Raman spectrum of 1T'-WTe₂ under tensile strain: A first-principles prediction

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Abstract

Monolayer WTe₂ attracts rapidly growing interests for its large-gap quantum spin Hall effect, which enables promising applications in flexible logic devices. Due to one-dimensional W-W chains, 1T'-WTe₂ exhibits unique anisotropic structure and promising properties, which can be modified by simply applying strains. Based on the first-principles simulations, we show that phonon branch undergoes soft down to negative frequency at special q points under different critical strains, i.e., $\varepsilon_a = 11.55\%$ along a-axis (with W-W chains) direction, $\varepsilon_b = 7.0\%$ along b-axis direction and $\varepsilon_{ab} = 8.44\%$ along biaxial direction. Before each critical strain, the Raman-shift of $A_{1g}$, $A_{3g}$ and $A_{4g}$ modes, corresponding to the main peaks in Raman spectra of 1T'-WTe₂, shows anisotropic response to uniaxial strain but most sensitive to biaxial strain. Interestingly, we find that the frequency shift of $A_{3g}$ mode show parabolic characters of strained 1T'-WTe₂, then we split it into two parts and it shows a Raman-shift transition at $\sim 5\%$ strains. While for the $A_{1g}$ and $A_{4g}$ modes, the frequencies change linearly. Through careful structure and vibration analysis, we try to explain these Raman irregularity in strained 1T'-WTe₂.

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I. INTRODUCTION

In a robust two-dimensional materials family of transition metal dichalcogenides (TMDs) \([1]\), monolayer \(1T'-\text{WTe}_2\) has large-gap quantum spin Hall (QSH) insulator \([2, 11]\), unconventional spin-torque \([12]\) and gate-tunable superconductivity \([13]\), which attracts rapidly growing interests, and enable promising applications in spintronics, dissipationless transport, and quantum computations. Among \(1T'-\text{TMDs—MX}_2\) with \(M = (\text{W, Mo})\) and \(X = (\text{Te, Se, S})\)—theoretically predicted to be a new class of QSH insulators \([2]\), \(\text{WTe}_2\) is the only one for which the \(1T'\) phase is most energetically favoured \([2]\) and can be observed under ambient conditions \([1, 14]\). \(1T'-\text{WTe}_2\) with a distorted orthorhombic crystal structure is distinct anisotropy in contrast to the other monolayer TMDs crystallized in \(1H\) (trigonal prismatic coordination) or \(1T\) (octahedral coordination) structures. In plane, the covalently bonded \(W\) atoms form a zigzag \(W-W\) chain, which makes \(\text{WTe}_2\) structurally one-dimensional and electronically a semimetal \([15]\). When cutting \(1T'-\text{WTe}_2\) into nanoribbons perpendicular to the \(W-W\) chains in our previous study \([16]\), the electronic band opens a gap, and semimetal transforms to semiconductor. Other theoretical studies also found that only 1% tensile strain along the \(W-W\) chains can lead to a semimetal to semiconductor or QSH insulator transition \([17, 18]\). Moreover, the Poisson ration, the in-plane stiffness and the absorption spectrum of monolayer \(1T'-\text{WTe}_2\) are strongly dependent on and tunable by tensile strain \([17]\).

Strain engineering in different orientations can lead to anisotropic modifications to the structure and properties of monolayer \(1T'-\text{WTe}_2\), which could play important roles in the application of flexible logic devices \([19]\). Theoretical and experimental studies on graphene \([20, 21]\), monolayer \(h\)-\(\text{BN}\) \([22, 23]\) and \(1H\)-\(\text{MX}_2\) with \(M = (\text{W, Mo})\) and \(X = (\text{Se, S})\) \([24-29]\) have found that the phonon spectra are significantly affected by external strains, and their response can be probed by Raman spectroscopy \([30]\). In contrast to these \(1H\) structures with in-plane isotropic, \(1T'-\text{WTe}_2\) under stain would exhibit more interesting anisotropic properties. The Raman spectrum of \(\text{WTe}_2\), from monolayer, few-layer to bulk as well as alloys \([31-40]\), has been studied to detect the crystal structure, lattice vibration, number of layers and in-plane anisotropy, however, the Raman spectrum of strained \(\text{WTe}_2\) has not yet been studied by either theory or experiment.

