Bull. Mater. Sci. (2023) 46:89
https://doi.org/10.1007/s12034-023-02933-3

Impact of compression on the crystal structure, electronic and magnetic properties for bulk MoS_2

ASMA BOUARISSA[1], HAGER MAGHRAOUI-MEHERZI[1], AHMED GUEDDIM[2] and NADIR BOUARISSA[3,*]

[1]Faculté des Sciences de Tunis, Laboratoire de Chimie Analytique et Electrochimie, LR99Es15, Université de Tunis El Manar, 2092 Tunis, Tunisia
[2]Faculty of Science, Materials Science and Informatics Laboratory, University of Djelfa, 17000 Djelfa, Algeria
[3]Laboratory of Materials Physics and its Applications, University of M'sila, 28000, M'sila, Algeria
*Author for correspondence (n_bouarissa@yahoo.fr)

MS received 3 December 2022; accepted 9 January 2023

Abstract. The impact of pressure on structural parameters, electronic structure and magnetic properties in MoS_2 bulk material has been investigated using spin-polarized full-potential linearized augmented plane wave method in the Tran-Blaha-modified Becke-Johnson gradient approximation approach. Our findings at zero pressure in MoS_2 bulk material are usually dealing with the obtainable experimental input. With increasing pressure, the lattice parameters of MoS_2 bulk material are reduced, the material of interest has tendency to a metallic character and the total magnetic moment is increased non-monotonically in both spin-up and spin-down conduits. The impact of pressure on structural properties is more important *vs. c*-axis than *a*-axis.

Keywords. Structural properties; electronic structure; magnetic domains; high-pressure; bulk MoS_2.

1. Introduction

MoS_2 is an inorganic material that is formed from molybdenum and sulphur. In the bulk crystal shape, it is a semi-conductor that has an indirect energy bandgap of approximately 1.29 eV [1–3]. The material of interest has a coating structure that has a van der Waals interplay among the layers [2]. Owing to a heavy absorption in the solar range district [4,5], MoS_2 has been utilized for photo-voltaic [6] and photo-catalytic [7] requests. Moreover, it is conduced as an important material for dry lubrication [3,8–11].

A comprehensive study of the lattice caloric transport conductivity of MoS_2 for two-dimensional crystals has been presented using molecular standard conjectures [12]. For that, a single Stillinger–Weber-type interplay aspiring parameter successfully accounts for the *ab-initio* mechanical and vibrational domains of these frameworks has been developed. The optimized inter-atomic aspiring parameters replicate the grid thermic transportation properties of these frameworks in enough well accord with *ab-initio* methods. The dissimilarity between the computed MoS_2 caloric conductivity and experiment is probably owing to isotropic disorder and constructional defects that are native to deliberated structures. The forecast caloric properties of both semiconductors are in very nice accord with those previously calculated with *ab-initio* methods. The inconsistencies between the calculated and experimental proceedings are further likely sourced by the perfect nature of the frameworks in their simulations [12].

Density functional theory (DFT) simulations are used to have the modulation of energy gaps by distortion bilayer MoS_2 leafs with separate turning angles [13]. Results of the electronic framework demonstrate that the turnings can perform bilayer MoS_2 leafs vary from semiconductor to metal. The energy gap is de-enhanced from 1.24 to 0.06 eV. This would spawn alternatives for its appliances in nano-electronic apparatus merely by the adjustment of the energy gaps of MoS_2 material with turning angles [13].

The electronic structure and optical characteristics of AlP and GaP graphene similar to frameworks have been studied under various biaxial compressive and tensile stump charges [14]. This study is based on full-potential DFT calculations. These new mono-layers showed a great stretchability and large mechno-sensitivity of their electronic and optical properties. The energy gaps of the studied materials *vs.* the exerted strain is found to be approximated by a second-order polynomial mathematical problem. It is also found that the energy bandgaps of mono-layers AlP and GaP can be adjusted by biaxial stump charges [14].

The effect of the thiourea condensation on the making and photoelectric estates of MoS_2 microspheres have also been reported and discussed [15]. The results demonstrate

Published online: 26 April 2023

that the crystallinity, microsphere framework, photoelectric transformation efficacy and catalytic action of MoS_2 material scope the leading condition when the Mo/S molar report is 1:4. Hence, the thiourea content has a significant impact on the structure, morphology and photoelectric properties of MoS_2 material. This ending is going to supply the foundation for us to ameliorate the electrode material showing for MoS_2 for replacing Pt timer electrode [15].

