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Thermal expansion coefficient of few-layer MoS₂ studied by temperature-dependent Raman spectroscopy

Zhongtao Lin^{1,2}, Wuguo Liu^{1,3}, Shibing Tian¹, Ke Zhu¹, Yuan Huang^{1✉} & Yang Yang^{1✉}

The thermal expansion coefficient is an important thermal parameter that influences the performance of nanodevices based on two-dimensional materials. To obtain the thermal expansion coefficient of few-layer MoS₂, suspended MoS₂ and supported MoS₂ were systematically investigated using Raman spectroscopy in the temperature range from 77 to 557 K. The temperature-dependent evolution of the Raman frequency shift for suspended MoS₂ exhibited prominent differences from that for supported MoS₂, obviously demonstrating the effect due to the thermal expansion coefficient mismatch between MoS₂ and the substrate. The intrinsic thermal expansion coefficients of MoS₂ with different numbers of layers were calculated. Interestingly, negative thermal expansion coefficients were obtained below 175 K, which was attributed to the bending vibrations in the MoS₂ layer during cooling. Our results demonstrate that Raman spectroscopy is a feasible tool for investigating the thermal properties of few-layer MoS₂ and will provide useful information for its further application in photoelectronic devices.

Two-dimensional (2D) transition metal dichalcogenides (TMDs), especially monolayer 2D TMDs, have attracted enormous attention in the past decade because of not only their striking physical properties^{1,2} but also their potential applications in electronic, photonic and thermoelectric devices^{3–6}. However, obtaining large-area single crystalline monolayer 2D TMDs is still challenging, hindering their applications in devices. Compared with monolayer 2D TMDs, few-layer 2D TMDs are much easier to achieve by physical or chemical methods. In recent years, few-layer 2D TMDs have received increasing attention due to their interesting physical properties and applications in electronic and optoelectronic devices^{7–11}. Neri and coauthors reported the strain induced semiconductor–metal transition in few-layer MoS₂⁷. High-speed vertical photodiodes based on few-layer MoS₂ have been fabricated using asymmetric metal contacts, exhibiting an external quantum efficiency of up to 7%⁹. A simple few-layer MoS₂-based photodetector employing vertical Schottky junctions of Au–MoS₂–indium tin oxide (ITO) was proposed by Gong et al.¹¹. It has been demonstrated that the physical properties of MoS₂ can be significantly affected by the interactions between MoS₂ and the substrate, which causes strain, doping and defects^{12–16}. One of the prominent substrate effects is the strain created on the MoS₂ layer due to the difference in binding energies and the lattice mismatch between the substrate and MoS₂. Additionally, the electronic structure of MoS₂ can be modulated by external strain, and the PL emission of MoS₂ will change as a result^{16–18}.

The self-heating effect occurs while a device is working under a current flow or light irradiation, so the thermal properties of few-layer MoS₂ are important criteria that affect the performance of related electronic and optical devices. For example, the thermoelectric energy conversion ability of MoS₂ is related to the low thermal conductivity¹⁹, whereas high performance of electronic devices requires high thermal conductivity²⁰. Alongside the thermal conductivity and thermal transport properties, the thermal expansion coefficient is another important thermal property of MoS₂. The thermal expansion coefficient (TEC) mismatch between the substrate and MoS₂ introduces additional internal strain to the MoS₂ layer. Consequently, the optical and electronic performances of MoS₂ devices supposedly change due to the thermal strain. Therefore, clear insight into the TEC of

¹Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P O Box 603, Beijing 100190, People's Republic of China. ²Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124, People's Republic of China. ³Department of Materials Science and Engineering, and State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum Beijing, No. 18 Fuxue Rd., Beijing 102249, People's Republic of China. ✉email: yhuang01@iphy.ac.cn; yang.yang@iphy.ac.cn

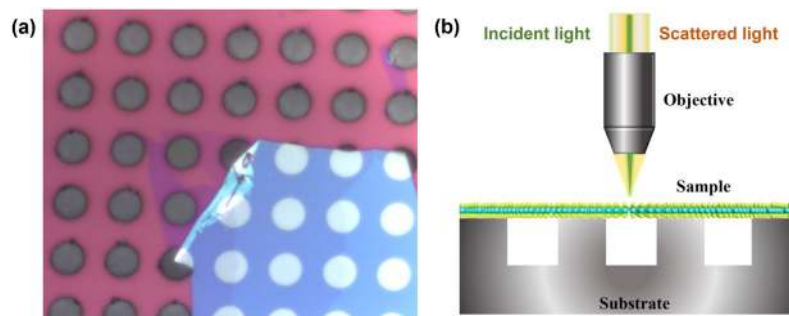


Figure 1. (a) Optical image of 2-layer MoS₂ on a prepatterned SiO₂/Si substrate with a 5 μm hole array. (b) Schematic illustration of Raman measurement for MoS₂ suspended on microholes.

