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Temperature Dependent Phononic Response of Few Layered MoS_2 Nanosheets

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ABSTRACT

From the temperature dependent phononic studies of few layered liquid phase exfoliated MoS_2 nanosheets we find that the E^1_{2g} (in-plane) and A_{1g} (out-of-plane) Raman modes follow red shift with increase in temperature and exhibits non-linear temperature dependence in the entire temperature range (80 to 600 K). The first-order temperature coefficients for E^1_{2g} and A_{1g} modes are found to be -0.0133 $cm^{-1}K^{-1}$ and -0.0092 $cm^{-1}K^{-1}$, respectively. The physical origin of the non-linear temperature dependence is analyzed using an analytical model that includes contribution of the thermal expansion and an-harmonic effects to the lattice potential. Our analysis suggests that the non-linear temperature dependence of E^1_{2g} and A_{1g} modes mainly originates from the an-harmonic contributions from three-phonon and four-phonon scattering.

1. Introduction

Recently, two dimensional layered materials (2DLMs) have gained increased research interests owing to their unique electrical, optical and thermal properties which do not exist in their bulk counterpart [1-5]. The atomically thin transition metal dichalcogenides (TMDs) like MoS_2, WS_2, $MoSe_2$, WSe_2 etc. are important members of 2DLMs vast family. Each layer of TMDs is tri-atomic thick (6-7 Å) with strong in-plane (covalent) bonding and weak out-of-plane (van der Waals) interactions. TMDs show layer dependent properties such as bulk MoS_2 is an indirect band-gap (1.3 eV) semi-conductor whereas its single layer nanosheets display a direct band-gap of 1.8 eV [1-8]. The presence of direct band-gap results in intense photoluminescence from monolayer MoS_2, which makes it useful for many optoelectronic applications. From application point of view, it is very important to investigate the thermal properties of TMDs to manage the performance loss due to self-heating of the device [6, 8].

The temperature-dependent phononic response of TMDs can provide prospective information about the thermal properties and related phonon-scattering processes [9-12]. These temperature-dependent changes are the result of contributions from pure temperature effects and volume effects [12-20]. The temperature dependent Raman studies of monolayer and few–layer MoS_2 (prepared by mechanical exfoliation or chemical vapour deposition (CVD) methods on different type of substrates) over a wide temperature range have been extensively studied [12,14,16-19]. The corresponding Raman peak shifts were described by considering first-order temperature coefficients that predict a linear red shift in the low temperature region [14-17]. At higher temperatures, the contribution of the higher order phonon scattering becomes significant and the non-linear temperature dependency is better described by cubic and quartic an-harmonic terms [16-20].

Here we present a combined experimental and quantitative analysis of the effect of temperature on the Raman-active modes (E^1_{2g} and A_{1g}) of few layered MoS_2 nanosheets (obtained by liquid phase exfoliation of bulk MoS_2 powder). While both peaks show an expected red shift with increase in temperature, the frequency shift is non-linear in the investigated temperature range. This non-linear temperature dependency of E^1_{2g} and A_{1g} modes can be explained by combined effect of lattice expansion and lattice an-harmonicity.

2. Experimental Methods

The single- and few-monolayer MoS_2 nanosheets from bulk MoS_2 powder were produced via hydrazine (N_2H_4) assisted mixed solvent strategy [21-23]. The dispersions containing MoS_2 nanosheets were used further for characterization and temperature dependent Raman studies.

