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Magnetism and magnetocystalline anisotropy of localized 1H/1T by S atom sliding

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Abstract: Monolayered MoS_2 is energetically most stable when it has a 1H phase, but 1H to 1T phase transition (1H→1T) is easily realized by various ways. Even though magnetic moment is not observed during 1H1T, 0.049 μ_B/MoS_2 is obtained in local 1T phase; 75% 2H and 25% 1T phases are mixed in (2 × 2) supercell. Furthermore, non-negligible magnetocrystalline anisotropy (MCA) energy is occured. Most magnetic moment as well as MCA are originated by 1T phased Mo atom in the supercell, while electronic structures of other atoms are similar to non-magnetic. Due to this, magnetic/non-magnetic boundary is created in the monolayered MoS_2. Our result suggests that MoS_2 can be applied for spintronics such as a spin transistor.

Keywords: DFT calculation, magnetism, MoS_2

1. Introduction

Recently, research on molybdenum disulfide (MoS_2), which is highly applicable to transistors and solar cells, has been actively conducted[1–6]. MoS_2 has a layered structure similar to that of graphite, but the S-Mo-S bonds in the layer are strong covalent bonds, but the layers and layers are weakly bound by van der Waals interactions, making the layers easily separated [7]. The crystal structures of the bulk Mo_2 are hexagonal symmetry (2H), tetragonal symmetry (1T), and rhombic symmetry (3R). The number before the letter indicates the number of MoS_2 layers contained in the unit cell. The electronic structure of MoS_2 is known to be highly dependent on the symmetry and thickness of the atoms. For example, the 2H phase of the bulk MoS_2 is a semiconductor having a band gap of about 1.2 eV[8], but the 1T phase is a conductor. The shape of the band gap also varies depending on the thickness of the thin film even for the 2H phase[9–11]. It will have an indirect band gap. The biggest advantage of MoS_2 is that it is easy to peel off to a single layer due to the weak interlayer bonding force. In addition, pure MoS_2 does not magnetize regardless of its bulk or thin film thickness, but it can be magnetized in the event of stress, atomic defects, or doping with a small amount of transition metals[9,12,13]. According to the paper, which studies the magnetic and magnetic anisotropy caused by atomic defects, it is observed that about 6% of atomic defects in the single layer MoS_2 generate about 1.989 μ_B of magnetic moment around the defects[14]. In addition, due to the MoS_2 characteristic of the 2H structure, it is possible to have several types of edge structures, such as armchair or zigzag, depending on the cutting direction. In this case, magnetic moments are measured. However, the method of creating defects or edges can lead to unpredictable deformation of the atomic structure and difficult control of the defective molecules and gas molecules adsorbed on the edges. It has been reported that the hydrogen gas is easily adsorbed where the bond is broken and the magnetic moment is greatly reduced when the hydrogen gas is adsorbed.

2. Method

As a solution to this problem, we focused on experimental papers that create 2H → 1T phase transitions by shifting the position of some S atoms in 2H MoS_2. According to this paper[15], some S atoms are horizontally shifted along a layer to make some 2H phases transition to 1T phases, thereby creating a boundary between semiconductors and metals. We have studied the change and magnetism of the electronic structure in the 1H → 1T phase transition in MoS_2. No magnetism was observed when the entire monolayer was in the 1T phase, but when the 1T phase was locally present in the 1S MoS_2 thin film, the Mo atoms in the 1T environment were about 0.160 μ_B and the Mo atoms in- the neighboring 1H environment were about 0.011 μ_B. It has a chair moment and an average magnetic moment of 0.049 μ_B/ MoS_2. This suggests that, unlike Y.C. Lin and others suggesting a semiconductor/metal interface by moving some S atoms in a single-layer Mo_2, a magnetic/non-magnetic boundary can be created. For the purpose of this study, spin-polarized total energy calculations were performed using the Viennaab-initio simulation (GGA)[16,17] established by Perdew-Burke-Ernzerhof, and pseudo potentials were generated by the Projector augmented wave (PAW) method. The base cutoff energy was adopted as a planar wave developed up to 400 eV, and two-dimensional BZ was represented as a 24 24 lattice point of Monkhorst-Pack for the Brillouinzone (BZ) integration[18].

In order to perform the film calculation, the distance between the monolayers was sufficiently given to 15 Å to neglect the interaction between the monolayers and the monolayers. In order to express a similar situation, the 1H → 1T phase transition was implemented by fixing the positions of the Mo atoms and the lower S atoms and shifting the positions of the upper S atoms collectively. Fig. As shown in 1 (a), yellow and orange, respectively, were used to distinguish between the lower S atoms fixed at the upper 1H and the upper S (hereinafter referred to as S') atoms moving to the 1T phase.

