Phase transitions via electron doping in WTe$_2$

Antonio Rossi,1, 2 Giacomo Resta,1 Seng Huat Lee,3 Ronald Dean Redwing,3 Chris Jozwiak,2 Aaron Bostwick,2 Eli Rotenberg,2 Sergey Y. Savrasov,1 and I. M. Vishik1,*

1 Department of Physics, University of California, Davis, CA 95616, USA
2 Advanced Light Source, Lawrence Berkeley National Lab, Berkeley, 94720, USA
3 Materials Research Institute, Penn State University, University Park, PA 16802, USA

WTe$_2$ is a multifunctional quantum material exhibiting numerous emergent phases in which the tuning of the carrier density plays an important role. Here we demonstrate two non-monotonic changes in the electronic structure of WTe$_2$ upon in-situ electron doping, realizing occupation near the chemical potential as a pathway for tuning structure of two-dimensional (2D) materials. The first phase transition is interpreted in terms of a shear displacement of the top layer, which realizes a local crystal structure not normal found in bulk WTe$_2$. The second phase transition arises from interactions between surface-dopant bands and the WTe$_2$ surface.

Semimetallic 2D materials, such as WTe$_2$, are highly tunable via numerous perturbations including hydrostatic pressure [1], uniaxial strain [2], gating [3, 4], alloying [5], THz excitation [6], and preparation as monolayer [7, 8]. For many emergent phenomena and transformations thereof in WTe$_2$, carrier concentration plays a key role. For example, this material initially gained attention for its large and nonsaturating magnetoresistance [9], which has been attributed to perfect compensation of electron and hole pockets in the bulk electronic structure [10], albeit not without controversy [11–13]. As a consequence of this near-balance of electrons and holes, the charge carrier concentration is also strongly temperature-dependent, yielding a Lifshitz transition near 160K [14]. More recently, WTe$_2$ has been proposed to be a type-II Weyl semimetal, characterized by tilted Weyl cones whose surface projections are connected by open segments of gapless excitations (Fermi arcs) [2], with some experimental support [15–21]. However, the Weyl points in WTe$_2$ lie $\approx 50$ meV above $E_F$, requiring gating or bulk electron doping to observe transport signatures of this behavior via the anisotropic chiral anomaly [19–21].

Recently, doping has been proposed as a mechanism for changing the structural phase of WTe$_2$ and related compound MoTe$_2$ [22], and given that different structural phases support different topological phases, these can also be viewed as topological phase transitions. Although the predicted structural phase transition is associated with hole-doping, several transformations in WTe$_2$, including the Lifshitz transition and the pressure-induced loss of large magnetoresistance and corresponding onset of superconductivity [23], are associated with an increased electron density, thus positing electron doping as an important independent tuning parameter.

Here we show that surface electron doping in WTe$_2$ can induce a shear displacement in the top layers, producing a crystal structure locally similar to a polytype typically not encountered in ambient conditions. This phase transition is evidenced by pronounced changes in low-energy surface electronic structure with support from first-principles calculations. A second phase transition at higher doping levels is associated with hybridization with dopant bands, and affects higher-energy band structure.

In the present angle-resolved photoemission spectroscopy (ARPES) experiments, in-situ electron-doping is achieved by depositing variable amounts of potassium on the cleaved WTe$_2$ surface (K-dosing). ARPES experiments were performed at the Microscopic and Electronic Structure Observatory (MAESTRO) at the Advanced Light Source (ALS). The synchrotron beam-spot size was $\approx 40 \mu m$ for the photon energies of 20 eV (Figs. 1, 2) and 90 eV (Fig. 3). First-principle density function theory calculations were performed using the localized pseudo-atomic orbital (PAO) method as implemented in OpenMX [24, 25]. High-quality bulk single crystals of 1T-WTe$_2$ were synthesized by chemical vapor transport (CVT) with bromine as the transport agent. More details about experiment and computation can be found in the Supplemental Materials (SM) [26].

WTe$_2$ is a layered van der Waal material consisting of stacked 2D sheets, and at ambient pressures the alignment between layers leads to a larger simple orthorhombic unit cell containing four formula units, called the $\gamma$ or $T_d$ phase [22, 27, 28]. This crystal structure breaks inversion symmetry along the c-axis in a subtle way, such that the average Te distance from the W plane is different above and below. This gives rise to different surface bands on opposing sides of the material. The different surfaces can be accessed by flipping a crystal over, and due to stacking faults, they can also be accessed with subsequent cleaves of a single orientation or different positions on an inhomogeneously cleaved surface [29]. The latter circumstance necessitates a sufficiently small ARPES beam spot to attain spectra on a single termination. Fig. 1(b)-(c) highlights the two types of spectra present when different surfaces are exposed: distinct bands are visible near $k_x = 0$ and $k_x = 0.3$, and in this work, we focus on the latter momentum region. Following the convention of Ref. 29, these surfaces are called face ‘A’ and type ‘B’.

