The topological insulator (TI) state, discovered fairly recently, is a new state of condensed matter.\(^1\)\textsuperscript{–7} It is characterized by the combination of an insulating bulk state and a quantized helical conducting edge state, which exhibits an intriguing quantum spin Hall (QSH) effect. The helical state provides an intrinsic spin lock localized at the edge and is robust against elastic backscattering, so it is ideal for various applications that require dissipationless spin transport.\(^6\)\textsuperscript{,7} Although the QSH state was first predicted in graphene, which is an ideal two-dimensional (2D) material, it is difficult to observe the QSH effect in graphene due to the weak intrinsic spin–orbit coupling (SOC).\(^8\)\textsuperscript{–10} In contrast, significant progress in the investigation of TIs in experiments has been made in quantum wells,\(^4\)\textsuperscript{,5,11,12\textsuperscript{) and three-dimensional (3D) TIs.}\(^13\)\textsuperscript{–16\textsuperscript{) However, transport properties in 3D TIs are more difficult to control than those in 2D TIs, due to the gapless side surface states in 3D TIs. Therefore, 2D TIs are more promising for practical applications, since quantized helical states only exist at the edges.

Many possible 2D TIs have been predicted in theory recently,\(^17\)\textsuperscript{–20\textsuperscript{) but most predicted 2D TIs must be decorated by anion atoms (such as H and the halogen elements) and kept away from the substrate. Freestanding 2D TIs are ideal, but they are difficult to grow in experiments. For example, freestanding honeycomb silicene was predicted to be a TI with a nontrivial gap of 1.55 meV, but honeycomb silicene has been fabricated only on some transition-metal surfaces, such as Ag(111) and Ir(111).\(^21\)\textsuperscript{–23\textsuperscript{) Unfortunately, there is no evidence yet that the honeycomb silicene on these transition-metal surfaces preserves the QSH state. Furthermore, large TI gaps are desired for possible applications of 2D TIs at room temperature. Therefore, it is urgent and important to search for 2D TIs that not only have large TI gaps but are also feasible to fabricate.

Recently, 2D transition-metal dichalcogenide (TMD) monolayers have attracted great attention, because they exhibit versatile electronic properties yet are chemically and physically stable.\(^24\)\textsuperscript{,25\textsuperscript{) Most importantly, 2D TMD monolayers can be obtained easily either through exfoliation of bulk materials or through bottom-up syntheses.\(^26\)\textsuperscript{,27\textsuperscript{) In this family, 2D Mo and W dichalcogenide monolayers—MoX\(_2\) and WX\(_2\) (X = S, Se or Te)—are semiconductors with sizable band gaps \(~\sim 1\) eV and fascinating valleytronic characteristics.\(^28\) Interestingly, QSH states were predicted in 2D MoX\(_2\) and WX\(_2\) monolayers either with structural distortion\(^29\) or in metastable phase.\(^30\) These studies provide new opportunities to explore the QSH effect in semiconducting 2D materials.

Alloying with exotic elements in semiconductors has been demonstrated as an effective method to engineer their electronic properties,\(^31\)\textsuperscript{–34\textsuperscript{) which may induce intriguing physical and chemical features such as dilute magnetism\(^32\) or adjustable SOC strength.\(^33\) Therefore, it is possible to produce QSH states in 2D MoX\(_2\) and WX\(_2\) by alloying. Meanwhile, QSH states are closely associated with the strength of SOC; hence strong SOC is desired to achieve large TI gaps. In this study, we investigated the electronic properties of 2D MoX\(_2\) and WX\(_2\) monolayers alloyed with 5d transition-metal elements, through first-principles calculations and tight-binding simulations. We found that Os is a good candidate for turning MoX\(_2\) and WX\(_2\) into TIs, with nontrivial band gaps ranging from 5.3 meV to 32.3 meV. Moreover, the TI gaps can be tuned by external strain.

