Strain-Induced Magnetism in Single-Layer MoS$_2$: Origin and Manipulation

Won Seok Yun and J. D. Lee*

Department of Emerging Materials Science, DGIST, Daegu 711-873, Republic of Korea

ABSTRACT: We investigate the strain-induced electronic and magnetic properties of single-layer (1L) MoS$_2$ with vacancy defects using the density functional theory calculation. When the tensile strain is applied, 1L-MoS$_2$ with vacancy becomes ferromagnetic and metallic. We elucidate that, from the electronic band structure of vacancy-defect-doped 1L-MoS$_2$, the impurity bands inside the gap play a role of seed to drive novel magnetic and electronic properties as the strain increases. In particular, we also find that 1L-MoS$_2$ with two-sulfur vacancy (V$_{2S}$) shows the largest magnetic moment at $\sim$14% strain among various vacancy types and undergoes a spin reorientation transition from out-of-plane to in-plane magnetization at $\sim$13% strain. This implies that the strain-manipulated 1L-MoS$_2$ with V$_{2S}$ can be a promising candidate for new spintronic applications.

INTRODUCTION

Tremendous research efforts have been focused on the layered transition-metal dichalcogenides (TMDCs) due to their potential applications in areas such as electronic, optoelectronic, and photovoltaic devices. Among those, interestingly, MoS$_2$ shows a strong dependence on the layer thickness in its electronic properties. A single-layer (1L) MoS$_2$, which is obtained by employing the micromechanical exfoliation, chemical exfoliation, liquid exfoliation, and chemical vapor deposition (CVD) methods, is a direct-gap semiconductor with a energy gap of $\sim$1.8 eV, whereas the bulk MoS$_2$ is an indirect-gap semiconductor with a energy gap of $\sim$1.3 eV. Furthermore, tuning the band gap of MoS$_2$ through the strain effect is one of the most feasible approaches to achieve a wide-range controllability of their electronic properties. Previous theoretical studies have shown that the single- and few-layer MoS$_2$ undergo not only the direct-to-indirect band gap transition but also a change of semiconducting to metallic phases under tensile strains. Subsequently, the strain-induced modulation of band gap was experimentally confirmed.

Great attention has been paid to the exploration of the magnetic properties of MoS$_2$ for the nanoscale spintronic applications. Manifestation of the ferromagnetic (FM) phase has been done in terms of various treatments: vacancy-defect formation, adsorption or substitution of transition metal or nonmetal elements, and nanoribbon with zigzag edges. For instance, Ataca et al. confirmed that vacancy defects of S, 2S, Mo, and Mo+S introduced in 1L-MoS$_2$ do not induce any magnetism; however, that of Mo+2S results in a sizable magnetic moment in the system. Nanoribbon with zigzag edges exhibit FM metallic phase regardless of its width. Such FM behavior is attributed to unpaired electrons that are mainly localized on the edge Mo atoms. Moreover, the magnetic property in those systems is made controllable through an application of the tensile strain, i.e., the strain engineering.

Recently, the strain-induced magnetism in 1L-MoS$_2$ with atomic vacancies has been proposed by Tao et al. and Zheng et al. They have been concerned about 1L-MoS$_2$ with single atomic vacancies under the tensile strain. In the present work, we have performed the first-principles calculations to investigate extensively the electronic and magnetic properties of 1L-MoS$_2$ with several types of vacancy defects under equibiaxial or uniaxial strain. Excavating the unfolded band structures of the supercell calculation for the vacancy-defective 1L-MoS$_2$, we have clarified that the strain-induced magnetism and the accompanying metallic nature are driven by the impurity bands inside the gap. Further, we have found that 1L-MoS$_2$ with two-sulfur vacancy (V$_{2S}$) shows an unexpectedly...
large spin magnetic moment up to 7.45 \( \mu_B \) per supercell at \( \sim 14\% \) tensile strain and it also shows a spin reorientation transition from out-of-plane to in-plane magnetization at \( \sim 13\% \) strain from a change of the magnetocrystalline anisotropy (MCA). This finding indicates an immediate significance of 1L-MoS\(_2\) with V\(_2\)S for new spintronic applications.

