Inorganic Chemistry

pubs.acs.org/IC



Reversible Iodine Intercalation into Tungsten Ditelluride

Patrick Schmidt, Philipp Schneiderhan, Markus Ströbele, Carl P. Romao,*^{,†} and Hans-Jürgen Meyer^{*,†}



ABSTRACT: The new compound WTe₂I was prepared by a reaction of WTe₂ with iodine in a fused silica ampule at temperatures between 40 and 200 °C. Iodine atoms are intercalated into the van der Waals gap between tungsten ditelluride layers. As a result, the WTe₂ layer separation is significantly increased. Iodine atoms form planar layers between each tungsten ditelluride layer. Due to oxidation by iodine the semimetallic nature of WTe₂ is changed, as shown by comparative band structure calculations for WTe₂ and WTe₂I based on density functional theory. The calculated phonon band structure of WTe₂I indicates the presence of phonon instabilities related to charge



density waves, leading to an observed incommensurate modulation of the iodine position within the layers.

INTRODUCTION

Transition metal dichalcogenides (TMDCs) are quasi-twodimensional layered materials, formed by monolayers of metal atoms sandwiched between layers of chalcogen atoms. Weak van der Waals interlayer bonding between building blocks of hexagonal chalcogen layers with nearly octahedral or nearly trigonal prismatically coordinated metal atoms allow many polytypes to form.^{1–3}

The weak interlayer bonding permits intercalations, quite akin to other layered materials such as graphite,⁴ allowing the incorporation of various metal atoms⁵⁻¹⁰ and organic molecules^{11,12} between the layers to form stoichiometric or nonstoichiometric compounds. Depending on the intercalated species, changes in the physical properties of the host can occur. In addition, such intercalated species can be used as precursors for the exfoliation of single TMDC layers.¹³⁻¹⁸

Tungsten ditelluride $(WTe_2)^{19}$ is a typical TMDC that crystallizes with the so-called distorted $1T(T_d)$ structure. The structure resembles a distorted derivative of the TiS_2^2 structure with distorted tellurium octahedra and tungsten atoms shifted away from octahedral centers, thereby forming W–W zigzag chains along the *a*-axis direction (Figure 1). The arrangement of tungsten atoms in the structure plays a significant role in the remarkable electronic properties of WTe₂. Electronic structure calculations have revealed WTe₂ to be a semimetal.²¹⁻²³ Physical studies have revealed many unusual properties of WTe2, including charge density wave (CDW)²⁴⁻³¹ formation, superconductivity,³² large magnetoresistance,³³ and the presence of nontrivial topological properties such as the appearance of type-II Weyl Fermions,³⁴ making this material interesting for a variety of electronic applications. Herein, we demonstrate that the oxidation of WTe₂ by iodine and the formation of the intercalated species

 WTe_2I modifies the electronic structure and therefore changes the properties of this material. According to our knowledge, this type of *anionic* intercalation has not been reported before in a TMDC and may be applicable to other TMDC systems as well.

EXPERIMENTAL SECTION

Synthesis of WTe₂ and WTe₂I. Manipulations of starting materials were performed in an argon-filled glovebox (MBraun, Labmaster 130, $O_2 < 1$ ppm, $H_2O < 1$ ppm). WTe₂ was prepared in a dry, vacuum-sealed silica ampule with a 1:2 molar ratio of tungsten powder (ABCR GmbH, 99.95%, 0.6–0.9 μ m) and tellurium pieces (Evochem, 99.999%) heated at 800 °C for 24 h (total mass = 1 g). An additional 0.1 equiv of WCl₆ (Arcos, 99.9+%) was added as an oxygen getter.

WTe₂I was prepared by heating a 1:2 molar mixture of WTe₂ and iodine (Honeywell, \geq 99.8%) in a dry, vacuum-sealed silica ampule at 100 °C for 16 h. The product appeared as black powder. Excess iodine aggregated at the top of the ampule.

Synthesis of WTe₂I Single Crystals. The as-prepared WTe₂ product contained some single crystals. Carefully selected single crystals of WTe₂ were heated with an approximately 4 molar excess of iodine at 120 °C for 16 h.

Powder X-ray Diffraction. PXRD patterns of products were collected with a Stadi-P (STOE, Darmstadt) powder diffractometer using germanium monochromated Cu–K_{a1} radiation ($\lambda = 1.5406$ Å) and a Mythen 1K detector.

Received: September 7, 2020 Published: January 15, 2021





pubs.acs.org/IC



Figure 1. Projection of the WTe₂ structure. View along the *c*-axis of the distorted T_d structure in which tungsten (gray) atoms follow a CDW along the *a*-axis. Tungsten atoms are shifted off the octahedral centers formed by tellurium (yellow) atoms.

