1D topological phases in transition-metal monochalcogenide nanowires†

Kyung-Hwan Jin a,b,c and Feng Liu c

The Su–Schrieffer–Heeger (SSH) model is a prototypical one-dimensional (1D) diatomic lattice model for non-trivial topological phases and topological excitations. Theoretically, many variations and extensions of the SSH model have been proposed and explored to better understand the novel aspects of topological physics in low dimensions on the nanoscale. However, the outstanding challenge remains to find real nanomaterials with robust structural stability for realizing the 1D topological states. Here, we develop an extended version of the SSH model with multi-atomic bases of four, six and eight atoms and an imposed screw rotation symmetry. Furthermore, based on first-principles calculations, we demonstrate the realization of this model in transition metal monochalcogenide $M_6X_6$ ($M = Mo$ and $W$; $X = S$, $Se$ and $Te$) nanowires. The topological features of the doped $M_6X_6$ nanowires are confirmed with non-trivial edge modes and $e/2$ fractional charges, representative of the 1D non-trivial Zak phase. Our finding not only sheds new light on our fundamental understanding of 1D topological physics, but also significantly extends the scope of 1D topological materials that will attract immediate experimental interest, since isolated $M_6X_6$ nanowires have already been synthesized in experiments.

Introduction

The concept of topological order in condensed matter physics provides a new theme for understanding the origin of various quantum phases and has promoted intense recent interest in searching for nontrivial topological materials. The topological phase is characterized by global properties rather than a local order, making it very robust against local perturbations; this topological robustness makes emergent topological excitations a promising candidate for quantum computing and devices. Since the discovery of topological phases in the 1980s, comprehensive theoretical and experimental studies have been carried out to create, classify, and comprehend these exotic phases. Among the wide variety of topological models, the Su–Schrieffer–Heeger (SSH) model1 serves as a paradigmatic model in describing the band topology. The SSH model describes spin-less fermions hopping on a one-dimensional (1D) lattice with staggered hopping amplitudes. The Zak phase, i.e., Berry phase in 1D, is used to classify two topologically distinct phases in the SSH model. The topological feature is characterized with zero energy states and fractionalized charges at the end of the non-trivial phase or domain walls between the two phases.3,4

One outstanding challenge is to realize 1D topological phases in nanomaterials with robust structural stability. 1D topological phases have been demonstrated in recent experiments, using optical lattice,5 cold atom6 or artificial lattice7 systems. But the electronic material platform for the SSH model is very rare. So far, the observation of increased conductivity due to solitons in polyacetylene1–8 and the chiral solitons in indium wires self-assembled on the Si (111) surface9 has been considered indicative of the 1D topological origin. However, polyacetylene is a polymer with weak structural stability, rendering the measurement of topological edge mode difficult. Indium wires are formed on a substrate corresponding to a quasi 1D structure due to its interaction with the surface. Therefore, it is highly desirable to find an isolated 1D system with strong structural stability for the realization of topological properties.

1D metallic transition metal monochalcogenide (TMM) nanowires, $M_6X_6$ [$M = Mo$ and $W$; $X = S$, $Se$ and $Te$], have shown structures and intrinsic anisotropic metallic properties as promising candidates for nanodevices. They have been theoretically studied10–13 and successfully synthesized both in isolated as
well as crystal (bundle) forms.\textsuperscript{14,21} For example, an isolated, nanometer-long M\textsubscript{6}X\textsubscript{6} nanowire has been fabricated using electron-beam irradiation methods.\textsuperscript{17,18} Isolated Mo\textsubscript{6}Te\textsubscript{6} nanowires encapsulated in carbon nanotubes were also synthesized.\textsuperscript{21} The fascinating properties of these single TMM nanowires are strong structural stability with a small diameter of about \(\sim 9\) Å and their tunable electronic properties by doping.\textsuperscript{11,12,22,23}

