Topological semimetals are one of the fast growing families in the frontier of material sciences and condensed matter physics due to their unique density of states, transport properties and novel topological surface states as well as potential applications for use in quantum computers and spintronics. To date, it is well-known that topological semimetals highlight several main types of interesting fermions in crystal solids, such as three-dimensional (3D) Dirac fermions, Weyl fermions, Dirac nodal lines and triply degenerate nodal points have been theoretically predicted and then experimentally discovered in the electronic structures of a series of solid crystals. In analogy of various typical fermions, topological mechanical states with two type of bosons, Dirac and Weyl bosons, were also experimentally reported in some macroscopic systems of kHz frequency and with a type of doubly-Weyl phonons in atomic vibrational framework of THz frequency of solid crystal was also recently predicted. However, to date no triply degenerate nodal point of phonon beyond the conventional Dirac, Weyl and doubly-Weyl phonons has been reported. Here, through first-principles calculations, we have reported on the prediction that the WC-type TiS, ZrSe, and HfTe commonly host the unique triply degenerate nodal point of phonon in THz frequency due to the occurrence of the phonon band inversion between the doubly degenerate planar vibrational mode and the singlet vertical vibrational mode at the boundary A point of the bulk Brillouin zone. Quasiparticle excitations near this triply degenerate nodal point of phonons are three-component bosons, different from the known classifications. The underlying mechanism can be attributed to the leading role of the comparable atomic masses of constituent elements in compounds in competition with the interatomic interaction. Additionally, the electronic structures in their bulk crystals exhibit the coexisted triply degenerate nodal point and Weyl fermions. The novel coexistence of three-component bosons, three-component fermions and Weyl fermions in these materials thus suggest an enriched platform for studying the interplay between different types of fermions and bosons.

Recently, the type of WC-type materials (Fig. 1a), including ZrTe, TaN, MoP and WC has been theoretically reported to host the coexistence of triply degenerate nodal points (TDNs) of electronic fermion and Weyl points (WPs) around the Fermi level. Interestingly, this type of coexisted fermions of TDNs and WPs have been recently confirmed in MoP. Within this context, here we further extend this family by proposing eight compounds (TiS, TiSe, TiTe, ZrS, ZrSe, HfS, HfSe and HfTe), which are isostructural to ZrTe. Among these eight compounds, four compounds of TiS, ZrS, ZrSe, and HfS, HfSe and HfTe, which are isostructural to ZrTe. Among these eight compounds, four compounds of TiS, ZrS, ZrSe, and HfS, HfSe and HfTe, which are isostructural to ZrTe. Among these eight compounds, four compounds of TiS, ZrS, ZrSe, and HfS, HfSe and HfTe, which are isostructural to ZrTe.
experimental data as shown in Table S1 (supplementary materials). Their enthalpies of formation are derived in supplementary Table S1, indicating their stabilities in the thermodynamic and their phonon dispersions have no any imaginary frequencies, revealing the stabilities in the atomic mechanical vibrations.

We have first elucidated the electronic band structures of these nine compounds. Interestingly, their electronic structures are in similarity to the case of ZrTe in Ref. 59. We have selected ZrSe as a prototypical example to show the crucial feature of electronic structures (details refer to Fig. S1-S3 in supplementary materials). Without the spin-orbit coupling (SOC) effect the two main features can be observed: In the first, a Dirac nodal line (DNL as marked in Fig. 1(c)) denoted by the Wilson loop method88 of electrons around the Fermi level when SOC is ignored. With the SOC inclusion each DNL is broken into two Weyl points with the opposite chirality, marked as blue (WP-) and red (WP+) balls and they coexist with the triply degenerate nodal point (TDNP) of electronic structure (namely, three-component fermion). Panel (d) shows the triply degenerate nodal point (TDNP) of phonon dispersions (namely, three-component boson) along the Γ-A direction.

FIG. 1: WC-type crystal structure of MX ($M = Ti$, Zr, Hf; $X = S$, Se, Te), crystallizing in the simple hexagonal crystal structure with the space group of P6/m2 (No. 187). $M$ occupies the 1a Wyckoff site (0, 0, 0) and $X$ locates at the 4d $(1/3, 2/3, 1/2)$ site. Panel (a) shows the phonon vertical vibrational mode (Mode$_{z}^{\text{mode}}$) along the $k_z$ direction at the boundary (the high-symmetry A (0, 0, $\pi$/2) point) of the Brillouin zone (BZ). Panel (b) denotes the phonon planar vibrational mode (Mode$_{x, y}^{\text{mode}}$) along the $k_x$ direction, which indeed is two-fold degenerate (called Mode$_{x, y}^{\text{mode}} = Mode_{z}^{\text{mode}}$) because of its hexagonal symmetry. Panel (c) The Brillouin zone (BZ) in which the closed loops around each K point denotes the Dirac nodal lines (DNLS) of electrons around the Fermi level when SOC is ignored. With the SOC inclusion each DNL is broken into two Weyl points with the opposite chirality, marked as blue (WP-) and red (WP+) balls and they coexist with the triply degenerate nodal point (TDNP) of electronic structure (namely, three-component fermion). Panel (d) shows the triply degenerate nodal point (TDNP) of phonon dispersions (namely, three-component boson) along the Γ-A direction.

