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Mechanical Properties of Monolayer Sulfides of TiS$_3$, HfS$_2$ and MoS$_2$

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In this study, motivated by the recent synthesis of hexagonal monolayers of Aluminum Nitride, we study it’s number of layer dependent electronic and optical properties. We also found that optical properties that is different for monolayer, fewlayer and bulk can utilized as an efficient way for the determination of the morphology of the synthesized materials. In this study, motivated by the recent synthesis of hexagonal monolayers of Aluminum Nitride, we study it’s number of layer dependent electronic and optical properties. We also found that optical properties that is different for monolayer, fewlayer and bulk can utilized as an efficient way for the determination of the morphology of the synthesized materials. In this study, motivated by the recent synthesis of hexagonal monolayers of Aluminum Nitride, we study it’s number of layer dependent electronic and optical properties. We also found that optical properties that is different for monolayer, fewlayer and bulk can utilized as an efficient way for the determination of the morphology of the synthesized materials. In this study, motivated by the recent synthesis of hexagonal monolayers of Aluminum Nitride, we study it’s number of layer dependent electronic and optical properties. We also found that optical properties that is different for monolayer, fewlayer and bulk can utilized as an efficient way for the determination of the morphology of the synthesized materials.

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I. INTRODUCTION

The high mechanical strength and electronic quality of transition metal sulphides (TMSs) have attracted understanding the chemistry and physics of these materials. Most of the TMSs form layered compounds where closely-packed layers are held together by weak van der Waals forces. However, Ultra-thin TMSs have recently emerged as promising materials for new nanoscale devices in a wide variety of applications. In these device applications, especially the semiconducting nature of ultra-thin sulphides make them superior to graphene, which is a semimetal. Chemical versatility of ultra-thin TMSs is another reason of growing interest on these materials.

The first synthesized member of ultra-thin TMSs is MoS$_2$. By using micromechanical cleavage method, successful synthesis of single layer MoS$_2$ was achieved by Novoselov et al. Shortly after this study, optical spectroscopy measurements on number of layer dependent properties of MoS$_2$ revealed that effect of quantum confinement leads to a crossover to a direct-gap material in the limit of the single monolayer. Significant enhancement in luminescence quantum efficiency of single layer structure attracted further interest on this material class. Furthermore the experiments on the stiffness and breaking strength of monolayer MoS$_2$ showed that its mechanical strength is comparable to that of steel. These findings on MoS$_2$ triggered the efforts on using TMSs for flexible electronic nanodevice applications.

Following MoS$_2$, several new elements of TMSs emerged such as WS$_2$, VS$_2$, HfS$_2$ and TiS$_3$. It was shown by several groups that sulphides of Mo and W have quite similar properties such as lattice parameter and electronic structure, although there were some findings on the high moisture responsiveness of ultra thin VS$_2$, the literature on the evidence of single layers of this material is sparse. In addition, dimensionality dependent electronic properties of HfS$_2$, from bulk to single layer, was reported. Differing from single layers of MoS$_2$, WS$_2$ and VS$_2$ which are in 1H phase where the metal atom have trigonal prismatic coordination, single layer HfS$_2$ forms a octahedral phase (1T) in its ground state. In addition to these, recent experiments reported the successful synthesis of single layer TiS$_3$ which has a entirely different crystal symmetry. It was shown that TiS$_3$ layers which are isolated by viscoelastic mechanical exfoliation have quite high photoresponsivity and therefore they are promising materials for nanoscale transistors and optoelectronic devices.

In this work we investigate the mechanical performance of single layer TMSs TiS$_3$, HfS$_2$ and MoS$_2$. Although the mechanical response of MoS$_2$ well-studied by experimental and theoretical groups in past few years, recently emerged structures TiS$_3$ and HfS$_2$ have not been investigated before. While our calculations on MoS$_2$ allow us to examine the reliability of the computational methodology, calculations on TiS$_3$ and HfS$_2$ reveal the mechanical characteristics of these novel structures.

