Raman tensor of layered WS₂

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Recently, van der Waals layered materials, such as MoS₂, WS₂, MoSe₂ and WSe₂, have attracted extensive attention due to their unique properties and potential applications in (optoelectronic) electronic devices [1]. Similar to graphene, the atoms of van der Waals materials in the layer are connected by covalent bonds, and the van der Waals' force is applied between the layers [2]. However, compared with graphene, van der Waals materials exhibit more excellent performance in sensors, lithium-ion batteries, photocatalysis and transistors [3–5] due to the rich variety, large adjustable bandgap, good mechanical flexibility, excellent chemical stability, no dangling bond on the surface, high intrinsic electron mobility [6–9], and their recent progress in synthesis, characterization and equipment manufacturing [10–13]. Compared with other van der Waals layered materials, WS₂ is one of the materials with high density and molecular weight, stronger spin-orbit coupling and bipolar electronic transport characteristics [9,14,15].

The introduction of phonons to investigate their interaction with carriers in crystals is a fundamental physics subject in semiconductor device technology [16]. Driven by these techniques, there are numerous studies on phonon vibration modes in crystals, including AlN, ZnO, GaN, WTe₂ and MoTe₂ [17–24]. For layered WS₂, there are a lot of studies on its optical and electrical properties [25–27], but the research on the basic physical parameter of Raman tensor related to phonon vibration is still very limited. Due to the special layered structure, the effects of Raman tensor on different test planes of WS₂ are different; especially the research on the Raman tensor of WS₂ on the cross plane is more difficult. Raman spectroscopy, as one of the main methods to study Raman tensor, is a characterization technique based on the Raman effect, and its source of information is mainly generated by the vibration and rotation of atoms [28–30]. According to the different orientations of different planes caused by the interaction of atoms in the WS₂ layer, the Raman tensor

and polarization of the material can be uniformly studied by using the angle-resolved polarized function of Raman spectroscopy, which will further the application of WS₂ in polarization devices [18,19,31,32].

In this article, the Raman tensor of a representative van der Waals layered material (WS₂) is studied *via* angle-resolved polarized Raman spectroscopy. By selecting the theoretical basis fitting experimental results suitable for the experimental system, the vibration symmetry of the phonon modes of the material can be explored, and a series of information such as the comprehensive Raman tensor and the differential polarizability of the WS₂ can be obtained. This work explores the differential polarization behavior of the van der Waals layered materials in the process of non-elastic light scattering, and provides a theoretical basis for a better understanding and application of the polarization of the van der Waals layered materials.

The bluk WS₂ used in the experiment was obtained directly from commercial purchase, and its atomic structure is shown in Fig. 1a. In the *c*-plane test, the material was laid on the glass slide. While in the *m*-plane test, the sample was prepared by the way of fracture at the cross-section grain boundary. All tests were carried out at room temperature. The angle-resolved polarized Raman measurements were performed by using a Renishaw micro-confocal laser Raman spectrometer with the resolution of 1 cm⁻¹, equipped with 50 mW, 488 nm Ar⁺ laser excitation light, objective lens of 50× Leica microscope head, and the charge-coupled device (CCD) with a polarizer inserted into the receiving light path to ensure that the incident laser is parallel to the scattered laser. The spectral peak position of the instrument was corrected by the standard Si sample provided by the manufacturer. When the *m*-plane was measured, the laser was incident along the *a*-axis to the side of the sample, and the angle between the polarization vector *e_i* of the incident laser and the *c*-axis is defined as the polarization angle *θ*. As

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Figure 1 WS₂ structure and the experimental structure diagrams. (a) The atomic structure diagram of WS₂, where blue stands for S atom and yellow stands for W atom. (b, c) The structure diagrams of *m*- and *c*-plane tests, respectively, and the angles θ and ω are the angles between the incident laser wave vector $\mathbf{e}_i$ and the *c*-/*a*-axis of the crystal, respectively.