## COMPUTATIONAL DETAILS

First-principles calculations based on the density functional theory (DFT) are performed using the Vienna \( \textit{ab initio} \) simulation package (VASP).\(^{30}\) The generalized gradient approximation (GGA) formulated by the Perdew–Burke–Ernzerhof (PBE) functional\(^ {31}\) and the projector augmented wave (PAW) potentials are used.\(^ {32,33}\) An energy cutoff of 450 eV was adopted for the plane-wave expansion of the electronic wave function and a \( 6 \times 6 \times 1 \) Monkhorst–Pack \( k \)-point grid used for an integration over the 2D Brillouin zone. The unit cell is optimized to obtain the equilibrium lattice parameter at the lowest total energy and atomic positions were fully relaxed until the force on each atom is less than \( 10^{-4} \) eV Å\(^{-1}\). The vacuum space along the \( z \) direction was taken to be more than 15 Å for all the considered systems and the convergence criterion in the self-consistency process set to \( 10^{-4} \) eV. The direct band gap at the K-point for the pristine 1L-MoS\(_2\) is estimated to be \( E_g = 1.7 \) eV, which is moderately consistent with the experimental optical band gap in the range 1.75–1.9 eV.\(^ {7,8}\) On the contrary, 2.14 eV at the K-point was recently reported with the hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional.\(^ {34,35}\)

In DFT, the calculated electronic band structure is important for an interpretation of the experimental measurement like the angle-resolved photoemission spectroscopy (ARPES). Meanwhile, the supercell calculation results in the folded band structure due to a shrinkage of the Brillouin zone, which makes an immediate interpretation of ARPES unavailable. Hence, we try to overcome this difficulty using the effective band unfolding technique\(^ {36,37}\) to recover a primitive cell picture. In this approach, it is important to construct a spectral function \( A(k;E) \), which is given by

\[
A(k;E) = \sum_{m} P_{\mathbf{k}m}^{\mathbf{k}n}(E_{mn} - E) \delta(E_{mn} - E)
\]

with the continuous variable energy \( E \) and the spectral weight

\[
P_{\mathbf{k}m}^{\mathbf{k}n}(E) = \sum_{n} |\langle \mathbf{k}m | \mathbf{k}n \rangle |^2,
\]

where \( |\mathbf{k}m \rangle \) and \( |\mathbf{k}n \rangle \) (\( n \) and \( m \) indicate band indices) are the eigenvectors in the primitive cell and the supercell, respectively. The spectral weight can be obtained by projecting \( |\mathbf{k}m \rangle \) on all primitive cell eigenstates \( | \mathbf{k}n \rangle \) of a fixed \( k \). From this, \( A(k;E) \) can be obtained, which is regarded as an effective primitive cell projection of the supercell band structure. The detailed description about the effective band unfolding method can be found elsewhere.\(^ {36-39}\) Further, the MCA calculation was also performed in the noncollinear mode with the spin–orbit coupling (SOC) term.\(^ {40}\)

We have considered two models for applying the tensile strain, i.e., the biaxial and uniaxial strain models. First, the biaxial strain model consists of a hexagonal \( 4 \times 4 \) supercell of 1L-MoS\(_2\) with 16 Mo and 32 S atoms. Subsequently, five

![Figure 1](image-url)
possible vacancy-defect types by removing Mo and/or S atoms in 1L-MoS2 (denoted by V1Mo, V1S, V1Mo+1S, and V1Mo+2S, e.g., V1Mo implies 1L-MoS2 with 1 Mo atom removed) are considered in the present study, which are displayed in Figure 1a. Note that the chemical compositions correspond to Mo0.9375 S2, Mo1.9375 S, Mo1.875 S, Mo1.9375 S1.9375, and Mo0.9375 S1.875 for defect types of V1Mo, V1S, V1Mo+1S, and V1Mo+2S, respectively. Next, for the uniaxial strain model, we have used a rectangular $4 \times 2\sqrt{3}$ supercell of 1L-MoS2 containing totally the same number of atoms as in the hexagonal $4 \times 4$ supercell. Again, five types of vacancy defects in the rectangular supercell are shown in Figure 1b.

