2H-TaS₂ and 4Hb-TaS₂. DFT results of the high symmetry lines in 2H-TaS₂ (left) and 4Hb-TaS₂ (right) of the top most 1H layer and the 1H layer beneath it in both polymorphs. The red (blue) lines represent spin-up (spin-down).

Supplementary Note 7: Spin-polarized Fermi-surface maps

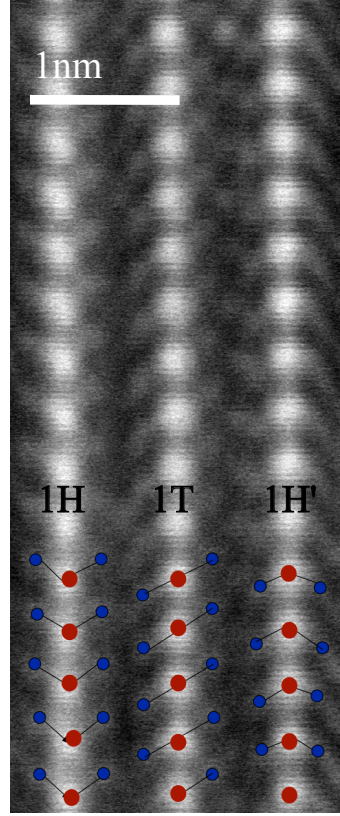
In addition to the spin polarized EDCs and MDCs, we show a spin polarized map of a part of the Fermi-surface of 4Hb-TaS₂. This map covers a part of the hole pocket around the Γ point, and a part of the pockets around the K point. Data was taken using $\hbar\nu=55$ eV photon energy. In Supplementary Figure 7(a,b) we show spin-integrated ARPES data and spin-resolved data of the Fermi-surface. Supplementary Figure 7(c,d) show the spin projection of spin up (down) of the same part of the Fermi-surface. We show that at the Fermi-level there is a strong spin polarization of the bands, as is predicted in DFT. The hole pocket around the Γ and inner K pocket have the same projection, while the two "dog-bones" from either side of the K point have the opposite projection.



Supplementary Figure 7. Spin polarized map at ϵ_F . (a) Spin-integrated ARPES map of a part of the Fermi surface of 4Hb-TaS₂. On the left the pocket around the K point is visible. Data taken with $\hbar\nu=55$ eV. (b) Spin polarization of the bands in the same field of view as in (a). (c, d) Spin up (down) projection in the out-of-plane direction of the same bands as in (a).

Supplementary Note 8: Crystal structure and actual Se concentration

The 4Hb structure is verified directly using transmission electron microscopy (TEM). In Supplementary Figure 8 we show a dark-field TEM image of a cross section of a crystal from the same growth batch as the crystals used in this study. The 1H-1T-1H' alternate stacking can be clearly observed.

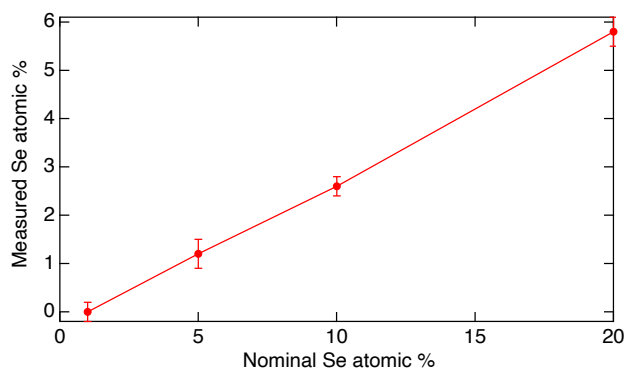


Supplementary Figure 8. TEM Dark field TEM image of a cross-section of 4Hb-TaS₂

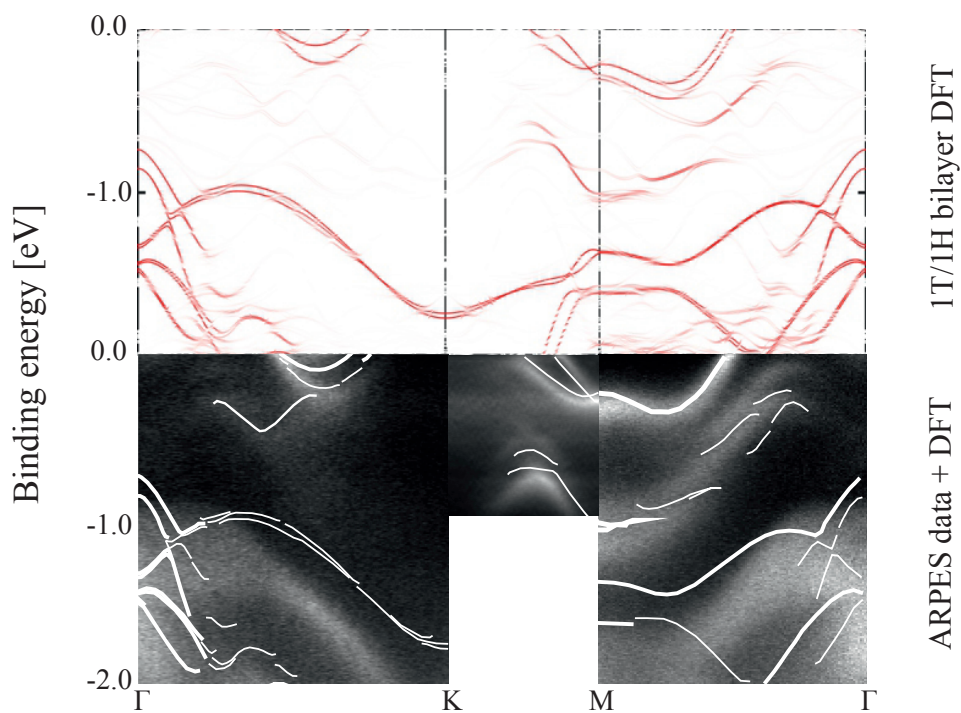
We found that substituting a small amount of S with Se greatly improves the quality of the superconductivity. This is reflected in the superconducting volume fraction and the transition width. Even a small amount of Se improves the crystals significantly. To measure the actual amount of Se in the crystals we used energy dispersive X-ray spectroscopy (EDS). In Supplementary Figure 9 we show the EDS measured concentration of Se versus the Se concentration in the mixture used to grow the crystals. The ratio is about 20%. Based on this trend we assume that the crystals used in this study have about 0.2% of Se.

Supplementary Note 9: Bi-Layer DFT and ARPES comparison

In Supplementary Figure 10 we show the bi-layer DFT results and compare them to the ARPES data. The bi-layer DFT results include the CDW flat bands around the Γ point. This calculations were done to analyze features related to CDW in 1T layers in 4Hb-TaS₂.



Supplementary Figure 9. Se concentration EDS measured Se concentration vs the Se concentration in the starting composition.



Supplementary Figure 10. High symmetry lines of Bilayer 1T-1H. ARPES spectra along the Γ -K-M- Γ line, Compared to DFT calculations of a 1T/1H bilayer.