EXPERIMENTAL AND THEORETICAL COMPARATIVE STUDY OF MONOLAYER AND BULK MoS₂ UNDER COMPRESSION

DEL CORRO Elena[1], MORALES-GARCIA Ángel[2], PEÑA-ALVAREZ Miriam[1,3], KAVAN Ladislav[1], KALBAC Martin[1], FRANK Otakar[1]

[1]*J.Heyrovsky Institute of Physical Chemistry of the AS CR, v.v.i., Prague, Czech Republic, EU,*
elena.delcorro@jh-inst.cas.cz
[2]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Czech Republic, EU*
[3] *Department of Physical Chemistry I, Faculty of Chemistry, Complutense University of Madrid, Spain, EU*

Abstract

Recently, a new family of 2D materials with exceptional optoelectronic properties has stormed into the scene of nanotechnology, the transition metal dichalcogenides (e.g., MoS₂). In contrast with graphene, which is a zero band gap semiconductor, many of the single layered materials from this family show a direct band-gap in the visible range. This band-gap can be tuned by several factors, including the thickness of the sample; the transition from a direct to indirect semiconductor state takes place in MoS₂ when increasing the number of layers from 1 towards the bulk. Applying strain/stress has been revealed as another tool for promoting changes in the electronic structure of these materials; however, only a few experimental works exist for MoS₂. In this work we present a comparative study of single layered and bulk MoS₂ subjected to direct out-of-plane compression, using high pressure anvil cells and monitoring with non-resonant Raman spectroscopy; accompanying the results with theoretical DFT studies. In the case of monolayer MoS₂ we observe transitions from direct to indirect band-gap semiconductor and to semimetal, analogous to the transitions observed under hydrostatic pressure, but promoted at more accessible pressure ranges (~25 times lower pressure). For bulk MoS₂, both regimes, hydrostatic and uniaxial, lead to the semimetallization at similar pressure values, around 30 GPa. Our calculations reveal different driving forces for the metallization in bulk and monolayer samples.

Keywords: MoS₂, High Pressure, Raman Spectroscopy, DFT Calculations, Optoelectronic Properties

1. INTRODUCTION

Recently, 2D materials are attracting great attention due to their exceptional properties and the possibility of tuning them by several factors. Specifically, single layer molybdenum disulphide (1L-MoS₂), presents remarkable optoelectronic properties, occasionally different from those in the bulk precursor [1]. Strain engineering [2] has been revealed as a promising method to modify the electronic properties of MoS₂, and a number of works, mainly theoretical, have appeared. Interestingly, strain may change the band-gap, but the strain direction and sign must be considered since only certain strain regimes lead to its closure. For instance, some theoretical works found in the literature predict that (i) biaxial in-plane strain has larger effect on the band-gap energy than uniaxial in-plane tension [3,4], (ii) for biaxial strain the effects are larger under the tensile regime in comparison with the compressive one [5], (iii) in the case of uniaxial in-plane stress the preferred direction for tuning the band-gap is the *yy* [6]. Additionally, in specimens with two or more layers, the strain-tuning gains another degree of freedom through the modification of the interlayer coupling [4,5,7]. Experimentally, small uniaxial strains (up to 2% of tension) were applied to 1L-MoS₂ via bending of their polymeric substrates and monitoring the changes with Raman spectroscopy [8,9] and photoluminescence [10,11]. It was observed that the direct optical gap of 1L-MoS₂ redshifted and the transition to an indirect band-gap took place at ~1.3% of strain. Concerning high pressure experiments using a diamond anvil cell we find recent works in both bulk [12-14] and monolayer [15,16] MoS₂, all of them exploring the hydrostatic regime. Photoluminescence measurements under pressure carried out in single layered samples showed the disappearance of the A peak with pressure, revealing an increase of the direct band-gap energy leading to the