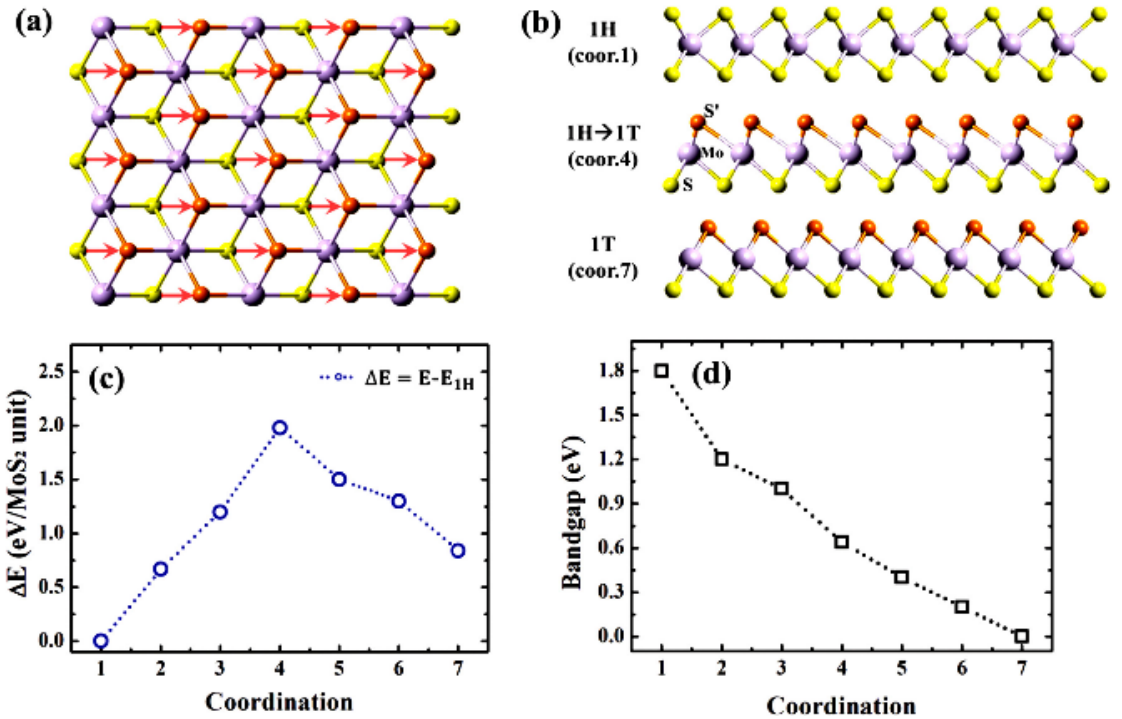

Figure 1. (a) Large sphere represents Mo, small yellow and orange spheres represent S and moved S (S'), respectively. Red arrows express moving path of S' atoms. (b) 1H, center of 1H → 1T path and 1T correspond to cood.1, 4 and 7, respectively. (c) Energy difference (ΔE = E - E_{1H}) and (d) band gap on the path of the 1H → 1T phase transition.

3. Results and discussion

To examine the electronic structure in the 1H $\rightarrow$ 1T phase transition intermediate process in a monolayer MoS_2 thin film. Calculate the energy and band gap at the midpoint of the path indicated by the arrow in Fig.1 (a). 1(c) and (d), respectively. ΔE of 1 (c) is the total energy calculated based on the 1H phase (EE_{1H}). The energy difference between 1H and 1T is approximately 0.84 eV/MoS_2, which is in good agreement with the results reported earlier. Intermediate of S' path. 4 is calculated to have about 1.98 eV/MoS_2 higher energy than 1H phase, indicating that the height of the barrier for 1H $\rightarrow$ 1T phase transition is higher than 1.98 eV/MoS_2. Fig. 1 (d) is a change in the band gap on the phase transition path. The band gap, which is about 1.8 eV at 1H, is steadily narrowed as it approaches 1T, and the band gap is completely closed at 1T to have a metallic electronic structure. The paramagnetic states were stable at all points along the path. To account for the local presence of 1T phase in the 1H phase, set the MoS_2 monolayer (2 $\times$ 2) superlattice and level one-quarter of the number of top S atoms. The method of moving was chosen. The top and side views of the local 1T structure are shown in Fig. 2 is shown. The dotted lines shown in the top and side views refer to the unit (2 $\times$ 2) superlattice used in this calculation.

