A Theoretical Investigation on the Physical Properties of Zirconium Trichalcogenides, ZrS₃, ZrSe₃ and ZrTe₃ Monolayers

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Abstract: In a recent advance, zirconium triselenide (ZrSe₃) nanosheets with anisotropic and strain-tunable excitonic response were experimentally fabricated. Motivated by the aforementioned progress, we conduct first-principle calculations to explore the structural, dynamic, Raman response, electronic, single-layer exfoliation energies, and mechanical features of the ZrX₃ (X = S, Se, Te) monolayers. Acquired phonon dispersion relations reveal the dynamical stability of the ZrX₃ (X = S, Se, Te) monolayers. In order to isolate single-layer crystals from bulk counterparts, exfoliation energies of 0.32, 0.37, and 0.4 J/m² are predicted for the isolation of ZrS₃, ZrSe₃, and ZrTe₃ monolayers, which are comparable to those of graphene. ZrS₃ and ZrSe₃ monolayers are found to be indirect gap semiconductors, with HSE06 band gaps of 1.93 and 1.01 eV, whereas the ZrTe₃ monolayer yields a metallic character. It is shown that the ZrX₃ nanosheets are relatively strong, but with highly anisotropic mechanical responses. This work provides a useful vision concerning the critical physical properties of ZrX₃ (X = S, Se, Te) nanosheets.

Keywords: ZrSe₃; electronic; mechanical; exfoliation energy; phonon dispersion

1. Introduction
After the experimental isolation of graphene [1–3] reported in 2004, two-dimensional (2D) nanomaterials have been extending continuously, owing to their exceptional physical and chemical properties. High surface-to-volume ratios in 2D systems can not only evolve to exceptional electronic and optical features, but are also highly appealing for practical chemistry-related applications, such as sensing and energy storage. In recent years, several 2D crystals with interesting physical properties have been fabricated, such as MoS₂N₄ [4,5], fluorinated diamane [6], penta-palladium phosphide selenide (PdPSe) [7], niobium oxide diiodide (NbOΙ₂) [8], penta-palladium phosphide sulfide (PdPS) [9], graphene-like BC₄N [10], and penta-nickel diazenide (NiN₅) [11] nanosheets. Highly bright prospects for the application of 2D nanomaterials in critical technologies and their outstanding physical and chemical features act as a continuous driving force for experimental endeavors to design and fabricate novel crystals. In line with continuous experimental accomplishments in the field of 2D nanomaterials, most recently Li et al. [12] succeeded in the exfoliation of the zirconium triselenide (ZrSe₃) nanosheets. Experimental observations and theoretical calculations confirm highly anisotropic and strain-tunable semiconducting excitonic effects in ZrSe₃ nanosheets [12]. This experimental advance also highlights the appealing possibility of the exfoliation of zirconium trisulfide and tritelluride (ZrS₃ and ZrTe₃)
nanosheets, also with anisotropic and strain-tunable electronic and optical properties. As a novel class of synthesizable 2D materials, which have been already predicted to yield appealing thermoelectricity [13,14], the objective of this study is to theoretically explore the structural, phonon dispersion relations, Raman spectra, single-layer exfoliation energies, and mechanical features of ZrX$_3$ (X = S, Se, Te) nanosheets by employing density functional theory (DFT) calculations.

2. Computational Methods

DFT calculations were carried out using the Vienna Ab-initio Simulation Package [15,16] with the GGA/PBE and DFT-D3 [17] vdW dispersion correction. The plane wave and self-consistent loop cutoff energies were set to 400 and 10$^{-6}$ eV, respectively. In order to find optimized geometries, atomic positions were relaxed using a conjugate gradient algorithm until Hellman–Feynman forces dropped below 0.001 eV/Å [18] with an 11 $\times$ 11 $\times$ 1 and 9 $\times$ 9 $\times$ 5 Monkhorst-Pack [19] K-point grid for the monolayer and bulk systems, respectively. The stress-free structures were acquired by isotropically changing the in-plane lattice dimensions. Periodic boundary conditions were considered in all directions, with a 23 Å box-size along the out-of-plane direction of the monolayers to avoid artificial interactions. Moment tensor potentials (MTPs) [20] were fitted to evaluate the phonon dispersion relations, using the same approach as that employed in our recent work [21]. Phonon dispersions on the basis of trained MTPs were acquired in conjunction with the PHONOPY [22] code over 4 $\times$ 5 $\times$ 1 supercells, as elaborately discussed in our previous work [23]. For the investigation of Raman activities of each phonon mode, firstly, the zone-center phonon vibrations were calculated in terms of the phonon frequencies and the vibrational displacements. For each optical phonon mode, the derivative of the macroscopic dielectric tensor with respect to the normal mode of each vibration was investigated using the finite-difference method.

