MoTe₂ is an exfoliable transition metal dichalcogenide (TMD) which crystallizes in three symmetries; the semiconducting trigonal-prismatic 2H-phase, the semimetallic 1T’ monoclinic phase, and the semimetallic orthorhombic Td structure. The 2H-phase displays a band gap of \( \sim 1 \) eV, making it appealing for flexible and transparent optoelectronics. The Td-phase is predicted to possess unique topological properties which might lead to topologically protected non-dissipative transport channels. Recently, it was argued that it is possible to locally induce phase-transformations in TMDs through chemical doping, local heating, or electric-field to achieve ohmic contacts or to induce useful functionalities such as electronic phase-change memory elements. The combination of semiconducting and topological elements based upon the same compound, might produce a new generation of high performance, low dissipation optoelectronic devices. Here, we show that it is possible to engineer the phases of MoTe₂ through W substitution by unveiling the phase-diagram of the Mo₀ₓWₓTe₂ solid solution which displays a semimetallic transition as a function of \( x \). We find that only \(~8\%\) of W stabilizes the Td-phase at room temperature. Photoemission spectroscopy, indicates that this phase possesses a Fermi surface akin to that of WTe₂.

The properties of semiconducting and of semimetallic MoTe₂ are of fundamental interest in their own right, but are also for their potential technological relevance. In the mono- or few-layer limit it is a direct-gap semiconductor, while the bulk has an indirect bandgap of \( \sim 1 \) eV. The size of the gap is similar to that of Si, making 2H-MoTe₂ particularly appealing for both purely electronic devices and optoelectronic applications. Moreover, the existence of different phases opens up the possibility for many novel devices and architectures. For example, controlled conversion of the 1T’-MoTe₂ phase to the 2H-phase, as recently reported, could...
enable circuits composed of a single material functioning as both semiconducting channels and metallic interconnects. More precise control of the phase change might also be used to minimize the metal-semiconductor Schottky barrier by continuous evolution of the electronic band structure, in order to overcome current limits on optoelectronic performance. In fact, recent work has reported contact phase engineering by laser processing and chemical modification.

The ability to phase-engineer MoTe₂ has many broader applications and potentially deeper implications. For instance, doping, temperature, strain, and electric fields can be used to drive metal-to-insulator transitions for sensors and nonvolatile information storage. More fundamentally, the electronic structure of mono-layers of semimetallic MoTe₂ (and of WTe₂) have been proposed to possess a Z₂ topological invariant characteristic of a quantum spin Hall-effect ground-state. Nevertheless, in Figs. 1c and 1d we also show the octahedral phase for these concentrations. Single crystals of the Mo₁₋ₓWₓTe₂ series were grown through a chemical vapor transport technique as described in Methods. Unless otherwise noted, samples were cooled slowly in order to obtain the equilibrium phase at room temperature. Their precise stoichiometry was determined through energy dispersive X-ray spectroscopy (EDS) and photoelectron spectroscopy (XPS), see Methods as well as Supplementary Fig. S1 for photodetection core level spectrum of a Mo₁₋ₓWₓTe₂ crystal and Supplementary Fig. S2 for details concerning the determination of the W content (x ± 0.01). Stoichiometric MoTe₂ (x = 0) and WTe₂ (x = 1) were synthesized through a Te flux method. For MoTe₂, samples were slowly cooled to yield the 2H—phase or quenched to room temperature to yield the metastable 1T’—phase.