MoS₂, especially the TEC mismatch between MoS₂ and the substrate, is a key for studying the thermal stability and intrinsic optical properties of few-layer MoS₂-based devices.

Raman spectroscopy has been demonstrated to be a versatile tool for investigating 2D TMDs^{21–23}. In the past decade, the temperature effects on the Raman modes of 2D TMDs have been widely investigated^{24–29}. However, the temperature behaviors of the Raman peaks of TMDs are still controversial. Some researchers reported that the peak positions varied linearly with increasing temperature^{24–27}. Late et al. reported that both monolayer and few-layer MoSe₂ and WSe₂ exhibit a linear temperature dependence²⁵. A linear temperature dependence of Raman modes was also observed in monolayer Mo_{1–x}W_xS₂²⁷. In recent years, some studies have demonstrated that the temperature dependence of the Raman peak positions for TMDs can be fitted by a nonlinear function. Su and coauthors employed temperature-dependent Raman spectroscopy to study the substrate bonding effects on MoS₂ and WS₂ and expressed the temperature dependence of Raman modes using a third-order polynomial function^{28–30}. Although the reported temperature dependences of Raman modes for 2D TMDs differ, the TEC mismatch between TMDs and substrates is widely accepted to play an important role in the temperature evolution of Raman modes. To eliminate the substrate effects, suspended TMDs have been used to study the intrinsic properties of TMDs in recent years^{31–36}. Two-ten times improvement of the mobility and on/off ratio was observed in suspended monolayer MoS₂³¹. The elastic coefficients, including the 2D elastic modulus and Young's modulus, were obtained for suspended multilayer WSe₂³². Moreover, the intrinsic thermal conductivity has been investigated for monolayer and few-layer MoS₂^{33,34}. However, to our knowledge, the TEC mismatch effect in few-layer MoS₂ has not been systematically studied, and the intrinsic TEC of few-layer MoS₂ has not yet been obtained.

In this work, suspended MoS₂ and supported few-layer (2–6 layer) MoS₂ was comprehensively investigated using Raman spectroscopy in the temperature range from 77 to 557 K. The temperature dependence of suspended MoS₂ exhibited different trends from that of supported few-layer MoS₂, which could be attributed to the TEC mismatch between MoS₂ and the substrate. Moreover, the temperature dependence of the Raman modes varied with the number of layers. Removing the substrate effect by adopting suspended MoS₂ as a freestanding MoS₂, the intrinsic TECs of few-layer MoS₂ was obtained. Prominent differences between our results and previous reports were observed and discussed in detail.

Results and discussion

The suspended and supported samples were fabricated by transferring MoS₂ with 2–6 layers onto microholes, which were prepared using a modified mechanical exfoliation method³⁷ (see “Methods”). Figure 1a presents the optical microscopy image of suspended 2-layer MoS₂ as an example.

Raman spectra were collected using a confocal micro-Raman spectrometer (Horiba Evolution) under back-scattering geometry, as exhibited in Fig. 1b. Figure 2 presents the room-temperature Raman spectra of suspended and supported few-layer MoS₂, which exhibit the typical spectral features of MoS₂ previously reported^{22,23}. Two high frequency peaks appear at approximately 380 cm⁻¹ and 405 cm⁻¹, originating from the lattice vibration of bulk MoS₂. Due to the crystalline symmetry changes between bulk, monolayer and few-layer MoS₂, the symmetric representations of these two Raman modes are different. For convenience, these two modes are identified as the E_{2g} and A_{1g} modes, respectively, following the assignments for bulk MoS₂²³. The bulk-vibrational Raman modes shift to higher positions with increasing number of layers. In recent years, ultralow frequency (ULF) Raman spectroscopy has attracted the interest of more researchers because it has been demonstrated to be a feasible tool for studying the interlayer vibrational modes of TMDs^{38–40}. The ULF Raman peaks originate from the in-plane (shear) and out-of-plane (breathing) vibrations of MoS₂, which have been used to identify the number of MoS₂ layers^{39,40}. The sharp peak is denoted as a shear mode (S1), while the broad peak is assigned as a breathing mode (B1), as shown in Fig. 2. Notably, the signal-to-noise ratio (SNR) of the Raman peaks, especially the ULF Raman peaks, of suspended MoS₂ is much better than that of supported MoS₂, and more detailed spectral information can be clearly seen. Both the S1 and B1 modes are clearly observed on suspended MoS₂, whereas only the S1 mode is detected on supported MoS₂. The MoS₂ layer is pinned on the substrate through van der Waals forces. The dielectric environment created from by the substrate may have effect on the local electromagnetic field due to the multiple reflection inside the monolayer¹⁶. The enhanced Raman signal of the suspended MoS₂ can be attributed to the isolation from the substrate effect³⁵. Moreover, the E_{2g} mode for the supported 2L MoS₂ is asymmetric, as shown in Fig. 2b. As Mignuzzi et al. reported, defects could induce not only an asymmetric line shape but also