The paper is organized as follows. Our computational details are given in Sec. II. Ground state structural and electronic properties of TiS$_3$, HfS$_2$ and MoS$_2$ outlined in Sec. III. We also calculate vibrational properties of these structures in Sec III. Our results on elastic parameters, ultimate strength and strain dependent electronic structure are presented in Sec IV. We discuss our results in Sec V.
II. COMPUTATIONAL METHODOLOGY

The calculations are performed using the frozen-core projector augmented wave method\textsuperscript{25} as implemented in the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{23,24} The generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE)\textsuperscript{26} is chosen as exchange-correlation functional. Energy cutoff for plane-wave expansion is set to 400 eV. Brillouin zone sampling is performed with Monkhorst-Pack (MP) special k-point meshes\textsuperscript{27} including the Γ-point. For MoS\textsubscript{2} and HfS\textsubscript{2} a grid of 12×12×1 is used, and for TiS\textsubscript{3} a grid of 7×11×1 is used. A vacuum layer larger than 10 Å is added to avoid interaction between adjacent images. All atoms are allowed to relax until the calculated Hellmann-Feynman force on each atom is smaller than 0.01 eV/Å.

III. GROUND STATE PROPERTIES OF TiS\textsubscript{3}, HfS\textsubscript{2} AND MoS\textsubscript{2}

A. Atomic Structure

1. paragraph MoS\textsubscript{2}
2. paragraph TiS\textsubscript{3}
3. paragraph HfS\textsubscript{2}

B. Vibrational Spectrum

1. paragraph MoS\textsubscript{2}
2. paragraph TiS\textsubscript{3}
3. paragraph HfS\textsubscript{2}

C. Electronic and Magnetic Properties

1. paragraph MoS\textsubscript{2}
2. paragraph TiS\textsubscript{3}
3. paragraph HfS\textsubscript{2}

IV. MECHANICAL RESPONSE OF TiS\textsubscript{3}, HfS\textsubscript{2} AND MoS\textsubscript{2}

A. Elastic parameters

In-plane stiffness and Poisson’s ratio are two important elastic parameters for 2D materials. The in-plane stiffness $C$ is defined as $C = (1/S_0)(\partial^2 E_s/\partial \varepsilon^2)$, where $S_0$ is the equilibrium area of the 2D material, $E_s$ is the strain energy (the energy difference between equilibrium and strained structures) and $\varepsilon$ is the applied strain. A material with smaller $C$ can be stretched more easily. The other parameter, Poisson’s ratio $\nu$, is the ratio of the transverse strain to the axial strain, namely, $\nu = -\varepsilon_{\text{trans}}/\varepsilon_{\text{axial}}$. $C$ and $\nu$ can be obtained through calculating the strain-energy relationship, as described in Ref.17. First, we construct rectangular unit cells of MoS\textsubscript{2}, TiS\textsubscript{3} and HfS\textsubscript{2}, as shown in Fig. 1. The two lattice vectors are along $x$ and $y$ directions, respectively. For hexagonal MoS\textsubscript{2} and HfS\textsubscript{2}, $x$ and $y$ correspond to the armchair and zigzag directions. By changing the lattice constants, we apply strains ranging from -0.02 to 0.02 along each directions, with a step of 0.01. Thus a data grid with 25 points is obtained. At each point we relax the internal atomic position, and calculate the strain energy $E_s$. The strain energy can be fitted by the formula $E_s = c_1\varepsilon_x^2 + c_2\varepsilon_y^2 + c_3\varepsilon_x\varepsilon_y$, in which $\varepsilon_x$ and $\varepsilon_y$ are the strain along $x$ and $y$ directions, respectively. The in-plane stiffness along $x$ and $y$ directions can be then calculated as $C_x = (1/S_0)(2c_1 - c_3^2/2c_2)$ and $C_y = (1/S_0)(2c_2 - c_3^2/2c_1)$. The Poisson’s ratio along $x$ and $y$ directions can be obtained by $\nu_x = c_3/c_2$ and $\nu_y = c_3/c_1$. For structures with hexagonal symmetry, $c_1$ equals to $c_2$ in the harmonic region. Therefore, along $x$ and $y$ directions, the in-plane stiffness and Poisson’s ratio of MoS\textsubscript{2} and HfS\textsubscript{2} are the same. On the other hand, TiS\textsubscript{3} exhibits anisotropic $C$ and $\nu$.