Figure 1 shows structural analysis via single crystal x-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and scanning tunneling microscopy (STM). For STEM, the crystals were exfoliated following a standard procedure and transferred onto a TEM grid, see Methods. Figures 1a and 1b display atomic resolution STEM images collected from two distinct multilayered crystals with compositions of Mo₀.₉₃W₀.₀₇Te₂ and Mo₀.₈₅W₀.₁₃Te₂, respectively. These crystals display distinct crystallographic structures: x ≃ 0.07 shows the hexagonal pattern characteristic of the trigonal prismatic or the 2H—phase, while x ≃ 0.13 shows a striped pattern consistent with either the 1T’— or the Td—phase. In Supplementary Fig. S3 we have included STEM and electron diffraction images for x ≃ 0.13 from whose analysis we conclude that it crystallizes in the orthorhombic Td—phase. Nevertheless, in Figs. 1c and 1d we also show single-crystal XRD patterns for x = 0.0 and x = 0.27, respectively. Analysis of these patterns confirms that crystals with x < 0.07 crystallize in the 2H—phase, whereas crystals with x > 0.07, in this case x = 0.27, display the orthorhombic Td—phase instead of the monoclinic 1T’—one. Supplementary Fig. S4 shows X-ray diffraction patterns for Mo₀.₉₁W₀.₀₉Te₂ and Mo₀.₈₂W₀.₁₈Te₂, also indicating the Td—phase for these concentrations. Our complete set of structural studies indicate that for all concentrations x > xₐ ≃ 0.08, W doping stabilizes the semimetallic Td—phase, confirming that the structural transition is sharp and occurs at a W doping level significantly lower than previously reported. Figure 1e shows a larger-scale STEM image of Mo₀.₉₃W₀.₀₇Te₂. In this image, bright dots surrounded by three additional dots (Te atoms) correspond to randomly distributed W atoms, as highlighted in Fig. 1f. Therefore, the STEM images clearly indicate that the Mo₁₋ₓWₓTe₂ series results from a homogeneous dilution of W atoms into a MoTe₂ matrix and not from the coexistence of 2H—MoTe₂ and
FIG. 1. Structural analysis of few-layered Mo$_{1-x}$W$_x$Te$_2$ crystals. a, Scanning transmission electron microscopy image of a few-layered crystal of Mo$_{1-x}$W$_x$Te$_2$ with $x \approx 0.07$ %. b, STEM image of a few-layered crystal of Mo$_{1-x}$W$_x$Te$_2$ with $x \approx 0.13$. Notice that its atomic arrangement is no longer consistent with the 2H– phase. All STEM images are lightly smoothed. c Single-crystal X-ray diffraction pattern for $x = 0.0$ (001) indicating that it crystallizes in the 2H–phase. d, Single-crystal X-ray diffraction pattern for $x = 0.27$ (00λ) indicating that it crystallizes in the $T_d$ phase (orthorhombic Pmn2$_1$). Powder X-ray diffraction indicates that for $x > 0.08$ the Mo$_{1-x}$W$_x$Te$_2$ series crystallizes in the $T_d$–phase. e, (8.25 nm)$^2$ area STEM image of monolayer 2H–Mo$_{1-x}$W$_x$Te$_2$. f, Brighter W atoms (indicated by red dots) are identifiable through their contrast with respect to the darker Mo atoms. g, Scanning tunneling microscopy image of a Mo$_{1-x}$W$_x$Te$_2$ single crystal with $x = 0.07$, corresponding to an area of (15 nm)$^2$ and showing a clear hexagonal pattern as expected for the 2H–phase. The spatial modulation in intensity reflects the local coupling between the layers. h, Magnification of a local area of (2.5 nm)$^2$ where one can detect a Te vacancy. i, STM image of a $x = 0.13$ single-crystal, also corresponding to an area of (15 nm)$^2$, showing a pattern of parallel chains as expected for the orthorhombic $T_d$–phase. j, Magnification of a local region of (2.5 nm)$^2$ revealing the intra-chain structure and illustrating the crystallographic positions of transition metal (black dots) and Te (yellow dots) atoms, respectively.

Mo$_{1-x}$W$_x$Te$_2$ domains. This lack of phase coexistence is further confirmed by room-temperature STM imaging of vacuum-cleaved crystals, as shown in Figs. 1g and 1h. For $x = 0.07$, see Fig. 1g, the equidistant distribution of Te atoms around the transition metal(s) forming an angle of $\theta = 120^\circ$ among them, indicates unambiguously the trigonal prismatic coordination of the 2H–phase. In contrast, for $x = 0.13$, see Figs. 1i and 1j, rows of atoms indicate a change in symmetry from triangular to (nearly) rectangular at the surface. In amplified images, e.g. Fig. 1h, one can clearly discern Te vacancies (indicated by a multicolored dot). Therefore, we have enough resolution to observe vacancies, but we do not observe the coexistence of distinct crystallographic phases.