Here, we demonstrate that the TMM nanowires offer an attractive new route to realizing 1D topological phases. We first develop an extended version of the SSH model with multi-atomic bases. A Dirac state at the zone-boundary is induced by using bases of four, six and eight atoms, instead of two atoms, and by imposing screw rotation symmetry along the axis of the 1D system. Considering the dimerization due to the Peierls instability, a topological gap is opened at the Dirac point, leading to non-trivial edge modes at the boundary. Furthermore, based on first-principles calculation, we demonstrate the topological phase in the M\textsubscript{6}X\textsubscript{6} nanowires and real materials to be represented by our extended SSH model with a six-atom basis. By doping the 1D TMM nanowires with Re (Cl, Br and I) atoms for transition metal (chalcogenide) atoms, the Dirac state can be adjusted as to the Fermi level, and meanwhile a Peierls distortion is induced. The resulting topological phase in the doped M\textsubscript{6}X\textsubscript{6} nanowires is confirmed with non-trivial edge modes and e/2 factional charges.

**Methods**

Structural and electronic properties of TMM nanowires are computed using the DFT scheme implemented in the Vienna \textit{ab initio} simulation package (VASP) code.\textsuperscript{24} The projector-augmented-wave method is used to describe the ionic core-valence electron interactions.\textsuperscript{25} The generalized gradient approximation (GGA) is employed to describe the exchange and correlation potential.\textsuperscript{26} Spin-orbit coupling is included in all electronic structure calculations. Electronic wave functions are expanded in plane waves with an energy cutoff of 500 eV. To describe isolated nanowires when using periodic boundary conditions, we arranged the nanowires with a large interwire separation of 20 Å. Geometries are optimized until the forces on each atom are less than 0.01 eV Å\textsuperscript{-1}. We used a \(1 \times 1 \times 15\) \(k\)-point grid to sample the 1D Brillouin zone. An electronic-temperature smearing of 0.02 eV was employed for the occupation of the electronic states. We constructed Wannier representations by projecting the Bloch states from the first-principles bands of TMM nanowires onto M d and X p orbitals.\textsuperscript{27} Based on Wannier representations, we further calculated the Zak phase and the edge states of a semi-infinite system for topological properties.\textsuperscript{28,29}

**Results and discussion**

Let’s begin with the well-known SSH model in its simplest form [Fig. 1(a)]. It consists of a chain of equally spaced atoms with an s or p\textsubscript{z} orbital. Considering the Peierls paring distortion, a topological phase transition occurs by tuning the ratio between inter- and intra-cell electron hoppings. If inter-cell hoppings are larger than the intra-cell hoppings, the Zak phase emerges and edge states appear as a consequence of bulk-edge correspondence.\textsuperscript{20,31} Now, we replace each atom with a molecule, such as a H\textsubscript{2} molecule or molecules with a ring configuration [Fig. 1(b)–(d)]. Specifically, in Fig. 1(b), the two atoms in the molecule are arranged in orientations perpendicular to each other, so that the whole system has time-reversal symmetry \(T\) and screw rotation symmetry \(S_z = \{C_{4z}\} 0,0,1/2\}; the latter combines a fourfold rotation and a half-lattice translation along the \(z\) axis. Similarly, for the other chain structures in Fig. 1(c) and (d), the screw rotation symmetry is \(\{C_{6z}\} 0,0,1/2\} and \(\{C_{8z}\} 0,0,1/2\}, respectively. The Hamiltonian of these chain structures with multi-atom bases is given as follows:

\[
H = \sum_{\langle ij \rangle} t_{ij} c_i^\dagger c_j + t_m \sum_{\langle ij \rangle} c_i^\dagger c_j + \text{h.c.},
\]

where \(c_i^\dagger(c_j)\) is the creation (annihilation) operator of the \(i\)-th atom. The first term represents the inter molecular hopping along the chain direction (\(z\)-direction) with the hopping parameter \(t_{ij}\). There are two types of hopping along the \(z\)-direction, \(i.e., t_{ij} = t + \delta\) and \(t_{ij} = t - \delta\) to account for the Peierls distortion. The second term represents the intra hopping within the molecule, and \([i,j]\) represents the hopping sites.