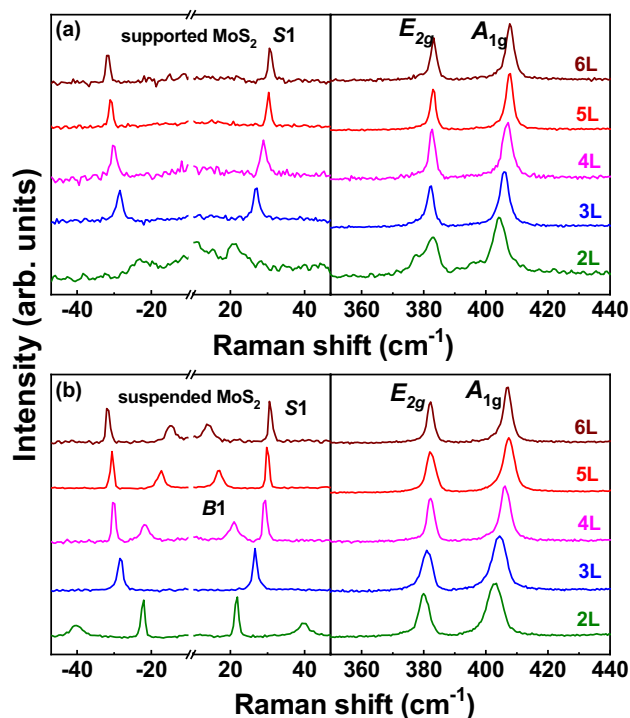


Figure 2. Raman spectra of (a) supported and (b) suspended MoS₂ with different numbers of layers collected at room temperature.

Raman peaks arising from zone-edge phonon modes⁴¹. In our work, no additional peak was observed in the spectrum for supported 2L MoS₂, suggesting that the strain is the dominant effect rather than defects. The E_{2g} mode of monolayer MoS₂ has been demonstrated to split into two singlets as the external strain is increased^{42,43}. As presented in Fig. S1b, the E_{2g} mode can be well fitted using two peaks, which can be attributed to the strain introduced by the substrate-MoS₂ interaction. We assume that the substrate-induced strain is the same for all the supported MoS₂ flakes. Therefore, the strain effect on the supported 2L MoS₂ is the most obvious because 2L MoS₂ is thinner than the other samples.

To deeply investigate the substrate effect, supported MoS₂ and suspended few-layer MoS₂ were studied in the temperature range of 77 K–557 K, and the results are displayed in Fig. 3. Prominent redshift and broadening of Raman peaks are noted for both suspended and supported MoS₂ with increasing temperature, as exhibited in Fig. 3. These phenomena can be attributed to the thermal expansion of the crystal lattice of MoS₂^{26,27}.

To obtain deeper insight into the difference between suspended and supported MoS₂, the Raman spectra were deconvoluted using a Lorentz/Gaussian mixed function. The peak positions of the E_{2g} and A_{1g} modes are plotted as a function of temperature in one figure for comparison. Figure 4 exhibits the fitting results for supported and suspended MoS₂, in which several remarkable phenomena should be addressed, as discussed below.

First, the temperature-dependent evolutions of the supported MoS₂ samples are similar, varying approximately linearly with increasing temperature at first sight. This suggests that the substrate effect is exerted on the MoS₂ flakes as a whole, although the substrate is only in direct contact with the bottom layer of a MoS₂ flake. The mechanically exfoliated MoS₂ layer is transferred and pinned on the substrate by the van der Waals force. As the temperature changes, the biaxial tensile or compressive stress induced by the TEC mismatch increases and becomes a prominent factor that modulates the frequency shift of Raman peaks. In addition to TEC mismatch, charge transfer between the film and the substrate or through interfacial states can impact the temperature evolution of Raman peak. As Su et al. discussed that accelerated redshift of A_{1g} mode with increasing temperature is associated with the enhanced charge injection from the substrate into the film and decomposition of adsorbed contaminants³⁰.

Second, the temperature-dependent evolutions of suspended MoS₂ are very different from those of supported MoS₂, exhibiting nonlinear behavior with increasing temperature. Moreover, the temperature dependence trends for the different suspended MoS₂ samples differ. As discussed previously, the TEC mismatch gives rise to a Raman shift with increasing temperature. However, suspended MoS₂, at least the part on the hole, is free of the substrate effect, suggesting that its Raman shift only originates from lattice expansion. Compared with the temperature dependence of supported MoS₂, suspended few-layer MoS₂ exhibits the intrinsic thermal properties of MoS₂ as expected.