Thus TEM, STM, and XRD analysis yield consistent results, namely a transition from the 2H phase to the $T_d$ phase at $x_c \sim 0.08$, with no phase coexistence even near the phase boundary. These observations stand in contrast to the early work in Ref. [30], which reported a higher critical W concentration and a region of phase coexistence near the boundary. This discrepancy is likely attributable to the difference between the methods of
FIG. 2. Raman spectra of the Mo$_{1-x}$W$_x$Te$_2$ series as a function of W doping. a, Raman spectra of $2H$–MoTe$_2$ (black trace), $1T'$–MoTe$_2$ (blue) and $Td$–WTe$_2$ (red) at room temperature using an excitation wavelength of 532 nm. 

The structural phase transition as a function of doping is accompanied by changes in vibrational modes, as probed by Raman spectroscopy (see, Fig. 2). Figure 2a shows room-temperature Raman spectra obtained from the $2H$– and $1T'$–MoTe$_2$ phases, and from WTe$_2$. The $2H$– structure displays two main Raman peaks at 174 cm$^{-1}$ and 235 cm$^{-1}$ corresponding to the $A_{1g}$ and $E_2^1$ modes, respectively. Reflecting its reduced symmetry, the $1T'$ phase displays several peaks at lower wave-numbers. For this structure the main peaks occur at 163 cm$^{-1}$ and 260 cm$^{-1}$ and have been indexed as the $B_g$ and $A_g$ modes, respectively. WTe$_2$ presents a spectrum having peaks occurring at 136 cm$^{-1}$ and 165 cm$^{-1}$ respectively, both of $A_g$ character, in addition to a peak at around 210 cm$^{-1}$ previously indexed as the $A_1^2$ mode. In Supplementary Fig. S6 we show Raman spectra for $Td$–Mo$_{0.88}$W$_{0.12}$Te$_2$ as the number of layers decrease, indicating that the $T_d$-phase is stable down to the single-layer limit despite its high Mo content. Figure 2b shows Raman spectra for several stoichiometries of the Mo$_{1-x}$W$_x$Te$_2$ series. Mo$_{1-x}$W$_x$Te$_2$ crystallizes in the $2H$–phase for concentrations up to $x \sim 0.08$. For concentrations beyond this value the spectra abruptly change, as indicated by the disappearance of the $A_{1g}$ and of the $E_2^1$ peaks at 174 cm$^{-1}$ and 235 cm$^{-1}$ respectively, which are observed when $x \lesssim 0.08$. These data support the conclusions reached by the structural probes above, namely a phase transition around $x_c \sim 0.08$ with no evidence for phase coexistence. Interestingly, as the W concentration increases beyond $x = 0.08$ we see the emergence of peaks which, at the first glance, would seem to be related to the $B_g$ and the $A_g$ modes of the $1T'$-phase. However, single crystal X–ray diffraction shown in Fig. 1d and in Supplementary Fig. S3 clearly indicate that the Raman spectra in Fig. 2b must be associated with the orthorhombic $T_d$-phase, with certain peaks shifted with respect to those of WTe$_2$ due to the high Mo content. An important observation is that Raman scattering yields nearly identical spectra for $1T'$–MoTe$_2$ and for $T_d$–Mo$_{1-x}$W$_x$Te$_2$, for reasons that will have to be clarified through theoretical calculations. We note that this similarity might lead to misidentification of the $1T'$ phase if Raman spectroscopy is the only method used to probe the crystal structure. In Supplementary Fig. S6, we show Raman scattering data as a function of the number of atomic layers for a crystal having $x = 0.12$, which is close to the critical concentration $x_c \sim 0.08$, indicating that it preserves its structure upon exfoliation despite its proximity to the phase-boundary. In Supplementary Fig. S7, we have include transport data, like the room temperature conductivity as a function of doping, which changes by orders of magnitude as one crosses the phase-boundary.