### RESULTS AND DISCUSSION

We have optimized the lattice parameter as $a_0 = 3.184\,\text{Å}$ for the pristine 1L-MoS2, which agrees with previous studies.11,28 In the same way, the optimized lattice constants of 1L-MoS2 with V1Mo, V1S, V1Mo+1S, and V1Mo+2S defects are determined to be 3.191, 3.166, 3.146, 3.183, and 3.152 Å, respectively, as listed in Table 1. The lattice constant in 1L-MoS2 with V1Mo defect is slightly increased compared to the pristine case, whereas those in 1L-MoS2 with other types of defects are a bit decreased. Except for 1L-MoS2 with the V1Mo+2S defect, there are not observed the magnetism at their equilibrium lattice constants.

To understand the defect-forming stability, we have carried out the calculation of the vacancy-defect formation energy $E_f$ using the following equation,

$$E_f = -E_{\text{pristine}} + E_{\text{defect}} + nE_{\text{Mo}} + mE_{\text{S}}$$

where $E_{\text{pristine}}$ and $E_{\text{defect}}$ are total energies of the $4 \times 4$ supercell of the pristine and defective 1L-MoS2, respectively, $E_{\text{Mo}}$, and $E_{\text{S}}$ are the total energy per atom of the bcc Mo and orthorhombic $\alpha$-S, respectively, and $n$ and $m$ are the numbers of removed Mo and S atoms, respectively. The results are listed in Table 1. The defect formation energy for the V1S-doped 1L-MoS2 is lowest among the considered systems. The sulfur (and even the two-sulfur) vacancy-defect formation is easier than the Mo-vacancy defect, which is consistent with previous reports.6,28 Point defects have been usually observed in the CVD grown MoS2 and can be easily made by the electron or proton irradiation method.17,41

We now examine the magnetic properties of the pristine and vacancy-doped 1L-MoS2’s under the tensile strain, which is more effective than the compressive strain for the present purpose.14,26,29 Figure 1c presents the calculation of total magnetic moment $m_{\text{total}}$ for the pristine and vacancy-defect-doped 1L-MoS2’s as a function of the tensile strain with a range from 0% to 20%. Here, the strain $\epsilon$ can be defined as $\epsilon = (a - a_0)/a_0 = \Delta a/a_0$, where $a_0$ and $a$ are the lattice constants of the unstrained (optimized) and strained systems, respectively. It is clear in the figure that the biaxial strain induces larger magnetic moment than the uniaxial strain. For this reason, we hereafter focus on the magnetic properties by the biaxial strain for 1L-MoS2.

It was in fact demonstrated that these 2D nanostructures can endure the strain to the intrinsic limit of $\sim 25%$.42,43 Moreover, according to the previous first-principles calculations, about 20% was also reported as the critical biaxial strain limit.44 Regarding an experimental realization of the strain-induced magnetism in this system, we would suggest another highly stretchable material as a substrate. A very recent work has reported that alginate–polyacrylamide hydrogels can be elongated over 20 times its initial length.45 Therefore, using such a materials with high flexibility and stretchability as a substrate, it would be available to achieve the necessary strain in 1L-MoS2.

Except for the V1Mo+2S case, the induced magnetic moments of all the considered systems are negligible for small (and zero) strains. In contrast, the V1Mo+2S defect leads to the magnetism ($\sim 2\mu_B$) even in the equilibrium (unstrained) state, in good agreement with previous theoretical investigations.15,17 A change from the nonmagnetic (NM) to FM state in 1L-MoS2 with V1Mo, V1S, V1Mo+1S, and V1Mo+2S defects occurs at approximately 6.5%, 8%, 9.5%, and 5.5% strains, respectively. It is noted that the magnetic phase transition for the molybdenum-vacancy-doped systems occurs earlier than the sulfur-vacancy-doped systems. Beyond the transition, the induced magnetic moments tend to increase gradually with respect to the applied tensile strain.

