

# Pressure-Induced Phase Transition in Weyl Semimetallic WTe<sub>2</sub>

Juan Xia, Dong-Fei Li, Jia-Dong Zhou, Peng Yu, Jun-Hao Lin, Jer-Lai Kuo, Hai-Bo Li, Zheng Liu, Jia-Xu Yan,\* and Ze-Xiang Shen\*

**T**ungsten ditelluride (WTe<sub>2</sub>) is a semimetal with orthorhombic  $T_d$  phase that possesses some unique properties such as Weyl semimetal states, pressure-induced superconductivity, and giant magnetoresistance. Here, the high-pressure properties of WTe<sub>2</sub> single crystals are investigated by Raman microspectroscopy and ab initio calculations. WTe<sub>2</sub> shows strong plane-parallel/plane-vertical vibrational anisotropy, stemming from its intrinsic Raman tensor. Under pressure, the Raman peaks at  $\approx 120 \text{ cm}^{-1}$  exhibit redshift, indicating structural instability of the orthorhombic  $T_d$ phase. WTe<sub>2</sub> undergoes a phase transition to a monoclinic T' phase at 8 GPa, where the Weyl states vanish in the new T' phase due to the presence of inversion symmetry. Such  $T_d$  to T' phase transition provides a feasible method to achieve Weyl state switching in a single material without doping. The new T' phase also coincides with the appearance of superconductivity reported in the literature.

J. Xia, Dr. J.-X. Yan, Prof. Z.-X. Shen **Division of Physics and Applied Physics** School of Physical and Mathematical Sciences Nanvang Technological University Singapore 637371, Singapore E-mail: jxyan@ntu.edu.sg; zexiang@ntu.edu.sg Dr. D.-F. Li, Prof. H.-B. Li Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education Jilin Normal University Changchun 130103, China J.-D. Zhou, Dr. P. Yu, Prof. Z. Liu **Center for Programmable Materials** School of Materials Science and Engineering Nanyang Technological University Singapore 639798, Singapore Dr. J.-H. Lin Materials Science and Technology Division Oak Ridge National Lab Oak Ridge, TN 37831, USA Prof. J.-L. Kuo Institute of Atomic and Molecular Sciences Academia Sinica Taipei 10617, Taiwan

Prof. Z. Liu

NOVITAS, Nanoelectronics Centre of Excellence, School of Electrical and Electronic Engineering Nanvang Technological University Singapore 639798, Singapore Prof. Z. Liu, Prof. Ze-X. Shen Centre for Disruptive Photonic Technologies Nanyang Technological University Singapore 637371, Singapore Dr. I.-X. Yan Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM) Nanjing Tech University (NanjingTech) 30 South Puzhu Road, Nanjing 211816, P. R. China Prof. Z.-X. Shen CINTRA CNRS/NTU/THALES, UMI 3288 **Research Techno Plaza** Singapore 637553, Singapore

# communications

Pressure is a clean and convenient tool to modify the physical properties of diverse transition metal dichalcogenide (TMDs) materials.<sup>[1–6]</sup> via strengthening the van der Waals interactions along *c*-axis and shortening the covalent bonds within the atomic plane. For instance, the typical first-order structural transition in MoS<sub>2</sub> (2H<sub>c</sub> to 2H<sub>a</sub>),<sup>[4,5]</sup> metallization in MoSe<sub>2</sub>,<sup>[6]</sup> and superconductivity in T'-MoTe2<sup>[7]</sup> have been reported under high pressure. Among the layered TMDs family, semimetallic WTe<sub>2</sub> have recently attracted considerable attention, with reports of the nonsaturating large magnetoresistance (LMR),<sup>[8-10]</sup> pressure-induced superconductivity,<sup>[11,12]</sup> and as the most promising candidate of a type-II Weyl semimetal.<sup>[13]</sup> Weyl Fermions were observed following the discovery of topological superconductors and semimetals, where they show low-energy excitation properties and have two types of Weyl points. A point-like Fermi surface are referred to as type-I, while a protected crossing appearing at the contact of electron and hole pockets are called type-II Weyl point. The type-II Weyl points in WTe2 endows many novel physical properties that are different to those of type-I Weyl semimetals.<sup>[13]</sup> So far, the pressure-driven superconductivity in WTe<sub>2</sub> has been attributed to a possible structural instability<sup>[11]</sup> or Lifshitz phase transition without structural transition.<sup>[12]</sup> Therefore, the structural evolution of WTe<sub>2</sub> under high pressure is still unclear and needs to be further clarified.