The structural and electronic properties were calculated according to density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package.\(^35\)\textsuperscript{,36\textsuperscript{) The interaction between valence electrons and ionic cores was described within the framework of the projector augmented-wave method.\(^37\)\textsuperscript{,38\textsuperscript{) The generalized gradient approximation (GGA) was used for the exchange–correlation potentials and the SOC effect was invoked self-consistently.\(^39\) The energy cutoff for the plane wave basis expansion was set to 500 eV. A \(2 \times 2\) supercell was employed and the 2D Brillouin zone was sampled by a \(27 \times 27\) k-grid mesh. The atomic positions were fully relaxed with a criterion that required the forces on each atom to be lower than 0.01 eV Å\(^{-1}\). The band topology was characterized by the topological invariant \(Z_2\), with \(Z_2 = 1\) for TIs and \(Z_2 = 0\) for ordinary insulators.\(^40\) We adopted the so-called \(n\)-field scheme to calculate \(Z_2\).\(^41\)\textsuperscript{–43\textsuperscript{) In addition, the band structure of a one-dimensional (1D) nanoribbon of a 2D TI exhibits edge bands within its nontrivial gap. We used the Wannier90 code\(^44\) to obtain the hopping parameters and the tight-binding model developed by Ref.\(^45\) to calculate the band structures of the 1D nanoribbons.

We first optimized the lattice constants and calculated the band structures of the Mo and W dichalcogenide monolayers. As listed in Table 1, the lattice constants are slightly larger than their bulk counterparts\(^24\) but in agreement with previous calculations.\(^46\) In addition, they increase as the anion changes from S to Te owing to the increasing atomic radii of the anions. However, the lattice constants do not differ visibly for MoX\(_2\) and WX\(_2\) monolayers with the same anion element. On the other hand, all MoX\(_2\) and WX\(_2\) monolayers...
are semiconductors with sizable band gaps \(E_g\) as seen in Table I. The gaps undergo an indirect-to-direct transition from the bulk to the monolayer and are enlarged due to quantum confinement in the monolayer.\(^{24,26}\) In addition, the calculated gaps are smaller than the experimental values. For instance, the calculated \(E_g\) of the MoS\(_2\) monolayer is 1.59 eV, while the experimental value is 1.8 eV.\(^{26}\) This is caused by the well-known problem of DFT calculations usually underestimating the band gaps of semiconductors. Nevertheless, the band structure plotted in Fig. 1(a) captures the main electronic feature of the MoS\(_2\) monolayer, that is, the MoS\(_2\) monolayer is a direct-band-gap semiconductor with the valence band maximum (VBM) and conduction band minimum (CBM) located at the K point. Moreover, the SOC effect results in the splitting of the valence bands around the K point as well as around the \(-K\) point. Owing to the time reversal symmetry, the splitting leads to a fascinating valley Hall effect known as valleytronics in these monolayers.\(^{28}\)

It has been proven that doping or alloying with other transition-metal elements in MoS\(_2\) is an effective way to engineer electronic properties.\(^{33,34}27\) Therefore, we choose MoS\(_2\) as a prototype to investigate the effect of alloying with 5d transition-metal elements on the electronic structures. One of the Mo atoms in a \(2 \times 2\) supercell is replaced by a 5d transition-metal atom, resulting in an alloyed compound with concentrations of Mo and the incorporated 5d transition-metal element of 75% and 25%, respectively, as shown in Fig. 1(b). We consider a series of 5d transition-metal elements from Ta to Ir and that alloying with W does not lead to visible change of the band structures, because MoS\(_2\) and WS\(_2\) have almost the same atomic structures and close band structures.\(^{33,34}\) Alloying with Ta, Re and Ir results in metallic properties. Interestingly, MoS\(_2\) alloyed with Os (notated as Mo\(_{0.75}\)Os\(_{0.25}\)S\(_2\)) shows an SOC-induced band gap near the middle point of the path from \(\Gamma\) to \(K\), which is commonly a signature of QSH states. Accordingly, we focus on Os-alloyed compounds in the following.