Also, the electronic estates of ultrathin crystals of S-Mo-S mono-layers are studied using the optical spectroscopy [16]. The quantum confinement effect on the electronic structure of the materials under investigation has been traced across characterization by soaking, photoluminescence and photoconductivity spectroscopy. The decrease of the thickness shifts the indirect energy bandgap upwards by additional 0.6 eV, thus leading to a crossing-over to a direct-band material in the boundary of the unique monolayer. Contrary to the bulk materials, the MoS_2 monolayer material radiates lighting greatly. The freestanding monolayer shows an augmentation in luminescence quantum effectiveness by further than a coefficient of 1000 confront to bulk materials [16].

The investigation of substances under elevated pressure had a significant theme, which displays explosive development for both experiment and theory [17–21]. This is essentially owing to the deployments of the diamond anvil techniques and the enlargement of the spectrum for optical and X-ray steps under static pressures up to 400 GPa and on high [17,22–24]. Adding to these experimental progresses, algorithms processing and quick rises in computer ability makes a considerable effect on great pressure physics [22,25–28].

This donation studies the action of pressure on the structural, electronic and magnetic properties of MoS_2 bulk material. The unbiased of the present employment is to point how these possessions of interest behave in MoS_2 when pressure is applied. The simulation is carried out through the full-potential linearized augmented plane wave (FP-LAPW) method within the generalized gradient approximation (GGA) framework. The pressure is varied from 0 up to 15 GPa using a step of 3 GPa. The obtained results are confronted with experimental and preceding theoretical findings reported in the literature, which show generally a good accordance.

2. Calculation method

An improvement to the local density approximation (LDA) can be made by considering the so-called GGA. While there is just one LDA there are diverse parameterizations for the GGA. Some of these methods are semi-empirical, in that tentative input (e.g., atomization energetics) is employed in their diversion. Others are established wholly from *ab-initio* calculations.

The wavefunctions of Kohn-Sham and energies have been obtained using DFT with GGA of Wu and Cohen (WC-GGA) induced exchange correlation potential scheme [29]. In order to ameliorate the precision of the bandgap energies, the GGA of Tran-Blaha amended Becke-Johnson (TB-mBJ-GGA) [30] is also worn for describing the potential of exchange-correlation. The source of the atomic and orbital of various electronic conditions in the band structure for MoS_2 material are recognized from their separate density of states (DOS). The structural, electronic and optical properties of MoS_2 material in their crystallographic phases have been obtained. We use the FP-LAPW process as performed in the Wien2K code [31], where wavefunctions are promoted in spherical harmonic functions interior to non-overlapping spheres enclosing the atomic locations and a plane wave foundation put in the residual interval of the unit cell (interstitial area).

A plane wave cutoff of $R_{MT}.K_{max} = 7$ is used, here R_{MT} is the littlest muffin-tin radius in the unit cell and K_{max} is the cutoff of the plane waves. The R_{MT} values are selected to be 1.6 and 1.5 a.u. for Mo and S atoms, respectively. The K-point sampling is chosen to be $10\times10\times10$.

The wurtzite structure possessing hexagonal primeval unit cell with space category P63/3 mmc is well-respected. The carried out pressure is carried in the spectrum 0 up to 15 GPa with a stage of 3 GPa. The error of total energy is less than 10^{-5} Ryd. In the geometry optimization, the atoms are permitted to wholly refresh where the force on each atom is inferior than 1 mRy/a.u. As reported earlier [2,32,33], spin–orbit interaction is important for MoS_2 and hence this effect is taken into consideration in the present work.

3. Results and discussion

In figure 1, a diagrammatic of MoS_2 atoms arrangements in its crystal has been drawn. The green spheres denote the Mo atoms, whereas the yellow ones denote the S atoms. This can also be seen in reference [34].

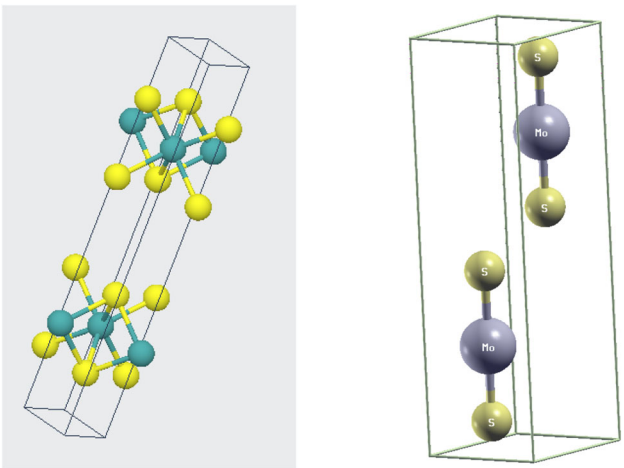

Figure 1. Bulk structure model of MoS_2.