Fig. 1(b)-(c) shows how in-situ K-dosing induces localized changes in the low-energy electronic structure on both non-equivalent crystalline faces of WTe$_2$, along a high-symmetry cut indicated in 1(a). The threshold K-
FIG. 1: (a) Schematic of 2D projection of Brillouin zone (BZ) of WTe$_2$ with bulk electron (red) and hole (blue) Fermi surfaces. Vertical dashed line is cut position in Fig. 3 and magenta dashed line is cut position for panels (b)-(c). (b)-(c) ARPES spectra taken on two opposite faces, along Γ-Y direction, called faces ‘A’ and ‘B’, respectively. (d)-(e) same as (b)-(c) but after K-dosing, called face ‘A*’ and ‘B*’, respectively. Note changes in band structure in boxed regions. Dashed curve in panels (c,d) highlights the band which disappears/appears with K-dosing. Panels (f)-(i) show DFT calculations in region of band structure indicated by colored boxes in (b)-(e). (f)-(g) show calculations relative to $\gamma$ structure, whereas (h)-(i) is relative to $\beta$ Color scale indicates bands that are of surface character (dark) versus bulk character (light). Pink ovals in (f)-(g) and blue ovals in (h)-(i) highlight changing surface bands.

dosing for this to occur corresponds to a shift in the chemical potential of around 0.03 eV. Along a high symmetry Γ−Y cut on face A (Fig. 1(b),(d)), a new band appears between the electron and hole pocket, at $k_x \approx 0.3$. The opposite is observed for face B (Fig. 1(c),(e)) where a band disappears at a similar momentum with K-dosing. The nonequivalent faces of the K-dosed structure are referred as A* and B*, respectively (Fig. 1(d),(e)). Density functional theory (DFT) calculations (Fig. 1(f)-(i), 4) are used to give a theoretical basis for the observed changes in the band structure, with the β (1T’) phase capturing the essential changes in the band structure upon dosing. The β crystal structure differs from the $\gamma$ phase via a small tilt in the unit cell of $\approx 4^\circ$ (Fig. 4(g)). The changing portions of the calculated band structure are highlighted with shaded ovals. In the $\gamma$ phase, the band structure of the two faces differs via a surface-dominated band which is located above $E_F$ on face A, hence not observable by ARPES, but below $E_F$ on face B. The opposite is true for the $\beta$ crystal structure where face A* shows a surface dominated band between the electron and hole pocket below $E_F$, but face B* has this band above $E_F$. Most of the other bands in Fig. 1(b)-(e) are unchanged by dosing, which is consistent with prior calculations showing that the $\beta$ and $\gamma$ phase yield very similar bulk bands [22].

The appearance/disappearance of bands between the electron and hole pockets is highlighted further via evolving fermiology, shown in Fig. 2. Prior to K-dosing, both faces show similar-sized electron and hole pockets, with

FIG. 2: Fermi surface maps with corresponding DFT calculations mirrored across $k_x = 0$, before and after K-dosing. (a)-(b) before dosing, faces A and B, with corresponding DFT of the $\gamma$ phase mirrored on left. (c)-(d) after K-dosing with DFT of the $\beta$ phase mirrored on the left. (e)-(f) difference spectra (A-A*, B-B*), where red (blue) indicates spectral weight increase (decrease) upon dosing. In all panels, green rectangle marks momentum region of interest where spectral weight increases (decreases) on face A* (B*). the hole pocket having weaker intensity at this photon energy due to matrix-element effects. Faces A and B differ by a segment of Fermi surface extending from the electron to the hole pocket, present only on face B (Fig. 2(a)-(b)). Earlier ARPES studies have demonstrated the 2D (surface-like) nature of these states via a lack of dis-
persion with varying photon energy [15, 29, 30]. Present DFT calculations, support the surface-dominated nature of the segments prominent on surface B. These surface states are sometimes misidentified as the topological Fermi arcs in literature, but they do not connect surface projections of Weyl points and are therefore trivial, though perhaps not irrelevant [31]. After K-dosing, these surface states on surface B\(^*\) are no longer observed (Fig. 2(d)). The opposite is seen on face A, where initially only electron and hole pockets are observed, but after dosing, new bands appear between them (Fig. 2(c)), which DFT calculations for the \(\beta\) phase indicate to be surface states. This phenomenon on face A/A\(^*\) was previously reported, but not explained [32]. The doping-induced change is highlighted by subtracting normalized spectra from one another (A-A\(^*\), B-B\(^*\)) in Fig. 2(e)-(f), where states near \(k_x = 0.3\) are shown to appear (disappear) on face A (B). Notably, while elevated temperature also leads to the diminishment of the hole-like band, associated with a Lifshitz transition near 160K, it does not appear to yield comparable changes in surface bands between the electron and hole pockets[17, 32, 33].