Third, the peak positions of supported MoS₂ are higher than those of suspended MoS₂ at each temperature, suggesting that the TEC mismatch induced compression of the crystalline lattice in supported MoS₂. That the larger attached area of supported MoS₂ compared with suspended MoS₂ would introduce more strain into the

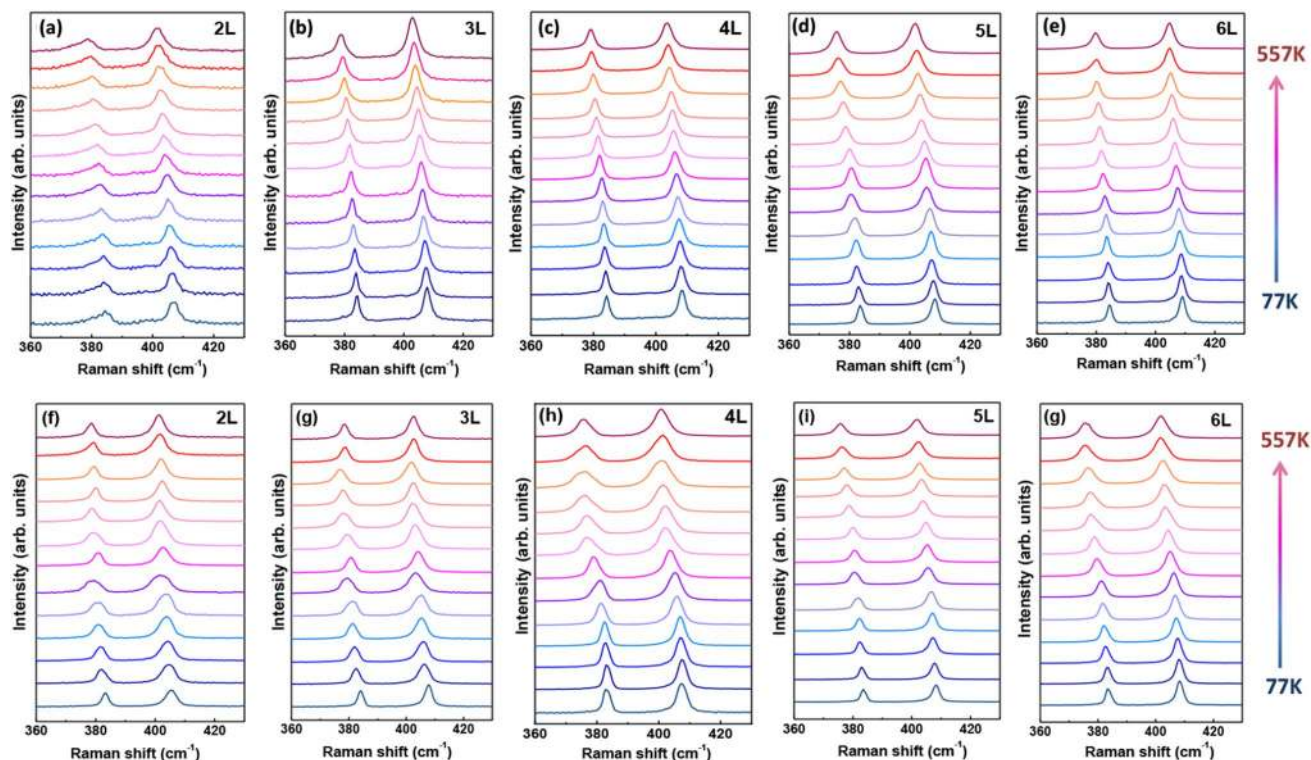


Figure 3. Raman spectra of (a–e) supported and (f–g) suspended few-layer MoS₂ for different temperatures.