3. Results and Discussion

Figure 1 depicts different views of the crystal structure of the ZrX$_3$ (X = S, Se, Te) monolayers. According to Figure 1, a ZrX$_3$ monolayer includes a rectangular primitive unit cell with a P21/M (No. 11) space group and highly anisotropic atomic arrangement along the x and y directions. A ZrX$_3$ monolayer can basically be considered laterally aligned (along the x direction) and alternatively inverted triangular prismatic ZrX$_3$ chains, which are connected through Zr-X bonds in the xz plane ($l_{Zr-X}^a$). The inter-chain Zr-X bonds ($l_{Zr-X}^b$) were found to be longer than the Zr-X bonds within the chain ($l_{Zr-X}^c$). This observation was expected to lead to anisotropic mechanical, optical, and electronic properties in the ZrX$_3$ monolayers. Table 1 summarizes the optimized lattice constants, bond lengths, and calculated band gap properties of each ZrX$_3$ monolayer. Our predicted lattice constants for ZrX$_3$ monolayers agree well with previous data: a = 5.138 Å and b = 3.619 Å for ZrS$_3$, a = 5.423 Å and b = 3.745 Å for ZrSe$_3$, and a = 5.942 Å and b = 3.909 Å for ZrTe$_3$ [12]. For the bulk structures the box size along the out-of-plane direction for the ZrS$_3$, ZrSe$_3$, and ZrTe$_3$ monolayers were found to be 9.01, 9.46, and 10.14 Å, respectively, with excellent agreement with corresponding experimental values of 8.98 [24], 9.43 [24], and 10.10 Å [24], respectively. In the Supplementary Materials document, the complete crystal data for the single-layer and bulk ZrX$_3$ systems are given. According to spin-polarized calculations, we found that these systems are not magnetic. Looking carefully to the crystal structure of a ZrX$_3$ monolayer, two different types of X atoms can be identified: surface X atoms, which exist in pairs ($X_2$), and the internal ones, which contribute to the inter-chain binding and only coordinate with the Zr atom. Our calculated bond lengths for $X_2$ were 2.07, 2.38, and 2.83 Å, which are only slightly different than the typical values for single covalent S-S, Se-Se, and Te-Te bonds [25,26]. According to Bader charge analysis, Zr atoms are positively charged and transfer electrons to the surface and internal chalcogen X atoms, indicating that electrostatic interactions play a key role in keeping the structural integrity of ZrX$_3$ monolayers. The amount of charge exchange decreased as the electronegativity of chalcogen
X atoms decreased: 1.77 \( e \) for ZrS\(_3\), 1.61 \( e \) for ZrSe\(_3\), and 1.33 \( e \) for ZrTe\(_3\). Although all chalcogen atoms were negatively charged, it was found that surface X atoms yielded almost twice the charge as those of the internal counterparts. The electron localization pattern along the Zr-X bonds shown in Figure 1b also supports the idea of the dominance of ionic interaction within the ZrX\(_3\) monolayers. The electron localization maps also show the gradual increase in electron localization in between adjacent surface X\(_2\) moieties from ZrS\(_3\) to ZrTe\(_3\) monolayers. For the case of ZrTe\(_3\), an appreciable electron localization was found in between adjacent surface Te\(_2\) moieties (find Figure 1d), indicating interactions between them. It is worth noting that our calculated distance between surface Te\(_2\) moieties in the ZrTe\(_3\) monolayer was 3.05 Å, which is only slightly larger than Te-Te bonds calculated for experimentally synthesized 2D \( \alpha \) and \( \beta \)-Te: 3.02 Å [27]. Therefore, surface Te\(_2\) moieties in the ZrTe\(_3\) monolayer can actually be considered infinite Te\(_2\) chains extended along the \( x \) direction. In other words, by comparing the ELF contours for the over-surface non-bonded X-X bonds, around the center of the Te-Te pairs (Figure 1d), the ELF values were considerably higher than those in the corresponding S-S (Figure 1b) and Se-Se (Figure 1c) pairs, which reveals the formation of stronger Te-Te interactions in the ZrTe\(_3\) monolayer.