The balance lattice parameters, that is $a = b$ and c of MoS_2 material are obtained by understating the complete energy for separate merits of the supercell volume and connecting the findings to the Murnaghan's equation of state in a suitable energy spectrum. This equation is a connection between the volume of corps and the pressure to that it is steadied. It implied two modifiable parameters: the modulus of incompressibility and its first derivative regarding the pressure, both deliberated at ambient pressure. The pressure in question is an hydrostatic one. At zero pressure, our findings yield values of 3.166 Å for $a = b$ and 12.345 Å for c. These securities slowly overvalues with regard to those of $a = b = 3.15$ Å and $c = 12.3$ Å announced by Wakabayashi *et al* [35]. Our performances are consistent with the general trend of the GGA approach [36,37]. Nevertheless, it ought to be eminent that the employment of WC-GGA oncoming improves the accuracy of the lattice parameters with respect to practice as confronted to that of the typical GGA approach [38]. The pressure dependence of $a = b$ and c for bulk MoS_2 is displayed in figure 2. We observe that when pressure is increased when going from 0 up to 15 GPa, the lattice parameters $a = b$ decrease non-linearly exhibiting a downward lattice constant bowing parameters, whereas the lattice parameter c decreases non-linearly presenting as well a downward lattice constant bowing parameter. In fact, applied pressure conducts to more cloud overlap of electrons, which increases the change transfer between Mo and S atoms. This reduces the bond length which results in the reduction of all a, b and c lattice parameters.

The electronic structure of semiconducting materials is a successful attitude for describing their physical parameters [39–42]. The accurate determination of these parameters permits valuable edition on their combination and devices manufacture [43–45]. In this employment, the bulk TB-mBJ-GGA oncoming is employed to compute the electronic structure of hexagonal wurtzite MoS_2 bulk material at different pressures scaling from 0 up to 15 GPa. The findings are displayed in figure 3. We observe that, at zero pressure the material of interest shows a semiconductor behaviour in a spin-up channel with a bandgap energy of 0.91 eV, whereas clearly seen the Fermi level does not pass through the energy bands. The nature of the gap seems to be indirect where the top of the valence band occurs at the Γ point and the lowest conduction band is layered among Γ and K dots in the Brillouin zone. The interlayer interaction makes the gap indirect for bulk MoS_2. Qualitatively, this agrees with the findings of Molina-Sánchez *et al* [33]. Nevertheless, the electronic band structure of bulk MoS_2 material exhibits a metallic behaviour in a spin-down channel, as can be shown in figure 3. Upon compression in the range 6–15 GPa, MoS_2 seems to exhibit a metallic behaviour in both spin-up and spin-down channels (see figure 3) for all pressures of interest. In fact, under pressure effect the valence and conduction bands of MoS_2 are both affected. At zero pressure, this affects the existing covalent bonds and results in fewer semiconductor-like matter that has a trend to a metallic disposition as far as applied pressure is enhanced.

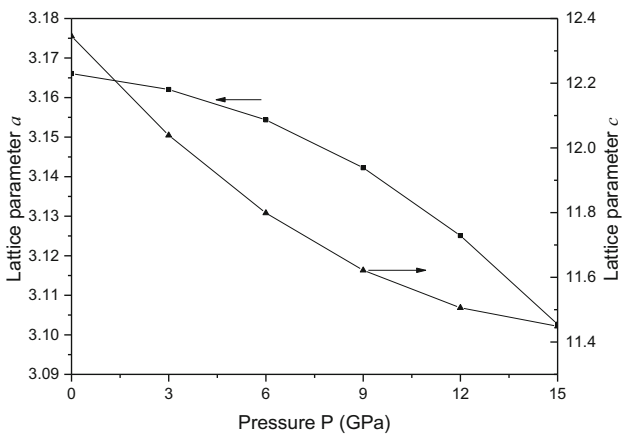

Figure 2. Lattice parameters a and c *vs.* pressure.

The properties of semiconductors are tightly linked to the electronic arrangement of molecules [46]. In these circumstances the total and projected DOS within valence bands are calculated for the hexagonal MoS_2 bulk material at various pressures up to 15 GPa in order to see the electrons delivery on numerous orbitals. The calculations are performed using the TB-mBJ-GGA method. The findings are illustrated in figure 4. At zero pressure, the first district of DOS is almost all tightly linked energy band (see figure 4). The S-p electrons have the predominant contribution for the energy bands close to the Fermi standard of the MoS_2 bulk crystal. Therefore, the S-p electrons are important for the conductibility in the crystal in question. In these districts, the DOS is composed principally of S-p and Mo-d states. Note as well that the bonding summits spanned from around –7 to –2.5 eV and those between around –2.5 and 4 eV are essentially overpowered by the Mo-d state. The undermost valence band is collected essentially from Mo-s orbitals, with a slight S-p feature. Upon compression, we note that the intensity of Mo-p and S-s orbitals increases. The projected DOS indicates that at the maximum of the valence band, the most important donations are due to the S-p electrons of the S atoms and the d electrons of the Mo atoms for all pressures being considered here.