In this paper, we investigate the effects of hydrostatic pressure on both plane-parallel and plane-vertical orientation of vibrational properties in WTe<sub>2</sub> as well as the corresponding electronic properties. A first-order structural transition from the T<sub>d</sub> phase to a monoclinic T' phase occurs above 8 GPa, marked by the vanishing of the Raman band at 120 cm<sup>-1</sup> where the Raman active  $B_2$  mode in the T<sub>d</sub> phase becomes Raman inactive  $(B_{2\mu}$  symmetry) in the T' phase. This  $B_2$  Raman mode can only be observed in the T<sub>d</sub> phase with incident laser beam perpendicular to the c-axis of WTe2 crystal, and it softens considerably with pressure, while all other Raman modes stiffen. Beyond the plane-parallel Raman studies generally conducted in 2D materials, our plane-vertical measurements can detect the inactive Raman modes, which may become the indicator of defects, stacking, or phase transition as the characteristic peaks. To the best of our knowledge, it is the first report on the anomalous redshift phenomenon of the T<sub>d</sub>-WTe<sub>2</sub> and the new T' phase under high pressure. We further show that these two phases have distinct electronic properties, especially in Weyl semimetallic states. Our findings offer the possibility to switch on/off the Weyl states in sole material via high pressure.

Unlike most other semiconducting TMDs with the hexagonal (2H) phase,<sup>[14–16]</sup> WTe<sub>2</sub> exhibits a unique distorted octahedral coordination of the W atom, referred to as  $T_d$ -polytype.<sup>[17–23]</sup> Its space group (*Pmn*<sub>21</sub>) endows the corresponding Raman tensors as:

$$R(A_{1}) = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix} R(A_{2}) = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$R(B_{1}) = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix} R(B_{2}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix}$$
(1)



Therefore,  $A_1$  and  $A_2$  modes can be detected under planeparallel configuration with incident laser along c-axis, while  $B_1$  and  $B_2$  modes can be observed with incident laser along a- or b-axis. In polarized Raman spectroscopy, A(BC)D are used to describe the excitation/collection configurations for sample measurements. In our case, A and D stand for the incident laser and output scattering direction, with respect to WTe<sub>2</sub> atomic plane. B and C stand for laser polarization and collection polarization direction, respectively. For perfectly plane-parallel aligned samples,  $A_1$  symmetry is obtained in the  $Z(XX)\overline{Z}$  and  $Z(YY)\overline{Z}$  configurations, while  $A_2$  symmetry is obtained in the  $Z(XY)\overline{Z}$  configurations.<sup>[24]</sup> In the case of plane-vertical configuration,  $B_2$  modes can only be observed in  $X(ZY)\overline{X}$  configuration, while for  $B_1$  symmetry modes, they are forbidden under both  $X(ZZ)\overline{X}$  and  $X(ZY)\overline{X}$ configurations. As far as we know, the latter Raman geometries with plane-vertical orientation in WTe<sub>2</sub> have not been reported in the literature. First, we address a full mode assignment in WTe2 crystal for both plane-parallel and planevertical orientations via the polarized Raman spectroscopy. For the scanning transmission electron microscope (STEM) experiments and plane-parallel property study, large-area monolayer WTe<sub>2</sub> samples with high quality are used to completely exclude the nonuniformity impact on Raman signals. As for the plane-vertical orientation, we vertically align the samples to achieve the  $X(ZZ)\overline{X}$  and  $X(ZY)\overline{X}$  geometries, so that the laser propagation direction is within the *ab*-plane of bulk WTe<sub>2</sub> sample, as shown in Figure 1c.