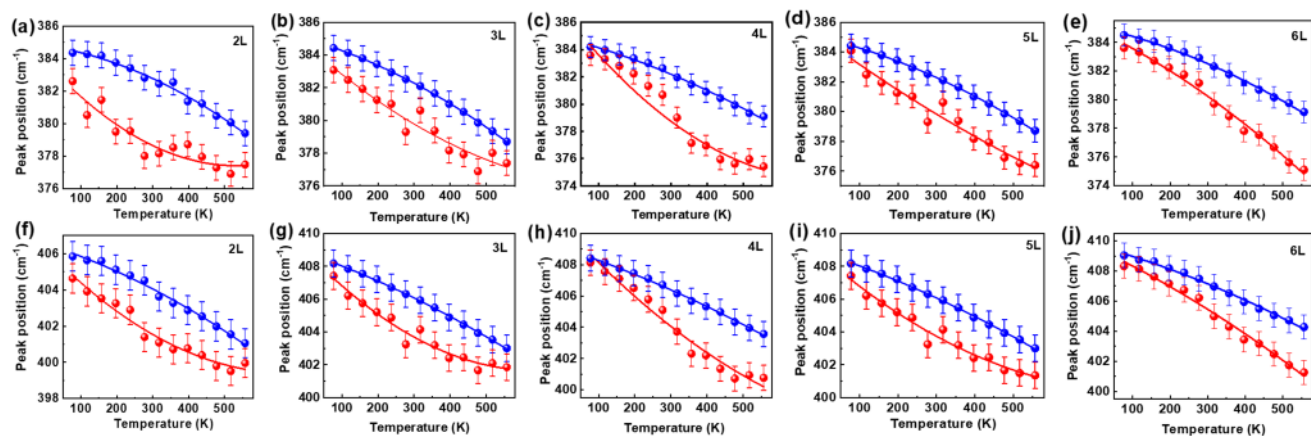


Figure 4. Temperature dependence of peak positions of the (a–e) E_{2g} and (f–j) A_{1g} modes for the suspended and supported MoS₂ with different numbers of layers. The blue spheres and red spheres represent the experimental results of supported and suspended MoS₂, respectively. The blue lines and red lines are the fitting results obtained using a second-order polynomial function of temperature.

MoS₂ layer is easy to explicate. As demonstrated previously, the strain in the MoS₂ layer is due to the TEC mismatch between the SiO₂ substrate and MoS₂.

The results shown in Fig. 4 demonstrate that the TEC of MoS₂ is strongly correlated with the number of layers, which can only be obviously exhibited after isolating it from the substrate effect.

Then, the peak positions of MoS₂ were fitted as a function of temperature to obtain the regularities of the temperature dependence of the peak positions. First, a linear function was employed to fit temperature evolution Raman peaks for the supported and suspended MoS₂ samples (see Fig. S2). The temperature evolution of Raman peaks for the supported MoS₂ shows a nearly linear behavior as a function of temperature. But there is a small deviation between the experimental results and fitting curve, as exhibited in Fig. S2. On the other hand, the temperature evolution for the suspended MoS₂ cannot be well fitted using a linear function, in which large discrepancies between the linearly fitted curves and experimental results are observed. According to previous literatures, the anharmonic effect caused by the phonon–phonon coupling leads to the nonlinear temperature-dependent behavior of the Raman peaks³⁸.

		E _{2g} mode			A _{1g} mode		
		ω ₀	χ ₁	χ ₂	ω ₀	χ ₁	χ ₂
2L	Sus	383.835	-0.024	2.249 × 10 ⁻⁵	406.271	-0.020	1.490 × 10 ⁻⁵
	Sup	384.812	-0.003	-1.153 × 10 ⁻⁵	406.550	-0.006	-6.557 × 10 ⁻⁶
3L	Sus	385.948	-0.029	2.622 × 10 ⁻⁵	409.181	-0.026	2.334 × 10 ⁻⁵
	Sup	384.995	-0.006	-8.833 × 10 ⁻⁶	408.843	-0.008	-5.139 × 10 ⁻⁶
4L	Sus	386.710	-0.033	2280 × 10 ⁻⁵	410.519	-0.025	1.168 × 10 ⁻⁵
	Sup	384.884	-0.007	-7.127 × 10 ⁻⁶	409.096	-0.008	-4.157 × 10 ⁻⁶
5L	Sus	384.990	-0.019	5.616 × 10 ⁻⁶	408.667	-0.020	1.236 × 10 ⁻⁵
	Sup	384.214	-0.008	-1384 × 10 ⁻⁵	409.105	-0.011	-5.266 × 10 ⁻⁶
6L	Sus	384.935	-0.013	-9.845 × 10 ⁻⁶	409.585	-0.012	-6.340 × 10 ⁻⁶
	Sup	385.099	-0.006	-8.738 × 10 ⁻⁶	409.719	-0.007	-5.627 × 10 ⁻⁶

Table 1. Temperature coefficients of the suspended and supported few-layer MoS₂ samples with polynomial fitting to the second order.