Upon subsequent dosing cycles, the system undergoes a second phase transition, as shown in Fig 3. In these spectra, the difference between faces A and B is not resolved, but the spectral changes largely occur at higher binding energy where the two faces yield identical spectra. Additionally, the spectral weight of bands differs from Fig. 1 because different photon energy was used. Several sudden changes occur at this higher dosing value, corresponding to a chemical potential shift of \(\approx 130\) meV. Initially, 4 bands are clearly visible between \(E_F\) and -1.5 eV at \(\Gamma\), and afterwards only 3 are resolved, with energy separation between bands also changing significantly (3(b)-(d)). The second phase transition is also seen in an off-high-symmetry cut (Fig. 3(e)-(g)), taken at momenta indicated in Fig. 1(a). Previous ARPES studies [33] have identified the observed Dirac-like dispersion as a surface state. Initial dosing trivially shifts the chemical potential and slightly broadens the band, but keeps the dispersion intact. After the second threshold dosing is reached, the upper branch of the dispersion is not observed. Additionally, spectral weight appears away from the initial dispersion, near -0.2 eV, marked by the arrow in Fig. 3(g). The spectral changes in the high-symmetry and off-high-symmetry cut are reproduced by considering bands from K hybridizing with bulk bands of WTe\(_2\), and a schematic of the simulated slab is shown in Fig. 3(a), with one K-adatom per unit cell donating 0.5 electron each. Overlays of calculated hybridized band structure are also shown in Fig. 3. Other sudden changes associated with the second phase transition include a shift in W core levels, a change in the K core levels, and a change in the shape of constant-energy maps at equivalent energies in the band structure [26].

The first phase transition manifests in changes in surface bands at low binding energy WTe\(_2\). Below, we will argue that this result can be reproduced by a shear shift of top layer for both terminations. We will also discuss the connection to the \(\beta\) phase which is used in corresponding DFT calculations in Figs. 1 and 2, and explain the rationale for considering this structural modification.

The transition from \(\gamma\) to \(\beta\) can be visualized as shear displacements of subsequent layers, and the change in energy when one WTe\(_2\) layer is subjected to variable amount of shear displacement is shown in SM [26] for both bulk and slab geometry, with very similar results. A shear displacement of zero corresponds to the WTe\(_2\) \(\gamma\) phase. A shear displacement of \(\approx 0.4\)A corresponds to a geometry where Te atoms on adjacent layers are closest. In the case of neutral or electron-doped WTe\(_2\), repulsion of Te antibonding orbitals leads to this configuration constituting a local maximum in energy and being unfavorable. Hole-doping has the opposite effect, removing electrons from the Te antibonding orbitals and stabilizing this configuration. A displacement of \(\approx 0.8\)A results in the Te atoms of adjacent layers adopting a lo-
cally mirrored configuration as compared to the WTe$_2$ γ state. With electron-doping, a shear displacement of $\approx 0.8\AA$ corresponds to a local minimum in energy, and is referred to as a metastable configuration, while the global minimum is found at $<-0.2\AA$, very close to the γ configuration.

Although the metastable configuration is not a global minimum in energy, the energy difference from the γ geometry is very small, $<2\text{meV}$, for one electron per unit cell. It should be noted that the DFT calculations cannot provide a reliable comparison of such small energy differences between the configurations, especially considering the difficulties in modeling the van der Waals interaction, such that it is possible that the metastable configuration actually has lower energy in the real system. Another possibility is that other aspects of the present experiment, such as the displacement field introduced by the ionization of the K atoms affects the energy landscape.

In Fig. 4(a)-(f), we consider how successive shear displacements of the top WTe$_2$ layer affect bulk and surface bands in the momentum region of interest. On surface A, the surface band located between the electron and hole pocket is initially above $E_F$ and hence not observable by ARPES, but is gradually pushed below $E_F$ by successive shear displacements of the top WTe$_2$ layer along the distortion direction of the 1T’ structure (W-W zig zag chains). A full series of shear displacements is shown in SM [26]. Between 0.6-0.8Å, the surface-derived band of interest is pushed below $E_F$ becoming visible to ARPES, and thus the metastable configuration captures this key feature of the data and of the β-phase electronic structure. On face B, the opposite is observed, with a surface band initially below $E_F$ between the electron and hole pockets, being pushed above $E_F$ for a shear displacement between 0.6-0.8Å.

