Experimental observations and density functional simulations on the structural transition behavior of a two-dimensional transition-metal dichalcogenide

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In this work, we show an obvious evidence of nondestructive Raman spectra for the structural transition, i.e., the existence of a charge density wave (CDW) in monolayer 2H-TaS2, which can exhibit a much higher transition temperature than bulk and results in additional vibrational modes, indicating strong interactions with light. Furthermore, we reveal that the degenerate breath and wiggle modes of 2H-TaS2 originated from the periodic lattice distortion can be probed using the optical methods. Since recently several light-tunable devices have been proposed based on the CDW phase transition of 1T-TaS2, our study and in particular, the theoretical results will be very helpful for understanding and designing electronic devices based on the CDW of 2H-TaS2.

Charge density waves (CDW), structural transitions from a normal to a distorted phase, have been extensively studied for many decades1. They are characterized by the competing influences of the energy cost associated with distortion of the crystal structure and liberation due to the opening of an electronic energy gap. CDW transitions are known to occur in wide variety of materials, a prominent example being layered transition-metal dichalcogenides (TMDs), which have received much attention due to the wealth of their novel optical and electronic properties. The properties of TMDs often show a strong dimensional dependence, including the CDW phase transition2,3. It has been suggested that it is possible to tune the CDW transition temperature of thin TMDs through dimensionality, electrostatic gating or strain engineering4. This would enable the quantum phase transitions to be controlled in a manner that is compatible with current semiconductor technology. Tantalum disulfide, TaS2, is an archetypal TMD material which exhibits CDWs. It consists of layers stacked by weak van der Waals bonding, with each covalently bound layer typically consists of a sheet of hexagonally arranged Ta atoms sandwiched between two S layers. 1T-TaS2 shows a $\sqrt{13} \times \sqrt{13}$ CDWs below 540 K. Upon cooling from 540 K, 1T-TaS2 undergoes several CDW transitions. It changes from incommensurate to nearly commensurate at 350 K and then to commensurate at 180 K5. Bulk 2H-TaS2 forms a 3 x 3 commensurate CDW at low temperature6. It undergoes an incommensurate in-plane CDW transition at about 78 K7,8 and a superconducting transition at about 0.8 K9. Previous studies of 1T-TaS2 have shown the importance of dimensionality for the CDW phase transitions3,8. It was found that as the thickness was reduced, the transition from the nearly commensurate to the commensurate CDW phase shifts toward lower temperatures during cool-down and suddenly vanished for a critical thickness. However, a recent study showed that the commensurate CDW phase is the ground state even for monolayer 1T-TaS210. CDW analysis of monolayer of 1T and 1H of TaS2 has been reported, and the complexity of the CDWs suggests that unexplored modes may be excited for different external driving frequencies11. While the thickness-dependent CDW in 1T-TaS2 has been intensively studied, less is known about the CDW structure in thin exfoliated 2H-TaS2, especially the CDW structure in mono- and few-layer 2H-TaS2. It is interesting to note that not only mono- and few-layer 2H-TaS2 exhibits strong interactions with light12. Moreover, CDWs in TaS2 spontaneously breaking lattice symmetry through periodic lattice distortion, and electron–electron and electron–phonon interactions may lead to a new type of electronic structure. Thus, optical methods provide a non-destructive and easy way to probe the electronic structure and transitions in 2H-TaS2.
Here, in combination with density functional simulations, we demonstrated that CDWs can exist in exfoliated monolayer 2H-TaS2, and the transition temperature is much higher than that of the bulk. A new peak appears at 155 cm$^{-1}$ below transition temperature, which corresponds to the breath mode and wiggle mode of the CDW of 2H-TaS2, suggesting that the charge density wave transition and periodic lattice distortion can be probed and determined by optical methods, such as temperature dependent Raman scattering.

Methods
Sample preparation and characterizations. TaS2 nanosheets with different thicknesses were mechanically exfoliated from bulk 2H-TaS2 purchased from HQ Graphene. Optical color contrast and Seiko SPI3800N Atomic Force Microscopy (AFM) measurements were combined to identify the thickness of the nanosheets. The temperature dependent Raman spectra were taken using a Bruker Senterra confocal spectrometer with an excitation wavelength of 532 nm. High-resolution transmission electron microscopy (HRTEM) was performed using a JEOL-TEM.