The magnetic properties of semiconductors are firmly important parameters for the reason that they combine two important constituents of present-day news technology, semiconductors for logic and magnetism for recollection [47–49]. In magnetic semiconductors, we may realize utilization of a diversity of spin-connected occurrences, not easily obtainable in other materials. A numeral exotic properties were spotted in these magnetic semiconductors, similar to colossal magneto-resistance and magneto-optical domains, having their origin play from the interaction amongst ferromagnetism and semiconducting estates [50]. The total magnetic moment of hexagonal wurtzite MoS_2 bulk material was computed at separate pressures spanning

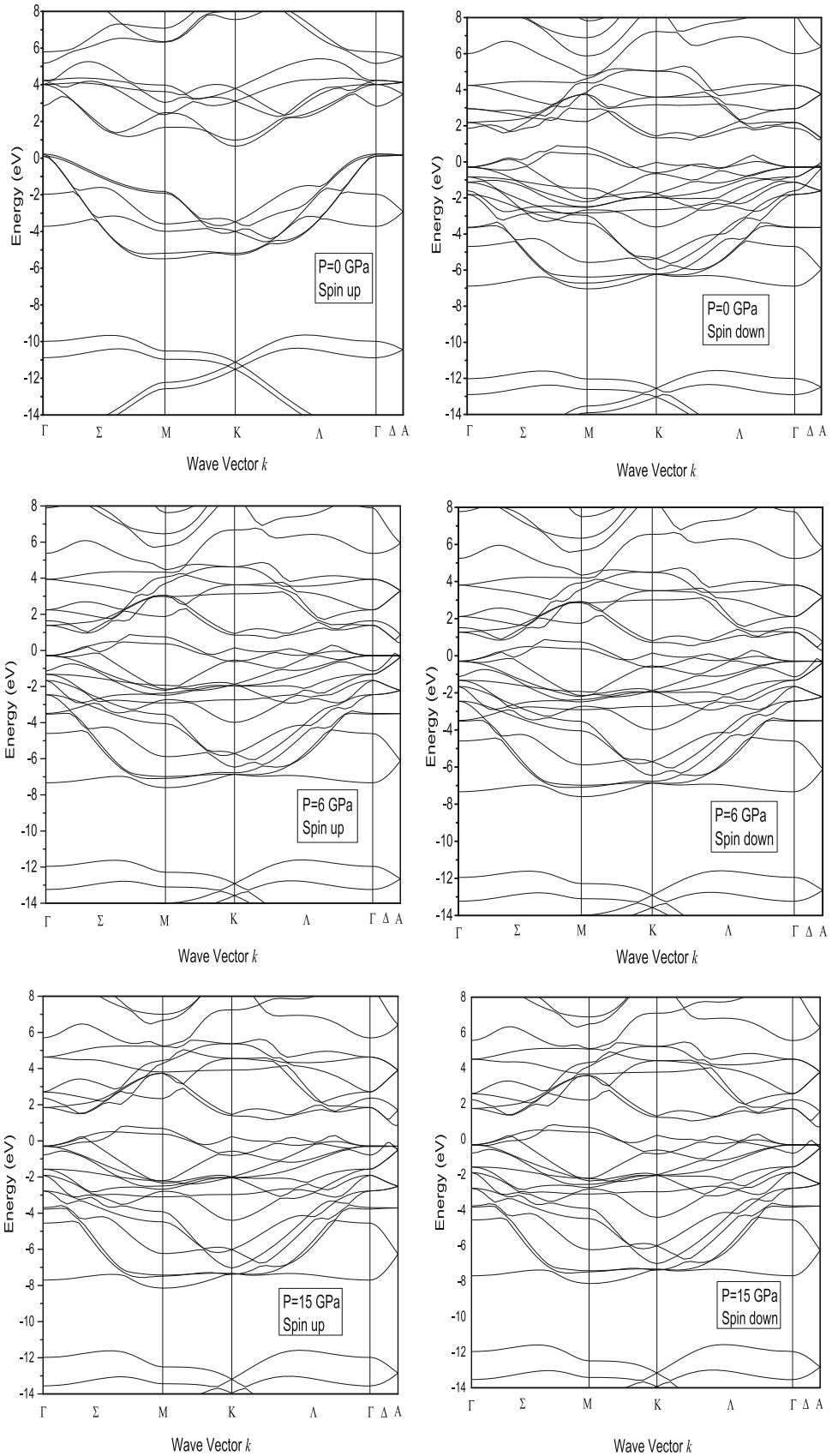

Figure 3. Electronic band structure of bulk hexagonal wurtzite MoS_2 at various pressures scaling from 0 up to 15 GPa.

