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High pressure anomalies in exfoliated MoSe$_2$: resonance Raman and x-ray diffraction studies

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Abstract

Detailed high pressure Resonance Raman (RR) Spectroscopy and x-ray diffraction (XRD) studies are carried out on 3–4 layered MoSe$_2$ obtained by liquid exfoliation. Analysis of ambient XRD pattern and RR spectra indicate the presence of a triclinic phase along with its parent hexagonal phase. Slope change in the linear behavior of reduced pressure ($H$) with respect to Eulerian strain ($f_E$) is observed at about 13 GPa in hexagonal phase and about 17 GPa for the triclinic phase. High pressure Raman measurements using two different pressure transmitting media (PTM) show three linear pressure regions, separated by pressure values around which anomalies in the structure are observed. A broad minimum in the FWHM values of $E_{1g}$ mode at about 10–12 GPa indicate to an electron-phonon coupling. Above 33 GPa the sample completely gets converted to the triclinic structure, which indicates the importance of strain in structural as well as electronic properties of two dimensional materials.

1. Introduction

Layered wide bandgap semiconductors have attracted interest as their electronic and optical properties can be modified by bandgap engineering. In recent years strain engineering or introduction of defects have been found to modify the band structure of these 2D materials leading to novel electronic properties. Introduction of strain has been found to induce electronic structural transition and enhance the electronic properties in TiS$_2$ and graphene [1, 2]. Tuning of optical band gap with strain in layered two-dimensional (2D) InSe has shown it to be a versatile optoelectronic material [3]. In a recent strain engineering work on the MoSe$_2$/WSe$_2$ heterolayers, it has been shown that decreasing the layer distance by application of uniaxial pressure can change the conductance by several orders of magnitude [4]. In a detailed study on layered MoS$_2$ transition-metal–dichalcogenide (TMD) Liu et al [5] have mapped the strain and structural heterogeneity with shift of Photoluminescence (PL) peak and have shown the importance of strain induced bandgap engineering. A theoretical simulation study based on state-of-the-art density functional calculations including vibrational energy corrections have shown relatively small amount of tensile strain under uniaxial conditions can induce semiconducting to metallic transition in Mo— and W—dichalcogenide compounds [6].

Pressure can be an excellent tool to study the structural and electronic phase transitions in layered TMD’s to understand their behaviour under strained conditions. There are several reports suggesting metallization of TMD’s under pressure [7–16]. Some of the above reports suggest possible structural transition along with metallization with pressure. High pressure Raman, electrical resistance, and synchrotron x-ray diffraction (XRD) studies on hexagonal 2H — MoSe$_2$ (single crystal and powder) do not report any evidence of structural transition accompanying the electronic phase transition [17–19]. Later a systematic high pressure investigation on single crystal MoSe$_2$ up to 60 GPa using multiple experimental techniques and ab-initio calculations reported pressure induced metallization above 40 GPa without any structural transition [11]. However, Aksoy et al [19] have observed a discontinuity in the ratio of $(\Delta c/c_0)/(\Delta a/a_0)$ (c and a are the lattice parameters with subscript 0 referring to ambient pressure) at 10 GPa. A recent theoretical study predict tetragonal phase with space group
In the present work, we have carried out a detailed high pressure investigation on exfoliated layered MoSe₂ using Raman spectroscopy and XRD measurements up to about 50 GPa. Anomalies in the positions and full width at half maximum (FWHM) of Raman modes are observed at about 13 GPa and 33 GPa, respectively. XRD studies in conjunction with Raman anomalies indicate to the presence of electronic transition at about 13 GPa followed by a phase transformation from hexagonal structure to a triclinic crystal structure at high pressures, similar to that observed in exfoliated WS₂.

2. Experimental

Few layers of MoSe₂ sample are prepared by liquid exfoliation [16, 22] of crystalline MoSe₂ (from Sigma Aldrich, powder, −325 mesh, 99.9% trace metals basis). After exfoliation samples of approximate size 10−15 μm are chosen for loading in the DAC. We have used a piston-cylinder type DAC from EasyLab Co. (UK) for our high pressure studies. Sample is loaded inside the central hole of diameter 100 μm of stainless gasket preintended to 45 μm. Mixture of methanol-ethanol at a ratio of 4:1 and silicone oil are used as pressure transmitting media (PTM) for high pressure Raman measurements. For the determination of pressure [23] few ruby chips (approximate size 3−5 micron) are loaded along with the sample. Raman spectra are collected in the back scattering geometry using a micro-Raman system (LabRam HR 800) with 1800 g mm⁻¹ grating and a spectral resolution better than 1.2 cm⁻¹. Appropriate edge filters are used for Raman measurements from 50 cm⁻¹, which are provided by Horiba Jobin Yvon. Ambient pressure Raman measurements are carried out at four different excitation wavelengths, 488, 532, 633 and 785 nm using a 100× microscope objective. High pressure Raman measurements are carried out using 488 nm excitation laser and 20× long working distance objective (infinitely corrected). The laser power is kept at 16 mW at ambient pressure and then increased to 40 mW at high pressure to obtain a good signal to noise ratio and also to avoid local heating of the sample.