Phonon dispersion calculation. The phonon dispersion calculations for bulk and monolayer of 2H-TaS2 were carried out using a supercell approach with the PHONOPY code. Before executing Phonopy package, the fully relaxed structures were obtained from the VASP relaxation procedure. To optimize the bulk and monolayer 2H-TaS2 by employing VASP, the lattice parameter for the bulk unit cell was set as 2.85 Å. Using the HRTEM results, the energy cut off of plane wave expansion was set to 500 eV, the k-points adopted from Monkhorst–Pack method were set to be 16 × 16 × 4 for bulk structure and 16 × 16 × 1 for monolayer structure, and the energy and atomic force convergence criteria for self-consistent was set to be 10$^{-9}$ eV and 10$^{-6}$ eV/Å, respectively. Moreover, the Van der Waal force interaction has been taken into account. For phonon dispersion calculations, the size of supercell has been chosen to be 4 × 4 × 4 for bulk and 4 × 4 × 1 for monolayer 2H-TaS2, respectively. In addition, we chose a 2 × 2 × 1 supercell extension for the calculating phonon dispersion of a 3 × 3 × 1 unit cell structure where the CDW phase of the monolayer 2H-TaS2 existed. Here it should be pointed out that the smearing parameter σ = 0.03 eV was used for the calculations of spectra since the depth of the negative peaks in the preceding spectra were smearing dependent.

Results and discussion
In the study, 2H-TaS2 nanosheets of different thicknesses (from 1 to over 100 nm) were exfoliated from a commercially grown 2H-TaS2, single crystal and then transferred onto SiO2/Si substrates by Scotch tape. Figure 1a shows the atomic structure of 2H-TaS2, where Ta atoms are in trigonal prismatic co-ordination with the S atoms. With increasing layer number, the interlayer Van der Waals force in 2H-TaS2 suppresses the out-of-plane vibration, so both the second-order scattering and $E_2^g$ modes can not be detected either because of selection rules for our scattering geometry ($E_2^g$) or because of the limited rejection of the Rayleigh scattered radiation ($E_2^g$). Remarkably, a strong band peaking at ~ 180 cm$^{-1}$ is observed for thick samples due to second-order scattering. With increasing layer number, the interlayer Van der Waals force in 2H-TaS2 suppresses the out-of-plane vibration, so both the second-order scattering and $E_2^g$ mode is stiffened (blue shift). While the red shift of the $A_{1g}$ mode indicates that long-range Columbic interlayer interactions may dominate variation of Raman mode, which is consistent with many other 2D materials. Noticeably, the Raman data of the thin sample (< 4 nm) shows two significant differences with respect to the thicker samples, where the second-order scattering peak degenerates and the $E_2^g$ mode shows a dramatic red shift.

Figure 2a presents the temperature evolution of the Raman spectra of a 2H-TaS2 monolayer measured at the same position during a cooling cycle. With decreasing temperature, the $E_2^g$ mode shows a red shift. Interestingly, apart from the peaks of the $A_{1g}$ and the $E_2^g$ modes, a new peak appears at ~ 155 cm$^{-1}$, when the temperature is below 100 K. Bulk 2H-TaS2 undergoes a phase transition at 75 K and the distorted CDW phase is formed below the transition temperature. Here it is noted that the 280 K spectrum shown in Fig. 2a is not identical to the 1 nm spectrum shown in Fig. 1d, e.g. the relative heights of the two peaks differ in the two figures, implying a dependence of temperature cycling. To confirm this, Fig. 2b plots the temperature-dependent electrical resistance curve for monolayer 2H-TaS2 during cooling. A sudden jump in resistance is observed at 93 K, indicating the CDW phase transition occurs even in monolayer 2H-TaS2, and the transition temperature is much higher than that for the bulk. The increased $T_c$ may be due to the reduced dimensionality, which enhances electron–phonon coupling and has been observed in other two-dimensional CDWs. Figure 2c further shows the Raman spectra of the same monolayer 2H-TaS2 during the heating cycle. Remarkably, the new peak can be clearly observed even at 140 K. The observed thermal hysteresis effect may be due to the presence of hidden CDW states or the roughness of the substrate. Figure 2d summarizes the intensity of the $A_{1g}$ mode as a function of temperature. It is found that the intensity of the $A_{1g}$ mode also shows a similar thermal hysteresis effect. We also measured...
2H-TaS₂ flakes of other thicknesses (figure S1). Similar effects were observed. We would like to stress that our work is the first to demonstrate that CDWs can exist in monolayer 2H-TaS₂.