The absorbance spectra of exfoliated dispersions were recorded using Jasco V-770 UV-Vis spectrophotometer in a matched pair of quartz cuvettes of path length 1 cm. Micro-Raman measurements were performed with a Jobin-Yvon LabRAM HR800 system with 473 nm as the excitation wavelength. The spectra were measured in the backscattering configuration using a 50X objective and 1800 grooves/mm grating. The laser power used on the sample was 25 mW to avoid any shifting in the both the in-plane and out-of-plane modes of the Raman signature. Single point Raman measurements were performed on the same location in the sample over the temperature range from 80 to 600 K using liquid nitrogen cooled heating stage. The samples used for Raman analysis were prepared by drop casting films on Si (100) wafer that were dried in hot air oven at 60 °C. The X-ray diffraction (XRD) studies were carried out using Panalytical's X'pert Pro diffractometer using Cu-Kα radiation. The transmission electron microscopic (TEM) studies were performed with the JEOL-JEM 2100 microscope operated at an accelerating voltage of 200 kV. Carbon-coated copper grids (300 mesh) were used in the TEM sample preparation.

3. Results and Discussion

The presence of single- and few monolayers in the exfoliated MoS_2 dispersion was confirmed using the optical absorbance spectroscopy as shown in Fig. 1. It was found that the MoS_2 dispersion displays characteristic absorption peaks, A and B, at λ = 670 and 608 nm, respectively, that can be assigned to the direct transitions (band edge excitons) in 2H-MoS_2 [1-5]. The peak labeled as C at λ = 460 nm originate from inter-band transitions from the occupied d_{z^2} orbital to the unoccupied d_{xy}, $d_{x^2-y^2}$ and $d_{xz,yz}$ orbitals in few-layered MoS_2 nanosheets [1-5].

Fig. 2(a) shows the X-ray diffraction (XRD) patterns of the bulk and exfoliated MoS_2 nanosheets. The bulk MoS_2 shows a number of strong diffraction peaks which can be indexed to the (002), (100), (101), (103), (006), (105), (008) and (110) planes of the 2H-MoS_2 (JCPDS card No. 37-1492). The XRD pattern of exfoliated MoS_2 nanosheets shows a single strong peak at 14.5°, which corresponds to diffraction from the (002) plane while the other peaks are absent or relatively weak. This confirms that the nanosheets have been exfoliated along (002) plane and are highly

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crystalline. The low magnification TEM image as shown in Fig. 2(b) further depicts the presence of single to few-layer MoS_2 nanosheets in the exfoliated dispersion. The high resolution lattice image from the MoS_2 nanosheets along with selected area electron diffraction (SAED) pattern is shown in Fig. 2(c). The SAED pattern shows diffused spots confirming the crystalline nature of MoS_2 nanosheets. The inter-planar spacing determined from lattice fringe separation (Fig. 2c) is found to be 0.27 nm, which is consistent with (100) plane of hexagonal phase of MoS_2. The Mo and S ratios determined at various local spots on the nanosheets using energy dispersive X-ray analysis was found to be 1:2.

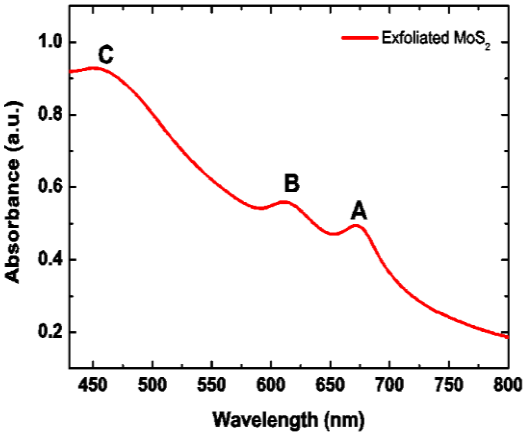

Fig. 1 A typical optical absorbance spectrum measured at room temperature from MoS_2 nanosheets dispersion