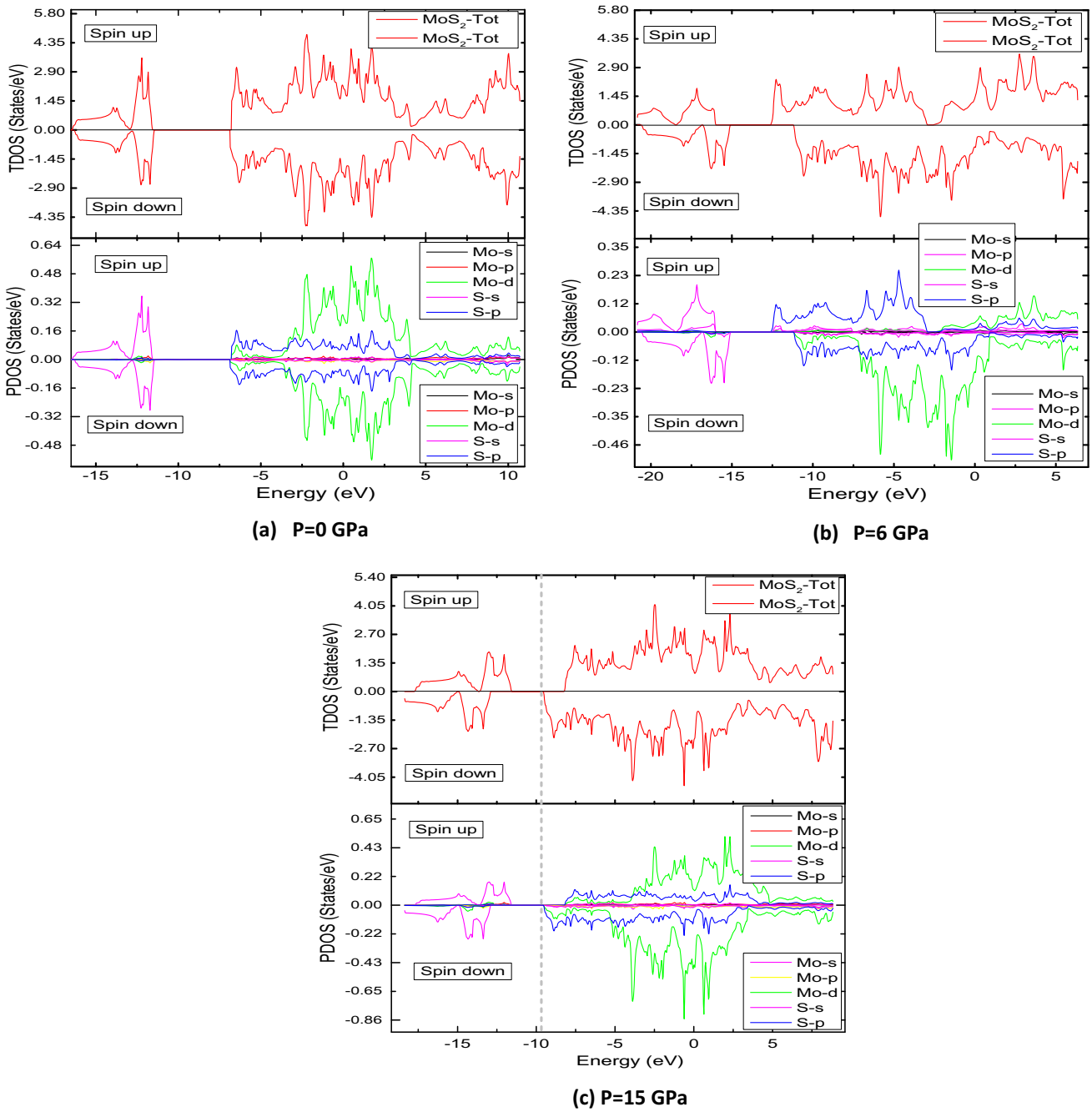

Figure 4. Density of states (DOS) of bulk hexagonal wurtzite MoS_2 within valence bands at various pressures scaling from 0 up to 15 GPa.

from 0 up to 15 GPa for spin-up and spin-down passages. The findings in both channels and for pressures raising from 0 up to 15 GPa are displayed in table 1 and presented in figure 5. At a pressure of zero, the findings donate a value of the total magnetic moment of –0.020 and 0.003 μB for spin-up and spin-down, respectively. Note that in both spin channels, the total magnetic moment of the material of advantage augments non-monotonically when augmenting pressure. Although a same qualitative trend can be observed for the total magnetic moment *vs.* pressure in both spin channels, by the quantitative viewpoint, the absolute values of the total magnetic moment in spin-up channel seems to be different from those in spin-down channel for all pressures being considered in the present work.