We now discuss the similarity between the metastable configuration and other crystal structures (Fig. 4(h)-(j)). The metastable crystal structure is superimposed on top of the γ phase, the inverted γ phase such that surface A and B are reversed, and the β phase. Boxes denote regions of qualitative agreement. The metastable structure agrees qualitatively with the β structure in the first three layers, which explains why the two structures yield qualitatively similar surface bands. The comparison of ARPES data to the β phase calculations is further justified by the surface-sensitivity of the technique. For photoelectrons with kinetic energy 20 eV, the mean free path is $\approx 6\AA$, such that $\approx 99\%$ of the photoemission signal comes from the first three WTe$_2$ layers. Additionally, the first two layers of the metastable structure agree well with the inverted γ structure, giving qualitative support for the observation that the electronic structures on the A and B surfaces seem to swap upon electron doping.

We have demonstrated that surface bands in WTe$_2$ can identify subtle structural changes in this material, even where these structural changes only minimally affect the bulk band structure. Additionally, these results suggest that the same shear mode which has been proposed to be activated with hole doping can also be activated with electron doping. Alkali metal dosing is a relatively ubiquitous means of surface manipulation in ARPES experiments, and usually it simply shifts the chemical potential. Here we demonstrate a distinct effect of K-dosing, and electron doping more generally, as a means of inducing surface structural changes which decouples the top layer structurally without intercalation.

**FIG. 4:** (a)-(c) Slab calculations with different shear displacements of top layer for face ‘A’ termination. Darker grey denotes more surface-like character, and lighter grey more bulk-like. Arrow points to surface-derived band to highlight changes as a function of shear displacement. (d)-(f) same for face ‘B’ g) definition of shear displacement in β unit cell, together with β unit cell (h)-(j) Overlay of metastable crystal structure (γ phase with the top layer displaced by 0.8Å) with other crystal structures with region of qualitative similarity indicated by a green box. (h) overlay with γ (i) overlay with inverted-γ, such that the opposite termination occurs (j) overlay with β crystal structure

We now turn to the second phase transition, achieved with a large amount of K dosing. Several scenarios were considered and are presented in SM [26], including additional structural transformations of WTe$_2$ and interactions between the K atoms and the host. The alternate structures either yield poor agreement with the data (hexagonal 2H) or are unstable (octahedral 1T). Interactions between K atoms and the WTe$_2$ surface yield better agreement, both considering intercalation and surface-hybridization, with the latter being more consistent with the evolution of K core levels [26]. The hybridized band
structure in Fig. 3 captures the reduction in number of bands at $\Gamma$, the loss of spectral weight near $E_F$ in the off-high-symmetry cut in Fig. 3(e)-(g), and the appearance of spectral weight away from the main bands in both cuts, which is marked by the arrow in 3(g). The $\beta$ structural phase is used in Fig. 3 because the large amount of K-dosing in Fig. 3 exceeds the amount which both cuts, which is marked by the arrow in 3(g). The off-high-symmetry cut in Fig. 3(e)-(g), and the appearance of spectral weight away from the main bands in both cuts, which is marked by the arrow in 3(g).

The sudden nature of the second transition is interpreted as reflecting a critical concentration where the bands from the 2D metal hybridize with those from the WTe$_2$ host surface.

In conclusion, we have demonstrated how surface dosing can induce two distinct changes in the electronic structure of WTe$_2$. The first transition is interpreted in terms of a metastable shearing of the top WTe$_2$ layer induced by electron-doping, which yields surface bands qualitatively similar to the $\beta$ phase. The second phase transition is consistent with electrons in a single layer of K atoms hybridizing with the WTe$_2$ host. Both results are broadly relevant to understanding effects of electrostatic gating and interactions with metallic contacts in devices constructed from semimetallic 2D materials.

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* ivishik@ucdavis.edu

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Phase transitions via electron doping in WTe$_2$: Supplementary Materials
MATERIALS AND METHODS

**First-principle calculations:** First-principle density function theory calculations were performed using the localized pseudo-atomic orbital (PAO) method as implemented in OpenMX [S1, S2]. All calculations were conducted using DFT with spin orbit coupling included and where the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) [S3] was used for the exchange-correlation energy. Fully relativistic norm-conserving pseudo-potentials [S4] and pseudo-atomic orbitals for each atomic type were taken from the 2013 OpenMX database (PBE13). The following radial cutoffs (in units of Bohrs) and orbital basis were used: 7.0-s3p2d2 for W, 7.0-s3p2d2 for Te, and 12.0-s2p2d2 for K. This basis was found to provide an optimal convergence for the bulk band structure as confirmed through comparisons with calculations using a larger radial cutoff and orbital basis (9.0-s3p3d3f1 for W and 9.0-s3p3d3f1 for Te). An energy cutoff of 200 Ry and a k-point sampling of $8 \times 15 \times 3$ was used for bulk calculations while a sampling of $8 \times 15 \times 1$ was used for surface state calculations.