Therefore, the polynomial function was adopted to fit the experimental results for the supported and suspended MoS₂ samples instead of the linear function. All the temperature dependence trends of the E_{2g} and A_{1g} modes were fitted using a second-order polynomial function of temperature *T*,

$$\omega(T) = \omega_0 + \chi_1 T + \chi_2 T^2 \quad (1)$$

where ω₀ is the frequency at 0 K and χ₁ and χ₂ are the first- and second-order temperature coefficients, respectively. The fitting results for supported and suspended MoS₂ with the same thickness are plotted in Fig. 4 for comparison, and the fitting parameters are listed in Table 1. As shown in Fig. 4, the polynomial curves better fit the experimental results for the supported and suspended MoS₂, compared with the linear curves. Remarkably, for the supported MoS₂, the residual sum of square (RSS) for the polynomial fitting is much smaller than that for the linear fitting (see Table S1 in the Supplementary Information). This implies that the polynomial function is a better and more reasonable choice for fitting the temperature-evolution of the Raman shifts for the supported MoS₂, although it exhibits an approximate linear trace.

As exhibited in Table 1, the fitting parameters for suspended MoS₂ are very different from those for supported MoS₂. The fitting parameter χ₁ for suspended MoS₂ is one order of magnitude larger than that for supported MoS₂. Moreover, the fitting parameters exhibit a layer number dependence. As exhibited in Table 1, for the 2L–5L MoS₂ samples, the χ₂ of suspended MoS₂ is positive, whereas the χ₂ of supported MoS₂ is negative. Interestingly, χ₂ is negative for both suspended and supported 6L MoS₂. This occurs because of the different temperature evolutions of 6L MoS₂ and thinner MoS₂. One can see in Fig. 4e and j that the peak positions for the 6L suspended MoS₂ linearly shift to low frequency, similar as the peak evolution for the supported MoS₂. Therefore, the fitting parameters for the curves are all negative. In contrast, the shift rates of the peak positions for the 2L–5L suspended MoS₂ vary in different temperature ranges. As exhibited in Fig. 4a–d, the peak positions shift faster in the low temperature range (< 350 K) than in the high temperature range (> 350 K). Therefore, the parameter χ₂ is positive to better fit the experimental results. The thermal stability of MoS₂ strongly depends on the competition between the energy barriers introduced by the MoS₂–substrate interface and by the MoS₂–MoS₂ interlayer interface⁴⁴. The few-layer MoS₂ flake as a whole changes with increasing temperature, the influence of the intrinsic thermal expansion of MoS₂ on the frequency shift increases as the number of layers increases. As a result, the temperature evolutions of the Raman peaks of the suspended and supported 6L MoS₂ samples become similar. These results suggest that the thermal behavior of few-layer MoS₂ become similar as that of bulk MoS₂ with increasing thickness.

The results in Table 1 indicate that the discrepancy in the frequency shifts between the suspended and supported MoS₂ originates from the TEC mismatch between the substrate and MoS₂. Taking advantage of the results shown in Figs. 3, 4 and 5, the TEC of few-layer MoS₂ can be obtained, and the details for the calculation of the TEC of few-layer MoS₂ will be discussed in the following section.

As has been reported, the temperature-dependent Raman frequency shift (Δω_{MoS₂}(*T*)) of freestanding MoS₂ can be commonly attributed to the thermal expansion of the lattice (Δω^E(*T*)) and the anharmonic effect (Δω^A(*T*)), which changes the phonon self-energy⁴⁵. Δω_{MoS₂}(*T*) can be expressed as

$$\Delta\omega_{\text{MoS}_2}(T) = \Delta\omega^E(T) + \Delta\omega^A(T) \quad (2)$$

Δω_{MoS₂}(*T*) can be obtained using the peak position at *T* (ω_{MoS₂}(*T*)) subtracted by the peak position at *T*₀ = 300 K (ω_{MoS₂}(*T*₀)).

For the thermal behavior of the supported MoS₂, both common thermal effects and strains induced by the TEC mismatch between the substrate and MoS₂ must be considered. As a result, the frequency shifts of supported MoS₂ can be written as

$$\Delta\omega_{\text{MoS}_2}^S(T) = \Delta\omega^E(T) + \Delta\omega^A(T) + \Delta\omega^S(T) \quad (3)$$

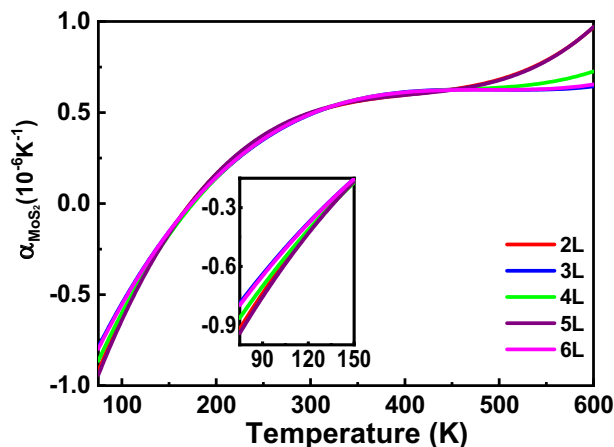


Figure 5. Calculated TECs of MoS₂ with different numbers of layers. The inset figure shows a magnified view of the TECs in the temperature range of 75–150 K.