![Figure 1](image_url)

**Figure 1.** (a) Crystal structure of the ZrX\(_3\) (X = S, Se, Te) monolayers. The primitive cell, first Brillouin zone, a prismatic chain of ZrX\(_3\) (red dashed-line rectangle), surface X\(_2\) moieties, and Zr-X bonds in \( zx \) and \( zy \) planes (\( l_{\gamma z}, X \), \( l_{\gamma z}, X \) ) are also distinguished. (b–d) Contour maps of electron localization function (ELF) for the ZrX\(_3\) monolayers. The regions in between surface X\(_2\) moieties are shown by red dashed-line ellipses. In this figure, green, yellow, orange, and dark yellow circles indicate Zr, S, Se, and Te atoms, respectively.

After an effective analysis of the structural and bonding characteristics of the ZrX\(_3\) monolayers, we next examined their dynamic stability by evaluating phonon dispersion relations. The predicted phonon dispersion along highly symmetrical points for the ZrS\(_3\), ZrSe\(_3\), and ZrTe\(_3\) monolayers are illustrated in Figure 2. As the first important finding, the phonon modes were free of imaginary frequencies, confirming the dynamic stability of these systems. By increasing the atomic number of chalcogen atoms in the ZrX\(_3\) nanosheets, it was clear that although preserving the general form of dispersions, the phonon modes showed narrower frequency ranges, which indicates lower group velocity. It is noticeable that all acoustic and optical modes appeared with considerable intersections, stimulating...
the scattering and reducing the lifetime for modes with higher frequencies. With generally lower group velocity and lifetime, it was expected that by increasing the atomic number of chalcogen atoms in ZrX₃ nanosheets, they would show lower lattice thermal conductivity, which is consistent with recent theoretical results for the ZrS₃ [13] and ZrTe₃ [14] systems.

Table 1. Structural and electronic properties of ZrX₃ (X = S, Se, Te) monolayers.

| Lattice   | a, b (Å) | \(d_{Zr-X}\) | \(d_{Zr-X}\) | \(Q(Zr,X_{\text{surface}},X_{\text{internal}})\) | \(E_{\text{PBE}}/E_{\text{PBE+SOC}}/E_{\text{HSE06+SOC}}\) (eV) |
|-----------|----------|---------------|---------------|-------------------------------------------------|-------------------------------------------------|
| ZrS₃      | 5.13,3.63| 2.72, 2.61    | 2.07          | 3.06                                            | 1.77/−0.41/−0.95                                 |
| ZrSe₃     | 5.41,3.76| 2.87, 2.74    | 2.38          | 3.03                                            | 1.61/−0.38/−0.85                                 |
| ZrTe₃     | 5.89,3.92| 3.16, 2.98    | 2.83          | 3.05                                            | 1.33/−0.34/−0.64                                 |

¹ PBE optimized lattice parameters along x and y directions, respectively (Figure 1). ² Bond lengths of those Zr-X bonds that are in the xz and yz planes, respectively (Figure 1). ³ Bond length of covalently bonded X₂ moieties (Figure 1). ⁴ Distance between adjacent X₂ moieties. ⁵ Average Bader charges on each of the Zr atoms, X atoms of X₂ moieties (X_surface), and internal X atoms (X_internal), respectively (Figure 1). ⁶ Band gaps using PBE functional (\(E_{\text{PBE}}\)) and PBE functional with inclusion of spin-orbit coupling (SOC) effect/HSE06 functional (\(E_{\text{PBE+SOC}}\))/HSE06 functional with inclusion of SOC effects (\(E_{\text{HSE06+SOC}}\)). For ZrS₃ and ZrSe₃, K-points at which valence band maximum and conduction band minimum occurs are shown in parentheses.

