Emergence of Topologically Nontrivial Spin-Polarized States in a Segmented Linear Chain

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Abstract — The synthesis of new materials with novel or useful properties is one of the most important drivers in the fields of condensed matter physics and materials science. Discoveries of this kind are especially significant when they point to promising future basic research and applications. van der Waals bonded materials comprised of lower-dimensional building blocks have been shown to exhibit emergent properties when isolated in an atomically thin form [1–8]. Here, we report the discovery of a transition metal chalcogenide in a heretofore unknown segmented linear chain form, where basic building blocks each consisting of two hafnium atoms and nine tellurium atoms (Hf2Te9) are van der Waals bonded end to end. First-principle calculations based on density functional theory reveal striking crystal-symmetry-related features in the electronic structure of the segmented chain, including giant spin splitting and nontrivial topological phases of selected energy band states. Atomic-resolution scanning transmission electron microscopy reveals single segmented Hf2Te9 chains within the hollow cores of carbon nanotubes, with a structure consistent with theoretical predictions. van der Waals bonded segmented linear chain transition metal chalcogenide materials could open up new opportunities in low-dimensional, gate-tunable, magnetic, and topological crystalline systems.

Introduction.—The isolation of single layers of van der Waals (vdW) bonded sheetlike materials has launched a new era of two-dimensional (2D) materials exploration, with the discovery of intriguing physical phenomena such as the fractional quantum Hall effect in graphene [1] and an indirect-to-direct band-gap transition for monolayers of the transition metal dichalcogenide MoS2 [2]. Recently, chain-like transition metal trichalcogenides have been examined at the one-dimensional (1D) limit inside carbon or boron nitride nanotubes, with, for example, charge-induced torsional waves appearing in single-chain NbSe3 [3].

Here, we investigate the transition metal chalcogenide (TMC) hafnium telluride (Hf-Te). Bulk HfTe3 is a semi-metal comprised of 2D layers with vdW bonds between layers [7,9], while bulk HfTe3 is a metal composed of 1D trigonal prismatic chains with vdW bonds between the chains [10,11]. Isolation of a monolayer of HfTe2 shows flattening of the valence band [7], while encapsulation of chains of HfTe3 within carbon nanotubes (CNTs) results in a size-driven metal-insulator transition as the chain number passes from 4 to 3 [4]. A single chain of HfTe3 encapsulated within a CNT supports a short-wavelength trigonal antiprismatic rocking distortion that drives a significant energy gap, but the chain is otherwise structurally robust [4].

We show here that an entirely new low-dimensional form of Hf-Te is possible. The new form consists of structurally coherent zero-dimensional “blocks,” each comprised of two Hf atoms and nine Te atoms (i.e., Hf2Te9), arranged end to end in a segmented linear chain, with vdW bonds linking the blocks or chain segments. The segmented chain resides inside the hollow core of a CNT, which protects the chain from oxidation and facilitates experimental characterization. First-principles calculations reveal an especially rich electronic structure for the segmented chain. The bands near the chemical potential are fully spin polarized in one direction and k-dependent giant spin splitting of the bands occurs due to one mirror symmetry which is broken by crystal momentum k and another mirror symmetry which is preserved for all k. Calculated Zak phases of the bands suggest externally tunable topological invariance.

Structural characterization.—Segmented chain Hf2Te9 specimens are synthesized using a method similar to that as described previously for the preparation of few-chain HfTe3 [4]. Briefly, end-opened multiwall carbon nanotubes are reacted together with Hf powder and Te shot, with...
FIG. 1. The linear segmented chain of Hf$_2$Te$_9$. (a) Aberration-corrected HAADF STEM image of a segmented chain of Hf$_2$Te$_9$ encapsulated within a double-walled CNT. A false color [Fire in the Look up Table (LUT) of ImageJ] is applied to visually aid the analysis. The structure consists of regularly spaced segments of Hf$_2$Te$_9$ (or Te$_3$-Hf-Te$_3$-Hf-Te$_3$). (b),(c) Atomic structure of the linear segmented chain of Hf$_2$Te$_9$ obtained from DFT calculations. (b) The obtained atomic structure of the segmented chain inside an (8,8) single-wall CNT is shown, where Hf and Te atoms are represented as red and blue spheres, respectively, and the chain direction is set to the $z$ direction. (c) The building block of a Hf$_2$Te$_9$ unit is shown without a CNT for clearer presentation of the atomic structure, in which the mirror planes perpendicular to $y$ and $z$ axes are represented by white dashed lines and denoted as $M_y$ and $M_z$, respectively. (d) Multislice simulated STEM image of a segment using the proposed atomic structure. (e) A composite STEM image generated from averaging experimentally collected 227 orientationally similar single segments (average cell).

iodine ($I_2$) as a transport agent, in a sealed ampule at 575 °C (see Supplemental Material [12] for details).

Figure 1 shows a structural characterization of a segmented Hf$_2$Te$_9$ chain encapsulated within a CNT. Figure 1(a) shows an atomic-resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image of the chain. The inner diameter of the CNT host [not easily visible in Fig. 1(a)] is 1.1 nm. The chain is clearly and strikingly segmented into regularly spaced blocks, each with distinct substructure. Almost all (>95%) of the blocks imaged contain two bright spots in the center, suggestive of transition metal atoms, surrounded by a handful of dimmer spots, suggestive of chalcogen atoms.