The optimized lattice constant of the Mo\(_{0.75}\)Os\(_{0.25}\)S\(_2\) alloy is listed in Table II, which expands by 1.9% compared to that of MoS\(_2\) due to the larger atomic size of Os than Mo's. To reveal the electronic properties of this alloy, we plot the atom- and orbital-resolved band structures in Fig. 2. From Fig. 2(a), it can be seen that the Os atom hybridizes strongly with the host MoS\(_2\), which induces two bands \("I" and "II"") in the gap of MoS\(_2\). Without including the SOC effect, these bands are degenerate at the \(\Gamma\) point and retain atomic orbital character as represented by the corresponding local charge density in the inset of Fig. 2. Clearly, the charge density has local \(C_3\) symmetry around the Os atoms and characterizes apparent in-plane components of the d orbitals (i.e. \(d_{xy}\) and \(d_{z^2-\gamma^2}\)) of the Mo and Os atoms. Note that the charge density around the Os atom has a round shape, mainly due to the large sizes of the \(d_{xy}\) and \(d_{z^2-\gamma^2}\) orbitals which hybridize strongly with the S atoms. Accordingly, we sort the d orbitals into three groups: (i) \(d_{z^2}\); (ii) \(d_{xz}\) and \(d_{yz}\); and (iii) \(d_{xy}\) and \(d_{z^2-\gamma^2}\). From the projections of these orbitals on the electronic bands in Figs. 2(b) and 2(c), we can see that the energy level at the \(E_F\) of the \(\Gamma\) point originates from the \(d_{xy}\) \(d_{z^2-\gamma^2}\) orbitals of both Mo and Os atoms and the weight of the Os atom is significantly larger than that of the Mo atom. As the bands propagate from the \(\Gamma\) point to the \(M\) or \(K\) point, the degeneracy at the \(\Gamma\) point breaks and the energy level evolves into two bands (notated as \"I\" and \"II\") in Fig. 2(c)]. Band I goes downwards, with the weight of the \(d_{xy}/d_{z^2-\gamma^2}\) orbitals decreasing and the weight of the \(d_{z^2}\) orbital increasing. Finally, band I near the \(K\) point is contributed only by the \(d_{z^2}\) orbital, and the weight of the Os atom is slightly larger than that of the Mo atom. Band II goes upwards and keeps the pure \(d_{xy}/d_{z^2-\gamma^2}\) state of the Os atom. For the \(d_{xz/yz}\) orbitals, those of the Os atom contribute to the bands \(\sim 0.5\) eV above \(E_F\), while those of the Mo atom do not have a notable contribution to the bands within the energy range in Fig. 2(b).

When the SOC effect is included, the degeneracy of bands I and II at the \(\Gamma\) point is removed with a large splitting of 0.45 eV, as shown in Fig. 2(d). Each of these bands further splits into two bands along the path of \(\Gamma - K - M\). Interestingly, band I-2 goes upwards faster than band I-1 from \(K\) to \(\Gamma\), so it crosses \(E_F\). Meanwhile, band II-2 goes downwards and crosses \(E_F\) at the same \(k\) point. As a

---

**Table I.** The lattice constants \((a, \text{in } \text{Å})\) and band gaps \((E_g, \text{in eV})\) of MX\(_2\) \((M = \text{Mo, W}; X = \text{S, Se, Te})\) monolayers. SOC is involved.

|     | Mo   | W       |
|-----|------|---------|
|     | S    | Se      | Te     | S    | Se      | Te     |
| \(a\) | 3.19 | 3.33    | 3.56   | 3.19 | 3.33    | 3.56   |
| \(E_g\) | 1.59 | 1.31    | 0.94   | 1.53 | 1.24    | 0.75   |

---

**Table II.** Properties of Mo\(_{0.75}\)Os\(_{0.25}\)X\(_2\) \((M = \text{Mo, W}; X = \text{S, Se, Te})\) monolayers: lattice constants \((a, \text{in } \text{Å})\), global and direct band gaps \((E_g\) and \(E_{ig}\), in eV), \(Z_2\) invariant, and formation energy \((\text{in } \text{eV}; \Delta H = E(\text{Alloy}) - \mu_\text{Mo} - E(\text{MX}) + \mu_\text{X}, \text{where } \mu \text{ stands for the chemical potential})\). SOC is involved.