The Raman spectrum of each ZrX₃ monolayer is shown in Figure 3. Apparently, due to the same crystal symmetry of each monolayer ZrX₃, the number of Raman active modes was the same in all structures. It is seen that there existed three prominent Raman active phonon modes for each monolayer structure. The three prominent peaks are labeled I, II, and III, as shown in the figure. As the chalcogenide atom changed from S to Te, which means the atomic radius increased, the frequency of each prominent peak displayed red shift due to the larger atomic mass. In addition, the motion of individual atoms showing the vibration of the corresponding phonon mode is also given in the right panel of the figure. The phonon mode I was calculated to be at the frequencies 522, 292, and 151 cm⁻¹ for ZrS₃, ZrSe₃, and ZrTe₃ monolayers, respectively. Apparently, mode I arose from the in-plane vibration of the outermost chalcogenide atoms against each other. On the other hand, modes II and III stemmed from the out-of-plane vibration of the Zr and chalcogenide atoms. The frequencies of modes II/III were calculated to be 321/274, 220/171, and 74/62 cm⁻¹ for the ZrS₃, ZrSe₃, and ZrTe₃ monolayers, respectively. The mode II phonon represents the out-of-plane vibration of the internal chalcogenide atoms against Zr atoms, whereas the outermost chalcogenide atoms made little contribution to the vibration. Finally, the mode III phonon arose from the out-of-phase vibration of each atomic level with respect to each other, that is, the outermost chalcogenide atoms vibrated against each other, and Zr atoms also moved out of phase. The three characteristic phonon peaks were quite important for the detection of the ZrX₃ monolayers.

Figure 2. Phonon dispersion relations of the ZrS₃, ZrSe₃, and ZrTe₃ monolayers.
we first acquired the energy-minimized six-layer slabs of the ZrX$_3$ (0.184210 Å)$^2$ and ZrSe$_3$ (0.218210 Å)$^2$. These findings reveal that the separate layers in these systems showed relatively weak interactions, and moreover highlight that by increasing the atomic number of chalcogen atoms, the exfoliation energy increased, consistent with earlier studies. We remind the reader that Li et al. [12] synthesized ZrSe$_3$ nanosheets via the mechanical exfoliation method. Taking into account our predictions for the exfoliation energies and the aforementioned experimental achievement, the experimental isolation of ZrS$_3$ and ZrTe$_3$ monolayers from their bulk structures is very bright.

Worth mentioning is that to prepare 2D materials, the common approaches include mechanical exfoliation, chemical vapor deposition (CVD), and liquid-phase exfoliation. The mechanical exfoliation of bulk 2D materials into single or multiple layers can be achieved by using external driving forces [28–30]. Before analyzing the electronic properties, it is thus very useful to investigate the mechanical exfoliation energy required for the isolation of the ZrS$_3$, ZrSe$_3$, and ZrTe$_3$ monolayers from their native bulk structures. For this purpose, we first acquired the energy-minimized six-layer slabs of the ZrX$_3$ nanosheets, with the same stacking pattern as that of their bulk systems. In the next step, the last layer was steadily separated toward the out-of-plane vacuum direction, with a small step of 0.25 Å. The change in the energy of the systems was subsequently calculated and the cleavage energy was recorded. As shown in Figure 4, the relative energies showed sharp initial increases and later reach converged values. According to our DFT-D3 simulations, the exfoliation energies of 0.32, 0.37, and 0.40 J/m$^2$ were predicted for the isolation of the ZrS$_3$, ZrSe$_3$, and ZrTe$_3$ monolayers, which are comparable to that of graphene: 0.37 J/m$^2$ [31]. These findings reveal that the separate layers in these systems showed relatively weak interactions and moreover highlight that by increasing the atomic number of chalcogen atoms, the exfoliation energy increased, consistent with earlier studies [32]. We remind that Li et al. [12] synthesized ZrSe$_3$ nanosheets via the mechanical exfoliation method. Taking into account our predictions for the exfoliation energies and the aforementioned experimental achievement, the experimental isolation of ZrS$_3$ and ZrTe$_3$ monolayers from their bulk structures is very bright.

