

## MATERIALS SCIENCE

## A room-temperature ferroelectric semimetal

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Coexistence of reversible polar distortions and metallicity leading to a ferroelectric metal, first suggested by Anderson and Blount in 1965, has so far remained elusive. Electrically switchable intrinsic electric polarization, together with the direct observation of ferroelectric domains, has not yet been realized in a bulk crystalline metal, although incomplete screening by mobile conduction charges should, in principle, be possible. Here, we provide evidence that native metallicity and ferroelectricity coexist in bulk crystalline van der Waals  $WTe_2$  by means of electrical transport, nanoscale piezoresponse measurements, and first-principles calculations. We show that, despite being a Weyl semimetal,  $WTe_2$  has switchable spontaneous polarization and a natural ferroelectric domain structure at room temperature. This new class of materials has tantalizing potential for functional nanoelectronics applications.

## INTRODUCTION

Ferroelectric materials have a spontaneous electric dipole moment, i.e., polarization, even in the absence of an external electric field. This spontaneous electric dipole moment can be repeatedly transitioned between two or more energetically equivalent states or directions upon application of an external electric field that breaks the degeneracy and forms the fundamental underpinning of numerous technological applications of ferroelectric materials (1). For piezoelectricity, noncentrosymmetric crystal structure is the only requirement (2). In contrast, for a polar material, not only must the crystal structure be noncentrosymmetric but also there should exist a unique polar axis. For a material to be considered a ferroelectric, it needs both to be polar and to show bistability of the polarization along the polar axis (2). Conventionally, ferroelectricity has often been associated with and observed in materials that are insulating or semiconducting rather than metallic because conduction electrons in metals screen out the static internal fields arising from a long-range dipolar order. In the 1960s, Anderson and Blount (3) proposed a new class of materials with these seemingly incompatible characteristics, i.e., metals with a polar axis and an inversion asymmetric crystal structure termed “ferroelectric metals.” Since then, an experimental demonstration of this concept for a room-temperature single-phase material has remained elusive. Metallic systems undergoing a centrosymmetric-to-noncentrosymmetric structural transition have been observed recently, e.g., in  $LiOsO_3$  at 140 K (4) and  $Cd_2Re_2O_7$  at 200 K (5), hinting at the possibility of sustaining ferroelectricity in a metal at room temperature. More progress has been made lately with a study (6) reporting on the observation of polar domains and strain-induced ferroelastic switching in bulk polar metal  $Ca_2Ru_2O_7$  at room temperature. Another strategy that has also been commonly used, besides investigating metallic systems with a noncentrosymmetric crystal structure (7), is to dope well-established ferroelectric materials, such as  $BaTiO_{3-\delta}$  (8, 9) and Nb-doped  $PbTiO_3$

(10). However, the ferroelectric instability weakens with increasing electronic density in these systems and will eventually be destroyed above a certain critical density (11). Furthermore, it is not clear that the ferroelectricity and metallicity coexist in a single phase in these materials (12), as other studies suggest a nanoscale phase separation into separate metallic and ferroelectric phases (13). Another approach to obtaining a ferroelectric metal has been to engineer interface-based polar metals in oxide heterostructures (14–16). Despite these investigations, the experimental realization of a native metal with bistable and electrically switchable spontaneous polarization states, the hallmark of ferroelectricity, is yet to be demonstrated. During the submission process of this manuscript, we became aware of a closely related work (17), in which ferroelectric switching has been demonstrated in device structures through electrical transport measurements for bilayer and trilayer  $WTe_2$ . Fei *et al.* (17) quantify and establish the temperature dependence of the polarization. However, a natural question arises as to whether ferroelectricity persists to samples thicker than three layers, or even to bulk crystals, and whether ferroelectric domains can be formed.

Here, we observe the coexistence of native metallicity and ferroelectricity in bulk crystalline  $WTe_2$  at room temperature. Bulk single crystals in their pristine state show ferroelectric domains that are visualized directly. We demonstrate that the bistable spontaneous ferroelectric polarization state is switchable under an external electrical bias and explain the mechanism for “metallic ferroelectricity” in  $WTe_2$  through a systematic study of the crystal structure, electronic transport measurements, and theoretical considerations. Density functional theory (DFT) calculations show that the ferroelectricity is related to the anisotropy of the crystal structure. A van der Waals material that is both metallic and ferroelectric in its bulk crystalline form at room temperature has potential for new nanoelectronics applications.