the sample stage rotates, the angle θ between the sample crystal axis and the incident laser polarization vector changes from -90° to 90° , with a step of 10° . During the *c*-plane test, the laser was incident along the *c*-axis to the sample surface, and the angle between the polarization vector $\mathbf{e}_i$ of the incident laser and the *a*-axis is defined as the polarization angle ω . The rotation angle ω increases from 0° to 180° and the step size is 10° . The experimental structure diagrams for the *m*- and *c*-plane tests are shown in Fig. 1b and c. Considering the stability of the sample and the comparability of the experiments, the test conditions on the *c*-plane are as follows: exposure time of 1 s, laser power 10%, and cumulative scanning for 5 times. The *m*-plane test conditions: exposure time of 1 s, laser power 50%, and cumulative scanning for 1 time. All those steps are in order to ensure the experiment's comparability.

2H-WS₂ belongs to D_{6h} point group and $P6_3/mmc$ space group, and its structure is shown in Fig. 1a. A primitive repetitive unit consists of 6 atoms of which the crystal structure is 2H hexagonal symmetry. There are 15 optical

phonon branches and 3 acoustic phonon branches in the center of Brillouin region [33]. The irreducibility is expressed as [30]

$$\Gamma = A_{1g} + 2A_{2u} + 2B_{2g} + B_{1u} + E_{1g} + 2E_{1u} + 2E_{2g} + E_{2u}. \quad (1)$$

According to the group theory, A_{1g} , E_{1g} and E_{2g} belong to Raman activities. Through the first-principles calculation, the dispersion relation and information of vibration modes inside the WS₂ lattice are obtained as shown in Fig. 2a and b. The A_{1g} mode is the vibration of S atom perpendicular to the *xy* plane, the E_{2g} mode is the relative movement between W atom and S atom, and the E_{1g} mode is the shear vibration between the rigid layers in plane. Therefore, Raman scattering experiments on different planes are beneficial to fully revealing the inelastic scattering process of each mode.

The Raman spectra of two-dimensional materials are related to the number of layers, but in the non-resonant Raman spectrum, with the change of the number of layers, the spectrum only shows the peak displacement [34–37], which does not affect the identification of the vibration modes. So the corresponding optical phonon Raman tensor R of the crystal structure for each mode is [17,38]

$$R(A_{1g}) = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} = \begin{pmatrix} |a|e^{i\varphi_a} & 0 & 0 \\ 0 & |a|e^{i\varphi_a} & 0 \\ 0 & 0 & |b|e^{i\varphi_b} \end{pmatrix}, \quad (2-1)$$

$$R(E_{1g}) = \begin{pmatrix} 0 & 0 & -c \\ 0 & 0 & c \\ -c & c & 0 \end{pmatrix}, \quad (2-2)$$

$$R(E_{2g}) = \begin{pmatrix} d & d & 0 \\ d & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (2-3)$$

Among them, a , b , c and d are Raman tensor elements

Figure 2 First-principles calculation results. (a) The phonon dispersion curve of WS₂ obtained from the first-principles calculation. (b) Schematic diagram of symmetry and atomic displacement of the three optical vibration modes of WS₂ with Raman activity.

of each Raman vibration mode, φ_a , φ_b denote the Raman tensor element multiphase, and all of these corresponding values can be obtained by fitting the experimental results.

According to the Raman selection rule defined by the unit polarization vectors $\mathbf{e}_i$ ($\mathbf{e}_s$) of incident laser (scattered laser), and the propagation and polarization characteristics of phonons under specific crystal symmetry, the Raman scattering intensity has the following relationship with Raman tensor [39,40]:

$$I \propto |\mathbf{e}_i \cdot \mathbf{R} \cdot \mathbf{e}_s|^2. \quad (3)$$

In the experiment, the polarization vectors of the incident laser and scattered laser are pre-set parallel, i.e., $\mathbf{e}_i // \mathbf{e}_s$ [41,42]. According to the polarization vectors (corresponding to Fig. 1b and c) selected from different observation points on the cross (m -) and basal (c -) planes of the test system, the polarization vectors can be marked as $\mathbf{e}_i = \mathbf{e}_s = (0, \sin\theta, \cos\theta)$ and $\mathbf{e}_i = \mathbf{e}_s = (\cos\omega, \sin\omega, 0)$. The experimental test planes refer to Ref. [25].