Next, we investigated the electronic phase-transition accompanying the structural phase transition. In particular, while the nature of the semiconducting $2H$–phase is well understood, it is not known whether the $T_d$ phase in the W-doped material is a conventional, or a Weyl, semi-metallic system. Therefore, we investigated the
FIG. 3. **Angle resolved photoemission spectroscopy (ARPES)** of Mo$_{1-x}$W$_x$Te$_2$. a, Bulk Brillouin zone of Mo$_{0.73}$W$_{0.27}$Te$_{1.99}$ indicating its high symmetry points. b, ARPES intensity plot at the Fermi level as a function of both the momentum and the photon energy. c, Topography of the Fermi surface at $k_z = 0$. One electron- and one hole-like pocket is observed at either side of the $\Gamma$-point. The resolution of our ARPES measurements limits our ability to identify possible points of contact between the electron and the hole pockets. d, ARPES band structure along $Y$-$\Gamma$-$Y$ direction acquired with a photon energy of 70 eV, i.e. corresponding to ($k_z = 0$). e, Plot of the energy distribution curve of the low energy bands. Blue dotted line serves as a guide to the eye, indicating the positions of peaks for the electron-like band. f, Second derivative of the band structure collected along the $Y$-$\Gamma$-$Y$ direction. g, ARPES band structure along $T$-$Z$-$T$ direction acquired with a photon energy of 57 eV, i.e. corresponding to ($k_z = \pi$). h, Second derivative of the band structure collected along the $T$-$Z$-$T$ direction.

Electrical structure of heavily doped Mo$_{1-x}$W$_x$Te$_2$ single crystals through angle-resolved photoemission spectroscopy (ARPES), as shown in Fig. 3. The core level spectrum, shown in the Supplementary Fig. S1, displays the characteristic peaks of W and Te elements, confirming that W is alloyed into the $1T'$-MoTe$_2$ crystal. As seen in this figure, the W 4$f$ core levels have one set of doublets at 31.4 eV and 33.6 eV (right inset in Supplementary Fig. S1) respectively, in perfect agreement with the values found in the literature. Meanwhile the Te $4d_{5/2}$ and $4d_{3/2}$ doublets split into four peaks (left inset in Supplementary Fig. S1). This suggests that the Mo/W layer is sandwiched by the Te layers, making the Te layer the exposed surface. To investigate the electronic structure along the $k_z$-direction of the three-dimensional Brillouin zone (BZ), which is depicted in Fig. 3a, we performed photon-energy-dependent ARPES measurements with energies ranging from 40 to 90 eV. Figure 3b shows the ARPES spectra at the Fermi level $E_F$ as a function of the momentum and photon energy from 55 to 75 eV. We extracted the positions of the $\Gamma$ ($k_z = 0$) and $Z$ ($k_z = \pi$) points from the dispersion as a function of $k_z$, as shown. Figure 3c shows the Fermi surface of Mo$_{0.73}$W$_{0.27}$Te$_2$ acquired at $h\nu = 70$ eV. The Fermi surface along the $Y$-$\Gamma$-$Y$ direction shows two hole-pockets and two-electron pockets at either side of $\Gamma$ which would seem to touch. This geometry for the Fermi surface of Mo$_{0.73}$W$_{0.27}$Te$_2$ (as well as its overall electronic band-structure) is remarkably similar to the one reported in Ref. 34 for WTe$_2$ and therefore remarkably different from the one already reported for orthorhombic MoTe$_2$. This difference is particularly striking given its considerably larger content of Mo relative to W. Notice that such a simple Fermi surface would be in broad agreement with our recent study on the quantum oscillatory phenomena observed in $T_d$-MoTe$_2$.