electronic transition from direct to indirect band-gap semiconductor at ~23 GPa [15]. In another recent study this transition is theoretically predicted as well as the semiconductor-semimetal one at ~68 GPa [16]. Bulk MoS_2 was subjected to hydrostatic compression and monitored with Raman spectroscopy and in-situ resistivity measurements; under these conditions the semiconductor to semimetal electronic transition, via an intermediate state, was observed (10 and 19 GPa, respectively) [12]. Interestingly, similar high pressure experiments using X-ray diffraction as characterization technique [13,14] observed abrupt discontinuities of the lattice parameters evolution at ~20 GPa (range of the semiconductor-metal transition observed in [12]), associated with a structural transition from the 2Hc to the 2Ha phase.

In this work, monolayer and bulk MoS_2 specimens are directly compressed along the out-of-plane direction up to 5 GPa using a gem anvil cell, in absence of pressure media, i.e. non-hydrostatic conditions, as previously reported [17], and the sample evolution is characterized with non-resonant Raman spectroscopy (488.0 nm). For the monolayer sample, according to the evolution of the Raman spectra, we could conclude that the transition from direct to indirect band-gap semiconductor takes place immediately after closing the anvil cell when the stress is increased ~0.5 GPa, while the metallization (to a semimetal) occurs at stress as low as 2.8 GPa; these results are confirmed by means of theoretical density functional theory (DFT) studies. In the case of bulk MoS_2 no discontinuities were observed in the Raman spectrum evolution, indicating no electronic transition in the achieved pressure range; as was also confirmed by DFT calculations, which showed a semiconductor to metallic transition at ~30 GPa. The comparison between previous hydrostatic pressure studies and our non-hydrostatic experiment reveals a clear difference for the case of the 1L-MoS_2, while the electronic properties of the bulk samples seem to change analogously regardless the pressure conditions. Our thorough theoretical analysis will shed some light to these phenomena revealing the efficiency of direct out-of-plane compression for tuning the electronic properties of this material.

2. METHODS

2.1. Experimental details

The MoS_2 samples are placed on Inconel discs and directly compressed in a moissanite (SiC) anvil cell and the pressure is estimated from the Raman shifts of the optical phonons of moissanite. The high pressure device is coupled to a LabRAM HR spectrometer (Horiba Jobin-Yvon) using the 1800 grooves/mm gratings. For the sample excitation we used an Ar/Kr laser (488.0 nm). A 50× objective was used, providing a laser spot of about 1 μm in diameter. The laser power on the sample was kept below 0.5 mW to avoid sample damage.

2.2. Theoretical calculations

First-principles calculations were carried out using DFT formalism implemented in VASP code, as already reported [17]. All-electron projector augmented wave (PAW) pseudopotentials represent the core electrons, while the valence electrons are explicitly treated using plane waves of cut-off 420 eV. The Perdew, Burke, and Ernzerhof (PBE-GGA) functional is used to solve the Khon-Sham equations. A well-converged Monkhorst and Pack k-points set (8x8x2 and 12x12x1 for bulk and monolayer, respectively) was used for the Brillouin zone sampling. This grid was increased to evaluate the electronic band structures. The hydrostatic pressure is defined as $p= -dE/dV$, and for bulk systems is easily implemented by changing the lattice parameters using a scale factor. To include the non-hydrostatic conditions on the bulk structure we change the c lattice parameter keeping constant the a and b parameters as constraints. On the other hand, the implementation of hydrostatic pressure in the monolayer configuration is done by the modulation of S-S distance and the a lattice parameter, while the uniaxial pressure is considered just by changing the S-S distance, keeping the a and c lattice parameters constant. The equivalent stress acting on the cell is obtained for both directions z and $x(=y)$. The ratio between the in-plane and out-of-plane stress is in good agreement with previous experimental results using moissanite anvil cells [18].