ICP-OES. After dissolution of WTe_2I in 2 wt % NaOH/H₂O₂, the W/Te/I ratio was determined by ICP-OES (iCAP 7400 Thermo Fisher Scientific).

Thermal Analysis. Differential thermal analysis (DTA) and thermal gravimetry (TG) measurements were performed with a Netzsch Jupiter, STA 449 F3 apparatus between room temperature and 350 °C with a heating and cooling rate of 2 K min⁻¹ in a bespoke silica crucible (height: 2 cm, inner diameter: 0.6 cm, thickness of wall: 0.1 cm).

DFT Calculations. Calculations were performed using the ABINIT software package with the projector augmented-wave (PAW) method and a plane-wave basis set.^{35,36} The Perdew–Burke–Ernzerhof exchange–correlation functional was used with the vdw-DFT-D3 dispersion correction.^{37,38} PAW data files were used as received from the ABINIT library.³⁹ Methfessel–Paxton smearing was used to determine band occupation.⁴⁰ Convergence studies and structural relaxation were performed prior to calculation of the electronic structure. Spin–orbit coupling was included by calculation of the electronic wave function of each spin separately, as described in ref 41. Example input files are available as part of the Supporting Information.

RESULTS AND DISCUSSION

Reactions of metal dichalcogenides with halides have been reported to yield mixed chalcogenide-halide cluster compounds. An example is the formation of $\text{Re}_3\text{Se}_2\text{Br}_5$ from ReSe_2 with Br_2 (at 450 °C).⁴² Following this example we have explored the reaction of WTe₂ with iodine. WTe₂ can be prepared from well-known transport reactions of the elements in fused silica tubing, like other transition metal chalcogenides.^{19,21,43-46} A detailed study of the reaction of WTe₂ with iodine in a fused silica ampule reveals several reaction steps with increasing temperature and iodine pressure. The first step is an intercalation of iodine into interlayers of the WTe₂ structure, yielding the new compound WTe₂I, which occurs following heating above 40 °C in a closed vessel. When heated above 200 °C, iodine and TeI₄ are released until (TeI₃)₂[WeI₁₄] is formed at 250 °C.⁴⁷

A chemical analysis of WTe_2I by inductively coupled plasma optical emission spectrometry (ICP-OES) confirmed the identity of the product with an average ratio of elements (from a number of measurements) corresponding to W:Te:I = 1:1.98:0.99.

The crystal structure of WTe_2I is closely related to that of WTe_2 but contains iodine atoms in interlayers and was refined by powder X-ray diffraction (PXRD) in the centrosymmetric space group *Pmmn* (Figure 2).

The structure refinement converged with a conclusive crystal structure model, revealing unusually high anisotropic displacement parameters (ADPs) of the iodine atoms (Table S2). A single-crystal X-ray analysis of the reciprocal a^*/b^* plane (Figure S2) revealed perturbations of some weak Bragg reflections away from the exact regularity of the basic lattice reflections. The PXRD pattern exhibits a few additional reflections (with $I/I_{max} \cong 1/100$, marked with asterisks in Figure 2) that could not be assigned to any known compound (and the purity of all starting materials was carefully checked by EDX, ICP-OES, and RFA).



Figure 2. PXRD refinement pattern of WTe_2I at 298 K with the experimental (red) and calculated (black) patterns of the Rietveld refinement. Bragg positions (green) of WTe_2I and the difference curve (blue) are also shown. Asterisks (*) are discussed in the main text.

The observation of large ADPs of the iodine atoms can be seen to be indicative of a modulation of the iodine atom arrangement in interlayers of the structure. Hence, based on our PXRD studies, we can only provide an average location of the iodine atoms relative to the WTe₂ lattice. Low-temperature PXRD measurements (at 120 and 12 K) did not introduce a significant change in the diffraction pattern, nor in the iodine ADPs (Figure S5, Figure S6, and Table S8).

The *a*, *b*, and *c* axes in WTe₂I correspond to the *c*, *a*, and *b* axes, respectively, in WTe₂. Individual WTe₂ layers and corresponding W–W and W–Te distances are nearly unchanged before and after the reaction with I₂ (Table 1). Therefore, the cell dimensions within the layers remain almost the same. However, due to the intercalation of iodine between adjacent WTe₂ layers, the lattice parameter along the stacking direction are approximately doubled (Table 1, compare the *c*-axis of WTe₂ and *a*-axis of WTe₂I) (Figure 3). The relative orientation of adjacent WTe₂ layers changes compared to WTe₂ in a way such that the tungsten chains are aligned parallel along the stacking axis.

Iodine atoms form nearly square (Figure 4), planar layers within the *bc*-plane with I–I distances of 3.18(1) Å and 3.48(1) Å. A similar arrangement of iodine layers with values of 3.32 and 3.84 Å was reported in the unusual intercalation compound $(Te_2)_2(I_2)^{49}$ Another, more closely related, TMDC intercalation compound containing a planar iodine network is AuTe₂I,⁵⁰ which has I–I distances of 4.06(1) and 4.74(1) Å.