The energy spectra of the chain configurations in Fig. 1(a)–(d) are displayed in Fig. 1(e). Without dimerization, there are Dirac bands (dashed lines) crossing at the zone boundary \(k_z = \pi/a\), where \(a\) is the lattice period along the \(z\)-direction. Since the \(T\) commutes with \(S_z\), \([T, S_z] = 0\), it ensures the twofold band degeneracy, \(i.e.,\) stability of the Dirac point at the \(k_z = \pi/a\)
point. When the Peierls distortion is included, this degeneracy is lifted to open a trivial or nontrivial gap depending on the sign of $\delta$ (or unit cell construction). The topological properties of 1D systems are characterized by the so-called Zak phase, i.e., the Berry phase picked up by a particle moving across the Brillouin zone. The Zak phase has been shown to be related to polarization.\(^2\) The Zak phase of the nth band $\gamma_n$ is integral over the Brillouin zone (BZ) of the Berry connection:

$$\gamma_n = \int_{G/2}^{G/2} \langle \hat{u}_{nk} | \partial_k | \hat{u}_{nk} \rangle dk,$$

where $\hat{u}_{nk}$ is the periodic part of the Bloch function of the nth band with the momentum $k$, and $G = 2\pi/a$ is the reciprocal lattice vector. The total Zak phase, $\varphi_{Zak}$, for a given 1D insulator is the sum of $\gamma_n$ over the occupied bands, i.e., $\varphi_{Zak} = \Sigma \gamma_n$. Once we obtain $\hat{u}_{nk}$ from first-principles calculation or tight-binding model Hamiltonians, we can evaluate $\varphi_{Zak}$ by numerically integrating the Berry connection over the 1D BZ (see ESI\(^\dagger\)).

Topological edge modes with fractional charge is one of the key signatures of the non-trivial Zak phase. Fig. 2(a) shows the two distinct Zak phases of the SSH model with a six-atom basis for the opposite sign of $\delta$. If the strong bond is inside the unit cell (phase A), the system is trivial ($\varphi_{Zak} = 0$). If the strong bond is located between the unit cells (phase B), it is a topological phase ($\varphi_{Zak} = \pi$). Fig. 2(b) and (c) show the calculated energy states of finite chains for phases A and B, respectively. The finite chain is constructed by 20 times the unit cell. For the trivial phase, there are no zero-energy edge states in the bulk gap. In contrast topological edge states marked as red dots appear in the topological gap, which are characterized by the $\pi$ Zak phase accompanying a fractional charge $e/2$ at the end of the chain. Furthermore, the topological domain-wall states appear between phase A and phase B (see ESI Fig. S1\(^\dagger\)). Therefore, these results demonstrate that the extended SSH model can indeed exhibit a topological state. Other multi-atom-based models also show topological edge modes in the bulk gap (see Fig. S2–S4\(^\dagger\)).

Next, we demonstrate a real material system to realize the newly developed extended 1D SSH model. The 1D topological material should meet the following conditions: (i) An alternating arrangement of the molecular structure with screw rotation symmetry; (ii) A Dirac point is isolated from other bands and located at the Fermi level. Specifically, we narrow down our search to transition-metal monochalcogenides (TMMs), which have a common formula $M_nX_6$, where $M$ is a transition metal atom (Mo and W) and X is a chalcogen atom (S, Se, and Te). As illustrated in Fig. 3(a), $M_nX_6$ nanowires are 1D materials composed of alternately stacked $M_nX_6$ triangles along the wire axis, with three capping X atoms located at the vertices of the triangles and three $\gamma$-M atoms located between the X atoms. The structure contains the screw rotation symmetry $S_6 = \{C_6, 0, 0, 1/2\}$. Thus, their structure satisfies the first condition. Their optimized lattice parameters are presented in Table 1, consistent with previous works.\(^{10,13,17,21}\)