3.   RESULTS AND DISSCUSION

Fig. 1 shows the evolution of the Raman spectra of monolayer and bulk MoS_2 with increasing uniaxial pressure. The broadening and blue-shift of the whole spectrum with increasing pressure can be observed. Interestingly, in the case of 1L-MoS_2 two additional contributions appear at pressures above 2 GPa, which are not observed in the case of bulk. As already reported, the appearance of these extra peaks indicates an electronic transition, maybe also structural, in monolayer MoS_2 under compression [17]. These extra peaks were also observed in bulk samples subjected to hydrostatic pressure, but at higher pressure conditions (~20 GPa) [13] than the ones achieved in this work. Such difference might indicate that in the case of the bulk sample there is no electronic transition promoted by pressure up to 5Gpa; but for a deeper insight of the changes under stress, the spectra are analysed as a sum of Lorentzian contributions, depicted in **Fig. 1**.
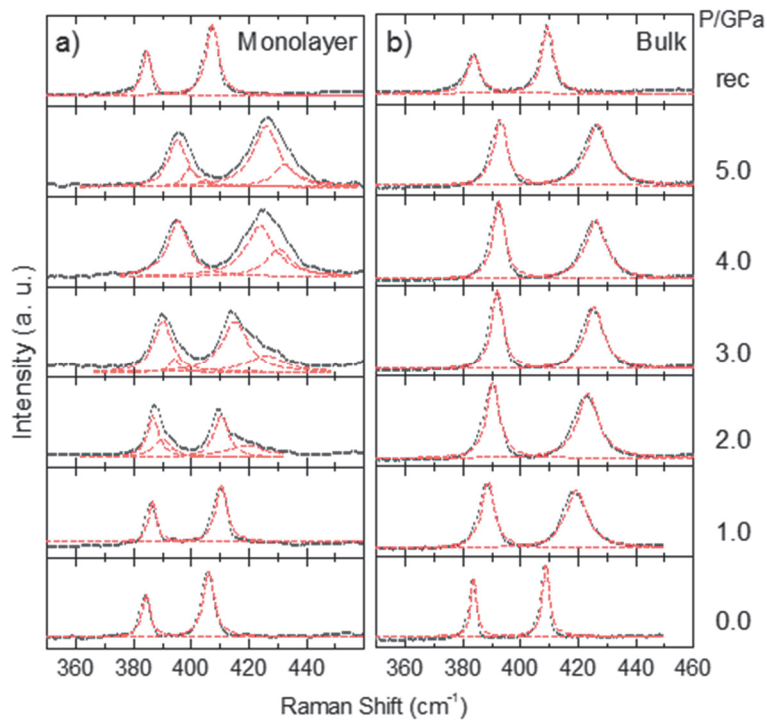