For high pressure XRD measurements, the exfoliated samples are loaded in the DAC using the same procedure described above. In this case, small amount of silver powder is loaded along with sample for pressure estimation [24]. XRD studies are carried out at room temperature at the XPRESS beamline in Elettra synchrotron source, Italy using monochromatic x-ray radiation of wavelength 0.495 7 Å. The x-ray beam is collimated to 20 micron and the diffracted x-rays are detected using a MAR 3450 image plate type detector aligned normal to the beam. The sample to detector distance is calibrated using LaB₆. The two dimensional diffraction images are integrated to get intensity versus 2θ profile using Dioptas software [25]. The XRD data are then indexed using the CRYSFIRE [26] and CHECKCELL program [27] followed by LeBail profile fitting using GSAS [28].

3. Results and discussion

Initially the exfoliated sample is placed on the diamond culet and Raman spectra are collected to have an idea of resonance condition and layer thickness. Raman spectra of the exfoliated sample at ambient condition and different excitation energies are shown in figure 1(a). In the right-inset of figure 1(a) we have shown the magnified image of the exfoliated sample of approximate size 10−15 μm on the diamond anvil culet of size 300 μm. 2H − MoSe₂ has a space group symmetry of D₆h and there are 12 modes of lattice vibrations at the centre of Brillouin zone [29, 30]: A₁g + 2A₂u + B₁u + 2B₂g + E₁g + 2E₁u + 2E₂g + E₂u. Among these A₁g, E₁g, E₂g, and E₂u are Raman active modes [17]. We find a prominent mode at 242 cm⁻¹ along with another broad mode at 147 cm⁻¹ using 633 and 785 nm excitation laser. At laser excitations of 532 and 488 nm, in addition to the above, few other prominent modes are observed at 169, 285, 352 cm⁻¹. Several other additional Raman modes are seen in case of 488 nm laser excitation (figure 1(b)). The mode at 147 cm⁻¹ can be seen in case of 532 nm laser excitation, however is not much prominent at 488 nm laser excitation due to several other sharp Raman modes below 200 cm⁻¹. The modes at 242 and 285 cm⁻¹ are identified as two first order Raman modes A₁g and E₁g, respectively [11, 17]. The mode at 147 cm⁻¹ is assigned as E₂g — LA, which is close to Stokes-anti-Stokes pair at the M point as indicated by Nam et al [30]. The laser excitation at 488 nm corresponds to the energy 2.54 eV, which is very close to the band-to-band transition at 2.5 eV [17, 29–31]. Therefore, additional modes are excited due to the resonance condition, which are in agreement with the other measurements on MoSe₂ [29, 30, 32]. Intensity of A₁g mode is found to be enhanced with respect to that of E₂g in agreement with the literature [29, 30]. Even though the E₁g mode is forbidden in back scattering geometry, it is found to be
prominent around 169 cm\(^{-1}\). The mode observed at 352 cm\(^{-1}\) can be indexed to the infrared active mode, \(A_{2g}\). Above anomalous observation of modes can be related to resonance condition [29–31]. Similar phenomena are also observed in nitrogen doped GaAs [33]. A close inspection reveals a shoulder on the left side of \(A_{1g}\) mode, which can be identified as a Raman mode centered at 239 cm\(^{-1}\) (see right-inset of figure 1(b)). This mode is labeled as \(B_{1u}\) [29, 30]. Splitting of \(A_{1g}\) mode has been shown to depend on the layer thickness [31]. In the present case double splitting of \(A_{1g}\) mode indicates to three to four layers of MoSe\(_2\) in our exfoliated sample [31]. Few additional modes in the range from 75 to 140 cm\(^{-1}\) and humps around 215 and 360 cm\(^{-1}\) are observed in the Raman spectrum (indicated inside dotted red rectangle in figure 1(b)). The prominent additional modes below \(E_{1g}\) mode are found at 91, 94, 99, 107, 116, 122, 130, 138, 147, 150 and 154 cm\(^{-1}\). Similar features are also found in 1–5 layers of MoSe\(_2\) using excitation wavelength 465 nm by Soubrelet et al [31] but remain unresolved. Additional Raman modes observed in earlier Raman studies on exfoliated WS\(_2\) and MoS\(_2\) are assigned to different crystal structures embedded in parent hexagonal phase [16, 21]. Therefore it is important to discuss XRD measurements before proceeding to further analysis of high pressure measurements.