## RESULTS

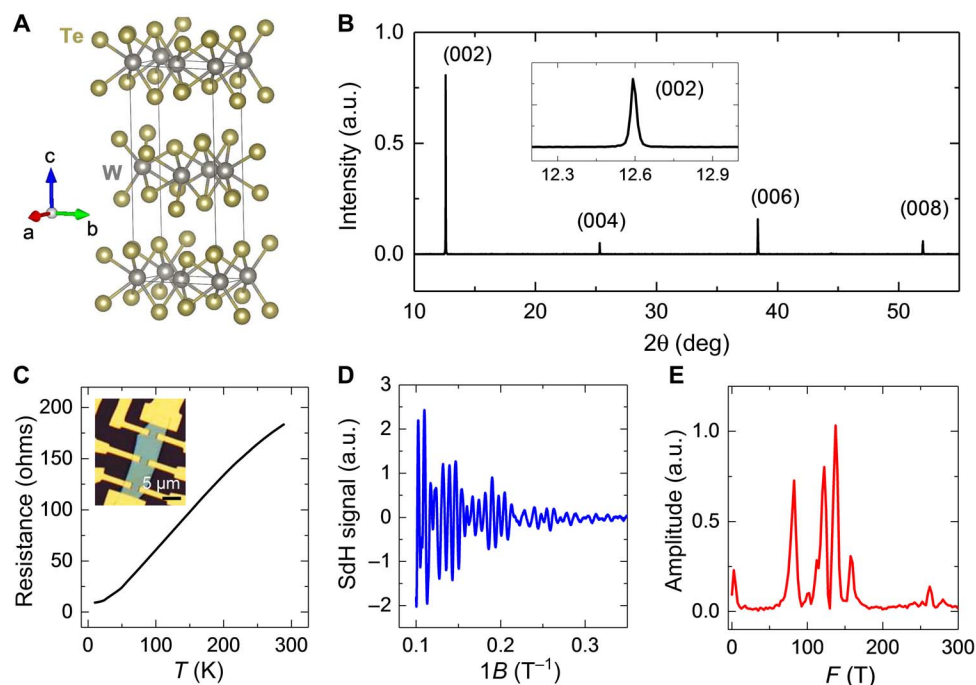
## Noncentrosymmetric crystal structure and semimetallic ground state

Tungsten ditelluride,  $WTe_2$ , belongs to the class of materials known as transition metal dichalcogenides (TMDCs). These materials exhibit many different crystal structures, such as hexagonal (2H), monoclinic (1T), and orthorhombic ( $T_d$ ) (18, 19).  $WTe_2$  crystallizes in a layered orthorhombic structure (also known as the  $T_d$  phase; Fig. 1A), in which the tungsten atoms are octahedrally coordinated by the tellurium atoms,

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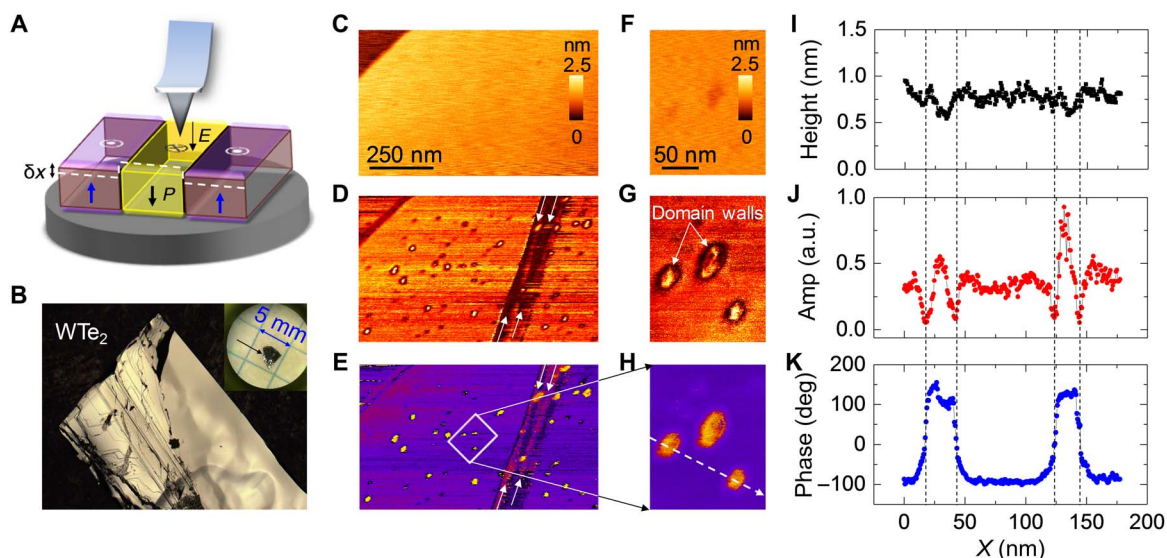
**Fig. 1. Crystal and electronic structure of  $\text{WTe}_2$ .** (A) Atomistic model of the  $T_d$  phase of  $\text{WTe}_2$ . (B) XRD  $\theta$ - $2\theta$  scan on a  $\text{WTe}_2$  single crystal. Inset shows a zoom-in on the (002) diffraction peak. a.u., arbitrary units. (C) Temperature-dependent resistance of a  $\text{WTe}_2$  sample with a thickness of  $\sim 50$  nm measured from room temperature to 10 K. Inset shows the optical micrograph of the sample. (D and E) SdH oscillations of a  $\text{WTe}_2$  sample with a thickness of  $\sim 30$  nm measured at 30 mK (D) and corresponding fast Fourier transform (E).