|     | Mo   | W       |
|-----|------|---------|
|     | S    | Se      | Te     | S    | Se      | Te     |
| \(a\) | 6.50 | 6.78    | 7.27   | 6.48 | 6.78    | 7.26   |
| \(E_g\) | 32.3 | 31.8    | 25.4   | 29.6 | 8.8     | 5.3    |
| \(Z_2\) | 1    | 1   | 1     | 3.55 | 2.85    | 1.55   |
| \(\Delta H\) | 3.53 | 2.98    | 2.02   | 3.55 | 2.85    | 1.55   |
invariant of the other cases is also 1, as invariant. So we calculate point. Second, it = of the Mo0.75Os0.25 level. (a,d) Projection on Os and MoS2. The color bar represents the weight (c) and with (d) Projection on Os 5d orbitals. For simplicity, the of the Os atom and the host MoS2. (b,e) Projection on Mo 4d orbitals. (c,f) the Brillouin zone marked by shading.

II-2, i.e. the consequence, band inversion occurs between bands I-2 and II-2, i.e. the d_{3z^2} and d_{3z^2-r^2} orbitals, which is a signature of the nontrivial topological phase in this material.4 Thus, bands I-2 and II-2 interact with each other through the SOC Hamiltonian, yielding a nontrivial band gap of 37.4 eV. Note that the actual CBM [i.e. the minimum of bands II-1 and II-2 as seen in Fig. 2(f)] is located at the K point rather than the crossing point, which suggests that the global gap of Mo0.75Os0.25S2 is actually an indirect band gap with a smaller amplitude of 32.3 eV. It is well known that GGA calculations usually underestimate the band gaps of semiconductors, but hybrid functionals such as the Heyd–Scuseria–Ernzerhof (HSE) functional45 can predict more accurate band gaps. Indeed, our HSE calculations for Mo0.75Os0.25S2 show that the nontrivial band gap can be as large as 116 meV. Furthermore, the E_F is located in this SOC-induced gap. Accordingly, we can conclude that the Mo0.75Os0.25S2 alloy is a natural TI which does not require the gate voltage to adjust the E_F. This is a good feature for both experimental investigations and practical applications.

For MoSe2 and MoTe2, alloying with Os also leads to lattice expansion as listed in Table II similar to MoS2. The band structures before and after including the SOC effect are plotted in Fig. 3. Clearly, the SOC has two effects on the electronic band structures. First, it eliminates the degeneracy of the two bands beside the E_F at the Γ point. Second, it induces band inversion when the bands propagate from Γ to K for both Mo0.75Os0.25Se2 and Mo0.75Os0.25Te2, which results in nontrivial band gaps of 31.8 and 25.4 meV, respectively. Note that both gaps are direct band gaps, with the VBM and CBM at the same K point in the Brillouin zone. The band structures of W0.75Os0.25X2 are similar to those of Mo0.75Os0.25Te2. However, the II-1 band of both W0.75Os0.25S2 and W0.75Os0.25Se2 decreases significantly and crosses E_F, which turns the alloys metallic. In contrast, W0.75Os0.25Te2 still possesses a nontrivial band gap of 5.3 meV. Furthermore, the direct band gap at the band inversion point between the I-2 and II-2 bands still follows the same trend as those of Mo0.75Os0.25X2, as listed in Table II.