In figure 2 we have shown the ambient pressure XRD pattern of the exfoliated sample and compared with XRD patterns collected at high pressures. All the intense reflection lines at ambient condition are indexed to a hexagonal structure with space group \(P6_3/mmc\) and lattice parameters \(a = 3.288(8)\) Å, \(c = 12.958(6)\) Å with volume = 121.36(6) Å\(^3\) and \(Z = 2\), which is consistent with the literature [11, 19]. In addition a few new peaks are observed in the ambient pattern, which are indicated by the black arrow in the figure 2 and could only be indexed to a triclinic cell. The triclinic phase is indexed to space group \(P\overline{1}\) with lattice parameters: \(a = 6.991(4)\) Å, \(b = 7.151(6)\) Å, \(c = 7.054(5)\) Å, \(\alpha = 126.1(2)^\circ\), \(\beta = 88.4(2)^\circ\), \(\gamma = 105.3(2)^\circ\), Volume = 271.04(7) Å\(^3\) and \(Z = 4\) and it is consistent with the literature [16, 34]. In figure 3(a) we have shown Le-Bail refinement of the triclinic phase along with the Rietveld fit of the hexagonal phase. Le-Bail refinement of the triclinic phase is carried out in the absence of a structural model. The fitting of XRD pattern indicates a mixed phase for exfoliated sample under ambient condition itself with a small amount of triclinic phase along with the parent hexagonal phase.

Pressure evolution of XRD patterns (figure 2) show that the intensity of all the Bragg peaks of our sample rapidly decrease with pressure above 12.3 GPa and start broadening extensively. A close inspection reveals that the Bragg-peaks corresponding to triclinic phase become more evident in expense of Bragg-peaks

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Figure 1. (a) Room temperature Raman spectra collected in back scattering geometry of exfoliated few layered MoSe\(_2\) placed on diamond anvil culet of 300 μm (magnified image shown in right-inset), using four different laser excitations. (b) Resonance Raman spectra taken using 488 nm laser source. Splitting of \(A_{1g}\) mode into two parts indicating the few-layered nature of the sample is shown in right-inset. Apart from the two major Raman modes (\(A_{1g}\) and \(E_{1g}\)) of MoSe\(_2\), several prominent resonance Raman modes are clearly seen at 147, 169, 239, and 352 cm\(^{-1}\) corresponding to \(E_{1g}^{2\text{−}x} - \text{LA}\), \(E_{1g}\), \(B_{1u}\), and \(A_{2g}\) respectively. Few additional modes in the range from 75 to 140 cm\(^{-1}\) and humps around 215 and 360 cm\(^{-1}\) are indicated inside dotted red rectangle.
corresponding to hexagonal phase with increase in pressure. Above 33 GPa the XRD patterns could only be indexed to triclinic crystal structure and the corresponding profile fit along with XRD pattern is given in figure 3(b). This represents a transition from a mixed phase to a pure phase. This result is in contrast to earlier high pressure XRD studies which did not report any structural transition in MoSe$_2$ [11, 19]. However a close inspection of data reported by Aksoy et al [19] shows presence of a Bragg peak close to (103) line (similar to our results), which however was ignored in the analysis.