and the successive layers in between are rotated by  $180^\circ$  (20, 21). Because of strong intermetallic bonding, the tungsten atoms form slightly buckled zigzag chains resulting in distortion of the tellurium octahedra (around each tungsten atom) (19). Figure 1B shows a typical x-ray diffraction (XRD) pattern of  $c$  axis-oriented  $\text{WTe}_2$  single crystals investigated in this work. The (00l) diffraction peaks confirm the presence of the single-crystalline  $T_d$  phase of  $\text{WTe}_2$  (20). The lack of inversion symmetry in the  $T_d$  phase of  $\text{WTe}_2$  (polar space group,  $Pmn2_1$ ) has played an important role in its identification as a type II Weyl semimetal (22). Unlike most TMDCs,  $\text{WTe}_2$  is a semimetal in its native ground state (23, 24), instead of being a semiconductor. We confirmed the semimetallic ground state of  $\text{WTe}_2$  by electrical transport measurements (Fig. 1C). The resistance of  $\text{WTe}_2$  decreases with decreasing temperature from room temperature down to 10 K, a behavior typical of metallic systems. Furthermore, magnetoresistance measurements at 30 mK with magnetic fields up to 10 T reveal pronounced Shubnikov-de Haas (SdH) oscillations with four main frequencies (Fig. 1, D and E). These oscillations confirm the existence of four well-defined Fermi surfaces, consisting of two sets of electron and hole pockets (25). The presence of both free electrons and holes is believed to be the origin of the extremely large, nonsaturated magnetoresistance in  $\text{WTe}_2$  (26–28). Given the existence of metallic conduction down to 30 mK, and the fact that noncentrosymmetry is a necessary but insufficient requirement for a material to be ferroelectric, an intriguing question arises: Is semimetallic  $\text{WTe}_2$  with a noncentrosymmetric space group ( $Pmn2_1$ ) a ferroelectric (7)?

### Ferroelectric domains in single crystals

To address this question and probe ferroelectricity in  $\text{WTe}_2$ , we used piezoresponse force microscopy (PFM) to spatially map the polar-

ization. PFM is a standard technique used extensively to investigate domain microstructure and dynamics of polarization in classical ferroelectric materials. It exploits the converse piezoelectric effect and detects lattice deformation due to an applied electric field (29, 30). To ensure pristine surfaces for the investigation, we prepared freshly cleaved  $\text{WTe}_2$  single-crystal samples (several tens of micrometers thick; Fig. 2, A and B, and see Materials and Methods for details). Measurements were performed in an inert dry  $\text{N}_2$  environment at room temperature immediately after the crystals were cleaved. In this experiment, the conductive nanoscale tip acts as a movable top electrical contact. Spectroscopic electrical transport measurements performed using conductive atomic force microscopy (c-AFM) reveal the expected metallic behavior of  $\text{WTe}_2$  and establish the ohmic nature of the electrical contacts (see fig. S1). The measured current-bias curves are linear and show appreciable conduction over a rather small bias range. Subsequently, we performed PFM imaging (see Materials and Methods for details). The PFM images (Fig. 2, C to H) show the presence of antiparallel ferroelectric domains. A few of these domains are visualized in more detail in the high-resolution PFM images (Fig. 2, G and H). The domains usually exhibit a distorted circular profile with an average domain size in the range of  $\sim 20$  to 50 nm. The domain shape resembles those of well-known ferroelectric materials such as strontium bismuth tantalate (29) and triglycine sulfate (31). The piezoresponse characteristics are textbook (29, 32) examples of ferroelectric behavior (Fig. 2, J and K): (i) Domain walls appear as dark lines (i.e., as a minimum in the PFM amplitude signal) in the amplitude image, and (ii) the PFM phase inverts by  $\sim 180^\circ$  between adjacent domains in the corresponding phase image. The surface of the sample is atomically flat (root mean square roughness,  $\sim 0.2$  nm) with occasional step edges (Fig. 2C) from the cleaving process. We note that, in some



**Fig. 2. Ferroelectric domains resolved in  $WTe_2$  single crystals.** (A) Schematic of the experimental setup for imaging domains in  $WTe_2$  single crystals. (B) High-magnification optical image of the  $WTe_2$  single crystal sample. Inset shows optical image of a bulk  $WTe_2$  single crystal. (C to E) Topography (C), corresponding PFM amplitude (D), and PFM phase images (E). (F to H) High-magnification imaging of small ferroelectric domains enclosed within the rectangle shown in (E), topography (F), corresponding PFM amplitude (G), and PFM phase images (H). (I to K) Cross-sectional profiles of topography (I), PFM amplitude (J), and phase (K) across the dashed white line shown in (H) for respective images in (F) to (H).

but not all cases, submonolayer surface variations close to the resolution limit of our measurement system were observed near the position of the domains (Fig. 2I). In addition to the small oval domains, micrometer-sized stripe-like domains (shown by arrows in Fig. 2D) were also resolved. This observation of domains in semimetallic  $WTe_2$  single crystals implies that  $WTe_2$  not only has a polar axis ( $c$  axis) but also has bistable polarization states manifesting as static antiparallel domains. Therefore, the above results strongly support the existence of ferroelectricity in semimetallic  $WTe_2$  at room temperature.