The calculated in-plane stiffness of MoS\textsubscript{2} is 124.24 N/m, which is in agreement with other DFT work.\textsuperscript{13} A recent experiment reported a in-plane stiffness of 180±60 N/m,\textsuperscript{18} which is also consist with our results. The effective Young’s Modulus can be deduced from $C/h$ by assuming a proper thickness $h$ of the monolayer. Taking $h=6.145$ Å, which is the interlayer spacing in bulk MoS\textsubscript{2}, the Young’s Modulus of monolayer can be determined as 202.18 GPa. The Poisson’s ratio of MoS\textsubscript{2} is calculated to be 0.25.

For TiS\textsubscript{3}, $C_x$ and $C_y$ are different. We found $C_x=83.33$ N/m and $C_y=133.56$ N/m, in agreement with other calculations.\textsuperscript{19} According to Ref.20, the interlayer spacing in bulk TiS\textsubscript{3} is 8.706 Å. So the effective Young’s Modulus are 95.72 GPa and 153.41 GPa along $x$ and $y$, respectively. The Poisson’s ratios are $\nu_x=0.11$ and $\nu_y=0.18$.

The in-plane stiffness of HfS\textsubscript{2} is found to be 79.86 N/m. Assuming a effective thickness as its bulk interlayer spacing 5.837 Å, the Young’s Modulus is 136.82 GPa. The calculated Poisson’s ratio is 0.19.

The calculated in-plane stiffness follows the trend TiS\textsubscript{3}(y) > MoS\textsubscript{2} > TiS\textsubscript{3}(x) > HfS\textsubscript{2}. This trend can be understood in view of bond length and bond density in different materials. A smaller bond length (thus a stronger bond) and a higher bond density per unit area would lead to a larger in-plane stiffness. In MoS\textsubscript{2} and HfS\textsubscript{2}, the metal-sulfur bond length is 2.41 Å and 2.55 Å, respectively. In TiS\textsubscript{3}, there are three different types of bonds. Along the $y$ direction there are two types, with bond length of 2.46 and 2.50 Å. The third type is along $x$ direction, with bond length of 2.67 Å. The order of bond length is TiS\textsubscript{3}(x) > HfS\textsubscript{2} > TiS\textsubscript{3}(y) > MoS\textsubscript{2}. Hence the in-
plane stiffness of MoS\(_2\) and TiS\(_3\)\((y)\) is larger than that of TiS\(_3\)(\(x\)) and HfS\(_2\), due to stronger bonds. On the other hand, in TiS\(_3\), each Ti is eight-fold coordinated, whereas the metal atoms are six-fold coordinated in the other two materials. In addition, the density of Ti per unit area is larger than that of Mo and Hf. As a result, the bond density in TiS\(_3\) is higher than those of MoS\(_2\) and HfS\(_2\). When bond strength is comparable, TiS\(_3\) would have larger in-plane stiffness because of higher bond density. Thus the in-plane stiffness of TiS\(_3\)(\(y\)) (TiS\(_3\)(\(x\))) is larger than that of MoS\(_2\) (HfS\(_2\)).