FIG. 2: Electronic structures of ZrSe. Panel (a): band structure without the SOC inclusion shows (i) the band inversion between $d_{z^2}$+$d_{x^2}$ and $d_{z^2}$+$d_{x^2}$+$d_{xy}$ at K and (ii) the band inversion between $d_{z^2}$ and $d_{x^2}$+$d_{xy}$ orbitals at A. Panel (b): Electronic band structure with the SOC inclusion. Panel (c) show the zoom-in visualization of two TDNP1 and TDNP2 along the Γ-A direction in panel (b), whereas Panel (d) shows the zoom-in bands crossing one WP (0.27314, 0.27314, ±0.01628) around the Fermi level with the SOC inclusion.
electronic features, including those coexisted TDNPs and WPs in their electronic structures of bulk phases. Because of the highly weak SOC effect in TiS, it is highly unique with the coexisted six DNLs and two six-fold degenerate nodal points in its electronic structure, which is exactly what happened for other eight compounds when the SOC effect is ignored.

Besides their coexisted TDNPs and WPs in their electronic structures, we have further found that the presence of the triply degenerate nodal points (TDNPs) of phonon in three compounds of TiS, ZrSe and HfTe after a systematic analysis of their phonon dispersions (supplementary Fig. S4). Because each primitive cell contains two atoms (Fig. 1(a)), its phonon dispersion has six vibrational branches consisting of three acoustic and optical ones, respectively. As compared with the computed phonon dispersions in Fig. 3(a, b, and c) and their phonon densities of states in Fig. 3(d, e, and f) of the isoelectronic ZrS, ZrSe and ZrTe compounds, it can be clearly seen that a well-separated acoustic-optical gap can be clearly observed in both ZrS and ZrTe with their smallest direct gap at the A point (0, 0, π/2) on the boundary of the BZ. The specified analysis uncovered that for both ZrS and ZrTe compounds the top phonon band of the gap at the A point is comprised with the doubly degenerate vibrational mode of phonons in which both Zr and S (or Te) atoms, oppositely and collinearly, displace along either x or y direction (Mode_{\tau z} as marked in Fig. 1(b)). The vibrational amplitude of the Mode_{\tau z} are contributed nearly 100% by the Zr atom, rather than S (or Te) atoms. The bottom phonon band of the gap at the A point is a singlet state originated from the vertical vibration mode at which both Zr and S (or Te) atoms collinearly move in the same k direction (Mode_{\perp} as marked in Fig. 1(a)). But its amplitude of this Mode_{\perp} are almost fully dominated by the displacement of S (or Te) atoms.

In contrast to both ZrS and ZrTe in Fig. 3 the case of ZrSe shows no acoustic-optical gap (Fig. 3(b)), as illustrated by its phonon density of states in Fig. 3(e)). It has been noted that the planar Mode_{\tau z} at the A point becomes now lower in frequency than the vertical Mode_{\perp}. Accordingly, this fact corresponds to the occurrence of so-called phonon band inversion at the A point, indicating its non-trivial topological mechanical property in ZrSe. It means the unusual fact that around A point the optical phonon bands inverts below the acoustic band which normally should have a lower frequency. Physically, within the (quasi)harmonic approximation the vibrational frequency, \( \omega \), have to be proportional to \( \beta/m \) at the boundary of the BZ. Here, \( \beta \) is the second-order force constant - the second derivative of the energy following a given vibrational mode as a function of the displacement and \( m \) the atomic mass. Therefore, as seen in Fig. 3(b) for ZrSe the occurrence of the phonon band inversion at the boundary A point is certainly induced by both \( \beta \) and \( m \) which are both determined by the planar Mode_{\tau z} and the vertical Mode_{\perp} at the A point. Following this consideration, we have defined the dimensionless ratio \( \tau \) as follows,

\[
\tau = \frac{\beta_{\perp}m}{\beta_{\parallel}m_{\perp}}.
\]