Another aspect that deserves mention here is the stability of  $WTe_2$ . It is well known that the surface of  $WTe_2$  is quite sensitive and can undergo oxidation in air. Previous works (33–36) have investigated in detail the physical and chemical properties of this surface oxide using a range of techniques including Raman spectroscopy, energy dispersive x-ray spectroscopy, cross-sectional transmission electron microscopy, x-ray photoelectron spectroscopy, and electrical transport studies. The surface oxide forms through evolution of  $W-O$  ( $WO_x$ ) and  $Te-O$  ( $TeO_2$ ) secondary bonds at the surface of  $WTe_2$  in air. The  $WTe_2$  oxidation is a self-limiting process (35) and results in an amorphous surface oxide layer, which is about 2 nm thick (34). To independently determine time-dependent thickness evolution of the surface oxide, we performed ellipsometry measurements (see section S2 and fig. S2). From our measurements, we find that the thickness of surface oxide saturates at about 2.5 nm after several hours of atmospheric exposure (fig. S2). These results thus are consistent with earlier published reports (34). The exposure time for surface oxide formation ranges from a few hours to days (37). The bulk crystals and relatively thick  $WTe_2$  samples are more stable in air compared to samples with just few layers, especially monolayer and bilayer  $WTe_2$  (35, 36). Moreover, there is no polar space group in amorphous materials, and ferroelectricity cannot arise as it exists only in crystalline materials. This is the very reason that, in the literature, there are no publications reporting on the observation of existing ferroelectric domains or domain-like features using PFM in amorphous materials. Nevertheless, we performed the measurements

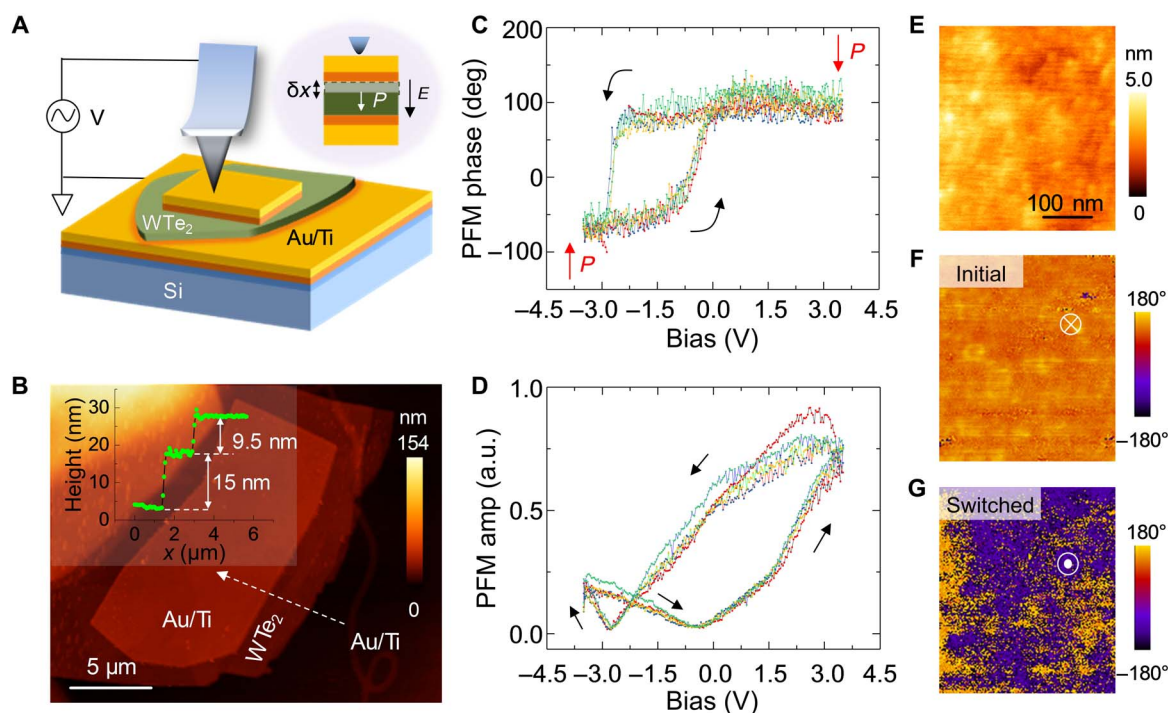
presented in Fig. 2 on a freshly cleaved atomically smooth  $WTe_2$  single crystal in a controlled  $N_2$  environment (see also fig. S1), and thus, the observed behavior cannot be ascribed to the surface oxide.

### Probing ferroelectricity and polarization switching

One of the defining aspects of ferroelectrics is the reorientation of polarization by means of an external electric field. However, unlike insulating ferroelectrics, switching the polarization is difficult in  $WTe_2$  because of its high conductivity: The applied bias induces electrical current rather than acts on the polar distortion (fig. S1). Nonetheless, if the flow of large electrical currents can be prevented, e.g., by insertion of a dielectric layer between the contacts, then it is possible to apply an electric field to  $WTe_2$  and realize ferroelectric switching. To achieve such a configuration and to preclude the possibility of direct charge injection (30) from the tip into the  $WTe_2$ , we prepared thin film samples in a capacitor geometry (Fig. 3A and see Materials and Methods for details). In these capacitor structures, current flow is inhibited by a dielectric layer at the ferroelectric/metal interface (see also section S3) (38), as the  $WTe_2$  sample surface briefly exposed to air before the metal deposition forms a very thin oxide layer (34). Figure 3B shows a metal-gated  $WTe_2$  flake on the surface of a Ti/Au-coated silicon substrate. The  $WTe_2$  flake is 15 nm thick, and the Ti/Au metal electrode on top of it is 9.5 nm thick (Fig. 3B, inset). In this configuration, the electrical current flow across the  $WTe_2$  is strongly suppressed (fig. S3), although the  $WTe_2$  flake is still metallic (25).