To explore the electronic characteristics of the ZrX$_3$ monolayers, we calculated electronic band structures using PBE and the more accurate HSE06 functional. The effect of spin-orbit coupling (SOC) on band gap properties of ZrX$_3$ monolayers was also examined. Figure 5 depicts the HSE06 band structures of the ZrX$_3$ monolayers without and with the inclusion of SOC effects. The corresponding PBE results are also given in Figure S1 in the Supplementary Materials. Band-gap values as well as transition k-points for HSE06 results are listed in Table 1. According to results shown in Figure 5 and Table 1, the ZrS$_3$ and ZrSe$_3$ monolayers were indirect gap semiconductors with HSE06 band gaps of 1.93 and 1.01 eV. In the ZrS$_3$ monolayer, VBM was located at a k-point on the Γ-X path (0.184210 $k_1$ + 0 $k_2$, $k_1$ and $k_2$ are lattice vectors of reciprocal space) and CBM was located at the Γ point. The direct gap at the Γ point in ZrS$_3$ was only 0.08 eV larger than the indirect

![Figure 3. The Raman spectrum of each monolayer ZrX$_3$ structure (on the left) and the vibrational characteristic of the individual atoms for the most prominent Raman active modes (on the right).](image-url)
gap, indicating that ZrS$_3$ may behave as a quasi-direct gap semiconductor. VBM and CBM in the ZrSe$_3$ monolayers were, however, located at the $\Gamma$ and X points, respectively. Both band gap values and transition k-points are in good agreement with previous data (1.92 eV for ZrS$_3$ and 0.92 eV for ZrSe$_3$) [33]. It can be seen that for each of the ZrS$_3$ and ZrSe$_3$ monolayers, PBE and HSE06 band structures looked similar, except the PBE band gaps, as expected, were underestimated. It was also observed that the inclusion of SOC did not yield a detectable effect on the band structure of the ZrSe$_3$, but it reduced the HSE06 (PBE) band gap of the ZrSe$_3$ monolayer by 0.08 (0.06) eV (find Figures 5 and S1). Unlike the ZrS$_3$ and ZrSe$_3$ monolayers, the ZrTe$_3$ monolayer exhibited a metallic character irrespective of the functional used, which is also in agreement with a previous report [33].

![Figure 4. Cleavage energy of the ZrS, ZrSe, and ZrTe monolayers as a function of separation distance.](image)