Figure 1a shows the Z-contrast STEM images of 1L and 2L WTe2 in the Td phase which vividly reveal that the T<sub>d</sub> phase 1L WTe<sub>2</sub> consists of zigzag W chains along *a*-axis as skeleton with Te chains connected therein, in excellent agreement with the atomic model of 1L WTe<sub>2</sub>. The STEM image of 2L WTe<sub>2</sub> indicates this stacking order is similar to that of 2H (AB) stacking for MoS<sub>2</sub> yet the atoms of top and bottom layers cannot perfectly overlap due to its distorted lattice structure. The optical images of 1L (grown by chemival vapor deposition (CVD) method) and single crystal bulk WTe<sub>2</sub> samples are shown in Figure 1b,c, where the atomic planes (010) are parallel and perpendicular to the substrate, respectively. Figure 1d shows the Raman spectra of the monolayer and bulk WTe2 samples with incident laser along c- (marked as P) and a-axes (marked as V) for the study of plane-parallel and plane-vertical anisotropies, respectively. All the Raman signals with both  $\vec{e}_{i} \parallel \vec{e}_{s}$  and  $\vec{e}_i \perp \vec{e}_s$  configurations can be detected. For plane-parallel configuration (P), the peaks located at 89, 110, 117, 160, and 210 cm<sup>-1</sup> (marked as P1, P2, P3, P4, and P5 in Figure 1d) can be assigned to  $A_2, A_2, A_1, A_1$ , and  $A_1$  symmetry, respectively. Compared with plane-parallel case, the plane-vertical configuration exhibits a different set of Raman peaks, where the four peaks V1, V2, V3, and V4 located at 93, 123, 141, and 170 cm<sup>-1</sup> are assigned as  $B_2$ ,  $B_2$ ,  $A_1$ , and  $A_1$  symmetry, respectively. The polarized Raman features of plane-parallel and plane-vertical configurations are further discussed both experimentally and theoretically in Supporting Information by using various setups, which reaffirms the precise attributions of each mode. Our experimental frequencies of the observed peaks are excellent agreed with the calculated

www.small-journal.com





**Figure 1.** a) Scanning transmission electron microscope (STEM) images of 1L and 2L WTe<sub>2</sub>. Optical image of 1L CVD grown WTe<sub>2</sub> b) vertically aligned bulk WTe<sub>2</sub> c). The white rectangle in (b) highlights the corresponding Raman intensity mapping at 210 cm<sup>-1</sup>, indicating its homogenous quality. The inset shows the atomic structures from the top view and the green arrows represent the reference sample orientation. d) Raman spectra of the monolayer (blue) and bulk (red) WTe<sub>2</sub> samples with incident laser along *c*- (marked as P) and *a*-axes (marked as V). The solid curves are from experiments, and the gray curves (doted and solid) are corresponding Lorentzian fitting results.

frequencies and the corresponding symmetry assignments match perfectly.<sup>[25–27]</sup>

Next, we utilize Raman spectroscopy to extend the highpressure study on plane-parallel and plane-vertical anisotropies of the vibrational properties, in which the *ab*-plane of bulk  $T_d$ -WTe<sub>2</sub> are parallel (P type) or vertical (V type) to the diamond anvil surface. **Figure 2**b shows the Raman spectra of bulk  $T_d$ -WTe<sub>2</sub> sample with the incident laser propagation along *c*- (P) and *a*- (V) axes at ambient pressure, respectively. The difference of Raman behaviors between P-type and V-type can be evidently noticed, that is, there is a particularly strong peak envelope at around 120 cm<sup>-1</sup> showing up under V-type configuration. Figure 2b,c shows the evolution of lattice vibrational properties of bulk  $T_d$ -WTe<sub>2</sub> with the increasing of pressure for P- type (b) and V-type (c) sample orientation, respectively. In the case of P-type, all the observed Raman peaks gradually blueshift with no discontinuities as the increasing of hydrostatic pressure from 0 GPa to final 17.0 GPa, indicating no structural phase transition within the whole studied pressure range. The stiffening and broadening phenomenon of Raman modes under pressure has been well known, similar to other layered materials.



**Figure 2.** a) Illustration of the diamond anvil cell loaded with parallelly (P) and vertically (V) aligned WTe<sub>2</sub> crystals. b,c) The evolution of Raman vibrations with pressure for different sample orientations.



**Figure 3.** a,b) Evolution of Raman peaks with pressure for perpendicular a) and parallel b) to the laser polarizations. The transparent lines indicate the linear fit of Raman peak center as a function of pressure. c) Calculated pressure dependence of the enthalpy difference between the  $T_d$  and T' unit cells. d) Calculated phonon dispersion curve of T'-WTe<sub>2</sub> at 12 GPa.