Incidentally, the calculated magnetic moments for 1L-MoS2 with V1Mo, V1S, V1Mo+1S, and V1Mo+2S defects have maximum values of 2.02, 4.07, 7.45, and 4.04 $\mu_B$ at roughly 14.5%, 14.5%, 13.5%, and 13% strains, respectively. The total energy difference between FM and NM states has been also calculated. In the calculation, the FM state is found to be favored by 101, 350, 1129, and 288 meV over the NM states for the case with V1Mo, V1S, V1Mo+1S, and V1Mo+2S defects, respectively. From the magnetic moments and total energy difference, we note that the V1S-doped 1L-MoS2 is found to have the largest magnetic moment and, at the same time, be energetically most stable.

Let us discuss the electronic and magnetic driving force originated by the vacancy defects in view of the electronic band structure. The zone folding of the electronic bands due to the supercell calculation has been a long-standing difficulty. In the present study, we have tried to overcome the difficulty for the immediate supercell calculation using the effective unfolding technique.36,37 Figure 2 illustrates the results of unfolded band structure for the pristine and five cases of defective 1L-MoS2’s at their equilibrium lattice constants. For the pristine 1L-MoS2, 4 $\times$ 4 supercell, the direct band gap at the K-point is estimated to be $E_g = 1.70\,\text{eV}$, which is very consistent with that of the primitive cell calculation.8,10 Compared with the pristine case, all defective cases introduce the flat impurity bands inside the band gap due to the atomic vacancies. In particular, it is worth noting that the impurity bands for 1L-MoS2 with V1S and V1Mo defects (i.e., only sulfur vacancy) are found near below the conduction band minimum (CBM). It is known that MoS2 on the bare SiO2 substrate has an unipolar n-type behavior.47 In contrast, the impurity bands of V1Mo, V1Mo+1S, and V1Mo+2S defects (i.e., including molybdenum vacancy) are located near above the valence band maximum (VBM). Further, it is revealed that the
impurity bands of $V_{2S}$ and $V_{1Mo}$ defects are derived by Mo d and S p characters near the vacancy sites. To gain more insight into the emergent electronic and magnetic properties of defective 1L-MoS$_2$'s under the tensile strain, the total density of states (DOS) are illustrated in Figure 3. Comparing the equilibrium DOS (shaded cyan lines of Figure 3) among the defective 1L-MoS$_2$'s with respect to the pristine, one can find clearly that the defect levels of the molybdenum vacancy lie close to the VBM, whereas those of the sulfur vacancy are close to the CBM. This is confirmed from the midgap impurity bands found in the corresponding unfolded band structures of Figure 2. In addition, in Figure 3, the systematic band narrowing of defective 1L-MoS$_2$'s occurs as the applied strain increases. In particular, after the magnetic transition, all the considered systems are shown to be metallic (see black dotted lines of Figure 3); i.e., the band gap collapses.

We have now calculated the bond lengths between Mo and S atoms ($d_{Mo-S}$) in the vicinity of the defect site of the $V_{2S}$-defective 1L-MoS$_2$, which are indicated in the inset of Figure 4a. It should be noted that the induced magnetism in this system is mainly localized in Mo atoms near the defect site. Consequently, the bond lengths between Mo and S atoms are calculated to be 2.392, 2.428, and 2.480 Å at the strain for the equilibrium (zero strain), magnetic transition ($\sim$10% strain), and maximum magnetization ($\sim$14% strain), respectively. Simultaneously, the bond lengths between Mo and Mo atoms ($d_{Mo-Mo}$) near the defect site are calculated to be 2.829, 3.452, and 5.079 Å at the strain for the equilibrium, magnetic transition, and maximum magnetization, respectively. Further, we have tried the unrelaxed calculation for the $V_{2S}$-defective 1L-MoS$_2$ at $\sim$14% strain (i.e., fixing the atomic distances as stretched ones by $\sim$14% strain from the pristine 1L-MoS$_2$ with two S atoms just removed). In this calculation, $d_{Mo-S}$ and $d_{Mo-Mo}$ are found to be 2.594 and 3.575 Å, respectively, and the states near vacancy defects to the created magnetization under the strain. In particular, as shown in Figure 4a, out-of-plane states (d$_{z^2}$ and d$_{xz/yz}$ orbitals) of the Mo atoms near the defect sites show appreciable unbalanced spin populations in spin-split impurity bands near the Fermi level. Quantitatively, the local spin magnetic moment of the Mo atom is calculated to be 2.09 $\mu_B$ per atom.