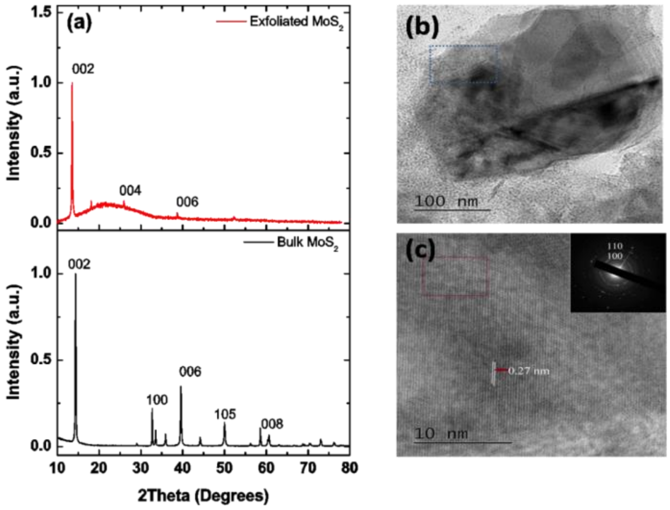

Fig. 2 (a) XRD pattern of bulk MoS_2 powder and exfoliated MoS_2 nanosheets (b) Low magnification TEM images of MoS_2 nanosheets showing its heterogeneous nature with thickness ranging from single- to few monolayers and (c) HRTEM image of MoS_2 showing lattice fringes. Also shown in the inset is the SAED pattern from the region marked with a dashed box

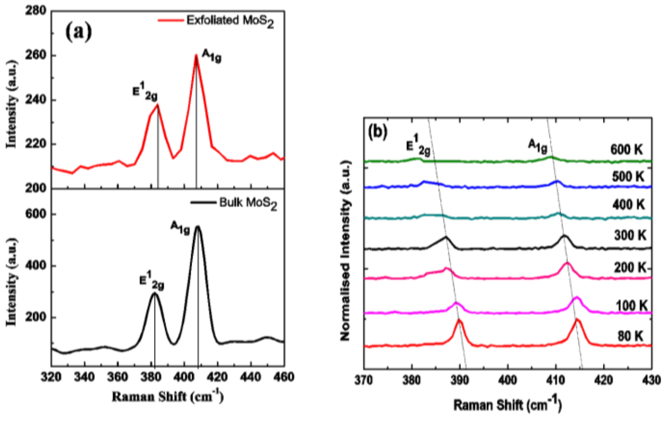

Fig. 3 (a) Raman spectra of bulk MoS_2 powder and exfoliated MoS_2 nanosheets measured at room temperature (b) Raman spectra of the MoS_2 nanosheets at different temperatures ranging from 80 to 600 K

Prior to discussing the effect of temperature on the in-plane and out-of plane Raman modes, we would like to compare the Raman spectra of bulk and exfoliated MoS_2 at room temperature (Fig. 3a). The Raman spectra for MoS_2 showed two principal modes: E^1_{2g} and A_{1g}. The E^1_{2g} mode is an in-plane optical mode, whereas the A_{1g} mode corresponds to out-of plane vibrations of the sulfur atoms. In bulk MoS_2, the E^1_{2g} and A_{1g} peaks were located at 382.75 and 408.62 cm^{-1}, respectively. As the bulk MoS_2 was exfoliated to MoS_2 nanosheets, the E^1_{2g} and A_{1g} peaks were located at 383.65 and 407.76 cm^{-1} respectively (Fig. 3a). The frequency difference, Δ between E^1_{2g} and A_{1g} modes is an indicator of number of layers in the sample and is found to be 24.10 cm^{-1} that corresponds to 4 monolayers in the exfoliated nanosheets [9,17].

Further, in order to study phononic response of E^1_{2g} and A_{1g} modes as function of temperature, the temperature dependent Raman measurements were performed from 80 to 600 K (Fig. 3b). The peak positions were determined using Lorentz fitting. As can be seen from Fig. 4, the position of the E^1_{2g} and A_{1g} mode decrease (red shift) with increase in temperature and exhibited non-linear temperature dependence in the investigated temperature range. The full width at half maxima (FWHM) of the respective peaks exhibited broadening with increasing temperature (not shown) and is in-line with the general expectations.