The E_{2g} mode arises from the in-plane relative vibration between the Mo and S atoms, which is more sensitive to the temperature-induced lattice expansion/shrinkage of 2D MoS₂. On the other hand, the frequency shift of A_{1g} mode not only closely depends on lattice variations, but also is related with the charge transfer from the substrate to MoS₂⁴⁶. The electron doping effect can induce the frequency shifts of A_{1g} mode due to the strong electron–phonon interaction⁴⁷. Consult to previous literature, the E_{2g} mode is not sensitive to the electron doping effect^{47,48}. So it is assumed that the electron doping effect induced Raman shift of E_{2g} mode did not change with temperature, or the changes can be neglected. For simplicity, the doping effect induced Raman shift of E_{2g} mode is defined as a constant that is independent of temperature in this work. Thus, in the calculation of the Raman frequency differences ($\Delta\omega_{\text{MoS}_2}(T)$) between the given temperatures and $T = 300$ K, the doping effect induced Raman shift is subtracted as a constant. So that there are still three terms in Eq. (3) when the doping effect induced Raman shift is not taken into consideration. Therefore, the $\Delta\omega_{\text{MoS}_2}(T)$ of E_{2g} mode was calculated and employed in the following equations.

The TEC mismatch-induced frequency shift can be obtained by subtracting the intrinsic frequency shift from the frequency shift of supported MoS₂,

$$\Delta\omega^S(T) = \Delta\omega_{\text{MoS}_2}^S(T) - \Delta\omega_{\text{MoS}_2}(T) \quad (4)$$

To apply Eq. (4), the frequency shift of freestanding MoS₂ should be provided. However, real freestanding MoS₂ does not exist. Therefore, Raman frequency shifts from theoretical calculations or suspended TMDs have normally been employed as those of freestanding samples^{31,35}. In this work, we assume that the strain induced by the substrate effect can be neglected in the center of the suspended MoS₂ layers, as the laser spot (1 μm) in the measurement is much smaller than the size of the hole (5 μm) below the suspended MoS₂. Therefore, the Raman shifts of suspended MoS₂ is adapt as the intrinsic frequency of freestanding MoS₂ in this work.

Based on above discussion, the TEC mismatch-induced frequency shift $\Delta\omega^S(T)$ for the supported MoS₂ can be obtained by

$$\Delta\omega^S(T) = \Delta\omega_{\text{sup}}(T) - \Delta\omega_{\text{sus}}(T) \quad (5)$$

where $\Delta\omega_{\text{sup}}(T)$ and $\Delta\omega_{\text{sus}}(T)$ are the Raman shifts of supported and suspended MoS₂, respectively.

In addition, the contribution to the Raman frequency shift from the substrate-induced strain ($\Delta\omega^S(T)$) can be expressed as

$$\Delta\omega^S(T) = \beta \int_{T_0}^T [\alpha_{\text{SiO}_2}(T) - \alpha_{\text{MoS}_2}(T)] \quad (6)$$

where β is the biaxial strain coefficient of the Raman mode and $\alpha_{\text{SiO}_2}(T)$ and $\alpha_{\text{MoS}_2}(T)$ are the temperature-dependent TECs of SiO₂ and MoS₂, respectively. As has been reported, β depends on the number of MoS₂ layers⁴⁹.

As the values of α_{SiO_2} and β are already known from previous literatures, the temperature dependence of α_{MoS_2} can be derived from Eqs. (5) and (6). The calculated $\alpha_{\text{MoS}_2}(T)$ can be expressed using a quadratic function, and then, the $\alpha_{\text{MoS}_2}(T)$ values for MoS₂ with different numbers of layers are plotted in Fig. 5.

As presented in Fig. 5, the curves of the calculated TECs of MoS₂ with different numbers of layers follow similar trends. Notably, the order of magnitude of the TECs is at the same level as those in previous reports^{22,28}, implying the validity of the calculation methods employed in this work. For example, the TEC at room temperature observed in this work is approximately $0.5 \times 10^{-6} \text{ K}^{-1}$. Su et al. claimed that the in-plane TEC of MoS₂ is $2.48 \times 10^{-6} \text{ K}^{-1}$ at room temperature²⁸, whereas Late et al. reported a TEC of $8.2 \times 10^{-6} \text{ K}^{-1}$ ²². The discrepancy in the TECs between our results and previous publications can be attributed to the diversity in β employed in the calculation and whether the substrate effect is considered. Remarkably, the TECs of few-layer MoS₂ are very close

in the temperature range of 150–450 K. These results clearly suggest the feasibility of using Raman spectroscopy in the investigation of the TEC of MoS₂, at least in the temperature range of 150–450 K.