However, in the case of V-type, upon increasing pressure, the new Raman modes ( $\approx 120 \text{ cm}^{-1}$ ) of bulk T<sub>d</sub>-WTe<sub>2</sub> redshift while all other modes blueshift. More interestingly, the peaks at around 120 cm<sup>-1</sup> nearly disappear with the pressure above 10.9 GPa. Both redshift and vanishing of Raman peaks cannot be observed under the P-type configuration, which confidently declares that there is a phase transition point at ≈10 GPa. Figure 3a,b is the statistic diagrams of peak center evolution of WTe<sub>2</sub> as a function of pressure for V-type (a) and P-type (b) configurations. Our experimental observation on pressure-dependent Raman frequencies shows good qualitative agreement with the calculated Raman frequencies as a function of pressure. The pressure-dependent lattice vibrational properties of the V-type WTe2 are sketched in Figure 3a, where the peaks, V2 and V3, show an anomalous redshift as the pressure increases while other peaks show a blueshift. We can also find the consistent blueshift of all the Raman peaks in Figure 3b, and yet the change slop for peak P1 is smaller than that of other peaks. This insensitive property of Raman peak P1 to pressure vibration indicates this kind of peak represents the Raman vibration within atomic plane, where the pressure has a weaker impact on this planeparallel vibration compared with plane-vertical vibration. This phase transition under high pressure (8 GPa) should strongly account for the dramatic change in magnetic and electronic properties of WTe<sub>2</sub> beyond a certain pressure as previously reported.[11,12]

To further identify the possible phase transition under high pressure, we have performed the molecular dynamics (MD) simulation to examine the evolution of the atomic structure of WTe<sub>2</sub> under 20 GPa (Figure S8, Supporting Information) at 0 and 15 ps, respectively, which certified that the T<sub>d</sub> phase of WTe<sub>2</sub> cannot stably exist under 20 GPa and a phase transformation from T<sub>d</sub> to T' phase actually happens. Besides, we have also calculated the enthalpy difference as a function of pressure between the T<sub>d</sub> and T' structures of WTe2, as shown in Figure 3c. Before 8 GPa, the value of  $H_{T'} - H_{T}$  is small and positive, and then it rapidly changes to negative after the pressure increasing above 8 GPa, which further elucidates that the phase transition of WTe<sub>2</sub> is from  $T_d$  phase to T' phase with the turning point pressure at around 8 GPa. Figure 3d shows the phonon dispersion curves for T'-WTe2 at 12 GPa, where all the phonon frequencies are positive, indicating the T' phase can stably exist under high pressure. The instability of T<sub>d</sub> phase at 12 GPa is also discussed in Figure S8 in the Supporting Information, with imaginary frequencies based on our calculations. Therefore, the MD simulation, enthalpy with increasing pressure, and phonon calculation for WTe2 at 12 GPa are also consistent with that the application of pressure tends to stabilize the T' phase for MoTe<sub>2</sub>.<sup>[7]</sup>

Furthermore, in order to explain the anomalous Raman behavior with V-type configuration, we have performed the first-principles calculations of the phonon modes at the Brillouin zone (BZ) center within the framework of the density functional perturbation theory (DFPT).<sup>[28]</sup> Figure S8c in the Supporting Information depicts the vibrational schematics of two Raman active  $B_2$  modes in V-type bulk T<sub>d</sub>-WTe<sub>2</sub> and T'-WTe<sub>2</sub> corresponding to the two redshifted peaks in pressure-dependent Raman spectra (Figures 2c and 3a). Compared with T<sub>d</sub> phase, T'-WTe<sub>2</sub> undergoes an opposite sliding within adjacent layers, leading to the unit cell change



**Figure 4.** a) Calculated band structures of  $T_d$  (left) and T' (right)  $WTe_2$  with SOC at 0 and 10 GPa. b) Artificially modification of the band structure of  $T_d$  (left) and T' (right)  $WTe_2$  along momentum space cut along the line *K*–*K*', where the Weyl points W1(-), (0.12314, 0.03455, 0) and W2(+)) (0.12185, 0.05280, 0) are given for  $T_d$ .

from orthorhombic to monoclinic symmetry. This phonon softening of the peaks at 120 cm<sup>-1</sup> can be explained by the intermediate states engagement before the phase transition point. These states originate from the electron–phonon interactions, where intervalence charge transfer between the WTe<sub>2</sub> layers plays an important role in the structural distortion of the crystal symmetry. Several materials have been previously reported to exhibit an intermediate state with soften phonon behavior while undergoing a transition from a semiconductor to a metallic state or when stress or strain is applied.<sup>[19]</sup> To the best of our knowledge, it is the first report on the anomalous redshift of the T<sub>d</sub>-WTe<sub>2</sub> Raman modes. Our calculations indicate that the two modes become inactive from T<sub>d</sub> to T' phase, in consist with our experimental findings that the peaks at around 120 cm<sup>-1</sup> finally vanish at 10 GPa.