By introducing the polarization vector and Raman tensor into the Raman selection rule, the correlation between the Raman intensity and the angle of different test surfaces can be obtained. The Raman intensity of the m -plane test is as follows [39]:

$$I_{A_{1g}}(\theta) \sim |a_m|^2 \sin^4\theta + |b_m|^2 \cos^4\theta + 1/2 |a_m| |b_m| \sin^2(2\theta) \cos(\varphi_{a-b}), \quad (4-1)$$

$$I_{E_{1g}}(\theta) \sim |c_m|^2 \sin^2(2\theta), \quad (4-2)$$

$$I_{E_{2g}}(\theta) \sim |d_m|^2 \sin^4\theta, \quad (4-3)$$

where $\varphi_{a-b} = \varphi_a - \varphi_b$, which is the phase difference between Raman tensor elements a and b [43], usually obtained from experiments, depending on both the internal properties of the crystal and the influence of external testing.

The Raman intensity of the c -plane test is as follows [39]:

$$I_{A_{1g}}(\omega) \sim |a_c|^2, \quad (5-1)$$

$$I_{E_{1g}}(\omega) \sim 0, \quad (5-2)$$

$$I_{E_{2g}}(\omega) \sim |d_c|^2. \quad (5-3)$$

The theoretical results show that when the m -plane is measured, the Raman intensity of each vibration mode is correlated with the polarization angle, while that of the c -plane is not.

In the first-order Raman scattering (only the phonon

with wavevector $q \approx 0$ is possible), the Raman susceptibility $\partial\chi_{ij}/\partial r_l(\mu)$ can be introduced to obtain the scattering cross section, which is positively correlated with the Raman tensor element R_{ij}^q , i.e., [44]

$$R_{ij}^q = V_{\text{prim}} \sum_{\mu=1}^N \sum_{l=1}^3 \frac{\partial\chi_{ij}}{\partial r_l(\mu)} \frac{e_l^q(\mu)}{\sqrt{M_\mu}}, \quad (6)$$

where M_μ is the atomic mass, $r_l(\mu)$ the atomic displacement, V_{prim} the volume of the cell, and $e_l^q(\mu)$ the eigenvector of the vibration mode. The polarizability tensor α_{ij} has a positive proportional relationship with the susceptibility coefficient χ_{ij} ($\alpha_{ij} = \epsilon_0 \chi_{ij}$), that is [44]

$$R_{ij}^q = V_{\text{prim}} \sum_{\mu=1}^N \sum_{l=1}^3 \frac{\partial\alpha_{ij}}{\partial r_l(\mu)} \frac{e_l^q(\mu)}{\epsilon_0 \sqrt{M_\mu}}. \quad (7)$$

The differential polarizability $\partial\alpha_{ij}/\partial r_l(\mu)$ can be obtained by calculating the scattering rate of all small deformation $r_l(\mu)$. Therefore, the Raman spectra of other atoms with the same bond can be explained by the bond polarizability obtained by fitting the Raman data of one or more molecules.

The non-resonant Raman spectra of WS_2 are usually dominated by three basic vibration modes at Γ point: E_{1g} (291 cm^{-1}), E_{2g} (352 cm^{-1}), and A_{1g} (420 cm^{-1}), as shown in Fig. 2a [30,45]. Except for the peak position of the low wavenumber which is difficult to detect under the polarization configuration of the device, the other peak positions are consistent with the theoretical values. At ambient temperature and pressure, the experimental structures of WS_2 along the a - and c -axes of the samples are shown in Fig. 1b and c.