In addition, the diversity in the TECs between the MoS₂ with different numbers of layers is also obvious. As presented in the inset figure of Fig. 5, the TECs of few-layer MoS₂ exhibit remarkable differences in the temperature ranges of 0–150 K and 450–600 K. Strikingly, the TEC becomes negative below 175 K. This is different from most previous reports^{25,28,50,51}, in which the TEC is positive in the entire temperature range. In 2015, Wang et al. obtained a negative TEC below 31 K for monolayer MoS₂ using first-principles calculation by taking the stiffness and charge transfer effect into consideration⁵². The ZA bending vibrations (acoustic modes) may cause negative thermal expansion in few-layer MoS₂^{52,53}. The negative value of the Grüneisen parameter for the transverse acoustic mode responds for the negative TEC⁵⁴. The larger the absolute value of the negative Grüneisen parameter is, the larger the negative TEC. The negative TEC below 175 K observed in our work suggests a larger negative Grüneisen parameter.

Moreover, the TEC of few-layer MoS₂ increases gently in the temperature range over 450 K, as shown in Fig. 5. This evolution of the TEC observed in our work is similar to that in previous studies^{50–52}. However, the high-temperature TECs for 4L and 5L MoS₂ exhibit a slight difference compared with the other thicknesses. Wang et al. reported that the threshold temperature for etching monolayer MoS₂ is lower than 513 K, which is closely related with defects⁴⁴. The abnormal behavior of the TECs for 4L and 5L MoS₂ in the high temperature range can be attributed to the lower thermal stability due to the defects initially existed in these MoS₂ samples. Identification of the TEC of few-layer MoS₂ requires further experimental and theoretical studies. In the future, the temperature-dependent Raman study carried with controllable electronic doping concentration is called to deeply investigate the doping and dielectric environment effects on the frequency shifts of Raman modes, especially the A_{1g} mode.

Conclusion

In this work, a comprehensive Raman study was carried out on supported and suspended MoS₂ with different numbers of layers in the temperature range from 77 to 557 K. Strikingly, the temperature behaviors of the Raman frequency shift for suspended MoS₂ are significantly different from those for supported MoS₂. The intrinsic TECs of 2–6-layer MoS₂ were calculated after eliminating the substrate effect. Strikingly, the TEC becomes negative below 175 K, which can be associated with the bending vibration in the MoS₂ layer as the temperature decreases. The TEC curves of MoS₂ with different numbers of layers follow similar evolution trends in the temperature range of 150–450 K. Compared with previous reports, the validity of the TEC obtained in this work suggests that Raman spectroscopy is a feasible tool for investigating the TEC of MoS₂. Our results provide useful information for understanding the thermal properties of MoS₂ and its further application in devices.

Methods

To fabricate suspended MoS₂ samples, a periodic hole array was first fabricated on a SiO₂ (300 nm)/Si substrate by UV lithography and reactive ion etching technology, in which the holes were 5 μm in diameter and 2 μm in depth. MoS₂ flakes with different thicknesses were prepared from a natural MoS₂ single crystal using a modified mechanical exfoliation method onto the prepatterned SiO₂/Si substrate previously cleaned by oxygen plasma.

The optical image of the suspended few-layer MoS₂ was obtained using an Olympus BX41 microscope equipped on the micro-Raman spectrometer, Horiba Evolution HR. In the Raman spectroscopy measurements, a solid-state laser with a 532 nm wavelength was used as the excitation source. The laser beam was focused using a 100× long-working distance objective with numeric aperture NA = 0.8, and the spot size was approximately 1 μm. To avoid significant frequency shifts induced by the local heating effect and ensure a sufficient SNR, the laser power was set at ~0.9 mW on the surface of the heating stage. The numbers of layers of MoS₂ were identified using ULF Raman spectroscopy. The sample was placed inside a cryostat cell (Linkam, THMS 600), and the Raman spectra were measured in the temperature range from 77 to 557 K at an interval of 20 K.

Received: 17 July 2020; Accepted: 4 March 2021

Published online: 29 March 2021

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Acknowledgements

The authors acknowledge the financial support received from the National Key Research and Development Program of China (Grant Nos. 2018YFB0703500, 2019YFA0308000, 2018YFA0704201), the National Natural

Science Foundation of China (Grant Nos. 11704401, 11874405), and the Scientific Equipment Development Project of the Chinese Academy of Sciences (Grant No. YJKYYQ20170027).

Author contributions

Z.L. and W.L. did the measurements, data analysis. K. Z. did part of the data analysis. S. T. and Y. H. prepared the samples. Y. Y. supervised the study and wrote the main manuscript text. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1038/s41598-021-86479-6>.

Correspondence and requests for materials should be addressed to Y.H. or Y.Y.

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