Based on the first-principles calculations, we provide a thorough study on the changes
of structures, phonon spectra, and Raman-active modes of monolayer $1T'\text{-WTe}_2$ under uni-
axial (parallel or perpendicular to the $W-W$ chains, respectively) and equibiaxial tensile
strains. Here, we only focus on $1T'\text{-WTe}_2$ under tension since a $1T'-1H$ phase transition will
occur under compression [41], which may be experimentally challenging to achieve without
incurring any buckling response. Through our phonon dispersion curve calculations, we
find that the acoustic branches of phonon are the most sensitive to tensile strains, and a
soft mode with negative frequency at different $q$ point under different critical strain occurs,
which indicate the structural instability and signify the ideal strength of $1T'\text{-WTe}_2$ with-
standing larger strain before rupture. Besides, we also find that the Raman-active modes
response quite different to external strains, and their corresponding frequency changes are
anisotopic. These results indicate that Raman measurements are sufficient to detect the
strain magnitudes and structural stability of $1T'\text{-WTe}_2$.

II. COMPUTATIONAL METHOD

Our calculations are based on density functional theory (DFT) and density functional
perturbation theory (DFPT) in pseudopotential plane-wave formalism, as implemented in
the Quantum ESPRESSO package [42]. The atomic positions and lattice constants for $1T'\text{-}
WTe_2$ are optimized by using Perdew-Burke-Ernzerhof (PBE) [43] functional, and the cutoff
energy of 40 Ry and 400 Ry ($1Ry \approx 13.6eV$) for the wave functions and the charge density,
respectively. A vacuum spacing $\sim 13\AA$ is used to prevent the interaction between the WTe_2
monolayers. A set of $24 \times 12 \times 1 k$-point sampling is used for Brillouin Zone (BZ) integration
over electronic states, and a set of $8 \times 4 \times 1 q$-point grid is used for the phonon calculations
to obtain the dynamic matrices. The self-consistent solution of the Kohn-Sham equations is
obtained when the total energy changed by less than $10^{-8}$ Ry and the Hellmann-Feynman
force on each atom is less than $10^{-6}$ Ry/bohr ($1bohr \approx 0.529177\AA$). The lattice constants
thus are determined with $a_0 = 3.49\AA$ and $b_0 = 6.31\AA$ and agree with the experimental
[14, 44] and theorietica [13, 17] values.
FIG. 1: (color online) Crystalline structure of monolayer $1T'$-WTe$_2$ with (a) side view, (b) top view and (c) front view. The distorted W atoms form one-dimensional zigzag chains indicated by the pink lines. The primitive cells (green rectangles) and the primitive vectors $a$ and $b$ (red arrows) used in the calculations are shown in (b).

III. RESULTS AND DISCUSSION

The primitive cell of $1T'$-WTe$_2$ is indicated by green rectangle, and its primitive vectors, $\overrightarrow{a}$ and $\overrightarrow{b}$, are indicted by red arrows as shown in Fig. 1(b). Along $a$-axis direction, the distorted W atoms form 1D zigzag chains indicated by the pink lines. In the W-W chains as show in Fig. 1(c), the stress (corresponding to $E_{bb} = 110.14 \text{N/m}$) is lager than one in the $b$ axis as shown in Fig. 1(a), based on our calculation of Young’s modulus matrix $E = \begin{pmatrix} 78.59 & 27.68 \\ 28.43 & 110.14 \end{pmatrix} \text{N/m}$ which are in agreement with the theoretical [18] and experimental [34] values. Due to the stronger bond strength in W-W chains, one can expect that $1T'$-WTe$_2$ could withstand lager strain along the $a$-axis direction compared to the $b$-axis direction. These two directions are the subject of our study. A state of uniaxial strain along $a$-axis and $b$-axis is constructed by applying the nominal strain and , respectively, where $a$ and $b$ are the strained lattice constants of $1T'$-WTe$_2$.