Fig. 1 Raman spectra of a) monolayer and b) bulk MoS_2 under uniaxial pressure

In **Fig. 2** we present the peak position of the two normal modes, the E' (E_{2g}) in-plane vibration and the A1' (A_{1g}) out-of-plane vibration in monolayer (bulk) MoS_2, as a function of increasing uniaxial pressure. For the monolayer specimen, **Fig. 2a**, we observe that the data follow a three trend behaviour, especially visible in the case of the A_1' band. At the first steps of compression, up to 0.5 GPa, the modes' frequencies suddenly upshift; however, when the pressure is continuously built up to 2 GPa, they remain almost unaltered. From approximately 2 GPa we start to witness a continuous upshift with pressure with coefficients of 2.8 and 5.0 cm^{-1}/GPa, for the E' and the A_1' bands, respectively. The three region behaviour shown by the monolayer is indicating the occurrence of two electronic transitions in the pressure range achieved: direct band-gap **-** indirect band-gap semiconductor **-** semimetal [17]. These electronic changes are confirmed by DFT calculations, depicted in **Fig. 3a**. At 0.8 GPa the indirect band gap (form the K point of the valence band (VB) to the Γ point of the conduction band (CB)) is smaller than the direct one at Γ; and at 2.8 GPa, both the VB at K and the CB at Γ touch the Fermi level indicating a semimetal state. It must be noted that the same kind of sample subjected to hydrostatic conditions undergoes electronic transitions at ~25 times higher pressure conditions, these transitions implying a slightly different evolution of the electronic dispersion curves with pressure [16]. This interesting fact, explained later on, demonstrates the efficiency of uniaxial compression for promoting electronic transitions in this kind of 2D materials.
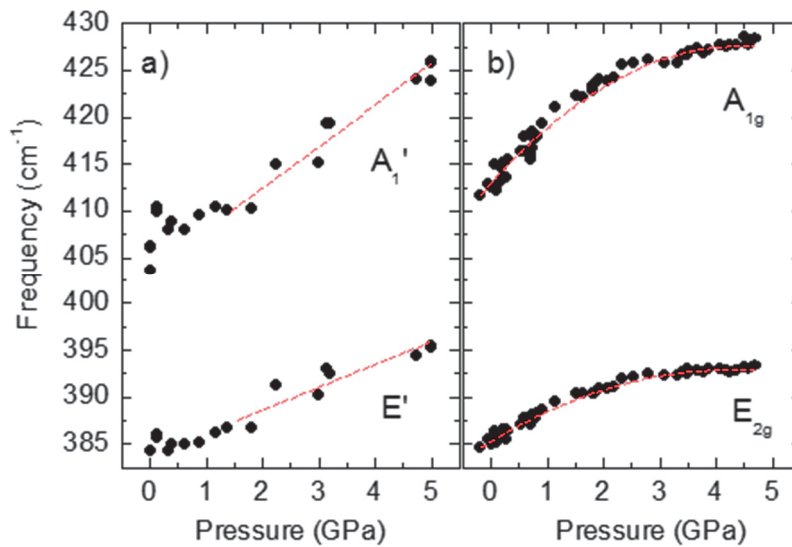
Fig. 2 Frequency of the A and E bands as a function of pressure for a) monolayer and b) bulk MoS_2

In contrast, the bulk MoS_2 crystal, **Fig. 2b**, shows a continuous upshift with pressure, following two polynomial functions with a first coefficient of 3.5 and 6.6 cm^{-1}/GPa, for the E_{2g} and the A_{1g} bands, respectively. This continuous upshift with pressure indicates the absence of electronic transitions in the pressure range from 0 to 5 GPa, as it is confirmed by the electronic dispersion curves shown in **Fig. 3b**. Bulk MoS_2 is an indirect band-gap semiconductor at normal conditions, from the Γ point of the VB to the Γ-K region of the CB (sometimes designated as the Q point); as the stress increases, the CB moves downwards in energy with higher rate than the VB moves upwards, thereby gradually closing the band-gap. The semimetallization is reached above 30 GPa, when the VB at K and the CB at Γ-K reach the Fermi level (differently to the semimetallic phase in 1L-MoS_2). A previous work concerning bulk MoS_2 under hydrostatic conditions [12] explores wider pressure ranges, but it must be mentioned that in the 0-5 GPa range the behaviour shown in [12] is very similar to the one presented here under uniaxial pressure: a continuous trend of the Raman shifts and analogous evolution of the electronic dispersion under pressure; moreover, the reported pressure threshold for the metallization is very similar to the theoretically predicted here for uniaxial conditions.
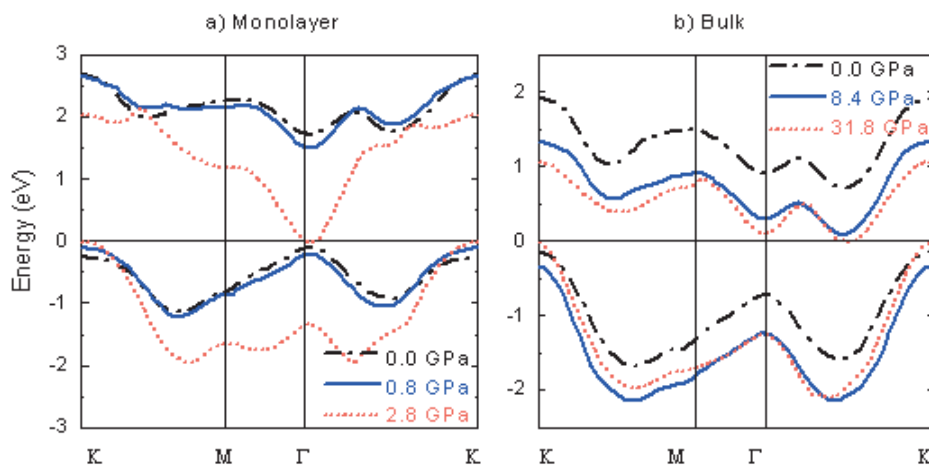