The electronic band topology can be characterized by the Z_2 invariant. So we calculate Z_2 of the Mo0.75Os0.25Se2 alloy with the n-field method.41–43 By counting the positive and negative n-field numbers over half of the torus as indicated in the inset in Fig. 2, we obtain Z_2 = 1 for the Mo0.75Os0.25S2 alloy, clearly demonstrating a nontrivial band topology. Similarly, the Z_2 invariant of the other cases is also 1, as listed in Table II. On the other hand, the TIs also manifest quantized edge states, which bring about the QSH effect.6,7 Therefore, we calculate the band structure of 1D nanoribbons of Mo0.75Os0.25X2 with zigzag edges. The nanoribbons consist of 60 cells and the outermost three cells are treated as the edge region. Figures 4(a) and 4(b) display the edge density of states of a 1D Mo0.75Os0.25Se2 nanoribbon. Apparently, there are linearly dispersive bands in the gap of 2D Mo0.75Os0.25Se2, and they are contributed by either the left edge or the right edge. In addition, the bands from the two edges are different, because one edge ends with Se atoms and the other edge with Mo/Os atoms. To determine how widely the edge bands are distributed, we project the wavefunctions of the edge bands (marked “A” and “B”) on each cell and plot the weights in Fig. 4(c). Clearly, the edge bands mainly localize within the outermost three cells and decay to zero until the 30th cell. Furthermore, the edge bands...
supercell (Color online) Nontrivial direct band gaps as a function of biaxial strain for Mo0.75Os0.25Te2. (a) Density of states of left and right edges, respectively. (c) Weight of each supercell (wsc) from one edge to the other (labeled from 1 to 60) for the wavefunctions of the states marked “A” and “B” in (a) and (b).

Fig. 4. (Color online) Edge states of the 1D Mo0.75Os0.25Se2 nanoribbon. (a,b) Density of states of left and right edges, respectively. (c) Weight of each supercell (wsc) from one edge to the other (labeled from 1 to 60) for the wavefunctions of the states marked “A” and “B” in (a) and (b).

Fig. 5. (Color online) Nontrivial direct band gaps as a function of biaxial strain for Mo0.75Os0.25X2 (X = S, Se and Te). The open square and circle indicate the indirect band gaps, which are smaller than the direct band gaps. The dashed lines denote that the systems become metallic. The inset shows the schematic band evolutions under compressive and extensile strains.

between 0 and π are from the majority spin channel, while the edge bands between π and 2π are from the minority spin channel. Therefore, there are two types of electrons with opposite spins on each edge and they are propagating along opposite directions, which are the main features of the QSH effect.

From Table II, we can see that the direct band gaps of both Mo0.75Os0.25X2 and W0.75Os0.25X2 decrease as the atomic sizes of the anions increase. This is because when the Os–X bond lengths increase, the interaction between bands I-2 and II-2 [Fig. 2(f)] weakens. Therefore, the band gap may be engineered by external strain, as indicated by the inset in Fig. 5. We calculate the band structures of Mo0.75Os0.25X2 alloys under biaxial strain from −2% to 4% and find that the bands near the direct gaps indeed undergo similar evolutions as indicated in the inset in Fig. 5. As plotted in Fig. 5, the nontrivial direct band gaps decrease slightly under extensile strain but increase significantly under compressive strain. For Mo0.75Os0.25S2, compressive strain leads to metallic electronic properties, because the II-1 band decreases significantly and crosses EF. For Mo0.75Os0.25Se2, a compressive strain of −1% turns the gap into an indirect band gap (33.2 meV), slightly larger than that without strain. When compressive strain increases to −2%, Mo0.75Os0.25Se2 becomes metallic. The band gap of Mo0.75Os0.25Te2 remains direct under compressive strain up to −2% and increases to 42.6 meV, 1.7 times as large as that without strain (25.4 meV). Therefore, compressive strain is an effective way to engineer a nontrivial band gap for Mo0.75Os0.25Te2.

Besides the electronic properties, structural stability is an important issue for the practical fabrication of Mo0.75Os0.25X2 and W0.75Os0.25X2 alloys, which can be estimated by calculating the formation energy (ΔHf). As listed in Table II, the formation energies of all the considered cases are positive and decrease from S to Te for both MoX2 and WX2. Therefore, these alloys could not be produced in equilibrium growth conditions. Nevertheless, the amplitudes of the formation energies are relatively small, especially for Mo0.75Os0.25Te2 and W0.75Os0.25Te2 (2.02 and 1.55 eV, respectively), so the alloys may be obtained with delicate non-equilibrium growth conditions. In fact, non-equilibrium growth processes are widely used to fabricate metastable states of materials.49,50