To obtain the phonon and Raman spectra of strained $1T'$-WTe$_2$, we firstly calculate the phonon dispersion curves of intrinsic one, and then analyse the characteristics of Raman-
FIG. 2: (Color online) Calculated phonon dispersion relations and atomic vibration displacements with their corresponding irreducible representations for nine typical Raman-active modes (marked by the red circles at Γ) in monolayer 1T′-WTe₂. Six $A_g$ modes with atoms vibrating in $bc$ plane are listed on the left panel, and three $B_g$ modes with atoms vibrating in $ab$ plane are listed on the right panel. The $q$ point labels Γ, X, S, Y correspond to (0,0), (1/2,0), (1/2,1/2), (0,1/2), respectively, in fraction of the reciprocal lattice vectors.

active modes based on the group theory. As shown in Fig. 2, there exist 18 phonon branches (3 acoustic and 12 optical branches) with 6 atoms (2 tungsten and 4 tellurium) in the primitive cell of 1T′-WTe₂. Because monolayer WTe₂ belongs to the No. 11 space group $P21/m$ and the point group $C_{2h}^2$, the irreducible representation of the normal modes at Γ point is $6A_g + 3A_u + 3B_g + 6B_u$, in which only 9 modes are Raman-active among 18 phonon modes based on the symmetry analysis of calculated atomic displacements. These nine Raman-active modes as shown in Fig. 2 are $6A_g + 3B_g$, whose frequencies are shown in Table I with other theoretical [31,32,35,45] and experimental counterparts [31–35]. Typical Raman spectrum of 1T′-WTe₂ exhibits three prominent Raman peaks at $\sim 210 cm^{-1}$, $160 cm^{-1}$, and $130 cm^{-1}$ denoted as $A^1_g$, $A^3_g$ and $A^4_g$, respectively. Later, we will focus our work exclusively on these three Raman-active modes.

Owing to strongly anisotropic mechanical properties of 1T′-WTe₂, we expect that the
three Raman-active modes exhibit diverse characteristics for WTe$_2$ under different-direction tensions. Therefore, we then calculate the phonon dispersion relations of strained monolayer WTe$_2$ along $a$-axis, $b$-axis as well as $ab$-biaxis direction, respectively. Interestingly, as red curves shown in Fig. 3, the phonon branches become soft and their frequencies become negative at special $q$ points under different critical strains. For example, when the tensile strain along $a$-axis direction approaches 11.55% ($\varepsilon_a = 11.55\%$), one of the acoustic modes of 1T$'$-WTe$_2$ becomes imaginary near $S$ point indicating structural instability, which consists with Torum’s ($\sim 11\%$) [17] and Xiang’s ($\sim 12.5\%$) [18] phonon spectra. In particularly, applying strains along $b$-axis direction, Torun et al [17] found that the strain-stress curve reaches a maximum at the critical strain of 15% (but without supporting phonon dispersion curves), and Xiang et al [18] found that a phonon branch becomes unstable near the Γ point (not pronounced) at the critical strain $\varepsilon_b = 12\%$. However, different from these two works, our study of tensile strain along $b$-axis direction shows that the ideal strength of monolayer 1T$'$-WTe$_2$ is 7% with the soft mode occurring at $Y$ point exactly, which is smaller than that of WTe$_2$ along $a$-axis direction with $\varepsilon_a = 11.55\%$. Such anisotropic phonons might be attributed to the 1D structure formed by the $W$-$W$ chains. Meanwhile, we also calculate the phonon dispersion curves of 1T$'$-WTe$_2$ under uniform biaxial strain, as shown in Fig.