To show the pressure impact on the structural properties of MoS_2, we have plotted the linear strain *vs.* pressure. Our findings are described in figure 6. The figure indicates the linear strain *vs.* pressure scaling from 0 up to 15 GPa of bulk hexagonal wurtzite MoS_2 along *a*- and *c*-axis. Note that along *a*-axis when pressure is augmented from 0 up to 15 GPa, the

Table 1. Total magnetic moment of bulk hexagonal wurtzite MoS_2 at different pressures ranging from 0 up to 15 GPa for spin-up and spin-down channels.

Pressure (GPa)	Spin	Total magnetic moment
0	Up	–0.01977
	Down	0.00283
3	Up	–0.01384
	Down	0.00347
6	Up	–0.0061
	Down	0.00070
9	Up	–0.0023
	Down	–0.00122
12	Up	–0.00316
	Down	0.00330
15	Up	0.00078
	Down	0.00735

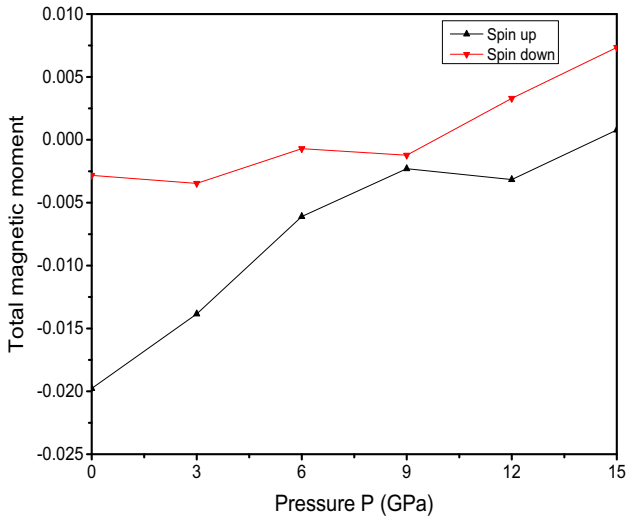

Figure 5. Total magnetic moment of bulk hexagonal wurtzite MoS_2 at various pressures scaling from 0 up to 15 GPa.

a-axis diminishes from 0 to about –0.015. However, along *c*-axis when augmenting pressure from 0 to 15 GPa, the *c*-axis diminishes from 0 up to about –0.075. Thus, we can conclude that the pressure impact on the structural properties is more significant *vs.* *c*-axis than *a*-axis. This can be seen as far as pressure is augmented. In our case we have obtained the mechanical properties, i.e., we have calculated the Young's modulus and the Poisson's ratio of MoS_2 material, which found to be 237.3 GPa and 0.26, respectively. Contrary to other semiconductors, the pliability of MoS_2 material prohibits the distortion and bandgap energy moves, which may occur to its crystalline framework when presented to strain. Nevertheless, the mechanical strain is utilized to change

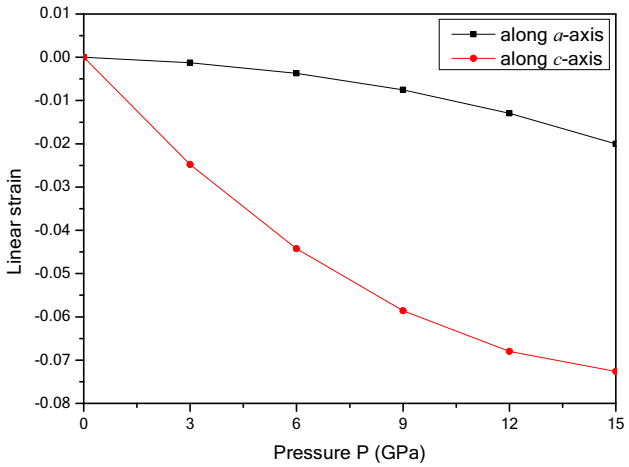

Figure 6. Linear strain *vs.* pressure scaling from 0 up to 15 GPa of bulk hexagonal wurtzite MoS_2 along *a*- and *c*-axes.