As noted above, the incorporation of iodine atoms into the structure of WTe₂ yields a significant increase of the interlayer W–W (from 7.01 Å in WTe₂ to 10.95 Å in WTe₂I) and Te–Te (from 3.911to 6.813 Å) distances. This increase is huge in comparison to cationic intercalation compounds like in WS₂In (increasing from 6.16 Å in WS₂ to 6.18 Å in WS₂In).⁵¹ As a result of this strong interlayer expansion and weak interaction forces between layers, dislocations are typically obtained (see Figure S1).

The intercalation reaction between iodine and WTe₂ in a sealed ampule proceeds without a detectable calorimetric feature. The deintercalation of iodine from WTe₂I under ambient pressure can be observed above 100 °C (Figure 5). The observed exothermic effect corresponds to the enthalpy of sublimation of the released iodine (in a constant argon flow of 60 mL/min) and has no correlation with the intercalation energy.

Electronic Structure. The calculated electronic band structure of WTe_2I is shown in Figure 6. This electronic structure calculation was performed on the average structure, as determined by XRPD; a discussion of the potential origins

Table 1. Crystallographic Data and W–W and W–Te Distances of WTe_2 and WTe_2I

	WTe2 ⁴⁸	WTe ₂ I
space group	$Pmn2_1$	Pmmn
a/Å	3.477(2)	21.8967(2)
b/Å	6.249(4)	3.4759(0)
c/Å	14.018(9)	6.3270(1)
$V/Å^3$	304.6(3)	481.54(1)
d(W−W)/Å	2.85(1), 3.48(1)	2.87(1), 3.48(1)
d(W−Te)/Å	2.70(1) - 2.80(1)	2.68(1) - 2.83(1)
d(Te−I)/Å	-	4.14(1) - 4.36(1)
$R_{\rm Bragg}$	-	5.0301



Figure 3. Perspective projection of the crystal structure of WTe_2I , showing a layered arrangement. Tungsten atoms are shown gray, iodine atoms in violet, and tellurium atoms in yellow.



Figure 4. Arrangement of a rectangular net of iodine atoms on top of a WTe_2 layer of the WTe_2I structure (W = gray, Te = yellow, I = violet).



Figure 5. DTA/TG measurement of WTe_2I in an open SiO₂ container up to 350 °C with complete iodine loss (DTA: red line, TG: black line).

and effects of a modulation of the iodine positions can be found below. Comparison of Figure 6 to the band structure of WTe₂ (Figure 7) shows that the addition of iodine layers into the structure increases the density of states (DOS) at the Fermi level significantly, leading to a transition from a semimetal to a metal. These additional states are largely located between the Γ ([0 0 0]), X ([1/2 0 0]), and Z ([0 0 1/2]) points in reciprocal space. The projected density of states



Figure 6. Electronic band structure and density of states of WTe_2I , calculated with spin-orbit coupling. The projected densities of states within the PAW spheres are shown as colored lines at right. Special points in the Brillouin zone are shown as an inset.



Figure 7. Electronic band structure and density of states of WTe_2 , calculated without spin-orbit coupling (see ref 8 c for the band structure with spin-orbit coupling). The projected densities of states within the PAW spheres are shown as colored lines at right.

shows that the states around the Fermi level have contributions from W, Te, and I atoms; many of the states project onto interatomic regions which cannot be assigned to a single atom.

Along the $\Gamma-Y-S-X-\Gamma$ path in reciprocal space (Figure 6), the calculated band structure of WTe₂I closely resembles that of WTe₂ along the $\Gamma-X-U-Z-\Gamma$ path, with the Fermi level shifted downward in energy by approximately 0.5 eV. The significant increase in the DOS at the Fermi level following the addition of iodine can therefore be partially attributed to the depletion of some electron density from the tungsten telluride layers into the iodine layers. The magnitude of this charge transfer can be estimated from the calculated density of states of WTe₂ and WTe₂I as 0.7 electrons per formula unit. In WTe₂, an avoided crossing of two bands due to spin-orbit coupling near the Fermi level along the $\Gamma-X$ direction gives rise to Weyl semimetal behavior.^{34,52} The addition of iodine to form WTe₂I moves the Fermi level away from the corresponding feature (located between Γ and Y), into a region with more conventional bands at the Fermi surface.