ARPES band-maps along the high symmetry directions of a Mo$_{0.73}$W$_{0.27}$Te$_2$ single crystal, as well as the corresponding plots of their second derivatives, are shown in Figs. 3d through 3h. Figs. 3d and 3f show band-maps, and corresponding second derivative, acquired with a photon energy of 70 eV ($k_z = 0$) along the $Y$-$\Gamma$-$Y$ direc-
tion. Figs. 3g and 3h correspond to band maps and second derivatives collected along the T-Z-T direction with a photon energy of 57 eV corresponding to \((k_z = \pi)\). The remarkable features near \(E_F\) are the flat hole-like band crossing \(E_F\) around \(k_{\parallel} \sim 0.2\ \text{Å}^{-1}\), and an electron-like pocket in the vicinity of \(k_{\parallel} \sim 0.4\ \text{Å}^{-1}\). The band connecting the hole- and the electron-like pockets is assigned to a surface state, which have already been claimed to be topologically nontrivial\(^{28,35}\). When compared to the calculations in Ref. \(^{28}\) the conduction band minimum is observed to be very close to the Fermi level, which makes this surface state not as easily detectable as one would expect from the calculations. The surface state is more clearly exposed in Supplementary Fig. S8. Notice that the bands near \(E_F\) at \(k_z = 0\) have higher binding energies than those at \(k_z = \pi\). As a result, the electron pocket and the surface state become more apparent in Figs. 3d and 3f.

Having established the room temperature boundary between the 2\(H\)– and \(T_d\)– phases and explored the electronic structure of the latter phase, we now turn to the temperature axis of the phase-diagram. Figure 4 shows powder XRD patterns for a sample with \(x \approx 0.05\), at different temperatures upon heating from room-temperature. Above \(T = 600\ \text{°C}\), the peaks associated with the 2\(H\)–phase disappear and new peaks that can be ascribed to the 1\(T'\)–phase appear. Similar studies for different compositions are shown in Supplementary Fig. S5. We find that the boundary is situated at \(T_{2H-1T'} \sim 650\text{°C}\) with a large, sample dependent uncertainty of the order of \(\sim 50\text{°C}\) previously attributed to variations in the Te stoichiometry. The variation of \(T_{2H-1T'}\) as a function of \(x\) remains within this uncertainty, therefore the boundary should be considered as doping independent. We do not see evidence for an extended region in temperature where both phases would coexist. The 1\(T'\)–MoTe\(_2\) phase continues to display a good degree of crystallinity at high \(T\)s indicating that the structural transition is not driven by an increase in the number of Te vacancies or material degradation.

![Figure 4](image_url)

**FIG. 4.** Powder X-ray diffraction as a function of angle for 2\(H\)-Mo\(_{95}\)W\(_{6}\)Te\(_2\). Notice the disappearance of the peaks associated with the 2\(H\)-phase and the emergence of new peaks, above \(T = 600\ \text{°C}\) which can be ascribed to the 1\(T'\)-phase. In a certain range of temperatures the coexistence of Bragg reflections associated to both phases results from the coexistence of domains and indicates a first-order phase-transition.

![Figure 5](image_url)

**FIG. 5.** Resulting temperature (\(T\)) as a function of the doping fraction, \(x\), phase-diagram of the Mo\(_{1-x}\)W\(_x\)Te\(_2\) series. Overall phase-diagram based on the array of experimental techniques used for this study. The phase-boundary between the 2\(H\)–, 1\(T'\) and the \(T_d\) phases were determined through powder X-ray diffraction measurements as a function of \(T\) and \(x\) up to \(x = 0.13\). Above 800 °C the samples decompose or lose their crystallinity.
The proposed phase diagram, shown in Figure 5, depicts a sharp phase-boundary between the $2H$ − and the $T_d$ phases at $x_c \sim 0.08$, and the boundary between the $2H$ − and $1T^\prime$ − phases at $\sim 650^\circ$C. In Supplementary Fig. S9 we compare X-ray powder diffraction data among samples crystallizing in the $2H$ − and in the $T_d$ −phases and the role of the temperature. The important point is that, in contrast to the $2H$ −phase, and even for samples with a W concentration very close to the critical one, we could not detect a structural phase-transition as a function of $T$ in samples crystallizing in the $T_d$ −phase. Given that the orthorhombic $T_d$ −phase becomes the ground state of $1T^\prime$ −MoTe$_2$ and the larger area occupied by it in the phase diagram, one is led to conclude that it is thermodynamically more stable than the latter phase. The most remarkable feature of the phase diagram is the very small concentration in W required to stabilize the orthorhombic semi-metallic $T_d$ −phase, and not the coexistence of the $2H$ − and the $1T^\prime$ − phases as predicted by Ref. 24, through a sharp boundary situated at $x = 0.08 \pm 0.01$. Such a sharp boundary points to a first-order phase-transition as a function of doping with the caveat that we could not detect phase coexistence.