### Table I: The phonon frequencies of nine Raman-active modes at Γ point for 1T$'$-WTe$_2$ from Raman experiments and first-principles calculations. The unit of frequency has been converted to $cm^{-1}$ for direct comparison with the Raman measurements.

| Symmetry | Exp.[31] | Exp.[32] | Exp.[33] | Exp.[34] | Exp.[35] | Cal.[31] | Cal.[32] | Cal.[35] | Cal.[45] | Cal.(this work) |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------------|
| $A^1_g$  | 213.2    | 217      | 212      | 216      | 222.6    | 219      | 221.9    | 208.9    | 210.3    |
| $A^2_g$  | 216.1    | 220.3    | 220.5    | 208.4    | 208.7    |
| $B^1_g$  |          | 185.7    | 173.7    | 161.3    | 158.5    |
| $A^3_g$  | 161.9    | 164      | 165      | 164      | 164.3    | 164.5    | 168      | 165.9    | 156.5    | 155.1          |
| $A^4_g$  | 132.8    |          | 135      | 137.2    | 135      | 136.9    | 129.9    | 128.9    |
| $A^5_g$  | 119.7    | 118.5    | 119      | 119.7    | 114.4    | 114.1    |
| $B^2_g$  | 109.4    | 108.5    | 110.4    | 105.8    | 105.1    |
| $B^3_g$  |          | 86       | 88.9     | 93.2     | 89       | 92.5     | 87.2     | 84.5     |
| $A^6_g$  | 81       | 85.7     | 81.4     | 84.6     | 80.0     | 81.4     |
FIG. 3: (Color online) Calculated phonon dispersion relations for monolayer 1T'-WTe$_2$ at different critical strains (a) $\varepsilon_a = 11.55\%$ and (b) $\varepsilon_b = 7.0\%$ uniaxial tension along $a$ and $b$ direction, respectively, and (c) $\varepsilon_{ab} = 8.44\%$ equibiaxial tension. The red phonon dispersion curves show negative-frequency modes (named soft modes) at special $q$ points, indicating the structural instability.

3(c), a soft mode occurs near X point at critical strain $\varepsilon_{ab} = 8.44\%$ indicating a possible phase transition with the 1T'-WTe$_2$ fracture.

Finally, we analyse the response of Raman-active modes ($A_g^1$, $A_g^3$ and $A_g^4$) on the three direction strains before 1T'-WTe$_2$ rupture. Due to $A_g$ modes containing double-rotation symmetry-axis operation $C_2(z)$ based on the character table for point group $C_{2h}$, they belong to tangential shear modes with opposite direction vibrations of W-W or Te-Te pairs. Moreover, the vibration displacements of $A_g$ modes (see Fig. 2) are in the $bc$ plane of 1T'-WTe$_2$, perpendicular to the $a$-axis direction, therefore, one can expect that the effects of $a$-axis strain on the $A_g$ modes would be weaker than that of $b$-axis strain. As a result, $A_g^4$ mode stays relatively unchanged when 1T'-WTe$_2$ under uniaxial strain along $a$-axis direction, with small slope value of $-0.29cm^{-1}/\%$, as the red line shown in Fig. 4(c). In order to make the frequency/strain ratio of three modes comparable, we put them in one figure with the same scale of the frequency and strain graduations, respectively. And in Fig. 4, we do find that the frequency shifts in three modes with $b$-axis strain are all much larger than that with $a$-axis strain, indicating a clear Raman modes anisotropy. This anisotropic Raman-strain response can facilitate the determination of the cristallographic orientation in 1T'-WTe$_2$. Moreover, when applying biaxial strain to 1T'-WTe$_2$, the frequencies of three
Raman modes also red-shift, but exhibit most sensitive to biaxial strain compared to uniaxial strains, with corresponding largest slope values. To explain this, we plot Figure 5. In Fig.5, one can find that, although the bond angle of W-W chain is almost unchanged when 1T'-WTe₂ under equibiaxial strain, the W-W bond length, the vertical distances in two pairs of Te atoms (c₁ and c₂, respectively) are all dramatically changed compared to the uniaxial strains. This structure modification under biaxial strain, in turn, leads to a considerable change in the Raman-active modes.