MoS_2 electronic typical and transform them from semiconductors to metals [51].

It should be noted that two-dimensional (2D) binary compounds have been newly recorded as undertaking materials for attaining topological insulation and dispersalless transport plans. On the grounding of *ab-initio* calculations consolidated with a tight-binding perfect, Teshome and Dutta [52] have examined a novel denomination of 2D bismuth arsenic (BiAs) polymorphs that are energetically and dynamically steady. The findings showed an undertaking for 2D topological insulators at room temperature [52].

Since the discovery of topological insulators, there has been much inquisition into prediction and experimentally findings separate classes of these materials, in which the bulk insulating but helical edge qualifications are driving in the non-attendance of magnetic range. Herein, using *ab-initio* calculations along with tight-binding model, methyl-decorated SiGe film is exposed to follow up a topological stage transition under overseas yielding stump. Furthermore, for designing and manufacturing of topological electronic plans, Teshome and Dutta [53] have nominated a bilayer of hexagonal boron nitride as appropriate substrate for encouraging $SiGeCH_3$ film without disturbing the nontrivial topology [53].

Topological insulating materials with dissipation-less surface states undertaking aspiring appliances in spintronic materials. Using DFT, Teshome and Dutta [54] have suggested a novel category of topological stage transition in Sb_2Mg_3 on the foundation of tensile stump. This survey increases the surroundings of topological insulators and current platforms for designing novel spintronic devices. These interesting findings perform Sb_2Mg_3 as a promising candidate material for performing a quantum spin Hall insulator at room temperature [54].

4. Conclusions

The structural parameters, electronic structure, DOS and magnetic moment of bulk MoS_2 in the hexagonal structure have been executed. Our computations were mainly based on the spin-polarized FP-LAPW procedure in the TB-mBJ-GGA oncoming. The impact of pressure on the lineaments of benefits has been inspected and discussed. At zero pressure, the obtained lattice parameters are accordant with experiment. In accord with previous calculations and with experimental evidence, our work showed that at a null pressure the bulk MoS_2 demonstrates a semiconductor behaviour in a spin-up channel, which has an indirect energy gap of 0.91 eV. The total magnetic moment was established to be –0.020 and 0.003 μB in spin-up and spin-down channels; respectively. Upon compression, the lattice parameters were found to decrease non-linearly. The material in question has tendency to a metallic character when it is compressed. The total magnetic moment was shown to increase non-monotonically in both spin-up and spin-down channels yielding values in spin-up channel that differs from those of spin-down channel. The pressure impact on the structural properties of MoS_2 material has also been obtained. For this purpose, the linear strain *vs.* pressure has been plotted. It is shown that the influence of pressure on the structural properties is further significant *vs. c*-axis than *a*-axis. The mechanical properties such as Poisson's ratio and Young's modulus have also been obtained at zero pressure.

References

[1] Gmelin L 1995 *GMELIN Institute for Inorganic Chemistry of the Max-Planck-Society for the Advancement of Science*, 8th edn. (Berlin: Springer-Verlag) vol B7

[2] Cheiwchanchamnangij T and Lambrecht W R L 2012 *Phys. Rev. B* **85** 205302

[3] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 *Phys. Rev. Lett.* **105** 136805

[4] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim C-Y *et al* 2010 *Nano Lett.* **10** 1271

[5] Bouarissa A, Gueddim A, Bouarissa N and Maghraoui-Meherzi H 2019 *Optik* **208** 164080

[6] Gourmelon E, Lignier O, Hadouda H, Couturier G, Bernede J C, Tedd J *et al* 1997 *J. Sol. Energy Mater. Sol. Cells* **46** 115

[7] Ho W K, Yu J C, Lin J, Yu J G and Li P S 2004 *Langmuir* **20** 5865

[8] Lee P A 1976 *Optical and electrical properties* (Dordrecht: Reidel) p 423

[9] Coehoorn R, Haas C and Degroot R A 1987 *Phys. Rev. B* **35** 6203

[10] Lebegue S and Eriksson O 2009 *Phys. Rev. B* **79** 115409

[11] Li T S and Galli G L 2007 *J. Phys. Chem. C* **111** 16192

[12] Kandemir A, Yapicioglu H, Kinaci A, Çağin T and Sevik C 2016 *Nanotechnology* **27** 055703

[13] Zhang Y, Xu W, Liu G and Zhu J 2020 *J. Phys.: Conf. Ser.* **1676** 012164

[14] Akbari A, Naseri M and Jalilian J 2018 *Chem. Phys. Lett.* **691** 181

[15] Ou H, Xu S, Xiao Z, Fu H and Luo Y 2019 *IOP Conf. Series: Mater. Sci. Eng.* **493** 012072