B. Ultimate strength

In this part we discuss the strain-stress relations of MoS\(_2\), TiS\(_3\) and HfS\(_2\). We employ rectangular unit cells as shown in Fig. 1. Uniaxial strain is applied along \(x\) or \(y\) direction, and the cell vector perpendicular to the strain, as well as the atoms, is fully relaxed. In many cases, nano-structure materials undergo reconstructions when applied strain is large enough. To explore possible reconstructions, in our calculations we break the symmetry limitation of the monolayers before structure relaxation in those works. With strain the symmetry of MoS\(_2\) is lowered from \(D_{3h}\) to \(C_{2v}\), therefore the mechanic response of MoS\(_2\) become anisotropic under higher strain value. When strain is along \(x\), the maximum stress of 23.48 GPa is achieved at \(\epsilon_x = 0.26\). This is in good agreement with the 27.35 GPa at \(\epsilon_x = 0.28\) in Ref.21 and the 24 GPa at \(\epsilon_x = 0.256\) in Ref.22. It is also notable that when \(\epsilon_x\) exceeds 0.26, there is a drop in the stress and strain energy, indicating a structure reconstruction of the monolayer. Indeed we find the \(C_{2v}\) symmetry is no longer preserved when \(\epsilon_x\) exceeds 0.26. The structure deformation is non-reversible in this region even when the applied strain is removed. This is not observed in previous studies,\(^{21,22}\) which probably results from the limitation of symmetry when doing structure relaxation in those works. With strain along \(y\), the ultimate strength of MoS\(_2\) is found to be 15.99 GPa at \(\epsilon_y = 0.20\), agrees with the the 16.9 GPa at \(\epsilon_y = 0.19\) in Ref.21 and the 15.6 GPa at \(\epsilon_y = 0.18\) in Ref.22. We observe no reconstructions up to \(\epsilon_y = 0.26\). The ultimate strength along the \(x\) and \(y\) directions shows obvious different. The anisotropy can be measured by a factor \(\phi = \sigma_x/\sigma_y\), where \(\sigma_x\) and \(\sigma_y\) are the ultimate strength along \(x\) and \(y\) directions, respectively. The \(\phi\) for MoS\(_2\) is 1.47.

In TiS\(_3\) monolayer, for strain along \(x\), the ultimate strength is 4.45 GPa, with a ultimate strain of 0.10. When strain is along \(y\), the ultimate strength and strain are 18.32 GPa and 0.22, respectively. In both cases, when the strain goes further than the ultimate strains, the monolayer undergoes non-reversible structure reconstructions which break the original \(C_{2h}\) symmetry, as indicated by a sudden reduce in strain energy and stress. The ultimate strength along \(x\) is much smaller than that of...
along y, with an anisotropy factor of 0.24. This can be attributed to the anisotropy in the structure of TiS$_3$. As mentioned above, the bond length of TiS$_3$ along x direction is much larger compared with the y direction. Therefore, the bond along x is weaker and easier to be break, leading to the small ultimate strength and strain.

For HfS$_2$, the ultimate strength and strain along x are 14.16 GPa and 0.15, respectively. Along y direction, these values are 12.38 GPa and 0.13. The anisotropy factor of ultimate strength is 1.14. Compared with 1-H MoS$_2$, the anisotropy in 1-T HfS$_2$ is smaller. Similar to TiS$_3$, reconstructions happen beyond the ultimate strain, breaking the C$_{2h}$ symmetry. The reconstructions with strain along x is non-reversible, proved by a decrease in strain energy. However, when strain is along y, we find the deformation is minor between the reconstructed and unreconstructed structures. Therefore, the strain energy continue to grow when strain is larger than 0.13, suggesting a reversible reconstruction. Once the strain is released, the monolayer may return to the structure at $\varepsilon = 0$.

C. Band gap response under strain

Finally we investigate the response of band structure with the applied strain. We focus on the strain range in which no reconstruction happens. For MoS$_2$ and HfS$_2$, we use the primitive unit cell to calculate the band structure instead of the rectangle unit cell. The variation of band gap and the band structure of the monolayers with uniaxial strain, are illustrated in Fig 2. For MoS$_2$, the band gap monotonously decreases when the strain increases, in consistent with previous study. When strain is less than 0.1, the effects of x-strain and y-strain on the band gap are almost the same. Beyond this value, the gap decreasing in y-strain case is slightly faster than in x-strain case. When strain along x becomes larger than 0.2, the gap saturates to 0.45 eV. Moreover, strain modifies the band edge position of MoS$_2$. Without strain MoS$_2$ has a direct band gap at the K(L) point. When strain is applied, the band gap becomes indirect. The CBM state is located on the L-M' path for strain along z, and on the K-Γ path for strain along y. Under small strain, the CBM is close to L or K. As the strain increases, the CBM moves towards M' or Γ. The VBM transfers to the Γ point with strain along both x and y.