where \( \tau \) indeed specifies the comparison between the frequencies of both Mode_{\tau z} and Mode_{\perp}. With \( \tau > 1 \) the material shows no band inversion, thereby being a trivial vibrational mechanical state, whereas \( \tau < 1 \) implies the topological non-trivial mechanical states exist due to the appearance of the phonon band inversion. If \( \tau \approx 1 \), the targeted material would locate at the phase boundary between trivial and non-trivial mechanical states. With such a definition, we further plot the \( \beta \) in Fig. 4(a) in the sequence of ZrS, ZrSe and ZrTe. It has been found that, only with the second-order force constants of \( \beta_{\parallel} \) and \( \beta_{\perp} \) (Fig. 4(a)) it is not enough to induce the phonon band inversion. This fact is in agreement with the Equ. (1) although the \( \beta_{\parallel} - \beta_{\perp} \) difference is the smallest in ZrSe among these three cases in Fig. 4(a). In further combination
with their atomic masses, the topological non-trivial mechanical property occurs for ZrSe because its \( \tau \) value is now 0.68, smaller than 1. Similar analysis has been performed for the trivial cases of both ZrS and ZrTe which all have a \( \tau \) value to be larger than 1, in agreement with no phonon band inversion. Furthermore, for all nine compounds in this family we compiled their \( \tau \) values as a function of the ratio \( \delta \) of the atomic masses related with \( \text{Mode}^{x,y} \) over \( \text{Mode}^z \) (namely, \( \delta = m(\text{Mode}^{x,y})/m(\text{Mode}^z) \)) in Fig. 4(b). With increasing the ratio of the atomic masses, the \( \tau \) value increases in a nearly linearity. This implies that if atomic masses in a targeted material highly differ its possibility to become topological non-trivial mechanical property is extremely low. However, if they have the comparable atomic mass with the \( \delta \) ratio close to 1 the possibility with the non-trivial topological property is high. Following this model, we have further uncovered that, because the \( \tau \) value is smaller than 1, both TiS and HfTe have topological non-trivial mechanical property as what ZrSe does (Fig. 4(b)). The findings for both TiS and HfTe are in accordance with the DFT-derived phonon dispersions in supplementary Fig. S4. However, the mechanical properties of other members in this family are trivial. These facts imply that in these materials the difference between the atomic masses of constituents in compound play a key role in inducing the phonon band inversion, as seen for three non-trivial cases of TiS, ZrSe and HfTe whose \( \delta \) value are all around 1.

![FIG. 4: Panel (a): DFT-derived second-order force constant at the A point for both the two-fold degenerate planar vibrational Mode\(^{x,y}\) and the vertical vibrational Mode\(^z\). Panel (b): The derived parameter \( \tau \) from Eqn. (1) as a function of the \( \delta \) value, as defined in the main text, for all nine compounds.](image)

Importantly, as accompanying with the occurrence of the phonon band inversion the TDNPs, featured by a linear crossing of the frequencies between the acoustic and optical bands, unavoidably appears at \( (0, 0, k_z = \pm 0.40769) \) along the \( \Gamma-A \) direction in the BZ (Fig. 4(b)) for ZrSe. It implies that at this phonon TDNP the planar Mode\(^{x,y}\) and the vertical Mode\(^z\) at \( (0, 0, k_z = \pm 0.40769) \) strictly have the same frequency of 183.9 \( \text{cm}^{-1} \). The TDNP locates at \( (0, 0, k_z = \pm 0.40382) \) with 293.4 \( \text{cm}^{-1} \) for TiS and at \( (0, 0, k_z = \pm 0.43045) \) with 133.3 \( \text{cm}^{-1} \) for HfTe. To elucidate the 3D TDNP shape of ZrSe, we also plotted the zoom-in dispersions within both \( k_y = 0 \) and \( k_y = 0 \) planes of BZ in Fig. 5.

![FIG. 5: Panels (a and b): DFT-derived phonon dispersions to elucidate phonon TDNPs of ZrSe along the \( X1 (-\pi/2, 0, 0) \) to \( X2 (\pi/2, 0, 0) \) and \( \Gamma-A \) directions, respectively. Panels (c and d): Zoom-in 3D visualization of phonon TDNPs in the \( k_z = 0 \) and \( k_y = 0 \) planes, respectively.](image)

From both Fig. 5(a) and (c) in the \( k_z = 0 \) the TDNP of phonon can be clearly visualized to have an isotropic shape. However, in the \( k_y = 0 \) plane the phonon bands around the TDNP are highly complex with the helicoid shape (Fig. 5(b) and (d)). Therefore, the topological surface states related to this TDNP of phonon may not be observed, since it indeed does not leave a bulk gap when projected onto any open surface.