To calculate the surface states in Figs. 1 and 2 of the manuscript, a supercell consisting of a 3-unit-cell (6-layer) thick (001)-oriented slab structure and a vacuum layer of 12 Å was constructed for both the WTe$_2$-$\gamma$ and WTe$_2$-$\beta$ phases, which was found to provide reasonable convergence for the surface states. A 6-unit-cell thick slab was used in Fig. 4 of the manuscript, and in this SM we show that the two yield similar agreement with ARPES data for the bands of interest.

The surface projected band structure was then determined by projecting the wavefunctions to the outermost two layers of the material.

**ARPES:** ARPES experiments were performed at the Microscopic and Electronic Structure Observatory (MAESTRO) at the Advanced Light Source. Samples were cleaved in glovebox and measured in microARPES end-station with a base pressure better than $5 \times 10^{-11}$ mbar. The synchrotron beam-spot size was on the order of 40 $\mu m$. Measurement temperature was 20K. Energy resolution was 5 meV for data taken with 20 eV photon energy and 80 meV for data taken with 90 eV photon energy. The data were collected using a hemispherical Scienta R4000 electron analyser equipped with custom-made deflectors that enable collecting ARPES spectra over a full Brillouin zone without moving the sample. Potassium-dosing experiments were carried out by evaporating potassium in situ from a
SAES getter source mounted in the analysis chamber such that dosing is performed without moving the sample from measurement position.

**Crystal growth:** High-quality bulk single crystals of 1T-WTe$_2$ were synthesized by chemical vapor transport (CVT) with bromine as the transport agent. Prior to the CVT growth, a stoichiometric mixture of high purity W (99.9%) and Te (99.9999+) was heated to 800°C for 72 hours in an evacuated quartz tube to form polycrystalline WTe$_2$. For single crystal growth, the pre-compounded polycrystals were ground into a fine powder and transferred into an evacuated 18 cm long, 10 mm inner diameter, 12 mm outer diameter quartz tube together with 3-6 mg/cc of bromine. Using liquid nitrogen, the volatile bromine was condensed with the powder at the bottom end of the ampoule during the quartz sealing process. To minimize oxide based W and Te growth, all sample preparation was done in an argon-filled glovebox to reduce the presence of oxygen and moisture. Additionally, the quartz ampoule was purged and vented with ultrahigh purity argon gas to further reduce the oxygen and moisture content prior to sealing the ampoule. The sealed ampoule was then placed in a four-zone tube furnace and heated up to 900°C and 840°C at the charges zone and growth zone, respectively, for 6 days. The size of our largest resultant flake was 36 mm$^2$.

The x-ray powder diffraction (XRD) pattern of the as grown single crystal is well-matched with the International Centre for Diffraction Powder Diffraction File (ICDD PDF) card 04-007-0799 and confirmed the WTe$_2$ single crystal is in the orthorhombic crystal system, space group Pmn2$_1$. Energy-dispersive x ray (EDX) elemental mapping showed that tungsten and tellurium are distributed evenly, and no other elements were detected except carbon and oxygen, whose presence is strongly believed to be from the vacuum chamber. van der Pauw resistivity measurements suggests that the carrier transport is dominated by electrons with a typical carrier density of $2.77 \times 10^{20}$ cm$^{-3}$ and specific electrical resistance of about 0.5 mΩ-cm.

**EFFECT OF CHARGE DOPING ON SHEAR DISPLACEMENT IN γ-WTe$_2$**

Fig. S1(a) considers the effect of charge doping on the WTe$_2$ γ phase under a bulk geometry, where one of the layers is shifted by various shear displacements. A shear displacement of zero corresponds to the WTe$_2$ γ phase. A shear displacement of approximately 0.4Å corresponds to a geometry where Te atoms on adjacent layers are closest and therefore the
FIG. S1: Effect of charge doping on the bulk (a) and slab (b) $\gamma$-WTe$_2$. Charge 1 corresponds to one hole per unit cell, 0 is pristine WTe$_2$, -1 is one electron per unit cell, and -2 is two electrons per unit cell. Bottom panel shows relative energy as a function of different shear displacements of the middle layer. Top panels show local crystal structure for select shear displacements of middle plane, with the relative alignment between the nearest Te-Te atoms indicated by black lines between planes.

Effects of antibonding orbitals is locally maximized. Finally a displacement of 0.8 Å causes the Te atoms of adjacent layers to adopt a locally mirrored configuration as compared to the WTe$_2$ $\gamma$ phase. In the absence of charge doping, zero shear displacement (WTe$_2$ $\gamma$) is the most stable state and that there is a small local maximum in configurational energy at 0.4 Å which is the result of the antibonding orbitals between Tellurium atoms of adjacent layers. In the presence of hole doping (charge = 1.0, i.e. one hole per unit cell), the local energy maximum at 0.4 Å vanishes completely and the most stable state has a shear displacement of around 0.3 Å. This is consistent with Ref. S5 in which hole-doping accelerates electrons away from antibonding orbitals between adjacent Te atoms, setting adjacent layers in relative oscillatory motion. It should be noted, however, that in the present calculations only one layer is shifted.