In summary, we predicted that alloying 2D MoX2 and WX2 monolayers with Os leads to a semiconductor-to-TI transition and produces sizable nontrivial band gaps of 5.3–32.3 meV, based on systematic first-principles calculations and tight-binding modeling. In these alloys, band inversion occurs between the dz2 and dyz2−xz2 orbitals of the Os atom caused by the SOC effect, which plays the most important role in the QSH state. Interestingly, the TI gaps can be tuned by external biaxial strain. In particular, the TI gap of Mo0.75Os0.25Te2 can be enhanced to 42.6 meV with compressive biaxial strain of −2%. It is worth pointing out that the band gaps are largely underestimated by GGA calculations, e.g. the nontrivial band gap of Mo0.75Os0.25S2 is 116 meV from HSE calculation, considerably larger than 32.3 meV (GGA). 2D MoX2 and WX2 monolayers have been successfully fabricated in experiments, which means our study has paved the way for engineering QSH states in 2D semiconductors.

Acknowledgments This work is supported by the National Natural Science Foundation of China (11574223), the Natural Science Foundation of Jiangsu Province (BK20150303) and the Jiangsu Specially-Appointed Professor Program of Jiangsu Province.

1) C. L. Kane and E. J. Mele, Phys. Rev. Lett. 95, 146802 (2005).
2) C. L. Kane and E. J. Mele, Phys. Rev. Lett. 95, 226801 (2005).
3) B. A. Bernevig and S. C. Zhang, Phys. Rev. Lett. 96, 106802 (2006).
4) B. A. Bernevig, T. L. Hughes, and S. C. Zhang, Science 314, 1757 (2006).
5) M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L. W. Molenkamp, X. L. Qi, and S. C. Zhang, Science 318, 766 (2007).
6) M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. 82, 3045 (2010).
7) X. L. Qi and S. C. Zhang, Rev. Mod. Phys. 83, 1057 (2011).
8) C. Weeks, J. Hu, J. Alicea, M. Franz, and R. Q. Wu, Phys. Rev. X 1, 021001 (2011).
9) J. Hu, J. Alicea, R. Q. Wu, and M. Franz, Phys. Rev. Lett. 109, 266801 (2012).
10) J. Hu, Z. Y. Zhu, and R. Q. Wu, Nano Lett. 15, 2074 (2015).
11) C. Liu, T. L. Hughes, X. L. Qi, K. Wang, and S. C. Zhang, Phys. Rev. Lett. 100, 236601 (2008).
12) I. Knez, R. R. Du, and G. Sullivan, Phys. Rev. Lett. 107, 136603 (2011).
13) L. Fu and C. L. Kane, Phys. Rev. B 76, 045302 (2007).
14) D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature 452, 970 (2008).
15) J. Hu, Z. Y. Zhu, and R. Q. Wu, Nano Lett. 15, 2074 (2015).
16) C. Liu, T. L. Hughes, X. L. Qi, K. Wang, and S. C. Zhang, Phys. Rev. X 1, 021001 (2011).
17) J. Hu, Z. Y. Zhu, and R. Q. Wu, Nano Lett. 15, 2074 (2015).
18) J. Hu, Y. N. Zhang, M. Law, and R. Q. Wu, J. Am. Chem. Soc. 134, 13216 (2012).
19) J. Hu, Z. Y. Zhu, W. B. Mi, Z. B. Guo, and U. Schwingenschlögl, Phys. Rev. B 87, 100401 (2013).
20) H. M. Weng, X. Dai, and Z. Fang, Phys. Rev. X 4, 011002 (2014).
21) P. Vogt, P. D. Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, and G. L. Lay, Phys. Rev. Lett. 108, 155501 (2012).
22) L. Meng et al., Nano Lett. 13, 685 (2013).
23) Q. H. Wang, K. Kalantar-Zadeh, J. N. Coleman, and M. S. Strano, Nat. Nanotech. 7, 699 (2012).
24) M. Chhowalla, H. S. Shin, G. Eda, L. J. Li, K. P. Loh, and H. Zhang, Nat. Chem. 5, 263 (2013).
25) K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105, 136805 (2010).
26) K. K. Liu et al., Nano Lett. 12, 1538 (2012).