It is quite remarkable that a semiconducting band gap as large as $\sim 1$ eV for $2H$ −MoTe$_2$, can be entirely suppressed by substituting just $x_c \approx 9 \pm 1$ % of Mo for W which stabilizes a semimetallic state, as clearly indicated by angle resolved photoemission experiments. Here, the situation bears a certain resemblance with the transition metal oxides such as the cuprates, whose charge or Mott-gap is estimated to be $\Delta \sim 2$ eV, but where a small concentration of dopants, in the order of 5 %, is enough to stabilize a metallic state (albeit anomalous) and even superconductivity. This clearly indicates that both the structural and the concomitant electronic phases of MoTe$_2$ are particularly susceptible to small perturbations. This suggests that it should be possible to reversibly induce structural-transitions through the application of strain or an electric field, particularly in $2H$ −Mo$_{1-x}$W$_x$Te$_2$ crystals with $x \leq x_c$. This would make the $2H$ −Mo$_{1-x}$W$_x$Te$_2$ series particularly appealing for the development of phase-change memory devices or for a new generation of optoelectronic devices, whose metallic interconnects could be created or “erased” at will through the application of an electrical signal, instead of a chemical treatment. Finally, the fact that the Mo$_{1-x}$W$_x$Te$_2$ series produce homogeneous alloys, is not only a major result of this study, but opens the unique possibility of exploring the evolution of their predicted topological/electronic properties, and of perhaps detecting topological phase-transitions in the bulk as well as in the surface state through the evolution of the Fermi surface. In effect, ARPES indicates that the Fermi surfaces of $T_d$ −MoTe$_2$ (Ref. 20) and of $T_d$ −Mo$_{1-x}$W$_x$Te$_2$ (this work) are remarkably different, a fact that can only be reconciled with an electronic/topological phase-transition as a function of W doping. In effect, since W doping tends to stabilize the $T_d$ −phase, it is reasonable to expect that one can stabilize it also in samples containing small amounts of W by quickly cooling the crystals to room temperature during the synthesis process. This would produce a phase-diagram not containing the region originally occupied by the $2H$ −phase. This set of orthorhombic samples would allow us to explore the evolution of the Fermi surface as a function of W doping to understand, for example, how the large hole-pocket seen by ARPES at the center of the Brillouin zone disappears to originate the hole-pockets seen by us at either side of zone center. Such electronic phase-transition should lead to either the suppression or the displacement of the Weyl-points already seen by ARPES, or to a concomitant topological phase-transition as a function of W doping.