The addition of iodine to WTe_2 also creates additional bands at the Fermi level between R ([1/2 1/2 1/2]) and S

([1/2 1/2 0]) and between Y ([0 1/2 0]) and T ([0 1/2 1/2]) (compare Figure 6 and Figure 8). These bands have very high dispersion, indicating small effective electron masses and large charge carrier mobility. They are associated with Dirac conelike anticrossings lying approximately 0.5 eV below the Fermi level. Several methods were used to investigate the nature of these highly dispersive bands. Projections of the wave functions near each atom onto spherical harmonics were used to determine the atomic and orbital character of the wave functions corresponding to the bands. As shown in Figure 10, this indicates that the bands of interest can be largely assigned to iodine p_z orbitals. To validate this result, the electronic band structure of the iodine layer alone was calculated, and the features between R and S and Y and T can also be found there (Figure 8).

Careful examination of the electron density around the iodine atoms (Figure 9) shows evidence of bonding (i.e., some interstitial electron density) in chains along c. Stronger bonding is indicated between iodine atoms with an interatomic distance of 3.148 Å in the XRD crystal structure. The



Figure 8. Electronic band structure of the iodine layers in WTe₂I.

pubs.acs.org/IC

Article



Figure 9. Density of valence electrons in a section through iodine atoms in the bc plane. A slight increase in electron density between iodine atoms along c evidence I–I bonding. The Te atoms above the plane are shown for comparison.

formation of dimers along c indicates that the bands with p_z character (Figure 10) correspond to σ bonding and antibonding orbitals.

The effects of modulation of the iodine layers upon the electronic band structure were investigated by calculation of the electronic band structure of WTe_2I with a displacement of the iodine atoms by -0.25 along *c* (Figure S3), in order to test the sensitivity of the band structure to the Te–I distances. The band structure was mostly unchanged, with the largest modification being a significant increase in energy of the valence band between R, S, Y, and T. This increase led to the valence band reaching the Fermi level at R and T, indicating that modulation of the iodine layers may introduce more states which contribute to electronic conductivity. Shifting the iodine atoms such that there is only one crystallographically independent I–I distance resulted in no noticeable effect on the electronic band structure (Figure S4).

Calculation of the phonon band structure of WTe₂I revealed the presence of several soft modes (modes with imaginary frequencies, shown as negative values in Figure 11). These modes indicate instabilities of the crystallographic *Pmmn* structure and can be identified as Kohn anomalies, that is, they indicate that a charge-density wave ordered structure is more stable at 0 K than the *Pmmn* structure.¹ The CDW ordering can be commensurate or incommensurate with the lattice vectors. The presence of these Kohn anomalies therefore offers



Figure 10. Projected contributions of p_z spherical harmonics to electronic bands in WTe₂I, shown in red as fatbands.



an explanation for the modulation of the iodine layers detected by X-ray diffraction and indicate that a phase transition to a CDW disordered state can be expected on heating (although decomposition could happen prior to such a transition).

The Kohn anomalies are related to nesting vectors of the Fermi surface (Figure 12); the introduction of additional sheet-like bands crossing the Fermi level therefore opens new possibilities for such nesting. The phonon band structure also shows numerous triply degenerate nodal points between R and S and Y and T, where optic bands invert and become lower in energy than the acoustic bands. These topological features can act as additional phonon scattering centers and lead to glass-like thermal conductivity.^{53,54} There are also numerous crossings and near-crossings of bands, especially near Γ , which may correspond to Dirac points which could, by breaking the inversion symmetry, be transformed into topologically charged Weyl phonons.^{53,54}

The nature of the CDW can be determined by examination of the eigenvectors of the soft modes, which are shown in cartoon form in Figure 13. These modes all involve oscillations of iodine atoms along b, with rocking motions of the Te₂ layers being incorporated in some cases. Since the soft modes involve motions of individual iodine atoms, not rigid I₂ units, we can conclude that the CDWs are related to instabilities of the weak I–I bonds seen in the average structure and in Figure 9. This offers an interesting parallel to the dissociation of I–I bonds under pressure in solid iodine, which involves the formation of a modulated structure where some of the I–I distances vary between the values seen in the average structure.⁵⁵



Figure 12. Calculated Fermi surface of WTe_2I . Nesting vectors (from left to right, $[0\ 0\ 0.52]$, $[0\ 0.34\ 0.20]$, $[0\ 0.28\ 0]$, and $[0\ 0\ 0.45]$) are shown as black arrows.



Figure 13. A cartoon view of several soft modes in WTe_2I . The modes with the largest imaginary frequency (most negative values in Figure 8) at the Z, T, R, and U points are shown. Linear oscillations of I atoms are shown as black arrows, and rocking motions of the WTe_2 layers are shown as curved arrows.

CONCLUSIONS

The reversible intercalation of iodine into the structure of WTe_2 is presented with an average crystal structure of WTe_2I obtained by PXRD. Iodide atoms in interlayers of the structure appear not fully ordered and show therefore anomalous large ADPs. Single-crystal studies have revealed additional reflections inconsistent with the Bragg reflections of the structure, leading to the assumption of the presence of an incommensurable structure.