To demonstrate switching of the ferroelectric polarization of  $WTe_2$ , spectroscopic PFM measurements were performed through the top electrode in a capacitor geometry, which has been successfully used before for subelectrode PFM measurements (29, 30). The acquired piezoresponse as a function of applied bias (Fig. 3, C and D) shows switchable hysteretic behavior consistent with that seen in traditional ferroelectrics such as  $BaTiO_3$  and  $Pb(Zr_xTi_{1-x})O_3$  (32). The PFM amplitude response displays a characteristic “butterfly” curve, while the corresponding phase response exhibits a phase inversion (i.e., a phase





**Fig. 3. Probing ferroelectricity in a metal-gated  $WTe_2$  thin film sample.** (A) Schematic of the experimental setup and geometry. Inset shows zoomed-in side view of the device structure. (B) Topography image of the metal (Ti/Au)-encapsulated  $WTe_2$  flake on a Si/SiO<sub>2</sub> substrate covered with a conductive buffer layer of Ti/Au. Inset shows the profile of surface morphology along dashed white line. (C and D) Spectroscopic bias-dependent piezoresponse phase (C) and amplitude (D) hysteretic curves acquired through the top metal electrode gating the  $WTe_2$  flake. (E and F) Topography image showing zoom-in on the metal-gated  $WTe_2$  (E) and the corresponding piezoresponse phase image (F). (G) PFM phase image after application of a bias pulse of  $-2.5$  V.

change of approximately  $180^\circ$ ) at minima of the amplitude response. To directly visualize these switchable polarization states, we applied switching bias pulses with the subsequent acquisition of PFM images to capture the remnant state. The bias-driven, oppositely oriented remnant polarization can be clearly seen in the PFM images of different color contrasts (Fig. 3, E to G). The initial near-uniform bright contrast of the phase image transforms to a predominant dark phase contrast. This bias-induced transformation between antiparallel equivalent polarization states of the  $WTe_2$  can be accomplished repeatedly and in a reversible fashion by inverting the polarity of the applied writing bias (fig. S4). These measurements therefore demonstrate that the polarization of  $WTe_2$  is switchable under an external bias.

### Theoretical insight into the ferroelectric instability

To gain further insight into electronic and structural origins of the ferroelectric instability of  $WTe_2$ , we performed first-principles DFT calculations.  $T_d$ -phase  $WTe_2$  ( $T_d$ - $WTe_2$ ) has a  $C_{2v}$  point group symmetry, corresponding to the noncentrosymmetric space group  $Pmn2_1$ . The  $C_{2v}$  point group contains mirror  $ac$  and  $bc$  planes precluding polarization along  $[100]$  or  $[010]$  direction. The mirror  $ab$  plane does not belong to this point group and therefore allows for polarization along the  $[001]$  direction. Theoretical predictions also show that polar axis orientation can be correlated with electronic anisotropy in layered materials (7). Figure 4A shows the electronic band structure of  $T_d$ - $WTe_2$  calculated by DFT (27, 39). The valence band maximum and the conduction band minimum cross the Fermi energy in the  $\Gamma$ -X direction, resulting in the formation of small hole and electron pockets, respectively. The valence band dispersion in the  $\Gamma$ -Z direction is very flat, consistent with nonuniform conduction charge densities in the  $[001]$