To further confirm that the additional peaks observed at low temperature originate from the formation of a CDW, we calculated the phonon dispersion for the lattice dynamics of bulk and monolayer 2H-TaS₂ with and without the CDW phase based on density functional theory²⁴–²⁶ and the PHONOPY code¹³–¹⁵. Details of the simulation can be found in “Methods” section. The bulk has a crystal symmetry belonging to the D₆h space group. Two molecular units of TaS₂ compose a unit cell of bulk 2H-TaS₂, resulting in a total of 18 phonon bands. From the symmetry point of view, the irreducible representations of vibrational modes for bulk 2H-TaS₂ of the D₆h space group are: A₁g + 2B₂g + E₁g + 2E₂g + 2A₂u + B₁u + 2E₁u + E₂u, where E₂g, E₁g, E₂₂g, and A₁g are Raman active modes¹⁸, as shown in Fig. 3a. Figure 3b shows the phonon dispersion of bulk 2H-TaS₂. Among them, three bands belong to acoustic branches and fifteen branches belong to optical branches, additionally, an obvious indirect phonon frequency gap of about 60 cm⁻¹ exists between the acoustic and optical branches. Significantly, with a smearing parameter σ = 0.03 eV, there is a segment of acoustic branches which has negative phonon frequencies, approximately less than 50 cm⁻¹ along the MΓ direction in bulk 2H-TaS₂. A similar phenomenon, with negative phonon frequencies, also occurs in monolayer 2H-TaS₂, as shown in Fig. 3c, where the maximum negative frequency approaches to 150 cm⁻¹ along the M-Γ-K direction. The calculated results show that the bulk and monolayer 2H-TaS₂ are mechanically unstable in their ground states. In VASP calculations, the smearing parameters were used to accelerate the convergence in electronic self-consistent calculations, and from physical point of view, the abrupt change in Fermi–Dirac distribution can be smeared out by changing the magnitude of σ in the ground state. As a result, this smearing parameter physically represents the electronic temperature and can qualitatively affect the phonon properties of the materials by considering temperature effects. Manifestly, from Fig. 3b,c, the dependence of the phonon bands of bulk and monolayer of 2H-TaS₂ on the smearing parameter demonstrates that the large negative phonon frequencies along the acoustic branches will eventually be overshadowed, and become wholly positive frequencies as smearing increases with temperature.

The emergence of negative phonon frequencies along the M-Γ-K direction in both bulk and monolayer 2H-TaS₂ provide a clue to obtain the phonon dispersion of monolayer 2H-TaS₂ in the CDW phase. Physically, negative phonon frequencies represent an unstable mechanical material structure, so in order to get rid of these negative phonon frequencies or to obtain the stable structure of the monolayer 2H-TaS₂, the unit cell should be extended along the ΓM direction. Significantly, such an extension of the unit cell along the ΓM direction basically behaves like the experimentally observed CDW phase in bulk 2H-TaS₂, where the CDW phase is close to a supercell of 3 × 3 × 1 of the unit cell structure²⁷,²⁸. Figure 3d shows the phonon dispersion plot for monolayer TaS₂ characterizations. (a) Schematic drawing of the atomic structure of TaS₂. (b) AFM image of mechanically exfoliated TaS₂ flakes with a thickness about 1 nm. (c) HRTEM of TaS₂ flakes. Inset: SAED of TaS₂. (d) Raman spectra of mechanically exfoliated TaS₂ flakes with various thicknesses. The excitation wavelength is 532 nm.
of 2H-TaS₂ with a 3 × 3 × 1 unit cell. The negative phonon frequencies have completely vanished along the path passing through high symmetry points. This firmly demonstrates that a 3 × 3 × 1 unit cell structure is mechanically stable. Secondly, two distinct phonon frequencies emerge at about 150 cm⁻¹ at the Γ point that are not observed for bulk 2H-TaS₂. From the above simulation results, one can confirm that the CDW phase of monolayer 2H-TaS₂ truly and stably exists in a 3 × 3 × 1 unit cell structure. Moreover, the two CDW-induced frequencies at ~155 cm⁻¹ from our numerical simulation coincide very well with the experimental results of the Raman spectra, as shown in Fig. 2.

To summarize this argument, for 2H-TaS₂ with a 1 × 1 × 1 unit cell, one cannot get CDW peaks at 155.6 cm⁻¹ as observed in experiments. However, for 2H-TaS₂ with a 3 × 3 × 1 unit cell, two CDW modes appear at frequency 155.6691 cm⁻¹ and 155.6718 cm⁻¹ from ab initio calculations, which are very close to experimental observations near 155 cm⁻¹. From the animations, there are two different modes near 155 cm⁻¹, the Ta atoms will come closer and farther away from the center sulfur atoms like a breathing action (Breath mode), while for the other CDW mode the Ta atoms wiggle back and forth around the central S atoms like a wiggling motion (Wiggle Mode) 29. The breath CDW mode and wiggle CDW mode can be viewed as degenerate modes.