For A₁⁠\textsubscript{g} and A₄⁠\textsubscript{g} modes, their frequencies decrease almost linearly with applied strains as shown in Fig. 4(a) and (c), respectively, therefore, the strain in 1T'-WTe₂ can be quantified by A₁⁠\textsubscript{g} or A₄⁠\textsubscript{g} mode in Raman spectra. However, for A₃⁠\textsubscript{g} mode, the frequency shift undergoes a sharp turn at about 5% for both uniaxial and biaxial strains, as shown in Fig. 4(b), for example, the calculated biaxial-strain coefficient for A₃⁠\textsubscript{g} mode is down from −2.22 cm⁻¹/% to −6.03 cm⁻¹/%. This redshift transition might be result from that the lattice symmetry is maintained before 5% strains and then broken after 5% strains applied. Because the A₃⁠\textsubscript{g} mode consists of both in-plane and out-of-plane motions as shown in Fig. 2, with regard to the relative motions in pairs of W atoms (in-plane) and pairs of Te atoms (out-of-plane), the parallelogram without W-W chains could maintain its shape, but the parallelogram with W-W chains might be flattened or prolongated. Moreover, the amplitudes of Te atoms are much larger than that of W atoms, especially external strains strengthen the motions of Te atoms but weaken the vibrations of W atoms, which would prompt the symmetry broken at last. So, for this particular A₃⁠\textsubscript{g} transition to external strains and A₃⁠\textsubscript{g} as the most significant peak with the largest intensity in Raman spectra, we hope this phenomena can be tested by future Raman experiments of strained 1T'-WTe₂.

IV. CONCLUSIONS

In conclusion, by using DFT and DFPT simulations, we have systematically obtained the Raman spectrum of monolayer 1T'-WTe₂ under tensile strains. Our results demonstrate that A₁⁠\textsubscript{g}, A₃⁠\textsubscript{g} and A₄⁠\textsubscript{g} modes, corresponding to the main peaks in Raman spectra of 1T'-WTe₂, are more sensitive to uniaxial strain along b-axis direction than that along a-axis (containing W-W chains) direction, exhibiting anisotropic Raman-strain response. In particular, biaxial strain induces the largest red-shift of the Raman modes compared to the uniaxial strains.
FIG. 4: (Color online) The phonon frequencies of (a) $A_1^g$, (b) $A_3^g$, and (c) $A_4^g$ modes (corresponding to three Raman peaks experimentally) versus strains along $a$-axis (red), $b$-axis (blue), and $ab$-biaxis (black) directions, respectively. The solid line are linear fits to the calculated frequencies (solid symbols) and the corresponding slope values are shown.

Through careful structure configuration analysis, we reveal that the irregularity comes from the dramatic change of the $W-W$ bond length as well as the vertical distances in two pairs of Te atoms under biaxial strain. More interesting, $A_3^g$ mode undergoes a Raman-shift transition at about 5% for both uniaxial and biaxial strains, different from the $A_1^g$ and $A_4^g$ modes whose frequencies show linear dependence on tensile strains. The underlying symmetry rea-
FIG. 5: (Color online) The calculated (a) W-W-W bond angle $\theta$, (b) W-W bond length $d$, (c) and (d) vertical distance of two pairs of Te atoms in $c$ axis, i.e., $c_1$ and $c_2$, respectively, as functions of $a$-axis strain (red lines), $b$-axis strain (blue lines) and biaxial strain (black lines). The inset crystal configurations are used to depict these calculated variables.

It is revealed that the competition and cooperation of the relative motions between W-atom pairs and Te-atom pairs modify the shape of $1T''$-WTe$_2$. The revealed Raman modes responses to tensile strain are useful for tracing or detecting operations on $1T''$-WTe$_2$ based flexible devices.

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