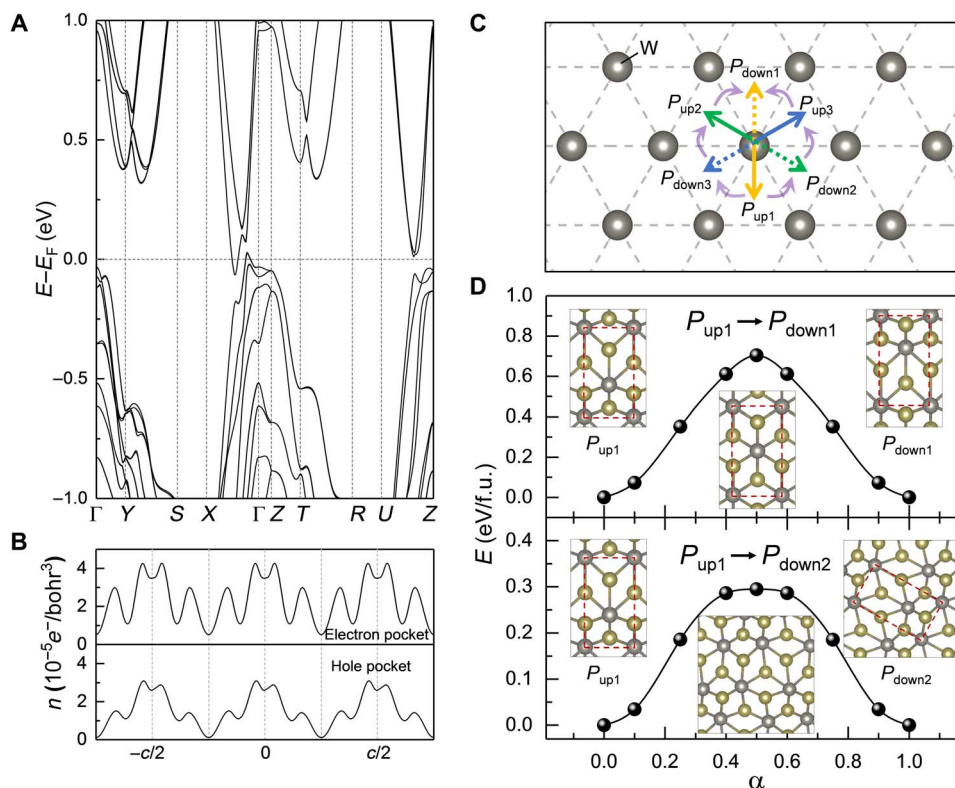
direction in Fig. 4B and the anisotropic transport in bulk  $WTe_2$  (40). Therefore, a spontaneous electrical polarization in  $T_d$ - $WTe_2$  along the  $[001]$  direction is feasible. In a ferroelectric material, the total polarization  $P$  can be split into contributions from ionic cores ( $P_{ion}$ ) and electrons below  $E_F$  ( $P_{electron}$ ). In  $T_d$ - $WTe_2$ ,  $P_{electron}$  can be further split into the contribution of the valence bands ( $P_{VB}$ ), the contribution of the electron pocket ( $P_{ep}$ ), and that of the hole pocket ( $P_{hp}$ ).

Therefore, the total polarization is

$$P = P_{ion} + P_{electron} = P_{ion} + P_{VB} - P_{hp} + P_{ep}$$

$P_{ion} + P_{VB}$  dominates the overall effect and is trivial to compute by the Berry phase method (41, 42) with fixed band occupations. We obtain  $P_{ion} + P_{VB} = 0.19 \mu C/cm^2$ . On the other hand, calculating  $P_{hp}$  and  $P_{ep}$  is not standard. Here, we take the method suggested by Filippetti *et al.* (7) to estimate  $P_{hp}$  and  $P_{ep}$  by calculating the dipole associated with the conduction electrons. As shown in Fig. 4B, the planar averaged charge density from the electron pocket for each  $WTe_2$  layer is almost symmetric, which does not contribute a dipole. On the other hand, the carriers in the hole pocket contribute a dipole within the layer. However, because of the tiny carrier density, the resulting polarization is negligible ( $<0.01 \mu C/cm^2$ ). The total estimated polarization  $P$  is  $\sim 0.19 \mu C/cm^2$ .

Normally, for a ferroelectric, the opposite (i.e., antiparallel)  $P_{up}$  and  $P_{down}$  polarization states can be transformed into one another by application of an inversion operation. The calculated energy barrier for such a transformation in  $T_d$ - $WTe_2$  is rather high [ $0.70$  eV/formula unit (f.u.)] (Fig. 4D, top). This is because such a transformation is



**Fig. 4. First-principles DFT calculations.** (A) Band structure of  $T_d$ -WTe<sub>2</sub>. (B) Planar averaged conduction charge densities contributed from the electron pocket (top) and the hole pocket (bottom). (C) Schematic of different distortion vectors in  $1T$ -WTe<sub>2</sub>. The solid straight arrows denote three equivalent distortion vectors for the polarization up states ( $P_{up1}$ ,  $P_{up2}$ , and  $P_{up3}$ ), while the dashed straight arrows denote three equivalent distortions vectors for the polarization down states ( $P_{down1}$ ,  $P_{down2}$ , and  $P_{down3}$ ). The purple curved arrows denote the possible transition paths from  $P_{up1}$  to  $P_{down1}$ , involving the switching of different distortion vectors. (D) The energy evolution between opposite polarization states of  $T_d$ -WTe<sub>2</sub>. The two opposite polarization states ( $P_{up1}$  and  $P_{down1}$ ) are connected by the inversion operation (top), while the polarization down state ( $P_{down2}$ ) has a different distortion vector, which can be obtained by application of a threefold rotation on  $P_{down1}$  (bottom). The energies of intermediate states are calculated using the atomic position  $r(\alpha) = r_{up} + \alpha(r_{down} - r_{up})$ , where  $0 < \alpha < 1$  and  $r_{up}$  and  $r_{down}$  are the atomic positions of  $P_{up}$  and  $P_{down}$ , respectively. Insets show the top views of the different states. The red dashed boxes in the insets denote the unit cell of  $T_d$ -WTe<sub>2</sub>.