METHODS

Sample synthesis

For the synthesis of pure $2H$ − and $1T^\prime$ −MoTe$_2$ as well as WTe$_2$ Mo, 99.9999%, W, 99.9999 % and Te 99.9999 % were placed in a quartz ampoule in a ratio of 1:25 for growth in a Te flux. Subsequently, the material was heated up to 1050°C and held there for 1 day. Then, the ampoule was slowly cooled down to 525°C to yield either $T_d$ −WTe$_2$ or $2H$ −MoTe$_2$ and then centrifuged. To produce the $1T^\prime$ −MoTe$_2$ phase crystals were centrifuged at 900°C. The “as harvested” single crystals were subsequently annealed for a few days at a temperature gradient to remove the excess Te. For Mo$_{1-x}$W$_x$Te$_2$, single crystals were synthesized through a chemical vapor transport technique using iodine or TeCl$_4$ as the transport agent. Samples were held at 750 °C with a 100 °C temperature gradient for 1 week, then subsequently cooled over 3 days to 400 °C and removed from the furnace. Each growth commonly yielded crystals of both structure types ($T_d$ − and $2H$ −), except for those crystals very rich in Mo, i.e. $x < 0.05$. Stoichiometry was determined by energy dispersive X-ray spectroscopy (EDS) analysis through a field-emission scanning electron microscope (FEI Nova 400). A more precise stoichiometric determination was achieved using X-ray photoelectron spectroscopy (XPS) either at the Shanghai Synchrotron Radiation Facility or at the Stanford Synchrotron Radiation Lightsource.

Scanning transmission electron microscopy

For scanning transmission electron microscopy imaging we used a JEOL 2200FS spherical aberration corrected tool operated under 200 kV. When using a 25.6 mrad convergence angle our probe size was 0.9 Å. Although 200 kV is most likely above the sample damage threshold, we used limited acquisition times and beam...
exposure to minimize the possible changes to the sample structure. Micro exfoliated few-layered samples were transferred onto TEM grids via a dry transfer method using polypropylene carbonate.

**X-ray diffraction as a function of the temperature**

Powder samples of Mo$_{1-x}$W$_x$Te$_2$ were prepared by sonicating chemical vapor transport grown bulk crystals in hexane. The Mo$_{1-x}$W$_x$Te$_2$ dispersion was then drop cast onto c-axis sapphire substrates. This preparation led to highly textured powders, with the c-axis of the sample roughly aligned with the substrate surface normal. Heating X-ray diffraction measurements were carried out in a PANalytical XPert 2 diffractometer with an Anton-Par dome hot stage that was purged with ultra pure nitrogen. The phase-transition temperature was found to be independent on the method used.

**Scanning tunneling microscopy**

Scanning tunneling microscopy (STM) measurements were performed with a home built variable temperature, ultra high vacuum STM system at $T = 82$ K. Single crystalline Mo$_{1-x}$W$_x$Te$_2$ was mounted onto metallic sample holders using a vacuum safe silver paste. Samples were transferred into the STM chamber and cleaved in-situ to expose a clean surface on which measurements were performed. The Pt-Ir STM tip was cleaned and calibrated against a gold (111) single crystal prior to the measurements.

**Angle resolved photoemission spectroscopy**

ARPES measurements were performed at the Dreamline beamline of the Shanghai Synchrotron Radiation Facility with a Scienta D80 analyzer. The energy and angular resolutions were set to 15 meV and 0.2°, respectively. The ARPES data were collected using horizontally-polarized light with a vertical analyzer slit. The samples were cleaved in situ and measured at $T = 40$ K in a vacuum better than $5 \times 10^{-11}$ Torr. The cleaved surfaces are observed to be flat at a scale $> 100 \mu$m while the beam spot size of the incident light is $30 \times 20 \mu$m$^2$, therefore the electronic structure probed by us is from a single domain.