To our knowledge, the example of WTe_2I represents the first reported halide intercalation into a dichalcogenide structure. Although other intercalation compounds of WTe_2 with alkali ions are known, no crystal structures have been reported in ICSD.⁵⁶ In light of the many unusual physical properties of WTe_2 , this intercalate with oxidized WTe_2 layers represents an interesting material for electronic applications. Electronic band structure calculations reveal WTe_2I to be metallic and to have steep bands with dominant iodine p-band character crossing the Fermi level. The phonon band structure indicates that modulation of the iodine layers is due to Kohn anomalies in the *Pmmn* structure. Halogen intercalation is therefore demonstrated to present a potential method to reversibly modify the physical properties of WTe₂.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02676.

DFT input (ZIP)

An image of a crystal of WTe_2I showing layer dislocations, PXRD patterns, and refinement information, a table of atomic coordinates, from refinement of XRD data and DFT structural optimization (PDF)

pubs.acs.org/IC

Calculated electronic band structure of WTe_2I with modified iodine positions (TXT)

Accession Codes

CCDC 2019336 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

- Carl P. Romao Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany; orcid.org/0000-0002-5519-2519; Email: carl.romao@mnf.uni-tuebingen.de
- Hans-Jürgen Meyer Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany; orcid.org/0000-0003-2450-4011; Email: juergen.meyer@uni-tuebingen.de

Authors

- Patrick Schmidt Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany
- Philipp Schneiderhan Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany
- Markus Ströbele Section of Solid State and Theoretical Inorganic Chemistry Institute of Inorganic Chemistry, Eberhard Karls University Tübingen, 72076 Tübingen, Germany; © orcid.org/0000-0002-5147-5677

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c02676

Author Contributions

[†]These authors contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors express their gratitude to Dr. Jochen Glaser (University of Tübingen) for performing ICP-OES analyses and Dipl.-Ing. Frank Adams, Dr. Sebastian Bette, and Prof. Dr. Robert Dinnebier (MPI Stuttgart) for low-temperature PXRD measurements on WTe₂I. Support of this research by the Deutsche Forschungsgemeinschaft (DFG-Bonn) through the project ME 914/31-1, by the state of Baden-Württemberg through bwHPC, and by the DFG through INST 40/467-1 FUGG (JUSTUS cluster) is gratefully acknowledged.

REFERENCES

(1) Han, G. H.; Duong, D. L.; Keum, D. H.; Yun, S. J.; Lee, Y. H. van der Waals Metallic Transition Metal Dichalcogenides. *Chem. Rev.* **2018**, *118* (13), 6297–6336.

(2) Atherton, M. J.; Holloway, J. H., Thio-, Seleno-, and Tellurohalides of the Transition Metals. In *Adv. Inorg. Chem. Radiochem.*, Emeléus, H. J., Sharpe, A. G., Eds.; Academic Press: 1979; Vol. 22, pp 171–198.

(3) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.

(4) Boehm, H. P.; Setton, R.; Stumpp, E. Nomenclature and terminology of graphite intercalation compounds (IUPAC Recommendations 1994). *Pure Appl. Chem.* **1994**, *66* (9), 1893.

(5) Ali, M. N.; Ji, H.; Hirai, D.; Fuccillo, M. K.; Cava, R. J. Synthesis and characterization of two crystallographic forms of Ag_{0.79}VS₂. J. Solid State Chem. **2013**, 202, 77–84.

(6) Ali, S. I.; Mondal, S.; Prathapa, S. J.; van Smaalen, S.; Zörb, S.; Harbrecht, B. Self-Intercalation and Vacancy-Ordering in 6R-Cu_xTa_{1+y}S₂ ($x \approx 0.23$, y = 0, 0.06). Z. Anorg. Allg. Chem. **2012**, 638 (15), 2625–2631.

(7) Ali, S. I.; Mondal, S.; van Smaalen, S. Synthesis, Superstructure, and Vacancy-Ordering in 2H-Cu_xTa_{1+y}Se₂ (x, y = 0.52, 0 and 0.16, 0.08). *Z. Anorg. Allg. Chem.* **2015**, 641 (2), 464–469.

(8) Crawack, H. J.; Pettenkofer, C. Calculation and XPS measurements of the Ta4f CDW splitting in Cu, Cs and Li intercalation phases of 1T-Ta X_2 (X=S, Se). Solid State Commun. 2001, 118 (7), 325–332.

(9) Rouxel, J. Structural chemistry of layered materials and their intercalates. *Physica* B+C **1980**, 99 (1), 3–11.

(10) Patel, S. N.; Balchin, A. A. Structural studies of lithium intercalated titanium di-telluride. *J. Mater. Sci. Lett.* **1985**, *4* (4), 382–384.