We have also calculated their band structures with spinorbit coupling (SOC) for T<sub>d</sub> and 1T' phase of WTe<sub>2</sub> obtained from different pressures, as shown in Figure 4. At 0 GPa, four pairs of Weyl Fermions exist in T<sub>d</sub> phase, while these Weyl states vanish in the monoclinic T' phase at 10 GPa, due to the presence of inversion symmetry. Such difference in band structure may pave a potential way for Weyl state tuning in diverse 2D materials by phase engineering. The type-II Weyl semimetal property in T<sub>d</sub>-WTe<sub>2</sub> was first reported by Soluyanov et al.<sup>[13]</sup> and then Tamai et al. also demonstrated that the MoTe<sub>2</sub> with 1T' phase also held the similar property as  $T_d$ -WTe<sub>2</sub>.<sup>[29]</sup> Moreover, one arc-tunable Weyl Fermion metallic state has been found in alloy materials,  $Mo_x W_{1-x}Te_2$ , in which they demonstrated that the Fermi arc length and topological strength can be modified by Mo concentration.<sup>[30]</sup> In our work, we propose a possibility of switching on/off the Weyl states in one material without doping.

In summary, we have investigated the high-pressure properties of WTe<sub>2</sub> single crystals by Raman microspectroscopy and ab initio calculations. WTe<sub>2</sub> shows strong plane-parallel/ plane-vertical vibrational anisotropy, stemming from its intrinsic Raman tensor. Under pressure, the Raman peaks at  $\approx$ 120 cm<sup>-1</sup> gradually soften upon increasing pressure and are totally suppressed above 10 GPa, indicating the phase transition from T<sub>d</sub> to T' phase. Reminiscent of the reported superconductivity emerging in WTe<sub>2</sub> at 10 GPa, one can expect that the phase transition from T<sub>d</sub> to T' phase at 10 GPa separates the LMR state and superconducting state. Our findings

may provide a potential way to switch on/off the Weyl states in one material through high pressure.

### **Experimental Section**

Sample Preparation: (1) The few-layer WTe<sub>2</sub> were synthesized by CVD method using  $WO_3$  and  $WCl_6$  (Sigma) as the W sources. The Te powder was used as the Te sources. The crystals were synthesized in guartz tube (1 inch diameter) with temperature from 700 to 850 °C. The mixed gas of H<sub>2</sub>/Ar with 15 and 150 sccm were used as the carrier gas, the silicon boat contained 30 mg mixed powders with  $WO_3$ :  $WCl_6$ : Te = 1:1:1 (weight ratio) was put in the center of the tube. The SiO<sub>2</sub>/Si substrate was placed downstream. Another silicon boat containing 0.5 g Te powder was put on the upstream. The temperature ramps up to the 820 °C in 17 min, and keeping at the reaction temperature for about 5–15 min. Then the furnace cooled down to room temperature gradually. (2) Bulk WTe<sub>2</sub> single crystals were prepared by chemical vapor transport method with iodide as the transporting agency. The stoichiometric amounts of W powder and Te lumps (300 mg) with iodide (30 mg) were sealed in a quartz tube under vacuum at  $10^{-6}$  Torr, which was placed in a three-zone furnace. The reaction zone was prereacted at 750 °C for 24 h with the grown zone at 850 °C, preventing the transport of the samples. The reaction zone was then programed at a higher temperature of 950 °C with the growth zone at a lower temperature of 850 °C for 7 d to give the temperature gradient in order to achieve the growth of single crystal. Finally, the furnace was naturally cooled down to room temperature and WTe2 single crystals were collected in the growth zone.

*TEM Characterization*: The STEM samples were prepared with a poly(methyl methacrylate) (PMMA) assisted method. A layer of PMMA of about 1 µm thick was spin coated on the wafer with WTe<sub>2</sub> samples deposited, and then baked at 180 °C for 3 min. Afterward, the wafer was immersed in NaOH solution (1 m) to etch the SiO<sub>2</sub> layer over night. After lift-off, the PMMA/WTe<sub>2</sub> film was transferred into (deionized water) DI water for several cycles to wash away the residual contaminants, and then it was fished by a TEM grid (Quantifoil Mo grid). The transferred specimen was dried naturally in ambient environment, and then dropped into acetone overnight to wash away the PMMA coating layers. The STEM imaging was performed on an aberration-corrected Nion UltraSTEM-100 operating at 100 kV.