In order to further rationalize the band-gap change trend in ZrX$_3$ monolayers, for each one, we calculated atom-type projected density of states (PDOS) and charge density distributions of valance band maximum (VBM) and conduction band minimum (CBM), as shown in Figure 5. For the three monolayers, VBM was mainly contributed by internal X-(p$_y$,p$_z$) with a minor contribution from Zr-(p$_y$,d$_{xy}$,d$_{xyz}$), representing a shallow bonding s(Zr-X) state. Considering the fact that the energy position of p orbitals of chalcogen X atom increased from S to Te, VBM in the ZrX$_3$ monolayers was expected to move upward in energy from the ZrS$_3$ to ZrTe$_3$ monolayer. This expectation was confirmed by the absolute energy positions of VBM of the ZrS$_3$, ZrSe$_3$, and ZrTe$_3$ monolayers, calculated to be −6.57, −5.68, and −5.21 eV, respectively. CBM in the ZrS$_3$ lattice was made of Zr-(s,d$_{xy}$,d$_{x^2-y^2}$), representing a bonding (Zr-Zr) state propagating along the y direction. The charge densities of CBMs in the ZrSe$_3$ and ZrTe$_3$ monolayers were, however, almost exclusively distributed over surface X$_2$ moieties, and they both represented bonding (X-X) states made of X-(s,p$_x$,p$_z$). As our electron localization analysis revealed, the strengths of interaction between adjacent X$_2$ moiety increased from ZrS$_3$ to ZrTe$_3$. The stronger the interaction between X$_2$ moieties, the lower the absolute energy position. Putting the conclusions together, from ZrS$_3$ to ZrTe$_3$, VBM shifted upward in energy whereas CBM shifted downward, leading to smaller band gaps (E$_g$(ZrS$_3$) > E$_g$(ZrSe$_3$) > E$_g$(ZrTe$_3$)).
Finally, we examined the mechanical responses by performing uniaxial tensile simulations along the \( x \) and \( y \) directions, as distinguished in Figure 1. Uniaxial stress–strain responses of the \( \text{ZrX}_3 \) monolayers along the \( x \) and \( y \) directions are illustrated in Figure 6. In these results, real volumes of the deformed lattices were considered in the conversion of the stress values to the standard GPa unit [34–36]. The real area of the deformed nanosheets can be obtained using the simulation box sizes along the in-plane directions. The real volume at every strain was calculated by finding the normal distance between boundary chalcogen atoms plus their effective vdW diameter. According to our geometry-optimized bulk lattices, the thickness of the stress-free \( \text{ZrS}_3 \), \( \text{ZrSe}_3 \), and \( \text{ZrTe}_3 \) monolayers were predicted to be 9.01, 9.46, and 10.14 Å, respectively, equivalent to the effective vdW diameters of 3.05, 3.20, and 3.26 Å for the S, Se, and Te atoms in the \( \text{ZrX}_3 \) monolayers, respectively. The stress–strain curves plotted in Figure 6 are uniaxial, which means that during the complete deformation and after the geometry minimization, these kagome monolayers exhibited a stress component only along the loading direction and showed negligible values along the two other perpendicular directions. As expected, and stemming from the anisotropic structure, the stress–strain curves along the \( x \) and \( y \) directions were considerably different, confirming highly anisotropic mechanical features. The elastic modulus of \( \text{ZrS}_3 \), \( \text{ZrSe}_3 \), and \( \text{ZrTe}_3 \) monolayers along the \( x \) (\( y \)) directions were predicted to be 93 (142), 90 (118), and 120 (56) GPa, respectively. The ultimate tensile strength of the \( \text{ZrS}_3 \), \( \text{ZrSe}_3 \), and \( \text{ZrTe}_3 \) monolayers along the \( x \) (\( y \)) directions were predicted to be 6.2 (16.5), 4.9 (17.4), and 4.6 (11.8) GPa, respectively. As expected, due to the existence of more connecting bonds along the \( y \) direction than the \( x \) counterpart, these systems showed considerably higher tensile strength along this direction. The same observation is also consistent for the elastic modulus of
the ZrS₃ and ZrSe₃ monolayers. The ZrSe₃ monolayers unexpectedly showed a higher elastic modulus along the x direction, which, as discussed earlier with the ELF results, was due to the formation of continuous over-surface Te-Te interactions along this direction in this system. As is clear, due to the multifaceted structural and bonding effects, the ZrX₃ nanosheets showed highly anisotropic and complex mechanical behavior. Worthy to mention that complex material properties can be explored using MTPs with high accuracy and accelerated computational costs [37–41].

Figure 6. True uniaxial stress–strain relations of the (a) ZrS₃, (b) ZrSe₃, and (c) ZrTe₃ monolayers elongated along the y and x directions.

4. Concluding Remarks

We studied the structural, phononic, electronic, and single-layer exfoliation energies and mechanical properties of ZrX₃ (X = S, Se, Te) monolayers. The acquired phonon dispersion relations revealed the dynamical stability of the aforementioned 2D systems. Exfoliation energies of 0.32, 0.37, and 0.40 J/m² were predicted for the ZrS₃, ZrSe₃, and ZrTe₃ monolayers’ isolation, which confirms bright prospects for the mechanical isolation of ZrS₃ and ZrTe₃ monolayers from their native bulk structures. ZrS₃ and ZrSe₃ monolayers were found to be indirect gap semiconductors, with HSE06 band gaps of 1.93 and 1.01 eV, whereas the ZrTe₃ monolayer yielded a metallic character. The elastic modulus of ZrS₃, ZrSe₃, and ZrTe₃ monolayers along the x (y) directions were predicted to be 93 (142), 90 (118), and 120 (56) GPa, respectively, and the corresponding ultimate tensile strength values were found to be 6.2 (16.5), 4.9 (17.4), and 4.6 (11.8) GPa, respectively. It is shown that because of multifaceted structural and bonding effects, ZrX₃ nanosheets showed highly anisotropic and complex mechanical behavior. The presented DFT results provide an effective overview of the key physical properties of the ZrX₃ (X = S, Se, Te) nanosheets, which can serve as valuable information for their practical application in nanodevices.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en15155479/s1, Figure S1: PBE band structures of the ZrX₃ monolayers without (purple solid lines) and with (red solid line) the inclusion of SOC effects.

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