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1. Revolins, E. & Beernisse, D. J. Electrical properties of α- and β-MoTe$_2$ as affected by stoichiometry and preparation temperature. J. Phys. Chem. Solids 27, 523-526 (1966).
2. Vellinga, M. B., de Jonge, R., & Haas, C. Semiconductor to metal transition in MoTe$_2$. J. Solid State Chem. 2, 299-302 (1970).
3. Voiry, D. Mohite, A. & Chhowalla, M. Phase engineering of transition metal dichalcogenides. Chem. Soc. Rev. 44, 2702-2712 (2015).
4. Keum, D. H., et al. Bandgap opening in few-layered monolimid MoTe$_2$. Nature Phys. 11, 482-486 (2015).
5. Ruppert, C. Aslan, O. B. & Heinz, T. F. Optical Properties and Band Gap of Single- and Few-Layer MoTe$_2$ Crystals. Nano Lett. 14, 62316236 (2014).
6. Soluyanov, A. A. et al. A New Type of Weyl Semimetals. Nature 527, 495-498 (2015).
7. Sun, Y. Wu, S.C. Ali, M. N. Felser, C. & Yan, B. Prediction of the Weyl semimetal in the orthorhombic MoTe$_2$. Phys. Rev. B 92, 161107 (2015).
8. Wang, Z. et al. MoTe$_2$: A type-II Weyl Topological Metal. Phys. Rev. Lett. 117, 056805 (2016).
9. Qian, X. F. Liu, J. W. Fu, L. & Li, J. Quantum spin Hall effect in two-dimensional transition metal dichalcogenides. Science 346, 1344 (2014).
10. Duerloo, K. A. N. Li, Y. Reed, E. J. Structural phase transitions in two-dimensional Mo- and W-dichalcogenide monolayers. Nat. Commun. 5, 4214 (2014).
11. Duerloo, K. A. N. & Reed, E. J. Structural Phase Transitions by Design in Monolayer Alloys. ACS Nano 10, 289-297 (2016).
12. Kuppera, R. et al. Phase-engineered low-resistance contacts for ultrathin MoS$_2$ transistors. Nature Mater. 13, 1128-1134 (2014).
13. Cho, S. et al. Phase patterning for ohmic homojunction contact in MoTe$_2$. Science 349, 625-628 (2015).
14. Li, Y., Duerloo, K.-A. N., Wauson, K. & Reed, E. J. Structural semiconductor-to-semimetal phase transition in two-dimensional materials induced by electrostatic gating. Nat. Commun. 7, 10671 (2016).
15. Zhang, C. et al. Charge Mediated Reversible MetalInsulator Transition in Monolayer MoTe$_2$ and W$_x$Mo$_{1-x}$Te$_2$ Alloy. ACS Nano 10, 73707375 (2016).
16. Pletikosić, I., Ali, M. N., Fedorov, A. V. Cava, R. J. & Valla, T. Electronic Structure Basis for the Extraordinary Magnetoresistance in WTe$_2$. Phys. Rev. Lett. 113, 216601 (2014).
17. Lezama, I. G. Ubaldini, A. Longobardi, M. Giannini, E. Renner, C. Kuzmenko, A. B. Morpurgo, A. F. Surface transport and band gap structure of exfoliated 2H-MoTe$_2$ crystals. 2D Materials 1, 021002 (2014).
18. Lezama, I. G. Arora, A. Ubaldini, A. Barreteau, C. Giannini, E. Potemski, M. Morpurgo, A. F. Indirect-to-Direct Band Gap Crossover in Few-Layer MoTe$_2$. Nano Lett. 15, 2336-2342 (2015).
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AUTHOR CONTRIBUTIONS

D.R. synthesized and characterized the single crystals through electron dispersive spectroscopy, Raman scattering and transport measurements. Y.-c.C., W.Z., and Q.R.Z. were directly involved in the synthesis and in the preliminary characterization of the crystals. D.C., T.K., A.M., M.C., M.D., N.F., A.A., and J.H. motivated the project, performed Raman, photoluminescence and device characterization. B.E.J. and P.Y.H. performed atomic resolution STEM transmission electron microscopy. W.J., J.Z.M., R.L., T.S., S.C.W., T.Q., H.D., J.I.D., and R.M.O. performed angle-resolved pho-
toemission spectroscopy measurements. Y.L., X.T., T.S., J.I.D., and R.M.O. performed x-ray photoemission spectroscopy measurements. D.E. and A.N.P. performed scanning tunneling spectroscopy measurements. C.N., E.M., F.E., and A.M.L. performed powder X-ray and electron diffraction measurements as function of the temperature. D.W.P. Performed single crystal X-ray diffraction. D. R., J. H. and L. B. wrote the manuscript with the input of all co-authors.

ADDITIONAL INFORMATION

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to L.B.

COMPETING FINANCIAL INTERESTS

The authors declare no competing financial interests.