[16] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 *Atomically thin MoS_2: a new direct-gap semiconductor* arxiv.org

[17] Holzapfel W B 1996 *Rep. Prog. Phys.* **59** 29

[18] Saib S, Bouarissa N, Rodríguez-Hernández P and Muñoz A 2008 *Physica B* **403** 4059

[19] Lukačević I and Kirin D 2010 *Croat. Chem. Acta* **83** 15

[20] Manjón F J and Errandonea D 2009 *Phys. Stat. Sol. B* **246** 9

[21] Boucenna M and Bouarissa N 2004 *Mater. Chem. Phys.* **84** 375

[22] Mujica J A, Rubio A, Muñoz A and Needs R J 2003 *Rev. Mod. Phys.* **75** 863

[23] Eremets M 1996 *High pressure experimental methods* (Oxford: Oxford University Press)

[24] Hemley R J, Mao H K and Struzhkin V V 2005 *J. Synchrotran Radiat.* **12** 135

[25] Yin M T and Cohen M L 1980 *Phys. Rev. Lett.* **45** 1004

[26] Payne M C, Teter M P, Alan D C, Arias T A and Joannopoulos J D 1992 *Rev. Mod. Phys.* **64** 1045

[27] Bouarissa N 2002 *Phys. Stat. Sol. B* **231** 391

[28] Bouarissa N 2002 *Mater. Chem. Phys.* **73** 51

[29] Wu Z and Cohen R E 2006 *Phys. Rev. B* **73** 235116

[30] Tran F and Blaha P 2009 *Phys. Rev. Lett.* **102** 226401

[31] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D, Luitz J 2014 *WIEN2k an augmented plane wave plus local orbitals program for calculating crystal proprieties* (Vienna University of Technology)

[32] Zhu Z Y, Cheng Y C and Schwingen Schlögl V 2011 *Phys. Rev. B* **84** 153402

[33] Molina-Sánchez A, Sangalli D, Hummer K, Marini A and Wirtz L 2013 *Phys. Rev. B* **88** 045412

[34] Abdul Rahman I and Purqon A 2017 *J. Phys.: Conf. Series* **877** 012026

[35] Wakabayashi N, Smith H G and Nicklow R M 1975 *Phys. Rev. B* **12** 659

[36] Saib S and Bouarissa N 2007 *Phys. Stat. Sol. B* **244** 1063

[37] Zerroug S, Ali Sahraoui F and Bouarissa N 2007 *Eur. Phys. J. B* **57** 9

[38] Algarni H, Gueddim A, Bouarissa N, Khan M A and Ziani H 2019 *Res. Phys.* **15** 102694

[39] Cohen M L and Chelikowsky J R 1989 *Electronic structure and optical properties of semiconductors* (Berlin: Springer-Verlag)

[40] Bouarissa N 1998 *Phys. Lett. A* **245** 285

[41] Martin R M 2004 *Electronic structure: basic theory and practical methods* (Cambridge University Press)

[42] Bouarissa N 2006 *J. Phys. Chem. Solids* **67** 1440

[43] Adachi S 2005 *Properties of group-IV, III-V, and II-VI semiconductors* (Chichester: Wiley)

[44] Adachi S 2009 *Properties of semiconductor alloys: group-IV, III-V and II-VI semiconductors* (Chichester: John Wiley & Sons Ltd.)

[45] Bouarissa N 2001 *Mater. Sci. Eng. B* **86** 53

[46] El Hassasna A, Bechiri A and Bouarissa N 2019 *Mater. Res. Exp.* **6** 085915

[47] Saib S, Bouarissa N, Rodríguez-Hernández P and Muñoz A 2010 *Eur. Phys. J. B* **73** 185

[48] Moulai N, Bouarissa N, Lagoun B and Kendil D 2019 *J. Supercond. Nov. Magn.* **32** 1077
[49] Harrache Y and Bouarissa N 2019 *Solid. Stat. Commun.* **295** 26
[50] Shinjo T 2009 (ed) *Nanomagnetism and spintronics* (USA: Elsevier Science) eBook ISBN: 9780080932163 https://doi.org/10.1016/C2009-0-18006-6
[51] Samy O, Zeng S, Birowosuto M D and Moutaouakil A E 2021 *Crystals* **11** 355
[52] Teshome T and Dutta A 2018 *J. Phys. Chem. C* **122** 15047
[53] Teshome T and Dutta A 2018 *J. Phys. Chem. C* **122** 25127
[54] Teshome T and Dutta A 2019 *ACS Omega* **4** 8701