In figure 4(a) we have shown the pressure evolution of $c/a$ value of the hexagonal phase. Large value of $c/a$ ratio shows that the crystal structure is composed of planes of atoms loosely packed along c-axis. Therefore one would expect continuous decrease in $c/a$ ratio with pressure. Instead the data show a step like characteristic with almost constant value in the pressure range 13–17 GPa indicating an anisotropic compression below 13 GPa and above 17 GPa. The anomalous change in the $c/a$-ratio starts just above the freezing pressure of methanol-ethanol pressure transmitting medium. Freezing of this liquid pressure transmitting media lead to quasi-hydrostatic environment inside DAC, that can produce deviatoric stress on the sample. This deviatoric stress is expected to increase as the pressure increases more. It should have lead to either a slope change or a sudden change in the behaviour of $c/a$-ratio at 10 GPa, the freezing pressure of pressure transmitting medium. Instead of we observe a step-like behaviour in the pressure range 13–17 GPa, with $c/a$ ratio reducing again above 17 GPa. Our XRD measurements are carried out by loading very small amount of sample compared to the total volume of the sample chamber and the XRD patterns are taken from the centre of the diamond anvil cell from an area of diameter 20 micron. Hence, the effect of quasi-hydrostatic component on the sample can be neglected. Therefore a large change in strain in the lattice is expected due to the anisotropic compression as the volume do not show any anomalous behaviour with pressure (figure 4(b)). To look into the effect of internal strain we have plotted reduced pressure $H \left( = \frac{p}{3b(1 + \frac{c}{a})^2} \right)$ with respect to the Eulerian strain $f_\varepsilon \left( = \frac{1}{2} \left[ \left( \frac{\nu}{V} \right)^{2/3} - 1 \right] \right)$ [35, 36] and shown in figures 4(c) and (d) for hexagonal and triclinic phases, respectively. $H$ vs $f_\varepsilon$ relation is linear as shown in the following equation considering third order Birch-Murnaghan equation of state [37, 38]:

Figure 2. Pressure evolution of XRD patterns of few layered MoSe$_2$ at selected pressure points. Arrows in the ambient pattern shows presence of new diffraction lines of triclinic structure. The star marks represent the silver pressure markers. Ambient XRD pattern is taken without adding silver.
where, \( V_0 \) is the volume at 1 bar and 300 K, \( V \) is the volume at pressure \( P \), \( K_0 \) is the bulk modulus, and \( \dot{K} \) is the first derivative of bulk modulus. However, slope changes in both the phases are observed around 13 GPa and 17 GPa for hexagonal phase and triclinic phase, respectively (shown by black arrow in the figures 4(c) and (d)). Similar anomalies have been observed in different systems during electronic topological transition (ETT) [36, 39–41]. It is important to note the coincidence of pressure values of the anomalies observed in the \( c/a \)-ratio in the hexagonal phase with the pressure values at the above slope changes. Fits to the data in the first linear in pressure range provide, \( K_0 = 37.4(7) \) GPa and \( \dot{K} = 10.1(4) \) for hexagonal phase. In the second linear in pressure range the fits provide \( K_0 = 53.4(5) \) GPa and \( K' = 4.6(1) \) for hexagonal phase and \( K_0 = 107(1) \) GPa and \( K' = 4.0(1) \) for triclinic phase. In both the cases bulk modulus values for the triclinic phase are found to be much larger than those for hexagonal phase. Reported values of Bulk modulus and its pressure derivative for MoSe\(_2\) are: (i) as reported by Zhao et al [11] are 62(1) GPa, 5.6(1), respectively and (ii) as reported by Aksoy et al [19] are 45.7(3) GPa, 11.6(1), respectively. These values are close to our results of the hexagonal phase. Hexagonal phase is found to be more compressible as expected, due to layered structure in comparison with triclinic phase. In fact the Eulerian strain value of hexagonal phase at 13 GPa is more than that of triclinic phase indicating increase in disorder in the hexagonal phase. This can be due to the growth of triclinic phase in expense of hexagonal phase. Larger pressure dependence of compressibility at low pressures can lead to disorder in the crystal structure.

\[
H = K_0 + \frac{3}{2} K_0 (K' - 4) f_E
\]

Figure 3. Lebail fit of synchrotron XRD patterns of exfoliated few layered MoSe\(_2\) (a) in mixed phases of hexagonal and triclinic structures at ambient conditions, and (b) triclinic phase at 43.4 GPa. Black filled circles represent the observed data points, red line shows the fit to the data, background is shown by the green line, upper vertical ticks indicates Ag Bragg peaks, with the Bragg peaks of samples marked by the ticks at a slightly lower level, and difference is marked by the blue line. The star marks represent the silver pressure markers. Ambient XRD pattern is taken without adding silver.
the modes harden with pressure as evident from the figure. The additional modes reduce in intensity and disappear as pressure increases. Pressure induced changes in lattice parameters can modify the band-structure of the sample, which is expected to affect inter-band transitions. Also growth of triclinic phase with pressure can affect the resonance condition. Therefore the low intensity resonance Raman modes observed at ambient condition reduce in intensity at high pressures and are masked by the background. Intensities of $E_{1g}$ and $A_{2u}$ modes decrease with pressure, while integrated intensity of $A_{1g}$ mode is found to show maximum at about 13 GPa. Since $c/a$-ratio is found to decrease by a large value, it affects the out of plane vibrations that are associated with $A_{1g}$-mode and it becomes stronger till about 13 GPa where the $c/a$ ratio levels off. Any change in relative intensities of Raman modes can be related to induced differential strain in lattice. The integrated intensities of $A_{1g}$ and $E_{g}$ modes show most changes with pressure, and hence in figure 6 we have shown the relative change in normalized intensity of these two modes. This data show a maximum at about 13 GPa followed by gradual decrease till about 45 GPa for experiments using both the pressure transmitting media, indicating the importance of internal strain in the out of plane vibrations of Se atom. It can be noted here that though the non-hydrostatic environment induced by silicone oil PTM starts at much lower pressures compared to methanol-ethanol mixture, the above anomalies are observed at the same pressure.