Figure 2. Unfolded band structures of the pristine and defective 1L-MoS$_2$'s at their equilibrium lattice constants. The color bar scale in the bottom represents the number of the primitive cell bands crossing the energy interval at a given primitive wave vector.

Figure 3. Total density of states (DOS) of the pristine and defective 1L-MoS$_2$'s. The positive (negative) values represent the majority (minority) spin bands. Cyan shading, black dotted lines, and red solid lines denote the total DOS at the strain for the equilibrium (i.e., zero strain), magnetic transition, and maximum magnetization, respectively.

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SUMMARY

We have explored the strain-induced magnetism in 1L-MoS₂ with various vacancy defects. When the tensile strain is applied, 1L-MoS₂ with vacancies result in magnetic and metallic phases. From the point of view of the electronic structure, we have found that the resultant impurity bands inside the band gap play a role of seed to drive novel magnetic and electronic properties as the strain increases. In particular, we have also found that the two-sulfur-vacancy-defective 1L-MoS₂ has the largest magnetization at ~14% strain among various defective 1L-MoS₂ and undergoes a switching of the magnetization direction at ~13% strain. Our finding indicates that the vacancy-defective 1L-MoS₂ promote the application of 2D transition metal dichalcogenides for the nanoscale devices and especially, the two-sulfur-vacancy-defective 1L-MoS₂ can be a promising candidate for the nanoscale spintronic application.

AUTHOR INFORMATION

Corresponding Author

*J. D. Lee. E-mail: jdlee@dgist.ac.kr.

Notes

The authors declare no competing financial interest.

REFERENCES


Figure 4. (a) Partial DOS of the Mo atom near vacancy-defect sites for the V₂S⁻₂-defective 1L-MoS₂ at ~14% strain. The inset illustrates the spin-density isosurfaces. The isosurface value is taken as S × 10⁻⁵ e Å⁻³ and the blue (red) distribution represents the net spin up (spin down) density. Orange and cyan two-headed arrows (↔) represent the bond lengths between Mo and S atoms (d_{Mo-S}) and between Mo and Mo atoms (d_{Mo-Mo}), respectively. (b) Magnetocrystalline anisotropy (MCA) energy E_{MCA} as a function of the tensile strain for the V₂S⁻₂-defective 1L-MoS₂. The blue arrow indicates the magnetization direction with respect to the surface.

net magnetic moment is 3.01 μB, which is smaller than that for the relaxed (atomic relaxation allowed) system (7.45 μB). This implies that the atomic relaxation and the bond length change could be a driving force of the strain-induced magnetism.29,48

MCA that originates from the spin-orbit interaction would be an interesting quantity to answer the question how the strain effect have an impact on the spin orientation of the V₂S⁻₂ defective 1L-MoS₂. In Figure 4b, we provide the MCA energy (E_{MCA}) of the system in a range of 10–20% of the tensile strain, where ~10% strain is the threshold of the magnetic transition. We note a sign change in E_{MCA}. The positive sign of E_{MCA} means the out-of-plane magnetization, whereas the negative sign the in-plane magnetization. As a result, the V₂S⁻₂-defective 1L-MoS₂ shows the spin reorientation transition (SRT) from out-of-plane to in-plane order at ~13% strain. This concludes that the tensile strain can be used as a new control tip not only for inducing the magnetization but also for switching the magnetization direction.

Finally, we remark that another important merit of our strategy is to prepare the intriguing nanostructure (i.e., the V₂S⁻₂-defective 1L-MoS₂) rather easily. As mentioned before, various point defects are naturally found in the CVD grown 1L-MoS₂. Most easily, one can always choose a piece of 1L-MoS₂ with defects of two-sulfur vacancies. Or, more elaborately, one may create two-sulfur vacancies using the scanning tunneling microscope (STM) regularly in 1L-MoS₂.


We have checked that the spin-polarized calculation for the V₂S₅ defect 1L-MoS₂ at ~14% strain using the hybrid HSE06 functional resulted in 7.99 μB per supercell, being very close to the present GGA result (7.45 μB per supercell).