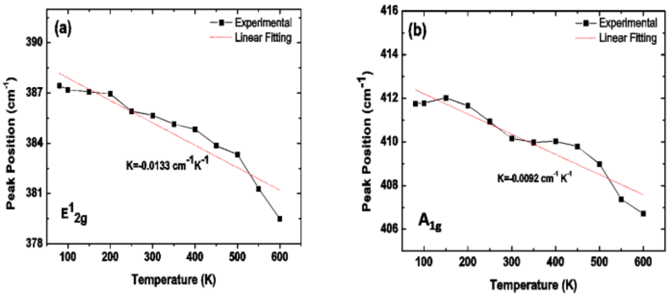

Fig. 4 Temperature dependence of the (a) E^1_{2g} and (b) A_{1g} peak positions observed for MoS_2 nanosheets. Linear fit to the data is also shown in the figure

The observed temperature dependence of E^1_{2g} and A_{1g} modes was first analyzed by considering the linear approximation. The following linear equation is used to fit the temperature dependence,

$$\omega(T) = \omega_o + \chi T \quad (1)$$

where ω_o is the extrapolated peak position at zero Kelvin, and χ is the first-order temperature coefficient which can be obtained from the slope of the fitted straight line. The extracted temperature coefficients of MoS_2 nanosheets for E^1_{2g} and A_{1g} modes are found to be -0.0133 cm^{-1}K^{-1} and -0.0092 cm^{-1}K^{-1}, respectively. The reported values of the temperature coefficient of these modes are -0.013 cm^{-1}K^{-1} and -0.016 cm^{-1}K^{-1} for CVD grown monolayer [17], and -0.015 cm^{-1}K^{-1} and -0.013 cm^{-1}K^{-1} for bulk MoS_2 [17].

In order to understand the origin of non-linearity in the temperature dependency of Raman shifts of E^1_{2g} and A_{1g} modes, an analytical model, that considers the effect of both volume expansion and an-harmonic effects is used [19,20]. The overall frequency shift defined in the model is expressed as,

$$\omega(T) = \omega_o + \Delta\omega_E + \Delta\omega_A \quad (2)$$

where $\Delta\omega_E$ and $\Delta\omega_A$ are Raman shift changes induced by pure volume effects (lattice thermal expansion) and pure temperature effects (an-harmonicity), respectively. Additionally, the thermal expansion mismatch between substrate (silicon) and MoS_2 also introduces a strain that induces shifts in Raman peak positions. However, the low thermal expansion coefficient for silicon and SiO_2 (2.6 x 10^{-6} °C^{-1}) will not result in considerable strain induced shifts in the peak position of MoS_2 over the temperature range investigated [19].

To estimate the contribution of volume effects to the frequency shifts, we consider Grüneisen constant model [19,20,24]. According to his model, $\Delta\omega_E$ can be expressed as,

$$\Delta\omega_E = \omega_o \exp\left(-n\,\gamma \int_0^T \alpha\, dT\right) - \omega_o \quad (3)$$

where ω_o is the extrapolated peak position at zero Kelvin, n is the degeneracy i.e. 1 for A_{1g} mode and 2 for E^1_{2g} mode, γ is the Grüneisen parameter, and α is the thermal expansion coefficient of the material. The Grüneisen parameter, γ has a shallow dependency on the number of layers of the material. The Grüneisen parameters of both E^1_{2g} and A_{1g} modes for bulk MoS_2 are theoretically reported to be γ (E^1_{2g}) = 0.21 and γ (A_{1g}) = 0.42, respectively [19,24]. Since our samples are few-layered thick (4

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monolayer thick), the values of Grüneisen parameters for bulk MoS_2 have been used to best fit Eq.(3) to the experimental data. The in-plane and out-of-plane thermal expansion coefficient 'α' for bulk MoS_2 can be derived by using the relationships given by El-Mahalawy [19,25]. The contribution of volume expansion to the phononic shift for both modes of vibration is estimated using Eq.(3) and is presented in Fig. 5 along with the experimental data. These results demonstrate that the linear contribution of the thermal expansion of the material is only significant for out-of-plane (A_{1g}) mode over the entire temperature range. For in-plane (E^1_{2g}) mode, thermal expansion makes a weak linear temperature dependent contribution.