# communications

Angle-Resolved Raman Spectra Measurements: A Witec CRM200 backscattering Raman system was used equipped with a solid-state (yttrium aluminum garnet) YAG laser at 2.33 eV (532 nm) with a proper power avoiding sample heating (below 1 mW). The size of the laser beam is around 250 nm which was focused on the sample using an objective (Olympus, 100×/NA0.95). To obtain stronger Raman signal with high (signal to noise) SN ratio, for the excitation path, the laser polarization was fixed and the sample was rotated from 0° to 360° with respected to the laser polarization direction. For the collection path, both the Raman scattering signals with z(xx)z and z(xy)z configurations can be detected simultaneously without any analyzer before output fiber. As the few-layer WTe<sub>2</sub> samples are easily degraded, all the related Raman experiments for each sample were completed within 2 h.<sup>[31]</sup>

High Pressure Measurements: The high-pressure cell used in this experiment is based on a symmetric diamond anvil cell (DAC) having two diamonds with 400  $\mu$ m culet size. The sample and pressure transmitting medium (methanol/ethanol, 4:1) with a small ruby chip (10  $\mu$ m) are loaded in a 150  $\mu$ m hole drilled in a 250 µm thick T301 gasket preindented to 60 µm thickness. The high-pressure Raman spectra were collected using a Renishaw InVia micro Raman system under backscattering configuration, with excitation laser wavelength of 532 nm and 20× objective lens. The laser power is controlled below 0.4 mW to avoid possible laser-induced heating. The signal was dispersed by a 2400 g mm<sup>-1</sup> grating under the triple subtractive mode with a spectra resolution of 1  $cm^{-1}$ . The acquisition time of each spectrum was 200 s. Frequency calibration of the Raman spectrum is realized using the characteristic 520 cm<sup>-1</sup> line of silicon. For WTe<sub>2</sub> sample loading in DAC, a very fine tip was used to cut the WTe<sub>2</sub> crystal and adjust its orientation within the punched gasket to obtain parallel and vertical alignments.

Ab Initio Calculations: The first-principles calculations including geometry optimization, vibrational properties, and molecule dynamics were all carried out using the projector-augmented wave<sup>[32]</sup> method as implemented in the Vienna ab initio simulation package (VASP) code<sup>[33]</sup> including the spin-orbit coupling effects. The exchange correlation potential was described using the Perdew, Burke and Ernzerhof functional within the generalized gradient approximation.[34] The kinetic energy cutoff was set to 500 eV. The BZ was sampled by a  $16 \times 8 \times 1$  k-point mesh using Monkhorst-Pack (MP) method. The energy convergence for the relaxation was chosen to be less than  $10^{-5}$  eV Å<sup>-1</sup>. To account for the interlayer van der Waals interactions, all the simulations were performed using the nonlocal vdW-DF-optB86b functional.<sup>[35]</sup> The phonon frequencies at the  $\Gamma$  point and Raman intensities were calculated within DFPT as introduced in Phonopy.<sup>[36]</sup> For the MD simulation study, a 96-atoms  $2 \times 2 \times 2$  supercell and  $2 \times 2 \times 2$  MP k-point sampling grid. To adopt Normal Pressure and Temperature (NPT) ensemble, the simulation system was coupled to an Parrinello-Rahman barostat<sup>[37]</sup> running with Langevin stochastic thermostat, as recently implemented in VASP code. The time step in the molecular-dynamics simulations was 1 fs and the external pressure maintains at 20 GPa. The Raman peak intensity of a particular normal mode v was calculated as<sup>[38]</sup>  $I^{v} \propto |e_{i} \cdot A^{v} \cdot e_{s}|(1/\omega_{v})(n_{v}+1)$ , where  $e_i(e_s)$  is the incident (scattered) light polarization,  $n_v$  is the Bose–Einstein distribution, and  $A^{\nu}$  is the Raman susceptibility associated with the vth normal mode. To do the spin projection calculations, the Wannier functions were computed by the



maximally localized algorithm<sup>[39]</sup> and were implemented in the package WANNIER90<sup>[40]</sup> using W s and d orbitals and Te p orbitals. The Weyl chirality was calculated by the software package WannierTools, which was based on the iterative Green's function.<sup>[41,42]</sup>

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

#### Acknowledgements

This research was supported by Ministry of Education (MOE) under Academic Research Fund (AcRF) Tier 1 (Reference No. RG103/16), AcRF Tier 2 (MOE2015-T2-1-148), and AcRF Tier 3 (MOE2011-T3-1-005) in Singapore. Z.L. would like to acknowledge the funding support from the Singapore National Research Foundation (NRF) under NRF RF Award No. NRF-RF2013-08. J.-H.L. acknowledge (Japan Society for the Promotion of Science) JSPS KAKENHI (P16823) for financial support. J.-X.Y. and J.X. acknowledge the technical support from H.-L.H at WITec. J.X. and D.-F.L. performed the experiments. J.-X.Y. performed simulation studies. J.-D.Z, P.Y., and Z.L. helped to prepare the samples. J.-H.L provided the STEM measurements. All authors discussed the results. J.X., J.-X.Y., and Z.-X.S. conceived the study. J.X. and J.-X.Y. wrote the paper.