(11) Dines, M. B. Intercalation of Metallocenes in the Layered Transition-Metal Dichalcogenides. *Science* **1975**, *188* (4194), 1210.

(12) Figueroa, E.; Brill, J. W.; Selegue, J. P. New intercalation compounds of transition metal dichalcogenides. *J. Phys. Chem. Solids* **1996**, 57 (6), 1123–1127.

(13) Budania, P.; Baine, P. T.; Montgomery, J. H.; McNeill, D. W.; Neil Mitchell, S.J.; Modreanu, M.; Hurley, P. K. Comparison between Scotch tape and gel-assisted mechanical exfoliation techniques for preparation of 2D transition metal dichalcogenide flakes. *Micro Nano Lett.* **2017**, *12* (12), 970–973.

(14) Sajedi-Moghaddam, A.; Mayorga-Martinez, C. C.; Saievar-Iranizad, E.; Sofer, Z.; Pumera, M. Exfoliated transition metal dichalcogenide (MX_2 ; M=Mo, W; X=S, Se, Te) nanosheets and their composites with polyaniline nanofibers for electrochemical capacitors. *Appl. Mater. Today* **2019**, *16*, 280–289.

(15) Cunningham, G.; Lotya, M.; Cucinotta, C. S.; Sanvito, S.; Bergin, S. D.; Menzel, R.; Shaffer, M. S. P.; Coleman, J. N. Solvent Exfoliation of Transition Metal Dichalcogenides: Dispersibility of Exfoliated Nanosheets Varies Only Weakly between Compounds. *ACS Nano* **2012**, *6* (4), 3468–3480.

(16) An, S.-J.; Kim, Y. H.; Lee, C.; Park, D. Y.; Jeong, M. S. Exfoliation of Transition Metal Dichalcogenides by a High-Power Femtosecond Laser. *Sci. Rep.* **2018**, *8* (1), 12957.

(17) Liu, X.; Chen, H.; Lin, J.; Li, Y.; Guo, L. Exfoliation of transition-metal dichalcogenides using ATP in aqueous solution. *Chem. Commun.* **2019**, *55* (20), 2972–2975.

(18) Jung, Y.; Zhou, Y.; Cha, J. J. Intercalation in two-dimensional transition metal chalcogenides. *Inorg. Chem. Front.* **2016**, 3 (4), 452–463.

(19) Brown, B. E. The crystal structures of WTe_2 and high-temperature MoTe₂. Acta Crystallogr. **1966**, 20 (2), 268–274.

(20) Chianelli, R. R.; Scanlon, J. C.; Thompson, A. H. Structure refinement of stoichiometric TiS_2 . *Mater. Res. Bull.* **1975**, *10* (12), 1379–1382.

(21) Kabashima, S. Electrical Properties of Tungsten-Ditelluride WTe₂. J. Phys. Soc. Jpn. **1966**, 21, 945–948.

(22) Augustin, J.; Eyert, V.; Boker, T.; Frentrup, W.; Dwelk, H.; Janowitz, C.; Manzke, R. Electronic band structure of the layered compound Td-WTe₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62*, 10812–10823.

(23) Dawson, W. G.; Bullett, D. W. Electronic structure and crystallography of MoTe₂ and WTe₂. J. Phys. C: Solid State Phys. **1987**, 20, 6159–6174.

(24) Rovira, C.; Whangbo, M. H. Factors governing the charge density wave patterns of layered transition-metal compounds of octahedral coordination with d^2 and d^3 electron counts. *Inorg. Chem.* **1993**, 32 (19), 4094–4097.

(25) Wilson, J. A.; Di Salvo, F. J.; Mahajan, S. Charge-density waves and superlattices in the metallic layered transition metal dichalcogenides. *Adv. Phys.* **1975**, *24* (2), 117–201.

(26) Ali, M. N.; Xiong, J.; Flynn, S.; Tao, J.; Gibson, Q. D.; Schoop, L. M.; Liang, T.; Haldolaarachchige, N.; Hirschberger, M.; Ong, N. P.; Cava, R. J. Large, non-saturating magnetoresistance in WTe₂. *Nature* **2014**, *514*, 205–208.

(27) Lu, N.; Zhang, C.; Lee, C.-H.; Oviedo, J. P.; Nguyen, M. A. T.; Peng, X.; Wallace, R. M.; Mallouk, T. E.; Robinson, J. A.; Wang, J.; Cho, K.; Kim, M. J. Atomic and Electronic Structures of WTe_2 Probed by High Resolution Electron Microscopy and ab Initio Calculations. J. Phys. Chem. C **2016**, 120 (15), 8364–8369.

(28) Canadell, E.; Whangbo, M.-H. Charge-density-wave instabilities expected in monophosphate tungsten bronzes. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1991**, 43 (3), 1894–1902.