Fig. 3 Electronic dispersion curves of a) monolayer and b) bulk MoS_2 at different pressure values

Such a complex behaviour observed for different samples (bulk or 1L) under different conditions (uniaxial or hydrostatic) was never observed before and a complete set of theoretical calculation were performed in order

to shed some light to these phenomena. The evolution of the band-gap energy was evaluated as a function of several parameters (S-S intra- and interlayer distance, S-Mo-S angle, S-Mo distance) and it was revealed that the driving force for the metallization in the case of bulk samples is the interlayer S-S distance (between S atoms of adjacent MoS_2 layers), for both hydrostatic and uniaxial conditions. According to this, in **Fig. 4a** we present the band-gap energy (E_{gap}) as a function of the S-S interlayer distance: the gap closes when adjacent layers are pressed closer, with the same rate regardless the pressure regime. This indicates that pressure causes the approaching of MoS_2 layers in a similar way under both hydrostatic and uniaxial conditions, thus explaining why the metallization pressure is similar in both regimes. The case of 1L-MoS_2 is more complex, as commented before, the evolution of the electronic dispersion curves with pressure is different for each regime and, therefore, the electronic transitions take place at quite different pressures thresholds. Moreover, when analysing the evolution of the band-gap energy with mentioned parameters of the atomic configuration no direct correlation between the individual parameters and band-gap evolution can be observed, hence it is their combination which matters. In the same time, the evolution of the intralayer S-S distance (between S atoms within one MoS_2 layer) with pressure points to the most crucial difference between the two regimes (**Fig. 4b**). The uniaxial conditions lead to an efficient closure of the band-gap when decreasing the S-S intralayer distance. Additionally, our theoretical study reveals that, while the monolayer becomes gradually less compressible under hydrostatic conditions, the compression is almost linear under uniaxial stress. At compression (along z) of ~15%, the stress needed under each regime differs by a factor of more than 4.
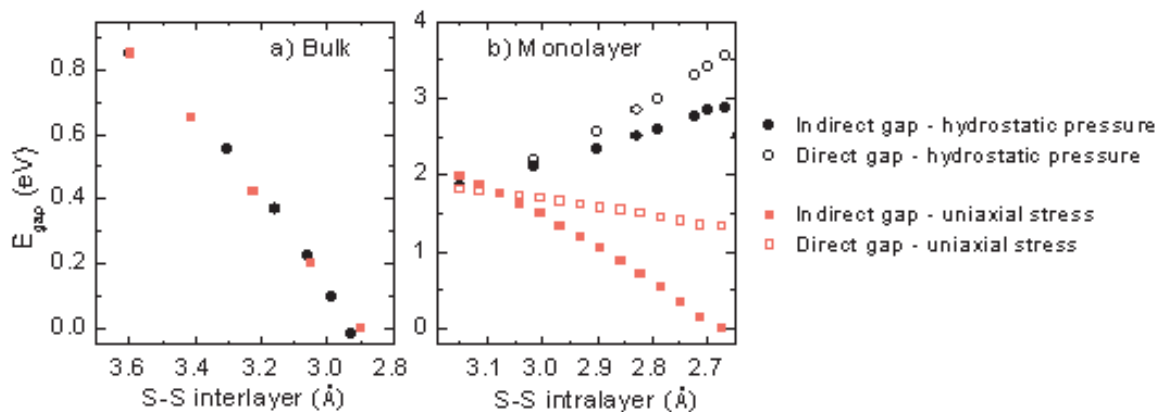