In the presence of electron doping, the local maximum near 0.4 Å is greatly increased.
This results from the fact that the additional electronic charge occupies the antibonding orbitals of adjacent Tellurium atoms near the $E_F$. We note that since the repulsion between the Te atoms is increased, the mirror geometry with a shear displacement of 0.8Å become meta-stable with a local minimum in the energy. However the most stable geometry remains the WTe$_2$ - $\gamma$ state with a displacement of at most -0.2Å.

Fig. S1(b) explores the effect of charge doping on the WTe$_2$ $\gamma$ phase under a slab geometry with the bottom layer shifted by various shear displacement. The results exhibit a similar qualitative energy profile as compared to the results for the bulk geometry in Fig. S1(a). Fig. S1(b) shows that in the case of zero charge doping the WTe$_2$ $\gamma$ phase is the global minimum in energy and therefore for energetically most favored state. Compared to the bulk calculations the local maximum at 0.4Å is approximately half as large. This is due to the fact that under a slab geometry the bottom layer has only half the number of adjacent Tellurium antibonding orbitals due to the presence of the vacuum layer on one side. In the absence of charge doping, we can see that the displacement potential for the bottom layer using a slab geometry with four layers is identical to the case of the slab geometry under a minimum of two layers which indicates that the presence of additional layers to first order does not modify the local potential significantly. In the case of electron doping we only consider the minimum geometry of two layers to ensure that the additional charge is entirely deposited on the two layers. Once again, the presence of electron doping increases the local maximum at 0.4Å, indicating that the additional charge occupies antibonding orbitals of Tellurium atoms in adjacent layers. The global minimum remains a state very similar to the $\gamma$ phase with a displacement of at most -0.2Å, and a local minimum in energy is found at the metastable geometry with a shear displacement of 0.8Å.

In both of the above calculations the $\gamma$ phase remains the most stable state with a shear displacement of at most -0.2 Å. However there are several limitations in the above calculations that prevent determination of energy changes down to several meV, such that the possibility of the meta-stable state (shear displacement of 0.8Å) being a global minimum in energy cannot be excluded. First the van der Waals interaction was modeled empirically using DFT+D3 which does not capture effects due to electron density and hence is fundamentally incapable of modeling the effect of a change in charge density. The second limitation in the case of the slab calculations is that only a minimal of two layers were considered to ensure that the added charge is fully localized on only two layers in a consistent
FIG. S2: Evolution of low-energy electronic structure as a function of shear displacement of the top layer with 'face A' termination. Labels above (a)-(h) indicate amount of shear displacement of top layer in Å, and (i) shows $\beta$ phase for comparison. Arrows point to surface states of interest.

fashion. In light of these limitations, the above calculations do not exclude the possibility that the meta-stable state in fact become the stable state. However, the above calculations illustrate that the addition or removal of charge modifies the strength of antibonding orbitals between Tellurium atoms in adjacent layers suggesting a mechanism for generating shear displacements using electron doping.
FIG. S3: Evolution of low-energy electronic structure as a function of shear displacement of the top layer with 'face B' termination. Labels above (a)-(h) indicate amount of shear displacement of top layer in Å, and (i) shows $\beta$ phase for comparison. Arrows point to surface states of interest.

Fig. S2 systematically shows the evolution of the 'face A' surface state as a function of various displacements of the surface layer from -0.4 to 1.0 Å. Displacements outside of this range are unlikely, due to the high energy barriers at -0.4 and 1.0 Å as illustrated Fig. S1(b). It is seen that the surface state between the electron and hole pockets, marked by an arrow, evolves from being below $E_F$ to being above $E_F$. Notably the meta-stable configuration reproduces the key experimental observable that this band is longer visible in
ARPES experiments that only measure occupied states. Also note the qualitative similarity between the metastable configuration (0.8 Å shear displacement) and the β phase.

Fig. S3 systematically shows the evolution of the ‘face B’ surface state as a function of various displacements of the surface layer from -0.4 to 1.0 Å. Again, the meta-stable configuration reproduces the key experimental observable that a surface band between the electron and hole pocket appears in ARPES spectrum, and also has qualitative similarity to the β phase.

![Fig. S4](image)

FIG. S4: Superposition of DFT calculated bands (colored, 3 unit cells (a) and 6 unit cells (b)) with measured band structure along Γ – Y direction. (i-ii) Band structure from Face A and B, respectively. (iii-iv) Band structure after doping induced transition from Face A* and B*, respectively.