Summarizing, through first-principles calculations we have discovered three WC-type materials of TiS, ZrSe and HfTe not only host three-component bosons featured by triply degenerate nodal points in its mechanical phonon dispersions but also exhibits three-component fermions feature by triply degenerated nodal points and six pairs of two-component Weyl fermions with opposite chirality in its electronic structures of the bulk crystal. Surprisingly, the novel coexistence of the main features of (i) three-component bosons, (ii) three-component fermions, and (iii) two-component Weyl fermions and, in particular, both three-component bosons and three-component fermions locate at the nearly same momentum (Fig. 5(c) and (d)) along the \( \Gamma-A \) direction could couple to each other through electron-phonon interactions, which would provide a wonderful platform to study the interplays between different types of topological electron excitations and topological phonons within the atomic scale for potential multi-functionality quantum-mechanical properties.

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Methods

Within the framework of the density functional theory (DFT) and the density functional perturbation theory (DFPT), we have performed the calculations on the structural optimization, the electronic band structures, the phonon calculations and surface electronic band structures. Both DFT and DFPT calculations have been performed by employing the Vienna ab initio Simulation Package (VASP) [99,102], with the projector augmented wave (PAW) pseudopotential [95,96] and the generalized gradient approximation (GGA) within the Perdew-Burke-Emrzerhof (PBE) exchange-correlation functional. The adopted PAW-PBE pseudopotentials of all elements treat semi-core valence electrons as valence electrons. A very accurate optimization of structural parameters have been calculated by minimizing the interionic forces below 0.0001 eV/Å. The cut-off energy for the expansion of the wave function into the plane waves was 500 eV. The Brillouin zone integrations were performed on the Monkhorst-Pack k-meshes (21×21×23) and were sampled with a resolution of 2π × 0.014Å⁻¹. The band structures, either with or without the inclusion of spin-orbit coupling (SOC), have been performed by the Gaussian smearing method with a width of smearing at 0.01 eV. Furthermore, the tight-binding (TB) through Green’s function methodology [97,99] were used to investigate the surface states. We have calculated the Hamiltonian of tight-binding (TB) approach through maximally-localized Wannier functions (MLWFs) [100,101] by using the Wannier 90 code [102].

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Supplementary Materials

1. **Table S1**: optimized lattice parameters of $MX$

2. **Figure S1**: Evolution of the electronic structure around the Weyl points (WPs) in ZrSe

3. **Figure S2**: Surface electronic band structures of (0001) and (1010) surfaces of ZrSe

4. **Figure S3**: Fermi surfaces of the (0001) and (10\bar{1}0) surfaces of ZrSe

5. **Figure S4**: DFT-derived phonon dispersions of the nine $MX$ compounds

### A. Supplementary Table S1

We have optimized the lattice structures of nine $MX$ compounds with the WC-type structure. Table S1 summarizes all optimized lattice constants as compared with the available experimental data. Among these nine compounds, five compounds of TiS, ZrS, ZrSe$_{0.90}$, ZrTe$_{0.92}$, and Hf$_{0.92}$Se$_{0.90}$ as well as ZrTe were experimentally reported to have the same WC-type structure\cite{80–87}. Because of no any experimental data available for the remaining four compounds of TiSe, TiTe, HfS, and HfTe, here we have assumed that they also crystallize in the same WC-type structure. For five experimentally known compounds TiS, ZrS, ZrSe, ZrTe and HfSe, our DFT calculations yield the good agreement of their equilibrium lattice parameters with the experimental data as shown in Table S1. Furthermore, their enthalpies of formation are derived in Table S1, indicating their stabilities in the thermodynamics.

### B. Electronic band structures

To elucidate the electronic band structure of these compounds, we have first repeated the calculations of ZrTe and obtained the electronic band structures are very similar to the reported data in Ref. [59], indicating the reliability of our current calculations. Remarkably, the derived electronic band structures of other compounds in this family are all similar to that of ZrTe.

The evolution of the derived electronic band structures around one of WPs for ZrSe is illustrated in supplementary Fig. S1(a,b,c) and it can be clearly seen that the WP appears around the Fermi level in supplementary Fig. S1c. The topological invariant can be identified using the so-called Wilson loop method\cite{88}. As shown in supplementary Fig. S1(d and e), the calculated evolution of the Wannier centers formed along the $k_z$ direction in the two $k_y = 0$ and $\pi$ planes. It can be seen that the $Z_2$ numbers (namely, counting the times of Wannier center crosses a reference line) of both these planes are odd, indicating their topological non-trivial feature.