Since the triclinic phase grows in expense of the hexagonal phase with pressure, the intensity of characteristic $A_{1g}$ mode does not increase again above 18 GPa where $c/a$-ratio decreases again. Above 33 GPa intensity of the $E_{1g}$ mode corresponding to the in plane vibrations of Mo and Se atoms is found to increase with respect to $A_{1g}$ mode as evident from the figure. At the same pressure the sample transforms completely to triclinic phase and this behaviour can be related to the same. A new mode at 103 cm$^{-1}$, and another one at the left shoulder of $E_{1g}$ mode at about 190 cm$^{-1}$ are found to emerge at about 12.5 GPa. Above 33 GPa one more new mode at 317 cm$^{-1}$ is found to emerge. These modes have not been observed in the previous studies [11, 17]. We name these modes as $M_1$, $M_2$, and $M_3$ and are marked by black arrows in figure 5. From XRD studies we have found the existence of a triclinic phase along with parent hexagonal phase, which grows with pressure. Therefore in all possibility these modes belong to the triclinic phase, which are masked at low pressures. They start showing up as the modes related to hexagonal phases start decreasing.

![Image](image-url)
For a comparison we have shown the pressure evolution of the prominent $A_{1g}$ and $E_{2g}$ Raman modes in figure 7 using two different types of PTM. It may be noted that for clear comparison we have shifted the Raman mode values obtained using the silicone oil PTM by a constant number. The modes show highly non-linear pressure behaviour in the complete pressure range. We have carried out linear fits of the Raman modes in three different regions of pressure (i) ambient to 9 GPa, (ii) 13 GPa to 27 GPa and (iii) 33 GPa and above and extrapolated the fitted lines to see the slope changes clearly. The fits show three linear regions separated by the pressure values where coinciding with the observed anomaly in Eulerian strain and complete transformation of hexagonal phase to triclinic phase. It may be noted here that the three linear regions coincide for even two different PTMs. Slopes at three different ranges of pressure for these modes are given in table 1. Similar change in the slope of the different modes are reported in other layered systems during electronic topological transition (ETT) \[40, 42, 43\]. But such anomalies in linear pressure behavior of Raman modes are not reported in the previous studies on single crystal MoSe$_2$ \[11, 44\]. However, a close inspection of their data do reveal the deviation from linear behavior.

Anharmonic lattice vibrations can be understood from the volume dependence of frequency through Grüneisen parameter ($\gamma$) values:

$$\gamma = \frac{\delta \ln \omega}{\delta \ln V} = K \frac{1}{\omega} \left( \frac{\delta \omega}{\delta P} \right)$$

where, $\omega$ is the Raman mode frequency, $V$ is the volume at pressure $P$, $K$ is the bulk modulus, and $\frac{\delta \omega}{\delta P}$ is the slope of the pressure dependent Raman modes. For $A_{1g}$ and $E_{2g}$ prominent modes the Grüneisen parameters values are given in the table 1. The values of $K$ and $\frac{\delta \omega}{\delta P}$ are taken from our study. It is evident from the table 1 that the Grüneisen parameter systematically decreases with pressure. As $\gamma$ is associated with the lattice anharmonicity, it seems to decrease with pressure. This implies increase in bond strength that is reflected in continuous structural change from layered hexagonal to three dimensional triclinic structure.