Fig. S4 shows the same data and calculations as in Fig. 1 of the main text, except with DFT Slab calculation of the β phase (3 unit cells, 6 layers (a)) overlaid on the ARPES data to qualify agreement, particularly with regards to evolving surface states. A calculation taking into account a thicker slab (6 unit cells) is shown in Fig. S4(b). Both agree with the general trend reported in the manuscript, justifying the use of the 3 unit cell system.

**SECOND PHASE TRANSITION: ADDITIONAL DATA**

The second phase transition is manifested in both W and K core levels, measured by x-ray photoemission spectroscopy (XPS). The XPS data in Fig. S5(a) show W core levels. These
data were fit with Voigt functions to track the position of the peaks, and the evolution as a function of doping cycle is shown in Fig. S5(b). In all core levels, an initial jump in peak position is observed after the first dosing cycle, due to the sudden change of overall chemical environment. With subsequent cycles, the binding energy downshifts due to the overall doping mechanism that involves the creation of a dipole field at the interface. However, when the second transition occurs (cycle 7), the W core level corresponding to the top W layer in the unit cell stops evolving monotonically and jumps to higher binding energy. Over subsequent cycles, the peak position again evolves monotonically.

![Graph showing the change in intensity with binding energy for different doping steps.](image)

**FIG. S5:** (a) W 4f⁵/² and 4f⁷/² core level at different doping steps. (b) W core level binding energies, fit from panel (a).

The K core levels (Fig. S6) also show a change at the same doping level. Both before and after the transition, two peaks are observed. The one at lower binding energy ($\approx -18.4\text{eV}$ in
FIG. S6: a-e) K 3p core level at different doping cycles. The peak is fit with two Voigt functions (green, blue) and a broad Gaussian. A Shirley function for the background is also used (not displayed). (f) K M3 − 3p3/2 core level at different doping cycles.

The present study) is consistent with the 3p core level in potassium metal, as measured and tabulated by earlier studies[S6, S7]. The one at slightly higher binding energy ($\approx -19.3eV$ in the present study) is interpreted as ionized potassium which has donated its electron to the substrate. Previous studies of potassium deposited onto metal surfaces have demonstrated a shift of the K 3p core level from slightly higher binding energy to the bulk value as monolayer coverage is approached[S8, S9]. The adsorption of alkali metals on a substrate is interpreted as initially being ionic (donating electrons to the substrate) and becoming more neutral (bonding among adatoms) with further dosing[S10]. The observed evolution of K core levels in Fig. S6(a-e) is consistent with this picture. The rise of the peak corresponding to neutral
K after the second transition is consistent with our interpretation of bonding within the K layer being one ingredient of that transition. K core levels for all dosing cycles are plotted in Fig. S6(f). A reduction in peak intensity is not observed after the second phase transition, indicating that intercalation is not likely.

The second phase transition is also manifested in the band structure beyond what is discussed in the main text. One example is constant energy contours which change orientation, as shown in Fig. S7 These contours are taken at equivalent energies in the band structure ($E_F$ and $-130\text{meV}$) before dosing and after the second phase transition. A clear change in the shape of the contours is observed. Initially Fermi surfaces are elongated along the $k_y$ direction, reflecting the quasi-1D tendency of the crystal structure induced by the W zigzag chains. Afterward, the contours are elongated along $k_x$. This change cannot simply be attributed to a Lifshitz transition due to a changing chemical potential, because the constant energy contour after the second phase transition are not taken at the chemical potential. Instead, it reflects a large rearrangement of the band structure.

![FIG. S7: Constant energy contours collected at 91 eV photon energy, for pristine crystal (left, $E = E_F$) and after the second transition (right, $E = -130\text{meV}$).](image)

Fig. S8 shows how two off-high-symmetry cuts evolve with K dosing across the second phase transition. The first cut (top row) is also shown in the main text, but additional panels are given here. The second cut (bottom row) is a different slice through the hole pocket. As discussed in the main text, the cut through the electron pocket is dominated by a nearly-dirac-like surface state which becomes clearly gapped across the second phase transition. This strong effect on a surface state is consistent with our interpretation of
FIG. S8: Evolution of two off-high-symmetry cuts as a function of dosing across second phase transition. Cut positions are indicated in constant energy contour on left. Top row: cut through center of electron pocket, showing additional panels from what is shown in main text. Bottom: cut through hole pocket taken at same dosing amounts. Vertical yellow line marks second phase transition.

the second phase transition being characterized by the loss of the WTe$_2$ surface and the emergence of a 2D K metal which hybridizes with the underlying WTe$_2$. The slice through the hole pocket is initially characterized by two hole-like dispersions near $E_F$ which can clearly be distinguished from one another. Across the second phase transition, the one at lower binding energy disappears and an additional feature appears at $E \approx -0.5$ eV.