associated with a large in-plane lattice displacement. However, the  $T_d$  phase is a distorted form of the hexagonal structure with a threefold rotation symmetry (Fig. 4C). Therefore, there are three equivalent distortion vectors (43). The switching between opposite polarization states with different distortion vectors (i.e.,  $P_{up}$  of one distortion vector and  $P_{down}$  of another distortion vector) should have smaller in-plane atomic displacements on average, leading to a smaller energy barrier. As shown in Fig. 4D (bottom), in this scenario, the energy barrier between opposite polarization states denoted as  $P_{up1}$  and  $P_{down2}$  is reduced to 0.29 eV/f.u. This value is smaller than (but comparable to) the energy barrier of  $\sim 0.43$  eV/f.u. for BiFeO<sub>3</sub> (44), a prototypical ferroelectric with a high Curie temperature ( $\sim 1000$  K). A transition path for polarization switching in WTe<sub>2</sub> with an even lower energy barrier has also been proposed recently (45). Hence, polarization switching in WTe<sub>2</sub> is achievable under normal experimental conditions from a theoretical point of view, supporting the theory that WTe<sub>2</sub> is not only polar but also ferroelectric.

## DISCUSSION

Using density functional perturbation theory (46) and the finite differences method (47), we calculated the magnitude of the piezoelectric coefficient of WTe<sub>2</sub> (see table S1 and fig. S5 for details). The calculated value of the longitudinal piezoelectric coefficient ( $d_{33}$ )

is about 6.5 pm/V. We find that this calculated value is about an order of magnitude larger than the experimentally measured value of  $\sim 0.7$  pm/V (see fig. S6 and corresponding text in section S5). However, the experimentally determined rather low value of the piezoelectric constant is understandable if one were to consider that we likely extract the piezoresponse within the Debye length of WTe<sub>2</sub>, which is  $\sim 1.6$  nm (see section S6 for details on the calculation of Debye length). Moreover, the calculation is done for a uniform system, while in the measurements, the electric field distribution is likely highly non-uniform. While the detection of piezoresponse at these small length scales of few nanometers is challenging, it is nevertheless not unrealistic. Furthermore, we are aware of electrically induced extrinsic mechanisms (e.g., electrostatic effects and/or electrochemical processes) that can manifest as a piezoelectric- or ferroelectric-like effect in PFM studies of nominally nonferroelectric materials. However, the experimental data in the present study of WTe<sub>2</sub> cannot be explained by these spurious extrinsic mechanisms (see section S7 for a detailed discussion). We note that the Debye length of  $\sim 1.6$  nm is relatively short compared to the material thicknesses investigated in our study. Nevertheless, one can obtain depth-sensitive data from electrical measurements for thicknesses larger than the Debye length in WTe<sub>2</sub> (48). In our study, we have observed ferroelectric domains in thick bulk crystals and ferroelectric switching in  $\sim 15$ -nm films. The question of the physical extent of these

domains is an interesting one. One possibility is that the piezoresponse and ferroelectric domains come only from within a Debye length of the surface. However, it is also possible that the ferroelectric domains extend much deeper into the material because ferroelectricity and ferroelasticity are often coupled in conventional ferroelectrics and because ferroelastic domains have been predicted for bulk  $\text{WTe}_2$  (43). In this latter scenario, ferroelectric domains could potentially propagate through elastically mediated wall motion, where fluctuation in bond lengths by electric fields initiated on the surface (within the Debye length) generates strain down into the bulk of the material and large domains could propagate through into the depth of the material (6). We hope that our study will stimulate further theoretical and experimental studies to answer this question.

In summary, the concept of ferroelectric metals predicted in the 1960s has been realized in a Weyl semimetal,  $\text{WTe}_2$ . A combination of experimental and first-principles DFT techniques demonstrates the coexistence of native metallicity and ferroelectricity at room temperature. Bulk crystalline  $\text{WTe}_2$  exhibits bistable polarization states that are switchable under an external electric field—thus, ferroelectricity is a bulk property of  $\text{WTe}_2$ —and is not just confined to few-layer samples. The investigation of ferroelectric domain walls (49, 50) in metallic systems constitutes an interesting aspect for future research and potential nanoelectronics applications, following recent findings in conventional ferroelectrics. Our findings also raise prospects for discovering ferroelectricity in other metallic layered materials.

## MATERIALS AND METHODS

### Sample fabrication details

All  $\text{WTe}_2$  samples were prepared from bulk crystals purchased from HQ Graphene, The Netherlands ([www.hqgraphene.com](http://www.hqgraphene.com)). For the PFM measurements on bulk samples, the  $\text{WTe}_2$  single crystals were first mounted on a metal disc using conductive Ag paste. To ensure a pristine surface for the measurements, the  $\text{WTe}_2$  single crystals were cleaved using the Scotch tape method. For measurements on  $\text{WTe}_2$  thin samples in a capacitor geometry, we first deposited 15 nm Ti/Au on the  $\text{SiO}_2$  surface of the doped Si substrates. The  $\text{WTe}_2$  thin flakes exfoliated from the bulk crystals were then transferred onto the substrates and were covered by poly(methyl methacrylate). Thereafter, electron beam lithography was used to pattern the area for subsequent metal deposition (10 nm Ti/Au). To remove any residual resist and control the surface oxides on the  $\text{WTe}_2$  sample, the patterned areas were briefly etched with an Ar plasma. The cleaned surface was exposed to air for ~10 min before loading into the vacuum chamber for the metal deposition, so that only a very thin oxide layer was formed at the surface.