(29) Guster, B.; Canadell, E.; Pruneda, M.; Ordejón, P. First principles analysis of the CDW instability of single-layer 1T-TiSe₂ and its evolution with charge carrier density. 2D Mater. **2018**, 5 (2), 025024.

(30) Whangbo, M. H.; Canadell, E.; Foury, P.; Pouget, J. P. Hidden Fermi Surface Nesting and Charge Density Wave Instability in Low-Dimensional Metals. *Science* **1991**, *252* (5002), *96*.

(31) Mitsuishi, N.; Sugita, Y.; Bahramy, M. S.; Kamitani, M.; Sonobe, T.; Sakano, M.; Shimojima, T.; Takahashi, H.; Sakai, H.; Horiba, K.; Kumigashira, H.; Taguchi, K.; Miyamoto, K.; Okuda, T.; Ishiwata, S.; Motome, Y.; Ishizaka, K. Switching of band inversion and topological surface states by charge density wave. *Nat. Commun.* **2020**, *11* (1), 2466.

(32) Huang, C.; Narayan, A.; Zhang, E.; Liu, Y.; Yan, X.; Wang, J.; Zhang, C.; Wang, W.; Zhou, T.; Yi, C.; Liu, S.; Ling, J.; Zhang, H.; Liu, R.; Sankar, R.; Chou, F.; Wang, Y.; Shi, Y.; Law, K. T.; Sanvito, S.; Zhou, P.; Han, Z.; Xiu, F. Inducing Strong Superconductivity in WTe₂ by a Proximity Effect. ACS Nano **2018**, *12* (7), 7185–7196.

(33) Lv, Y.-Y.; Zhang, B.-B.; Li, X.; Pang, B.; Zhang, F.; Lin, D.-J.; Zhou, J.; Yao, S.-H.; Chen, Y. B.; Zhang, S.-T.; Lu, M.; Liu, Z.; Chen, Y.; Chen, Y.-F. Dramatically decreased magnetoresistance in non-stoichiometric WTe₂ crystals. *Sci. Rep.* **2016**, 6 (1), 26903.

(34) Li, P.; Wen, Y.; He, X.; Zhang, Q.; Xia, C.; Yu, Z.-M.; Yang, S. A.; Zhu, Z.; Alshareef, H. N.; Zhang, X.-X. Evidence for topological type-II Weyl semimetal WTe₂. *Nat. Commun.* **2017**, *8* (1), 2150.

(35) Gonze, X.; Jollet, F.; Abreu Araujo, F.; Adams, D.; Amadon, B.; Applencourt, T.; Audouze, C.; Beuken, J. M.; Bieder, J.; Bokhanchuk, A.; Bousquet, E.; Bruneval, F.; Caliste, D.; Côté, M.; Dahm, F.; Da Pieve, F.; Delaveau, M.; Di Gennaro, M.; Dorado, B.; Espejo, C.; Geneste, G.; Genovese, L.; Gerossier, A.; Giantomassi, M.; Gillet, Y.; Hamann, D. R.; He, L.; Jomard, G.; Laflamme Janssen, J.; Le Roux, S.; Levitt, A.; Lherbier, A.; Liu, F.; Lukačević, I.; Martin, A.; Martins, C.; Oliveira, M. J. T.; Poncé, S.; Pouillon, Y.; Rangel, T.; Rignanese, G. M.; Romero, A. H.; Rousseau, B.; Rubel, O.; Shukri, A. A.; Stankovski, M.; Torrent, M.; Van Setten, M. J.; Van Troeye, B.; Verstraete, M. J.; Waroquiers, D.; Wiktor, J.; Xu, B.; Zhou, A.; Zwanziger, J. W. Recent developments in the ABINIT software package. *Comput. Phys. Commun.* 2016, 205, 106–131.

(36) Torrent, M.; Jollet, F.; Bottin, F.; Zérah, G.; Gonze, X. Implementation of the projector augmented-wave method in the ABINIT code: Application to the study of iron under pressure. *Comput. Mater. Sci.* **2008**, 42 (2), 337–351.

(37) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865; *Phys. Rev. Lett.* **1997**, *78* (7), 1396–1396.

(38) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion

correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 2010, 132 (15), 154104.

(39) ABINIT. www.abinit.org (accessed March 19, 2020).

(40) Methfessel, M.; Paxton, A. T. High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1989**, 40 (6), 3616–3621.

(41) Gonze, X.; Beuken, J. M.; Caracas, R.; Detraux, F.; Fuchs, M.; Rignanese, G. M.; Sindic, L.; Verstraete, M.; Zerah, G.; Jollet, F.; Torrent, M.; Roy, A.; Mikami, M.; Ghosez, P.; Raty, J. Y.; Allan, D. C. First-principles computation of material properties: the ABINIT software project. *Comput. Mater. Sci.* **2002**, *25* (3), 478–492.