In figure 8, we have plotted FWHM of prominent $A_{1g}$ and $E_{2g}$ Raman modes with pressure. FWHM of $A_{1g}$ mode show a sudden drop at about 34 GPa for silicone oil PTM and 39 GPa for methanol-ethanol mixture as PTM (figure 8(a)). The two different pressure of minimum can be related to two different non-hydrostatic component of the two PTMs. Similar sudden discontinuity in FWHM of Raman modes are observed in layered
WS₂ and MoS₂ at metallization pressure [8, 16]. FWHM of \( E_{2g}^1 \) mode start showing a minimum in the range 10–12 GPa, followed by a sudden jump at about 33 GPa with stronger pressure dependence. Similar minimum in the FWHM of \( E_{2g}^1 \) mode has been observed in crystal powder of MoSe₂ [44] around 18 GPa but remain unexplored. The minimum in FWHM in the Raman mode behaviour is observed in other layered compounds during ETT [40, 42, 43]. The FWHM of Raman peaks (\( \Gamma \)) are related to lifetime of phonon modes (\( \tau \)) as:

\[
\Gamma = \frac{1}{\tau}
\]

In the absence of any structural transition, pressure induced minimum in Raman mode bandwidths are generally associated with an increase in the life time of phonon-modes due to electronic topological transitions [39, 45]. The life time of a phonon mode can be related to its electron phonon coupling (\( \lambda \)) via the FWHM (\( \Gamma \)) of its Raman mode via

\[
\lambda = \frac{\Gamma}{\pi \hbar N(E_f) \omega_i^2}
\]

where \( \omega_i \) is the peak position and \( N(E_f) \) is the density of states which we can consider to be constant for a 2D material giving us a much simpler relation:

\[
\lambda \propto \frac{\Gamma}{\omega_i^2}
\]

In figure 8(c) we have shown the change in electron phonon coupling of \( E_{2g}^1 \) mode with pressure. We clearly see the electron phonon coupling changes with pressure, showing a broad minimum reflecting similar behaviour of FWHM. Similar dip in electron phonon coupling was observed in Black Phosphorus and attributed to ETT [46]. Pressure dependent resistivity measurements by Zhao et al [11] show a step like characteristic in the pressure range about 12–20 GPa similar to the \( c/a \)-ratio of the hexagonal phase. Our studies show that there is an ever increasing strain component with pressure (figure 4). This in combination with the broad minimum observed in FWHM of Raman mode and electron phonon coupling (taking in to account the scatter in the data around 10–12 GPa) may be related to an ETT around 13 GPa. However at this moment it is difficult to confirm it without any detailed theoretical study. Similar anomalies have been observed earlier during ETT in other

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systems [36, 39, 40, 42, 43, 45, 46] and are probably a precursor to semiconductor to metallic transition. It may be noted that the triclinic phase, which is known to be metallic also shows a slope change in Eulerian strain at 17GPa, which matches well with the end of plateau region in $c/a$-ratio of the hexagonal phase. It seems that the pressure behaviour of the structural and the electronic properties of the triclinic phase are intimately related to the parent hexagonal phase. This may be due to the fact the electronic clouds of valence electrons participating in formation of bonds between Mo and Se atoms try to absorb the large pressure induced stress and gives rise to excited electronic states. Our study shows the importance of careful structural characterization of the 2D layered systems to understand the effect of lattice strain and its relation to the electronic properties and further experimental and theoretical studies are needed to address these issues.

4. Conclusions

In the present study, we have carried out detailed high pressure Raman and XRD investigations on exfoliated $\text{MoSe}_2$. Raman spectroscopy measurements indicate the exfoliated sample to consist of 3 to 4 layers. The
An exfoliated sample is found to have triclinic phase embedded with its parent hexagonal phase, even at the ambient condition. Change in the slope of prominent Raman modes, anomalies in the FWHM of Raman modes, and the change in the slope in the reduced pressure behavior with Eulerian strain indicate to a possibility of an electronic transition at about 13 GPa. High pressure Raman spectroscopy studies show the emergence of a new modes $M_1$, $M_2$, $M_3$, which along with XRD measurements show a continuous change from hexagonal to triclinic crystal structure driven by internal lattice strain.

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Figure 8. Pressure evolution of FWHM of $A_{1g}$, $E_{2g}$ Raman modes are compared for two different pressure transmitting media in (a) and (b), respectively. FWHM of $A_{1g}$ shows a minimum at about 34 and 39 GPa for silicone oil and methanol-ethanol mixture, respectively. FWHM of $E_{2g}$ soften with pressure and reach a broad minimum above about 10 GPa followed by a sudden jump around 33 GPa. Pressure behaviour of electron phonon coupling for $E_{2g}$ Raman mode is shown in figure 8(c).
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