It is worth discussing the origin of the degeneracy of the oscillation frequency for these two modes. To clearly show the vibrational patterns it is necessary to consider a cell size 3 times larger in both the a and b directions for the CDW 3 × 3 × 1 unit cell. Figure 4 offers a top-down view of the lattice with the direction of the atomic displacements shown for both the breath and wiggle modes. The arrows denote the directions along which the atoms oscillate back and forth. Realistically, both the tantalum (Ta) and sulfur (S) atoms oscillate, however the displacement is comparatively small for S, thus we need only consider the movement of the Ta. Although the Ta atoms apparently oscillate in very different manners for the breath and wiggle modes, they are indeed the same at the larger scale if consider the collective motion of individual nearest atom triangular sub-units defined by 3 S atoms around a Ta atom. This equivalence can be more clearly recognized if we shift the origin of the wiggle mode by −½ b. Therefore, to analyze the origin of the degenerate frequencies, we only need to focus on the triangular cells, as shown in Fig. 3. The oscillations are regulated by the force exerted by the restorative potentials and can effectively be treated as a system or lattice of Ta atoms connected by several springs. As the lowest order approximation, we need consider only the nearest S atoms effecting spring forces from the Ta-S bonds, and all the spring constants are the same since the S atoms are equidistant. There are 6 S atoms around each Ta atom. Since the 2H-TaS₂ structure has a honeycomb structure, from the top view 3 S atoms situated are above the other 3 S atoms, thus the movements of Ta atoms for both modes are in-plane, and the S atoms can be further simplified by treating them as 3 in-plane atoms. If the spring constant between the actual S atoms and the Ta atom is $K$,
the combined force of by the two vertically aligned S atoms is $|F_s| = |F_{s1} + F_{s2}| = 2 \cos \theta K \Delta x$ (Fig. 5c), where $|F_{s1}| = |F_{s2}| = K \Delta x$ and $\Delta x$ is the atomic displacement of Ta from its equilibrium point. The contribution from two vertically aligned S atoms is equivalent to an in-plane atom with effective spring constant $k = 2\cos \theta K$.

For the breath mode shown in Fig. 5a, the Ta atoms oscillate along the line connecting a Ta and S atom. The net force exerted on the displaced Ta atom is the sum of the spring force from the 3 neighboring atoms, which is $F = F_1 + F_2 + F_3$, where 1, 2, and 3 label the three simplified S atoms and their respective directions. The Ta atom is shifted toward S1 by $\Delta x$, and thus $F_1 = -k\Delta x v_1$, where $v_1$ is the unit vector toward S1 (Fig. 2d).
Considering the lowest order approximation, the spring constant is assumed to be isotropic. Therefore, the effective displacement with respect to S2 is $|R_{Ta-S2}| - a = \sqrt{a^2 + \Delta x^2} - 2a\Delta x \cos \Phi = a - \Delta x/2$, and its direction is along $v_2$ since the displacement $\Delta x$ is very small. Similarly, the effective displacement from S3 atom is $\Delta x/2$ along $v_3$. Therefore, their spring forces are $F_2 = k\Delta x v_2$ and $F_3 = k\Delta x v_3$, respectively. The total spring force on the Ta atom is therefore $F = -3k\Delta x v_1$. Assuming the Ta atom has mass $m$, the oscillation frequency for breath mode is obtained to be $\omega = \sqrt{\frac{3k}{2m}}$. Displacement along $v_2$ and $v_3$ would be equivalent. For the wiggle mode Ta atom displacement is not directed towards the S atoms but rather towards the next adjacent Ta atom. Performing the same geometric analysis in this case, the displacement is along the x direction, the force due to the 3 simplified S atoms are $F_1 = \sqrt{3}k\Delta x v_1$, $F_2 = 0$, and $F_3 = \sqrt{3}k\Delta x v_3$. Therefore, the resultant force $F = (\frac{-3k}{2m})x$. Thus to concluded, at the lowest order both the breath and wiggle modes are degenerate, displaying the same oscillation frequency. However, here we have assumed that the three Ta-S bonds have same bond energies, thus conferring the degeneracy of the breath and wiggle modes. However, internal effects (e.g. defects) or external effects (e.g. applied stress) can introduce anisotropy into the CDW modes, the degeneracy can be lifted, and three Ta atoms will vibrate incoherently and several nearby peaks should be observed around 155.6 cm$^{-1}$.

Conclusions

Charge density waves can exist in exfoliated monolayer 2H-TaS$_2$ and the transition temperature can reach 140 K, which is much higher than that of the bulk. Moreover, the degenerate breath and wiggle modes of 2H-TaS$_2$ originated from the periodic lattice distortion have been probed by the optical methods. Our results open an avenue to investigate charge density wave phase in two-dimensional transition-metal dichalcogenides and will be helpful for understanding and designing devices based on charge density waves.

Data availability

All data, models, and code generated or used during the study appear in the submitted article.
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Author contributions

W.L. designed the work, Z.D. and C.Z. wrote the main manuscript text, X.X.H. and J.B.C. conducted analysis and interpretation of data, L.J.L. prepared figures, and L.L. revised the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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