Fig. S9(a-f) shows a comparison of WTe$_2$ intercalated with K, K/$\gamma$-WTe$_2$ surface hybridization, and K/$\beta$-WTe$_2$ surface hybridization. In all cases, there is one K-atom per unit cell contributing 0.5 electrons. The hybridized band structure is very similar considering the $\gamma$ or $\beta$ phase of WTe$_2$, notably reproducing the extra spectral weight away from the main bands in high-symmetry and off-high-symmetry cuts.

Other scenarios that were considered are shown in Fig. S9(g,h). The 2H phase is metastable and reached in some parameter regimes. For example, electrostatic doping in MoTe$_2$ induces a structural phase transition at room temperature which was identified as a transition from the 1T' phase to the 2H phase[S11]. However, this band structure does not have good agreement with what is observed after the second phase transition. The T phase
FIG. S9: DFT calculation overlayed on ARPES data considering intercalation (a,d), K-adlayer hybridizing with \( \gamma \) (b, e), and K-adlayer hybridizing with \( \beta \) (c, f). (a)-(c) are high-symmetry \( \Gamma - Y \) cut and (d)-(f) are off-high-symmetry cut used in top row of Fig. S8. Other bulk band structure calculations. (g): Crystal structure and calculation for semiconducting hexagonal 2H phase. (h): Crystal structure and calculation for undistorted T-phase.

(undistorted octahedral) is not stable and also has poor agreement with the data.

**FIRST-PRINCIPLES CALCULATIONS: LATTICE PARAMETERS AND TYPE-II WEYL SEMIMETAL**

Non-relaxed experimental crystal parameters were used to determine all layered WTe\(_2\) structures as it was found that geometric relaxation worsened the agreement with ARPES measurements. As noted in previous studies [S12], empirical van der Waals correction schemes such as DFT-D2 and DFT-D3 are not able to accurately model the interlayer interaction and therefore lead to inaccurate layer separations. Several experimental parameters have been reported for the WTe\(_2\)-\( \gamma \) phase of which two sets of parameters [S13, S14] are widely referenced through the literature and were taken at different temperatures. Consistent with previous studies [S15], we find that the room temperature crystal structure for WTe\(_2\)-\( \gamma \) reported by Brown [S13] does not exhibit Weyl points although the system is re-
markably close to realizing them. Although not the focus of the manuscript, the type-II Weyl semimetal phase, which is only supported by the $\gamma$ crystal structure was also studied. It was found that approximately a 1.5% compression along the c-axis of the unit cell is required for the Weyl points to emerge (see Fig. S10). The effect of uniaxial compression is consistent with several previous works which have reported that compression along the c-axis increases the Weyl point separation, thereby stabilizing the Weyl-semimetal state [S12, S16]. This sensitivity to c-axis parameters makes the bulk Weyl points of WTe$_2$ even more elusive for ARPES experiments, as they may already be annihilated at temperatures high enough to thermally populate their location above $E_F$.

FIG. S10: (a) Effect of c-axis compression on Weyl points and topological phase transition. Each column shows the evolution from the $\gamma$ to the $\beta$ phase (bottom to top), similar to Fig. 3 in main text. Each column differs by amount of c-axis compression. Sufficient compression supports Weyl points in the $\gamma$ phase. (b) Calculated positions of Weyl points (red) in the Brillouin zone. Axes $k_1$ and $k_2$ are scaled such that $\pm 1$ is the Brillouin zone boundary.

In contrast with results reported in [S16], we find that the experimental parameters measured at a lower temperature [S14], although slightly closer to realizing Weyl point crossings, exhibits only small changes in the band structure. This result was further confirmed using the all-electron full-potential linear augmented plane wave method (FP-LAPW) as implemented in ELK [S17]. It should be noted that [S16] reported exceptionally small Weyl point separations, far beyond spectroscopic experimental resolution. Consequently, taking into consideration the similarity between the band structures of the two crystal parameters, in
this study we have use the crystal structure for WTe$_2$-$\gamma$ reported by Brown [S13] in all calculations as it is more commonly used though out the literature and enables for a more direct comparison to the structures of MoTe$_2$-$\gamma$ and MoTe$_2$-$\beta$ reported in the same article. An approximate crystal structure for the WTe$_2$-$\beta$ phase was obtained by replacing Mo with W in the experimental structure for MoTe$_2$-$\beta$ [S13] and rescaling the lattice constants to be consistent with those of WTe$_2$-$\gamma$.

The positions of the Weyl points in the Brillouin zone for 1.5% compression along the c-axis is shown in Fig. S10(b). As acknowledged in previous literature, Weyl points of opposite chirality are very close to each other, making it very difficult to observe Fermi arcs connecting them.

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