Fig. 3(b) and (c) show the calculated band structures of $M_nX_6$ nanowires. $M_6S_6$ and $M_6Se_6$ nanowires show a metallic character, whereas $M_6Te_6$ is insulating. The metal–insulator transition can be explained by the TB model. In eqn (1), there are two hopping parameters: one is the inter-molecular hopping $t$ and the other is the intra-molecular hopping $t_\gamma$. If $t > t_\gamma/2$, the 1D system is metallic, while if $t < t_\gamma/2$, the system turns to be insulating. As the halogen atomic mass increases, $t$ is decreased, turning metallic bands into the insulating state (see ESI Fig. S5\(^\dagger\)). All the bands near the Fermi level are contributed from the $d$ orbitals of the transition-metal (Mo or W) atoms. Interestingly, all the $M_6X_6$ nanowires have a hole-doped Dirac band, with the Dirac point at the zone boundary ($k_z = \pi/a$) point located above the Fermi level $\sim 1$ eV. These Dirac states mainly originate from $d_{xz}$ and $d_{yz}$ orbitals of transition-metal atoms [see the left panel of Fig. 3(b)]. The Dirac state has a Fermi velocity ($v_F$) of about $4.6-4.8 \times 10^5$ m s$^{-1}$ and $5.3-6.0 \times 10^5$ m s$^{-1}$ for $M_6X_6$ and $W_6X_6$ nanowires, respectively (Table 1), which is comparable to that of graphene\(^{15}\) and edge states of quantum spin Hall insulators.\(^{34-36}\)
To realize the topological phase, the Dirac point needs to be moved to the Fermi level, in order to meet the second condition. Then, the band will be half-filled and $2k_F$ phonons of the 1D lattice will be condensed to induce a lattice distortion with a period $\lambda = 1/2k_F$, known as the Peierls instability.\(^\text{37}\) In doing so, the electrons gain energy via dimerization that opens a gap at the Dirac point. Therefore, electron doping is needed, specifically two electrons per unit cell, since there are two degenerate bands in between the Fermi level and Dirac point gap. This can be achieved by using a Re atom as an electron donor to substitute $1/3$ of transition metal atoms. It is worth noting that the Re-doped 2D transition metal dichalcogenides (TMDs) such as MX\(_2\) (MoS\(_2\), MoSe\(_2\), etc.) have been successfully synthesized by a facile hydrothermal reaction and an annealing process.\(^\text{38–42}\) Also it is reported that doping of TMDs with elements from Groups V–VII energetically favors substitutional doping instead of dopants occupying interstitial or defect sites.\(^\text{38}\) To test the feasibility of the electron doping, we have replaced one of the transition metal atoms in the stacked M\(_2\)X\(_3\) triangles with a Re atom to form M\(_4\)Re\(_2\)X\(_6\). Then, one may consider the reaction energy $\Delta H$ of the substitution reaction

$$\text{Mo}_6\text{X}_6 + \frac{x}{2} \text{Re}_2 \rightarrow \text{Mo}_{6-x}\text{Re}_x\text{X}_6 + \frac{x}{2} \text{M}_2,$$

(3)

The reaction energies of all the checked M\(_4\)Re\(_2\)X\(_6\) nanowires are presented in Table 1. Clearly, the desired reaction is exothermic for $x = 2$, confirming its feasibility. Moreover, it is reported that Mo\(_6\)X\(_6\) with $x = 2$ are particularly stable and rigid with the metallic linear band.\(^\text{11}\) A separate use of the doped M\(_4\)Re\(_2\)X\(_6\) nanowires as a building block for device application is its 1D Dirac state with good conductance [see Fig. 3(a) and ESI Fig. S6†]. All doped-TMD nanowires are metallic with a constant density of states near the Fermi level; we can observe quantized conductance in the transport measurement.