Angle-resolved polarized Raman spectroscopy of the m - and c -planes of WS_2 was measured under the same test conditions. The non-resonant pseudocolor Raman maps and waterfall diagrams with the range of $250\text{--}450 \text{ cm}^{-1}$ as shown in Fig. 3 can be obtained at each angle. When tested in the m -plane, the WS_2 spectrum shows that three modes, E_{1g} , E_{2g} and A_{1g} , can be observed in 297 , 355 , and 419 cm^{-1} , and according to the test of the c -plane, E_{2g} and A_{1g} modes at about 356 and 420 cm^{-1} are observed, consistent with the theoretical calculation results [46]. The theoretical discussion of Raman selection rules on the c -plane shows that the Raman intensity of E_{1g} mode keeps zero with the angle varying, so the E_{1g} mode cannot be observed when tested in this plane. Through the WS_2 spectral collection diagram (Fig. 3), it can be clearly distinguished that the Raman intensity of the m -plane is obviously correlated with the angle, while that of the c -plane is constant and polarization-independent.

Figure 3 The Raman intensity set of different polarization angles in the range of 250–450 cm⁻¹. (a, b) A set of pseudocolor Raman maps for WS₂ in the *m*- and *c*-plane tests, respectively. (c, d) Waterfall diagrams of WS₂ when tested in the *m*- and *c*-plane, respectively. And the strength scale settings are consistent for comparison.

Besides, compared with the Raman intensity of the three vibration modes, the Raman intensity of A_{1g} mode is the most identifiable, while that of E_{1g} mode is relatively weak.

In order to obtain more accurate angular polarization, Lorentz fitting was carried out for the Raman peak intensity of each vibration mode at each test angle, and the Raman intensity-polarization angle curve was obtained. As shown in Fig. 4a, the angle-resolved polarized Raman intensity of WS₂ in the A_{1g} mode of *m*-plane appears to be the smallest at about -50° and 50° in the range of -90°–90° without totally returning to zero. In the range of -90°–0° and 0°–90°, the Raman intensity decreases first and then increases. By fitting the experimental results with Equations (4-1), the normalized values of a_m and b_m are 1.00 and 1.36, respectively, and the phase angle φ_{a-b} is 90.44°. When the E_{2g} mode is tested in the *m*-plane (Fig. 4b), the Raman intensity decreases first and then increases in the whole range with an axial symmetry. When the polarization vector of the incident laser is perpendicular to the *c*-axis ($\theta = -90^\circ$ and 90°), the Raman intensity reaches the maximum; when the e_i is parallel to the *c*-axis ($\theta = 0^\circ$), the Raman intensity reaches the minimum, close to zero. The normalized Raman tensor d_m is 0.73 by fitting Equation (4-2). The E_{1g} mode has a trend of $|\sin|$ in the range of -90° to 90°, centered at 0°, via careful treatment (Fig. 4c). The minimum value is

close to zero at -90°, 0° and 90°, and the maximum value is at about -45° and 45°, respectively. The c_m is 0.10 by fitting Equation (4-3).

Compared with the obtained Raman tensor elements of WS₂ (as shown in Table 1), after normalization, the differential polarizability $\partial\alpha_{zz}/\partial r_i(\mu) \propto R_{zz}^{A_{1g}}$ (i.e., *b*) corresponding to the vibration of A_{1g} mode along the *c*-axis is larger than that of *a*(*b*)-axis differential polarizability $\partial\alpha_{xx}/\partial r_i(\mu) \propto R_{xx}^{A_{1g}}$ (i.e., *a*), that is, the corresponding Raman tensor matrix element $a < b$ [42]. The differential polarizabilities of E_{2g} and E_{1g} modes are smaller than that of A_{1g}, which shows that the identifiability of the relative vibration of S atom along the *c*-axis is the best.

Fig. 4d shows the intensities of E_{2g} and A_{1g} modes measured for WS₂ on the *c*-plane. The sample shows that the peak intensity corresponding to the *c*-plane is independent of the sample's rotation angle, which is consistent with the theoretical results. The relative values of the Raman tensor elements are extracted by dividing the square root of the average value of the fitting region, of which the a_c and d_c are 1.00 and 0.67, respectively. It can be found that the relative values $|d_m/a_m|$ of the Raman tensor element is very close to the $|d_c/a_c|$ by comparing the test results of *c*- and *m*-planes horizontally, which shows that the results of the two tests can be verified by each other, and the experimental results are in accordance

Figure 4 Raman intensity-polarization angle curves fitted by Raman selection rule. (a–c) Raman intensity-polarization curves of A_{1g} , E_{2g} and E_{1g} modes for WS_2 in the m -plane test, respectively. (d) Raman intensity-polarization curves of the vibration modes for WS_2 in the c -plane test. The points are the experimental data points and the curves are the fitting curves.