Compared with MoS$_2$, the band response to strain in TiS$_3$ is very different. In the strained structures, the CBM and VBM states remain at the Γ point. Furthermore, it shows strong anisotropy, as seen in Fig. 2. With increasing x-strain, overall the band gap shows a decreasing trend, and the magnitude is not large. From $\varepsilon_x = 0$ to $\varepsilon_x = 0.1$, the band gap reduction is about 0.1 eV. In case of y-strain, as the strain increases, the band gap becomes larger at first, and reaches 0.81 eV at $\varepsilon_y = 0.12$. When the strain further increases, the band gap become smaller. To explore the origin of such a non-monotonously behavior, we look into the orbital character of the CBM and VBM states. We find the CBM state of TiS$_3$ is from the $d_{xz}$ orbitals of Ti atoms, and this character doesn’t change with strain. The effect of strain on CBM energy is also found to be small. However, the situation of VBM is different. When $\varepsilon_y$ is smaller than 0.12, the VBM state consists of the $d_{xz}$ orbitals of Ti atoms and $p_x$ orbitals of the four-fold coordinated S atoms. Whereas when $\varepsilon_y$ is larger than 0.12, the dominated orbitals of VBM state are the $d_{xz}$ orbitals of Ti atoms and $p_x$ orbitals of the two-fold coordinated S atoms. Due to the different orbital character, the response of VBM state to strain is different in these two cases. For $\varepsilon_y < 0.12$, the VBM energy decreases as strain increases. When $\varepsilon_y > 0.12$, the VBM energy increases with increasing strain. Therefore, the band gap increases at first, and then decreases.

In the case of HfS$_2$, without strain the monolayer is a indirect gap semiconductor with CBM at M (M') and VBM at Γ. When x-strain is smaller than 0.1, the CBM is at M' and the VMB is at Γ. The gap value slightly increases with increasing strain, as shown in Fig. 2. When x-strain is larger than 0.1, the CBM moves to the Γ point, while the VBM is still at Γ, leading to a indirect-direct gap transition. Because of the change of CBM character, the band gap now decreases with increasing x-strain. In the y-strain case, the VBM is also found at the Γ point in the whole range considered. When $\varepsilon_y$ is smaller than 0.08, the CBM is at M. At $\varepsilon_y=0.1$, the CBM changes to the M' point. At $\varepsilon_y=0.12$, the CBM is located at the Γ point, and indirect-direct gap transition happens. The variation of gap value with $\varepsilon_y < 0.1$ is very similar to that in the x-strain case. It is slightly larger with larger strain. From $\varepsilon_y=0.1$ to 0.12, the gap decreases a little. The origin is again the change of CBM, as in the x-strain case. Overall, the anisotropy of band gap variation with strain in HfS$_2$ is also small, especially in the small-strain range, similar to the case of MoS$_2$. In addition, the strain-induced indirect to direct gap transition may lead to possible applications of HfS$_2$ in optoelectronics.

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1 Electronic address: jun.kang@uantwerpen.be
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3 F. Hulliger Crystal chemistry of the chalcogenides and pnictides of the transition elements
4 D. W. Bruce, Transition Metal Sulphides: Chemistry and Catalysis, T. Weber, R. Prins and R. A. van Santen (eds),
FIG. 2: The variation of band gap of MoS$_2$, TiS$_3$ and HfS$_2$ with strain, and the band structure under different strain. The corresponding Brillouin zones and high symmetry k-paths are also shown.