### Conflict of Interest

The authors declare no conflict of interest.

- [1] X. Dou, K. Ding, D. Jiang, B. Sun, ACS Nano 2014, 8, 7458.
- [2] A. P. Nayak, T. Pandey, D. Voiry, J. Liu, S. T. Moran, A. Sharma, C. Tan, C.-H. Chen, L.-J. Li, M. Chhowalla, J.-F. Lin, A. K. Singh, D. Akinwande, *Nano Lett.* **2015**, *15*, 346.
- M. Peña-Álvarez, E. del Corro, Á. Morales-García, L. Kavan, M. Kalbac, O. Frank, *Nano Lett.* 2015, 15, 3139.
- [4] A. P. Nayak, S. Bhattacharyya, J. Zhu, J. Liu, X. Wu, T. Pandey, C. Jin, A. K. Singh, D. Akinwande, J.-F. Lin, *Nat. Commun.* **2014**, *5*, 3731.
- [5] Z.-H. Chi, X.-M. Zhao, H. Zhang, A. F. Goncharov, S. S. Lobanov, T. Kagayama, M. Sakata, X.-J. Chen, *Phys. Rev. Lett.* **2014**, *113*, 036802.
- [6] Z. Zhao, H. Zhang, H. Yuan, S. Wang, Y. Lin, Q. Zeng, G. Xu, Z. Liu,
   G. K. Solanki, K. D. Patel, Y. Cui, H. Y. Hwang, W. L. Mao, *Nat. Commun.* 2015, *6*, 7312.
- [7] Y. Qi, P. G. Naumov, M. N. Ali, C. R. Rajamathi, W. Schnelle,
  O. Barkalov, M. Hanfland, S.-C. Wu, C. Shekhar, Y. Sun, V. Susz,
  M. Schmidt, U. Schwarz, E. Pippel, P. Werner, R. Hillebrand,
  T. Forster, E. Kampert, S. Parkin, R. J. Cava, C. Felser, B. Yan,
  S. A. Medvedev, *Nat. Commun.* 2016, *7*, 11038.
- [8] M. N. Ali, J. Xiong, S. Flynn, J. Tao, Q. D. Gibson, L. M. Schoop, T. Liang, N. Haldolaarachchige, M. Hirschberger, N. P. Ong, R. J. Cava, *Nature* **2014**, *514*, 205.
- [9] I. Pletikosić, M. N. Ali, A. V. Fedorov, R. J. Cava, T. Valla, Phys. Rev. Lett. 2014, 113, 216601.