To aid in the identification of the precise atomic structure of the blocks, we perform density functional theory (DFT) calculations. Several candidate structures of the segmented chain with various chemical formulas isolated in a vacuum region of 50 Å × 50 Å perpendicular to the chain are constructed, and the atomic positions of the candidate structures are fully relaxed by minimizing the total energy. Using the relaxed atomic positions of the segmented chain isolated in the vacuum and those of a pristine (8,8) CNT (with inner diameter 1.1 nm), we construct the atomic structure of the segmented chain inside the (8,8) CNT. The atomic positions of the segmented chain are relaxed further by minimizing the total energy, while those of the CNT are fixed. The encapsulation does not alter the atomic structure of the segmented chain appreciably. Among all of the candidate structures investigated, only one relaxed structure, with a chemical formula of Hf$_2$Te$_9$, matches well with the experimental data.

Figures 1(b) and 1(c) show the theoretically predicted structure of the segmented chain encapsulated inside the (8,8) CNT. Figure 1(b) shows the segmented chain together with the CNT, while Fig. 1(c) shows the detailed structure of a single block (see Supplemental Material [12], Fig. S1, as well). The length of a block is 7.89 Å, and blocks are separated by 3.65 Å. The block atomic structure has two mirror symmetries, and the mirror planes perpendicular to the $y$ and $z$ axis are, respectively, denoted as $M_y$ and $M_z$ in Fig. 1(c). Each block has two Hf atoms and nine Te atoms, with the sequence Te$_3$-Hf-Te$_3$-Hf-Te$_3$ along the chain ($z$) direction. As shown additionally in Supplemental Material [12], Fig. S1, the adjacent three Te atoms form isosceles triangles. The isosceles triangle at the center of the block is on the mirror plane $M_z$, perpendicular to the chain direction, while those on the sides of the block cant toward the center of the block. Each Hf atom is surrounded by six Te atoms, forming a trigonal prismatic structure (Supplemental Material [12], Fig. S1), notably unlike the single-chain HfTe$_3$, which prefers a trigonal antiprismatic form [4]. (More details about the atomic structure models and symmetry are presented in Supplemental Material [12], Fig. S1.)

To further validate the proposed block atomic structure, we simulate a block STEM image, as shown in Fig. 1(d). To compare this prediction to experimental STEM data, we first generate a composite STEM image by averaging 227 orientationally similar experimental STEM single-block images, as shown in Fig. 1(e). Comparison of Figs. 1(d) and 1(e), as well as the dimensions of a block and the separation gap, shows good agreement between the theory and experiment. We have also performed electron energy loss spectroscopy (EELS) on segmented chain samples (see Supplemental Material [12]). The Te $M$ edges of the EELS spectra are consistent with the atomic structure shown in Fig. 1(c). We note that previous studies have shown that CNTs can be filled by pure metals and pure chalcogens. We have performed control experiments and found no evidence for segmented chain structure within CNTs using only Hf, only Te, or only $I_2$ as feedstock.

Electronic structure.—We investigate the electronic structure of the segmented Hf$_2$Te$_9$ chain by DFT calculations. Because of the presence of the mirror symmetry with respect to the $M_y$ plane [Fig. 1(c) and Supplemental Material [12], Fig. S1(b)], which is not broken by the crystal momentum $\mathbf{k}$, the $x$ and $z$ components of spin and orbital angular momentum (OAM) with respect to the...
atom positions on the plane should be zero regardless of \( k \) [21]. However, the crystal momentum \( k \) breaks the mirror symmetry with respect to the \( M_z \) plane, and the energy eigenstates are not the eigenstates of \( M_z \), so the \( y \) component of the OAM of the states can have a finite value except for the time reversal invariant momentum points, the center, and the edge of the Brillouin zone (\( k = 0, \pi / a \), where \( a \) is the unit cell length).

Figures 2(a) and 2(d) show the electronic band structure of the segmented chain isolated in a vacuum obtained without considering spin-orbit interaction (SOI). The bands in Fig. 2(d) are colored with the expectation value of the \( y \) component of OAM \( \langle L_y \rangle \) \( \text{in (d)} \) and spin \( \langle S_y \rangle \) \( \text{in (e)} \). In (a)–(f), the chemical potential is set to zero and marked with a horizontal dashed line.

transition metal dichalcogenides [22,23]. The calculated band gap is 100.3 meV, and the states near the chemical potential mostly derive from Te atoms, as shown in Figs. 2(c) and 2(f).