Fig. 4 Evolution of the band-gap energy as a function of the S-S distance under hydrostatic (black circles) and uniaxial (red squares) stress conditions. a) Bulk MoS_2, indirect band-gap energy as a function of the interlayer S-S distance. b) Monolayer MoS_2, direct and indirect band-gap energy as a function of the intralayer S-S distance (empty and filled symbols, respectively).

4.   CONCLUSIONS

The evolution of the Raman spectrum with uniaxial pressure for single layer and bulk MoS_2 is presented; first, the monolayer specimen shows additional Raman peaks at high pressures not detected in the bulk, and second, the frequencies of the normal modes follows a three region behaviour in the case of the monolayer but a shows a continuous increase in the bulk sample. These results indicate that monolayer MoS_2 experiences two electronic transitions in the pressure range from 0 to 5 GPa, not observed for the bulk sample. DFT calculations confirm the existence of a direct to indirect band-gap transition and the semimetallization of 1L-MoS_2 at 0.5 and 2 GPa, respectively, and predict the semimetallization of bulk MoS_2 at ~ 30 GPa, so confirming the absence of electronic transitions in the pressure range achieved. Our theoretical calculations also provide useful information to understand the different behaviour found in monolayer and bulk under hydrostatic and uniaxial pressure; while in the bulk sample the driving force to get the semimetallic phase is the interlayer distance, in single layered specimens the decrease of the S-S intralayer distance seems to play a key role for the electronic change.

ACKNOWLEDGEMENTS

REFERENCES

[1]   BUTLER, S.Z., HOLLEN, S.M., CAO, L., CUI, Y., GUPTA, J.A., GUTIÉRREZ, H.R., HEINZ, T.F., HONG, S.S., HUANG, J., ISMACH, A.F., JOHNSTON-HALPERIN, E., KUNO, M., PLASHNITSA, V.V., ROBINSON, R.D., RUOFF, R.S., SALAHUDDIN, S., SHAN, J., SHI, L., SPENCER, M.G., TERRONES, M., WINDL, W., GOLDBERGER, J.E. Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene. *Acs Nano*, 2013, vol. 7, nr. 4, p. 2898-2926.

[2]   BISSETT, M.A., TSUJI, M., AGO, H. Strain engineering the properties of graphene and other two-dimensional crystals. *Physical Chemistry Chemical Physics*, 2014, vol. 16, nr. 23, p. 11124-11138.

[3]   CHANG, C.-H., FAN, X., LIN, S.-H., KUO, J.-L. Orbital analysis of electronic structure and phonon dispersion in MoS_2, $MoSe_2$, WS_2, and WSe_2 monolayers under strain. *Physical Review B*, 2013, vol. 88, nr. 19, p. 195420.

[4]   PEELAERS, H., VAN DE WALLE, C. Effects of strain on band structure and effective masses in MoS_2. *Physical Review B*, 2012, vol. 86, nr. 24, p. 241401.

[5]   SCALISE, E., HOUSSA, M., POURTOIS, G., AFANAS'EV, V., STESMANS, A. Strain-induced semiconductor to metal transition in the two-dimensional honeycomb structure of MoS_2. *Nano Research*, 2012, vol. 5, nr. 1, p. 43-48.

[6]   LI, T. Ideal strength and phonon instability in single-layer MoS_2. *Physical Review B*, 2012, vol. 85, nr. 23, p. 235407.

[7]   BHATTACHARYYA, S., SINGH, A. Semiconductor-metal transition in semiconducting bilayer sheets of transition-metal dichalcogenides. *Physical Review B*, 2012, vol. 86, nr. 7, p. 075454.