(42) Solodovnikov, S. F.; Mironov, Y. V.; Yarovoi, S. S.; Virovets, A. V.; Fedorov, V. E. Crystal chemistry of octahedral clusters of rhenium chalcohalides $\text{Re}_{6}X_{4}Y_{10}$ (X = S, Se, Te; Y = Cl, Br). *Khim. Interesakh Ustoich. Razvit.* **2000**, *8*, 285–290.

(43) Zhou, Y.; Pondick, J. V.; Silva, J. L.; Woods, J. M.; Hynek, D. J.; Matthews, G.; Shen, X.; Feng, Q.; Liu, W.; Lu, Z.; Liang, Z.; Brena, B.; Cai, Z.; Wu, M.; Jiao, L.; Hu, S.; Wang, H.; Araujo, C. M.; Cha, J. J. Unveiling the Interfacial Effects for Enhanced Hydrogen Evolution Reaction on MoS_2/WTe_2 Hybrid Structures. *Small* **2019**, *15* (19), 1900078.

(44) Brixner, L. H. Preparation and properties of the single crystalline AB₂-type selenides and tellurides of niobium, tantalum, molybdenum and tungsten. *J. Inorg. Nucl. Chem.* **1962**, *24*, 257–263.

(45) Al-Hilli, A. A.; Evans, B. L. The preparation and properties of transition metal dichalcogenide single crystals. *J. Cryst. Growth* **1972**, *15* (2), 93–101.

(46) Ueno, K. Introduction to the Growth of Bulk Single Crystals of Two-Dimensional Transition-Metal Dichalcogenides. *J. Phys. Soc. Jpn.* **2015**, *84* (12), 121015.

(47) Schmidt, P.; Siai, A.; Schneiderhan, P.; Ströbele, M.; Meyer, H.-J. Synthesis of $(TeI_3)_2[W_6I_{14}]$ via Iodination of WTe₂. *Eur. J. Inorg. Chem.* **2020**, 2020 (8), 716–719.

(48) Mar, A.; Jobic, S.; Ibers, J. A. Metal-metal vs tellurium-tellurium bonding in WTe₂ and its ternary variants TaIrTe₄ and NbIrTe₄. *J. Am. Chem. Soc.* **1992**, *114* (23), 8963–8971.

(49) Kniep, R.; Beister, H.-J. $(Te_2)_2(I_2)$ - An Unusual Intercalation Compound. Angew. Chem., Int. Ed. Engl. 1985, 24 (5), 393–394.

(50) Haendler, H. M.; Mootz, D.; Rabenau, A.; Rosenstein, G. The crystal structures of $AuTe_2Cl$ and $AuTe_2I$. J. Solid State Chem. 1974, 10 (2), 175–181.

(51) Srivastava, S. K.; Avasthi, B. N. Synthesis and characterization of indium intercalation compounds of tungsten disulphide: In_xWS_2 ($0 \le x \ge 1$). Synth. Met. **1985**, 10 (3), 213–221.

(52) Das, P. K.; Di Sante, D.; Cilento, F.; Bigi, C.; Kopic, D.; Soranzio, D.; Sterzi, A.; Krieger, J. A.; Vobornik, I.; Fujii, J.; Okuda, T.; Strocov, V. N.; Breese, M. B. H.; Parmigiani, F.; Rossi, G.; Picozzi, S.; Thomale, R.; Sangiovanni, G.; Cava, R. J.; Panaccione, G. Electronic properties of candidate type-II Weyl semimetal WTe₂. A review perspective. *Electron. Struct.* **2019**, *1* (1), 014003.

(53) Li, J.; Xie, Q.; Ullah, S.; Li, R.; Ma, H.; Li, D.; Li, Y.; Chen, X.-Q. Coexistent three-component and two-component Weyl phonons in TiS, ZrSe, and HfTe. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, 97 (5), 054305.

(54) Singh, S.; Wu, Q.; Yue, C.; Romero, A. H.; Soluyanov, A. A. Topological phonons and thermoelectricity in triple-point metals. *Phys. Rev. Mater.* **2018**, *2* (11), 114204.

(55) Kenichi, T.; Kyoko, S.; Hiroshi, F.; Mitsuko, O. Modulated structure of solid iodine during its molecular dissociation under high pressure. *Nature* **2003**, 423 (6943), 971–974.

(56) Zhu, L.; Li, Q.-Y.; Lv, Y.-Y.; Li, S.; Zhu, X.-Y.; Jia, Z.-Y.; Chen, Y. B.; Wen, J.; Li, S.-C. Superconductivity in Potassium-Intercalated T_d -WTe₂. *Nano Lett.* **2018**, *18* (10), 6585–6590.