To further clarify the topological feature in ZrSe, we have calculated the surface electronic structures on its (0001) and (10\bar{1}0) surfaces (see supplementary Fig. S2), clearly indicating the topological surface states. In addition, we also plot the Fermi surface of both surfaces in supplementary Fig. S3.

### Table 1: (Supplementary Table S1)

| Compound | $a$ (Å) | $c$ (Å) | $\Delta H$ (eV/atom) |
|----------|---------|---------|----------------------|
| TiS      | 3.287   | 3.210   | -1.50                |
| TiSe     | 3.419   | 3.402   | -1.28                |
| ZrS      | 3.446   | 3.445   | -0.64                |
| ZrSe     | 3.551   | 3.615   | -0.91                |
| ZrTe     | 3.670   | 3.860   | -1.49                |
| HfS      | 3.395   | 3.447   | -0.92                |
| HfSe     | 3.4958  | 3.6069  | -1.32                |
| HfTe     | 3.739   | 3.885   | -0.68                |

| Compound | $a$ (Å) | $c$ (Å) | $\Delta H$ (eV/atom) |
|----------|---------|---------|----------------------|
| TiS      | 3.267   | 3.223   | -1.50                |
| TiSe     | 3.460   | 3.475   | -1.65                |
| ZrS      | 3.464   | 3.475   | -1.65                |
| ZrSe     | 3.584   | 3.649   | -1.49                |
| ZrTe     | 3.696   | 3.860   | -1.32                |
| HfS      | 3.395   | 3.447   | -1.54                |
| HfSe     | 3.5173  | 3.6365  | -1.32                |
| HfTe     | 3.739   | 3.885   | -0.68                |

### FIG. 6: (Supplementary Figure S1)

Electronic band structures around the WP node at $k_z = 0.005$ in panel (a), $0.010$ in panel (b), and $0.01628$ (exactly corresponding to the WP node) in panel (c), respectively. Panels (d and e) denote the derived Wilson loops of ZrSe which show the $k_z$ evaluation of the Berry phases of all occupied bands along the $k_z$ direction in both $k_y = 0$ and $k_y = \pi$ planes, respectively.
tial to 155 meV, the Fermi surface gives rise to the clear visualization of six projected nodes in supplementary Fig. S3(c). In order to visualize the Weyl nodes, we further calculated (10\(\bar{1}0\)) Fermi surface at the energy level of 155 meV above the Fermi level in supplementary Fig. S3(d). On this surface, the six pairs of WPs with opposite chirality are projected to different positions. Two WPs with same chirality are projected to the same point on the (10\(\bar{1}0\)) surface (called WP1) and the projected points of other WPs are labeled as WP2. It can be clearly seen that the projected Weyl points are connected by Fermi arcs. For each WP1 point, there is one arc connecting it by going through the \(\Gamma - \bar{M}\) path, whereas, for each WP2 there are two arcs connecting them in supplementary Fig. S3(d). In addition, on both (0001) and (10\(\bar{1}0\)) surfaces it is impossible to see TDNPs because the projection of TDNPs are all overlapped with bulk electronic bands, as illustrated in Fig. supplementary Fig. S3(c).

Through our calculations the other eight members in this family all exhibit the similar electronic structures with the coexisted TDNPs and WPs in their bulk phases, except for TiS. Because of the weak SOC effect, TiS is highly unique with the coexisted six Dirac nodal lines (DNLs) and two six-degenerated nodal points, which is exactly what happened for ZrSe without the SOC effect.

C. Phonon dispersions of MX

Supplementary Figure S4 compiles the DFT-derived phonon dispersions of all nine MX compounds. Among them, only three compounds of TiS, ZrSe and HfTe exhibit the non-trivial topological phonon states with the appearance of the triply degenerate nodal points (TDNPs as marked in supplementary Figure S4, which refers to three-component bosons.
FIG. 7: (Supplementary Figure S2) Calculated surface electron structures of both (0001) and (10\bar{1}0) surfaces of ZrSe.

FIG. 8: (Supplementary Figure S3) The Fermi surfaces of (0001) (panels: a and c) and (10\bar{1}0) (panels: b and d) surfaces of ZrSe. Panels (a) and (b) denote the Fermi surfaces at the Fermi level, while panels (c) and (d) refer to the Fermi surfaces with a chemical potential of 155 meV above the Fermi level. The solid circles indicate the projected WPs in the (10\bar{1}0) surfaces.
FIG. 9: (Supplementary Figure S4) DFT-derived phonon dispersions of all nine MX compounds with the WC-type structure at their optimized equilibrium lattices.