Figure 3 shows the calculated atomic and electronic structures of the segmented chain encapsulated inside an (8,8) CNT. The encapsulation does not alter the electronic structure of the segmented chain significantly except for the band repulsion at \( \sim 0.3 \) eV above the Fermi energy. The states near the chemical potential remain fully spin polarized in the \( y \) direction, and the energy difference between the top of the highest occupied band and the bottom of the lowest unoccupied band remains at \( \sim 100 \) meV, similar to that of the chain isolated in a vacuum. No appreciable covalent bonding between the chain and CNT is found. Mölliken charge analysis [24] reveals that the amount of charge transferred from the CNT to the segmented chain is 0.118 \( e / \text{Hf}_2\text{Te}_9 \) formula unit (f.u.), where \( e \) is the electron charge. The binding energy of the chain, \( E_b \), is calculated to be 3.32 eV/f.u., which is defined as \( E_b = E_{\text{Hf}_2\text{Te}_9} + E_{\text{CNT}} - E_{\text{Hf}_2\text{Te}_9/\text{CNT}} \), where \( E_{\text{Hf}_2\text{Te}_9}, E_{\text{CNT}}, \) and \( E_{\text{Hf}_2\text{Te}_9/\text{CNT}} \) are the total energies of the segmented chain isolated in a vacuum, an empty CNT, and the
Topological properties.—We now consider the topological properties of the segmented chain. Because of the presence of time-reversal symmetry and mirror symmetry with respect to \( M_x \), the Zak phase of the \( n \)th band, \( \gamma_n \), is quantized to 0 or \( \pi \) (mod \( 2\pi \)) [25], corresponding to a topologically trivial or nontrivial band, respectively. The symmetry-protected topological invariance \( Z_2 \) can be obtained by \( (-1)^{Z_2} = e^{i\sum_{\gamma_n} \gamma_n} = e^{2\pi i P^I/e} \), where the sum of the Zak phase is over the occupied bands in only one channel \( \{u_{nk}\} \) out of two time-reversal channels \( \{u'_{nk}\} \), \( s = I \) and II, and \( P^I \) is the partial polarization over channel I [26,27]. Since the sum of the Zak phase over one channel is nothing but the partial polarization of the channel, the \( Z_2 \) invariance can be obtained alternatively by \( Z_2 = 2P^I/e = Q \mod 2 \), where \( Q \) is the end charge of the finite-length chain [27,28].

We find that the topological invariance \( Z_2 \) of the segmented chain can be tuned by doping as shown in Fig. 4. As shown in Figs. 4(a) and 4(b), in the neutral state \( Z_2 = 0 \) for the infinite length Hf\(_9\)Te\(_9\) segmented chain, meaning the chain is a trivial insulator. We construct a finite length chain (\( \sim 15 \) nm) and calculate the end charge \( Q \) (see Supplemental Material [12]); here \( Q = 0 \), confirming the topological trivialness of the undoped material [27,28]. On the other hand, the highest occupied band is nontrivial and well separated from other bands as shown in Fig. 4(b). Therefore, if the system is hole doped (\( h \) doped) so that the chemical potential lies between the energy levels of the highest and the second-highest occupied band as illustrated in Figs. 4(c) and 4(d), it becomes a topological mirror insulator, provided that the Zak phases of the bands remain unchanged and that Hamiltonian of the \( h \)-doped system may be obtained adiabatically from the neutral chain without closing the band gap. That is, the number of nontrivial occupied bands in one channel changes from even to odd, and the sum of the Zak phase of the \( h \)-doped chain in one channel differs from that of a neutral chain by \( \pi \), owing to the emptying out of the nontrivial highest occupied band. Hence, upon doping, \( Z_2 \) changes from 0 to 1, meaning the segmented chain experiences a transition from a trivial insulator to a topological mirror insulator.

We verify this topological richness with an explicit calculation of \( Z_2 \) invariance for an \( h \)-doped chain as shown in Figs. 4(c) and 4(d) (see Supplemental Material [12] as well). To simulate the hole-doped system, we subtract \( 2e/\text{f.u.} \) from the neutral system in the DFT calculation. With the subtracted number of electrons, the topological invariance is \( Z_2 = 1 \), and the end charge of the finite length chain (\( \sim 15 \) nm) is \( Q = 3e \). Many studies for related systems have shown that the chemical potential can be readily altered by chemical doping [29–31], electrostatic gating [6,32,33], or application of pressure [34]. This suggests that the segmented chain Hf\(_9\)Te\(_9\) represents a versatile, highly unusual, and externally tunable topological material. We note that the Hf\(_9\)Te\(_9\) segmented chain is, to our knowledge, the first example of a vdW-bonded crystalline material with spatial-symmetry topological invariants [35,36]. Our discovery thus expands the class of realized topological states of matter.

Conclusion.—In conclusion, a TMC-based, vdW-bonded segmented linear chain Hf\(_9\)Te\(_9\) material has been synthesized within a protective CNT cage and its structure determined via STEM analysis and complementary DFT calculations. Theory also reveals giant spin splitting and crystal-symmetry-protected topological properties, which are promising for applications such as spintronic nanodevices and topological transistors. The segmented linear chain is a realization of a TMC in the quasi-0D limit, where 0D blocks are vdW end-to-end bonded in a linear chain. This quasi-0D material completes the family of dimensionally reduced TMCs, where bulk MX\(_2\) compounds are typically quasi-2D and MX\(_3\) compounds are typically quasi-1D (\( M = \) transition metal and \( X = \) chalcogen).
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The authors declare no competing interests.


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