www.small-journal.com

# **ADVANCED**

www.advancedsciencenews.com

- [10] L. R. Thoutam, Y. L. Wang, Z. L. Xiao, S. Das, A. Luican-Mayer, R. Divan, G. W. Crabtree, W. K. Kwok, *Phys. Rev. Lett.* **2015**, *115*, 046602.
- [11] X.-C. Pan, X. Chen, H. Liu, Y. Feng, Z. Wei, Y. Zhou, Z. Chi, L. Pi, F. Yen, F. Song, X. Wan, Z. Yang, B. Wang, G. Wang, Y. Zhang, *Nat. Commun.* **2015**, *6*, 7312.
- [12] D. Kang, Y. Zhou, W. Yi, C. Yang, J. Guo, Y. Shi, S. Zhang, Z. Wang, C. Zhang, S. Jiang, A. Li, K. Yang, Q. Wu, G. Zhang, L. Sun, Z. Zhao, *Nat. Commun.* **2015**, *6*, 7804.
- [13] A. A. Soluyanov, D. Gresch, Z. Wang, Q. Wu, M. Troyer, X. Dai, B. A. Bernevig, *Nature* **2015**, *527*, 495.
- [14] X. Zhang, X.-F. Qiao, W. Shi, J.-B. Wu, D.-S. Jiang, P.-H. Tan, Chem. Soc. Rev. 2015, 44, 2757.
- [15] C. Tan, H. Zhang, Chem. Soc. Rev. 2015, 44, 2713.
- [16] J. Ribeiro-Soares, R. M. Almeida, E. B. Barros, P. T. Araujo, M. S. Dresselhaus, L. G. Cançado, A. Jorio, *Phys. Rev. B* 2014, *90*, 115438.
- [17] A. Mar, S. Jobic, J. A. Ibers, J. Am. Chem. Soc. 1992, 114, 8963.
- [18] B. Brown, Acta Crystallogr. 1966, 20, 268.
- [19] E. Lorchat, G. Froehlicher, S. Berciaud, ACS Nano 2016, 10, 2752.
- [20] D. Wolverson, S. Crampin, A. S. Kazemi, A. Ilie, S. J. Bending, ACS Nano 2014, 8, 11154.
- [21] D. A. Chenet, O. B. Aslan, P. Y. Huang, C. Fan, A. M. van der Zande, T. F. Heinz, J. C. Hone, *Nano Lett.* **2015**, *15*, 5667.
- [22] R. He, J.-A. Yan, Z. Yin, Z. Ye, G. Ye, J. Cheng, J. Li, C. H. Lui, Nano Lett. 2016, 16, 1404.
- [23] S. Yang, C. Wang, H. Sahin, H. Chen, Y. Li, S.-S. Li, A. Suslu, F. M. Peeters, Q. Liu, J. Li, S. Tongay, *Nano Lett.* **2015**, *15*, 1660.
- [24] W.-D. Kong, S.-F. Wu, P. Richard, C.-S. Lian, J.-T. Wang, C.-L. Yang, Y.-G. Shi, H. Ding, Appl. Phys. Lett. 2015, 106, 081906.
- [25] Y. C. Jiang, J. Gao, L. Wang, Sci. Rep. 2016, 6, 19624.
- [26] Y. Zhao, X. Luo, H. Li, J. Zhang, P. T. Araujo, C. K. Gan, J. Wu, H. Zhang, S. Y. Quek, M. S. Dresselhaus, Q. Xiong, *Nano Lett.* 2013, 13, 1007.

- [27] J. Yan, J. Xia, X. Wang, L. Liu, J.-L. Kuo, B. K. Tay, S. Chen, W. Zhou, Z. Liu, Z. X. Shen, *Nano Lett.* **2015**, *15*, 8155.
- [28] M. Lazzeri, F. Mauri, Phys. Rev. Lett. 2003, 90, 036401.
- [29] A. Tamai, Q. S. Wu, I. Cucchi, F. Y. Bruno, S. Ricco, T. K. Kim, M. Hoesch, C. Barreteau, E. Giannini, C. Besnard, A. Soluyanov, F. Baumberger, *Phys. Rev. X* 2016, *6*, 031021.
- [30] T. R. Chang, S. Y. Xu, G. Chang, C. C. Lee, S. M. Huang, B. Wang, G. Bian, H. Zheng, D. S. Sanchez, I. Belopolski, N. Alidoust, M. Neupane, A. Bansil, H. T. Jeng, H. Lin, M. Zahid Hasan, *Nat. Commun.* 2016, 7, 10639.
- [31] Y. Kim, Y. I. Jhon, J. Park, J. H. Kim, S. Lee, Y. M. Jhon, *Nanoscale* **2016**, *8*, 2309.
- [32] P. E. Blöchl, Phys. Rev. B 1994, 50, 17953.
- [33] G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169.
- [34] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **1992**, *46*, 6671.
- [35] J. Klimeš, D. R. Bowler, A. Michaelides, Phys. Rev. B 2011, 83, 195131.
- [36] A. Togo, I. Tanaka, Scr. Mater. 2015, 108, 1.
- [37] M. Parrinello, A. Rahman, Phys. Rev. Lett. 1980, 45, 1196.
- [38] D. Porezag, M. R. Pederson, Phys. Rev. B 1996, 54, 7830.
- [39] N. Marzari, D. Vanderbilt, Phys. Rev. B 1997, 56, 12847.
- [40] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, N. Marzari, Comput. Phys. Commun. 2008, 178, 685.
- [41] WannierTools: An Open-Source Software Package for Novel Topological Materials, arXiv:1703.07789 [physics.comp-ph], https:// github.com/quanshengwu/wannier\_tools.
- [42] M. P. Lopez Sancho, J. M. Lopez Sancho, J. M. L. Sancho, J. Rubio, J. Phys. F: Met. Phys. 1985, 15, 851.

Received: June 5, 2017 Revised: July 14, 2017 Published online: August 28, 2017