To take into account the contribution from an-harmonic effects due to phonon scattering, a semi-quantitative model developed by Klemens is used [26]. This model comprises the contributions of three- and four-phonon processes to the frequency shift and can be expressed as,

$$\Delta\omega_A = A\left[1+\frac{2}{e^x-1}\right]+ B\left[1+\frac{3}{e^y-1}+\frac{3}{(e^y-1)^2}\right] \qquad (4)$$

where $x = \hbar\omega/2kT$, $y = \hbar\omega/3kT$, A and B are fitting constants and were estimated from the best fit. The contribution of three- and four-phononic effects to the frequency shift for both Raman modes are estimated using Eq.(4) and is shown in Fig. 5.

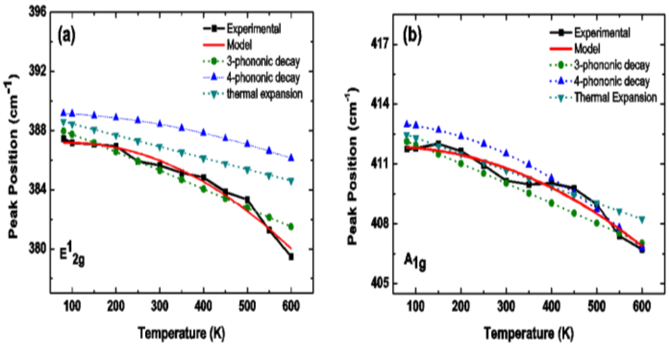

Fig. 5 The modelling of temperature dependence of Raman shift (red solid line) and the individual contribution from thermal expansion (marked by cyan), three-phonon (marked by green) and four-phonon (marked by blue) processes as compared to the experimental results (black solid line) of few layered MoS_2 in (a) E^1_{2g} and (b) A_{1g} modes

The simulated temperature dependent profiles (contributions of thermal expansion, three- and four-phonon processes) of E^1_{2g} and A_{1g} modes have been plotted along with the observed experimental data in Fig. 5(a) and Fig. 5(b), respectively. One can see that the model calculations (red solid line) are in good agreement with the experimental temperature dependent non-linear Raman shifts for both the modes. For E^1_{2g} mode, our model calculations suggests that non-linear temperature dependence of Raman shift mainly originates from three-phonon process and thermal expansion mainly act as a weak linear temperature-dependent component. However, for A_{1g} mode, we find that the contributions from three-phonon process and thermal expansion compete with each other at low temperatures. However, the contribution from four-phononic process is only dominant at higher temperatures (> 300 K). As a result, non-linear temperature dependence of Raman shifts for both in-plane and out-of-plane modes mainly originate from an-harmonic effect of three- and four-phonon process in the entire temperature range.

4. Conclusion

The temperature-dependent phononic response of the liquid phase exfoliated MoS_2 nanosheets have been investigated over a wide range of temperature (80-600 K) and it reveals the softening of vibrational modes (E^1_{2g} and A_{1g}) with an increase in temperature. The calculated first-order temperature coefficient of E^1_{2g} and A_{1g} Raman modes for few-layer MoS_2 nanosheets are found to be -0.0133 $cm^{-1}K^{-1}$ and -0.0092 $cm^{-1}K^{-1}$, respectively. The physical origin of the non-linear temperature dependency of the phononic modes is analyzed quantitatively using an analytical model that takes into account the thermal contribution (volume) and an-harmonic effects. From the results, it is evident that the an-harmonic effects play a vital role in deciding the vibrational properties of 2DLMs.

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