### XRD characterization

XRD  $\theta$ - $2\theta$  scans were performed with a PANalytical X'Pert Pro diffractometer using  $\text{Cu K}\alpha$ -1 radiation.

### Electrical transport measurements

The temperature-dependent resistance of  $\text{WTe}_2$  was measured in a home-built variable temperature system. The SdH oscillations were measured in an Oxford dilution fridge with a base temperature of 30 mK and magnetic fields up to 10 T. The magnetic field direction was perpendicular to the  $ab$  plane of the  $\text{WTe}_2$  sample.

### Scanning probe microscopy measurements

The scanning probe microscopy measurements were implemented on a commercial AIST-NT SmartSPM 1000 atomic force microscope at room

temperature in an inert atmosphere (i.e., controlled  $\text{N}_2$  environment). The PFM measurements were performed at an AC imaging bias of 1 V (peak to peak) and a frequency of approximately 700 kHz. The spectroscopic piezoresponse hysteresis loops were acquired at fixed spatial locations by supplying a triangular DC waveform with a superimposed low-amplitude AC modulation.

### Ellipsometry measurements

The ellipsometry measurements to determine surface oxide thickness were performed using a variable-angle spectroscopic ellipsometry system (J.A. Woollam Co. Inc.) under ambient conditions. The incident angle of light used in the study was  $70^\circ$ , and the wavelength range was from 300 to 2000 nm with wavelength increments of 10 nm.

### First-principles DFT calculations

First-principles DFT calculations have been performed using Quantum ESPRESSO (51) and Vienna Ab initio Simulation Package (VASP) (52, 53). In Quantum ESPRESSO, the optimized norm-conserving Vanderbilt pseudopotentials (54, 55) were used. In VASP, the projector augmented wave method (56) was used. The exchange and correlation effects were treated within the generalized gradient approximation (57). The lattice constant and atomic coordinates were relaxed until the force on each atom was less than  $0.001 \text{ eV}/\text{\AA}$ . For the calculation of bulk  $\text{T}_d\text{-WTe}_2$ , we used a  $16 \times 12 \times 8$   $k$ -point mesh in the irreducible Brillouin zone. Spin-orbit coupling was included in the electronic structure calculations. For the simulation of  $\text{T}_d\text{-WTe}_2$  with different distortion vectors, we used supercells ( $2 \times 2\sqrt{3}$ ) of a monolayer and a  $k$ -point mesh (12 by 8 by 1). We used the lattice constants and atomic positions of the supercells reported in (43) as the initial input for the structure relaxation.

## SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/5/7/eaax5080/DC1>

Section S1. Electrical transport behavior of  $\text{WTe}_2$  single-crystal samples in c-AFM

Section S2. Ellipsometry measurements on a  $\text{WTe}_2$  single-crystal

Section S3. Electrical transport behavior of  $\text{WTe}_2$  thin films in a capacitor geometry

Section S4. Polarization switching in the metal-gated  $\text{WTe}_2$  thin film sample

Section S5. Piezoelectric coefficient of  $\text{WTe}_2$

Section S6. Calculation of Debye length of  $\text{WTe}_2$

Section S7. Extrinsic mechanisms as the origin of PFM response in  $\text{WTe}_2$ ?

Table S1. The calculated piezoelectric constant  $e_{31}$  ( $\text{C}/\text{m}^2$ ) and  $d_{31}$  ( $\text{pm}/\text{V}$ ) for  $\text{WTe}_2$  with a polarization along +z direction.

Fig. S1. Spectroscopic current-bias curves recorded in c-AFM mode on a pristine surface of a freshly cleaved  $\text{WTe}_2$  single-crystal sample in a controlled  $\text{N}_2$  environment.

Fig. S2. Ellipsometry measurements determining the thickness of the surface oxide on  $\text{WTe}_2$ .

Fig. S3. Current-bias characteristics of metal-gated  $\text{WTe}_2$  thin film samples.

Fig. S4. Polarization switching in a metal-gated  $\text{WTe}_2$  thin film sample.

Fig. S5. The polarization change  $\Delta P$  with respect to the strain  $\xi$  along z direction.

Fig. S6. The calibrated piezoresponse measurements versus bias for a metal-gated  $\text{WTe}_2$  thin film sample.

Fig. S7. Stable ferroelectric domains in a  $\text{WTe}_2$  single crystal.

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performed the electrical transport measurements. F.-X.X., D.Z., and P.S. performed the XRD structural characterization. D.-F.S. and E.Y.T. conducted and/or analyzed the first-principles DFT calculations. D.Z., P.S., and J.S. collected and/or analyzed the ellipsometry data. P.S. and F.-X.X. wrote the manuscript with input from J.S. and A.R.H. All authors reviewed and contributed to the manuscript preparation. **Competing interests:** The authors declare that they have no competing financial or non-financial interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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## A room-temperature ferroelectric semimetal

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