![Fig. 3](image)

**Table 1** Optimized lattice parameters [\(a\) and \(h\) are marked in Fig. 3(a) in the unit of Å] of TMD nanowires, Fermi velocity \(v_F\) in the unit of \(10^5\) m s\(^{-1}\), band gaps \(E_g\) in the unit of eV, and the reaction energies \(\Delta H\) in the unit of eV of Re-doped TMD nanowires

<table>
<thead>
<tr>
<th>Material</th>
<th>(a)</th>
<th>(a_{\text{exp}})</th>
<th>(H)</th>
<th>(v_F)</th>
<th>(E_g)</th>
<th>(\Delta H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(_6)S(_6)</td>
<td>4.35</td>
<td>4.5(^a)</td>
<td>4.30</td>
<td>4.81</td>
<td>0.19</td>
<td>-1.39</td>
</tr>
<tr>
<td>Mo(_6)Se(_6)</td>
<td>4.44</td>
<td>4.5(^a)</td>
<td>4.53</td>
<td>4.62</td>
<td>0.20</td>
<td>-1.42</td>
</tr>
<tr>
<td>Mo(_6)Te(_6)</td>
<td>4.58</td>
<td>4.8(^b)</td>
<td>4.87</td>
<td>4.59</td>
<td>0.16</td>
<td>-1.36</td>
</tr>
<tr>
<td>W(_6)S(_6)</td>
<td>4.37</td>
<td>4.4(^a)</td>
<td>4.35</td>
<td>5.99</td>
<td>0.18</td>
<td>-0.81</td>
</tr>
<tr>
<td>W(_6)Se(_6)</td>
<td>4.46</td>
<td>—</td>
<td>4.59</td>
<td>5.73</td>
<td>0.18</td>
<td>-0.87</td>
</tr>
<tr>
<td>W(_6)Te(_6)</td>
<td>4.56</td>
<td>—</td>
<td>4.95</td>
<td>5.26</td>
<td>0.01</td>
<td>-0.72</td>
</tr>
</tbody>
</table>

\(^a\) From ref. 17. \(^b\) From ref. 21.
Therefore the two different gaps. We constructed a finite size of Mo₄Re₂S₆ nanowires. Zak phase is the emergence of the zero-energy modes in the bulk state. We have evaluated the electronic/topological properties of the TMM nanowires. We also studied the effect of uniaxial strain on the electronic/topological properties of the TMM nanowires. For 1D TMM nanowires, one may wonder if the correlation effect of d electrons of transition metal elements would influence the topological properties. So we have investigated the correlation effects of d electrons in Mo₆S₆ and Mo₄Re₂S₆ by employing the GGA + U approach (with the onsite Hubbard U term). Using different U values from 0 to 4 eV for Mo and Re atoms, we found that both systems remain in the nonmagnetic ground state and their nontrivial topological properties persist.

Finally, we extend our discussion to the experimental feasibility of topological modes in 1D TMM nanowires. The Re doped MₓX₆ nanowire is described by Peierls-dimerized chains with two degenerate ground phases, i.e., A and B phases, which would appear with equal probability. Therefore, one may expect that upon the phase transition, the dimers will form along the chain direction with both phases present and naturally there will be domain walls (stacking faults) in between two different phases. These topological boundary modes can be mobile, but are occasionally trapped by struc-
tural defects or impurities. Consequently, the oppositely charged topological end modes, as trapped by defects, experience Coulomb attraction, which would shrink the size of a trapped soliton significantly. The topological boundary or end modes trapped by defects can be resolved through STM and STS measurements.

Conclusions

In conclusion, an extended 1D SSH model is theoretically developed and used to elucidate the 1D topological phase in transition metal monochalcogenide nanowires, as predicted by first-principles calculations of the non-trivial Zak phase and in-gap topological edge states. Because the transition metal monochalcogenide nanowires have already been synthesized in experiments, we envision that our results will draw immediate experimental attention to detect the exotic 1D topological states in real materials. Moreover, other promising material platforms might be searched for based on the newly developed extended 1D SSH model, such as van der Waals-wired materials and group-IV metal chalcogenide nanowires.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

KJ acknowledges the support from Korea Research Fellowship Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT [Grant No. 2019H1D3A1A01071056] and the Institute for Basic Science (Grant No. IBS-R014-Y1). F. Liu acknowledges financial support from DOE-BES (No. DE-FG02-04ER46148).

References