Table 1 Relative values of Raman tensor matrix elements for three vibration modes of WS_2 . Among them, $|A_c|$ and $|A_m|$ are the values of the non-normalized Raman tensor elements a_m and a_c from the c - and m -planes of WS_2 , respectively, which are 35.97 and 58.77. “*” indicates the unknown tensor element in the c -plane test.

Raman mode	c -plane	m -plane
A_{1g}	$ A_c \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & * \end{pmatrix}$	$ A_m \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1.36e^{0.50\pi i} \end{pmatrix}$
E_{2g}^l	$ A_c \begin{pmatrix} 0.67 & 0.67 & 0 \\ 0.67 & -0.67 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$ A_m \begin{pmatrix} 0.73 & 0.73 & 0 \\ 0.73 & -0.73 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
E_{1g}		$ A_m \begin{pmatrix} 0 & 0 & -0.10 \\ 0 & 0 & 0.10 \\ -0.10 & 0.10 & 0 \end{pmatrix}$

with facts.

All the above results are compared with our previous work on MoS_2 Raman tensor [47,48]. It is shown that due to the same structural symmetry and Raman tensor form, the phenomena of van der Waals layered materials MoS_2 and WS_2 in the angle-resolved polarized Raman spectra

are almost the same. The results of both c - and m -planes tests show different polarization dependences, which are isotropic and anisotropic, respectively. The experimental results are consistent with the Raman selection rule. At the same time, their dominant orientations of differential polarizability caused by vibration asymmetry are also very close. Therefore, the materials with known point group symmetry can be used to predict the angle-resolved polarization according to the Raman selection rules, and thus the differential polarizability of the materials can be discussed. This conclusion is also applicable to other van der Waals materials.

In this article, according to the crystal point group structure and Raman selection rule of WS_2 , the correlation between Raman intensity and polarization angles of m - and c -planes in parallel polarization configuration is discussed. Based on theoretical and experimental results, the Raman tensor elements and the corresponding differential polarizabilities of E_{1g} , E_{2g} and A_{1g} modes are determined. WS_2 exhibits anisotropy at the m -plane due to the special layered structure, with the differential polarizability corresponding to the vibration of A_{1g} phonon mode along the c direction being the largest and the identification degree being stronger than that of E_{1g} and E_{2g} modes. However, for the c -plane, both samples show

isotropism and the Raman scattering intensity is not related to the polarization angle. Furthermore, the relative values of Raman tensor elements on the *c*- and *m*-planes are very close, which shows that the experimental results are in accordance with objective facts. At the same time, combining with the previous work on the MoS₂ Raman tensor, the reliability of this method is confirmed, and the unified law of van der Waals crystals in angle-resolved polarized Raman is revealed.

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层状 WS_2 的拉曼张量

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摘要 为完善范德瓦尔斯层状材料有关于拉曼张量的基本信息, 本文采用角分辨偏振拉曼光谱对二硫化钨的拉曼张量进行研究. 根据拉曼选择定则, 我们分析了角分辨拉曼光谱与偏振的依赖关系, 并结合实验结果获得了面内和面外各振动模式的拉曼张量元和与张量元对应的微分极化率等信息. 实验结果表明, 截面测试得到的拉曼强度具有偏振依赖性, 其中沿 c 轴振动的 A_{1g} 模式引起的微分极化率明显大于 E_{1g} 和 E_{2g} 模式, 并且 A_{1g} 模式自身在沿 c 轴的极化率也较沿 a 轴或 b 轴的大. 这种通过角分辨偏振拉曼光谱研究拉曼张量的方法对其他范德瓦尔斯层状材料具有普遍性.