[8]   CONLEY, H.J., WANG, B., ZIEGLER, J.I., HAGLUND, R.F., PANTELIDES, S.T., BOLOTIN, K.I. Bandgap Engineering of Strained Monolayer and Bilayer MoS_2. *Nano Letters*, 2013, vol. 13, nr. 8, p. 3626-3630.

[9]   RICE, C., YOUNG, R., ZAN, R., BANGERT, U., WOLVERSON, D., GEORGIOU, T., JALIL, R., NOVOSELOV, K. Raman-scattering measurements and first-principles calculations of strain-induced phonon shifts in monolayer MoS_2. *Physical Review B*, 2013, vol. 87, nr. 8, p. 081307.

[10]   ZHU, C., WANG, G., LIU, B., MARIE, X., QIAO, X., ZHANG, X., WU, X., FAN, H., TAN, P., AMAND, T., URBASZEK, B. Strain tuning of optical emission energy and polarization in monolayer and bilayer MoS_2. *Physical Review B*, 2013, vol. 88, nr. 12, p. 121301.

[11]   HE, K., POOLE, C., MAK, K.F., SHAN, J. Experimental Demonstration of Continuous Electronic Structure Tuning via Strain in Atomically Thin MoS_2. *Nano Letters*, 2013, vol. 13, nr. 6, p. 2931-2936.

[12]   NAYAK, A.P., BHATTACHARYYA, S., ZHU, J., LIU, J., WU, X., PANDEY, T., JIN, C., SINGH, A.K., AKINWANDE, D., LIN, J.-F. Pressure-induced semiconducting to metallic transition in multilayered molybdenum disulphide. *Nature Communications*, 2014, vol. 5, p. 3731.

[13]   AKSOY, R., MA, Y., SELVI, E., CHYU, M.C., ERTAS, A., WHITE, A. X-ray diffraction study of molybdenum disulfide to 38.8 GPa. *Journal of Physics and Chemistry of Solids*, 2006, vol. 67, nr. 9-10, p. 1914-1917.

[14]   CHI, Z.-H., ZHAO, X.-M., ZHANG, H., GONCHAROV, A.F., LOBANOV, S.S., KAGAYAMA, T., SAKATA, M., CHEN, X.-J. Pressure-Induced Metallization of Molybdenum Disulfide. *Physical Review Letters*, 2014, vol. 113, nr. 3, p. 036802.

[15]   DOU, X., DING, K., JIANG, D., SUN, B. Tuning and Identification of Interband Transitions in Monolayer and Bilayer Molybdenum Disulfide Using Hydrostatic Pressure. *Acs Nano*, 2014, vol. 8, nr. 7, p. 7458-7464.

[16]   NAYAK, A.P., PANDEY, T., VOIRY, D., LIU, J., MORAN, S.T., SHARMA, A., TAN, C., CHEN, C.-H., LEE, L.-J., CHHOWALLA, M., LIN, J.-F., SINGH, A.K., AKINWANDE, D. Pressure-Dependent Optical and Vibrational Properties of Monolayer Molybdenum Disulfide. *Nano Letters*, 2015, vol. 15, nr. 1, p. 346-353.

[17]   PEÑA-ÁLVAREZ, M., DEL CORRO, E., MORALES-GARCÍA, Á., KAVAN, L., KALBAC, M., FRANK, O. Single Layer Molybdenum Disulfide under Direct Out-of-Plane Compression: Low-Stress Band-Gap Engineering. *Nano Letters*, 2015, vol. 15, nr. 5, p. 3139-3146.

[18]   DEL CORRO, E., IZQUIERDO, J.G., GONZALEZ, J., TARAVILLO, M., BAONZA, V.G. 3D Raman mapping of uniaxially loaded 6H-SiC crystals. *Journal of Raman Spectroscopy*, 2013, vol. 44, nr. 5, p. 758-762.