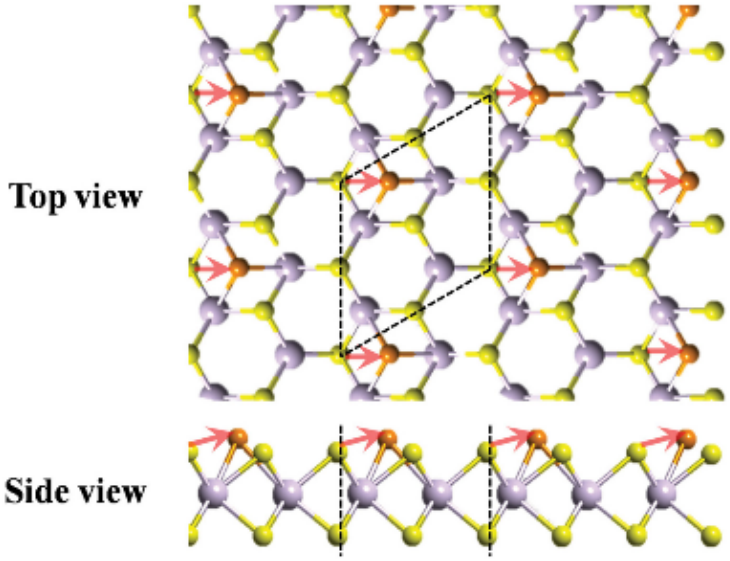

Figure 2. Atomic structure of the local 1T phase MoS_2. Upper (bottom) panel represents top-view (side-view). Dotted lines in both upper and under panels represent the unit cell of the local 1T phase. The moving path of the S' atom is schematically denoted by red arrows.

Similar to 1 (a), the S atom immobilized on 1H is yellow and the S' atom that moves to the 1T phase is represented by an orange sphere. The optimal two-dimensional lattice constants were obtained by loosening the atoms on the z-axis with fixed experimental values for the bulk. The lengths of Mo-S bonds on the 1H and 1T phases in the local 1T structure were 2.38 Å and 2.44 Å respectively. The bond length of the 1H portion is reduced compared to that of Mo and S on the pure 1H phase of 2.41 Å whereas the bond length in the 1T portion is increased.1H $\rightarrow$ (local 1T) The band gap is calculated and the results are shown in Fig. 3 (a) and (b). As shown in Fig. 3 (a), the energy difference between 1H and local 1T is 1.04eV / MoS_2, which is 0.20 eV/MoS_2 higher than that of the entire 1T phase. coor. 4 shows that the total energy is higher than about 2.50 eV/MoS_2 1H phase, and higher than the 1H$\rightarrow$1T energy barrier (1.98 eV/MoS_2), so that the impact of particles with high energy such as electron beam is required to realize local 1T. Fig. 3 (b) shows the band gap and the magnetic moment on the movement path of S' simultaneously. The band gap, like the 1H $\rightarrow$ 1T phase transition, gradually decreases to have a metallic electronic structure even in the local 1T structure.

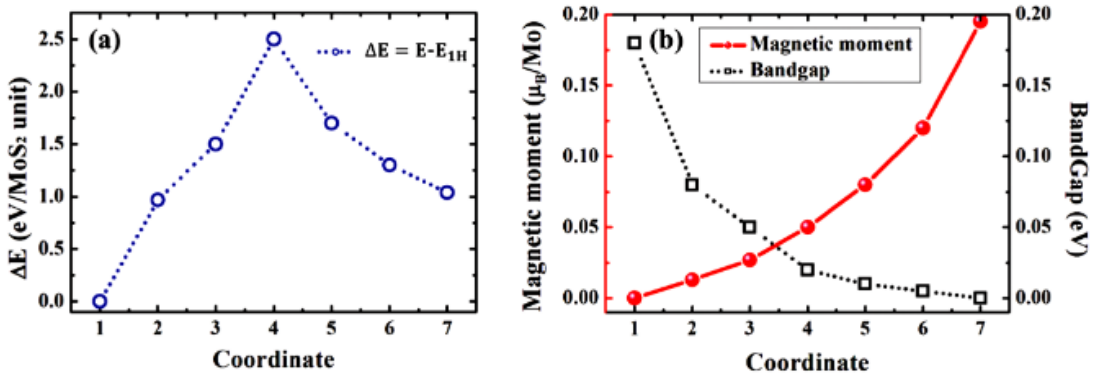

Figure 3. (a) Energy difference ($\Delta E = E - E_{1H}$) and (b) band gap and magnetic moment on the path of the 1H $\rightarrow$ (local 1T) phase transition.

On the other hand, in contrast to 1H $\rightarrow$ 1T phase transitions, the magnetic moments of the 1H $\rightarrow$ (local 1T) phase transitions increased steadily as the S′ atoms moved, and the magnetic moments of about 0.195 μ_B were observed in the fully Korean cattle 1T structure. In order to analyze the Figure 4 shows the spin polarization density of each atom of the local 1T structure. The left figure shows Mo and S′ atoms in the 1T environment within the local 1T, and the right figure shows S closest to the Mo and S′ on the 1H. The contribution of s or p orbits in the state density of Mo is negligible compared to the contributions of d orbits, so only the d orbits are represented. On the other hand, the S atom showed only the p orbit because the contribution of the s or d orbit was smaller than the p orbit. As can be seen from the density of states, most magnetic moments calculated at 0.049 μ_B/MoS_2 are mostly at 1T Mo atoms. The magnetic moment of the S atoms is negligibly small. Therefore, when considering the spin polarization density of Mo atoms in the 1T environment, in the energy region below -1.0 eV, the state densities of many spins and few spins are almost the same, and the difference is higher only in the energy region.

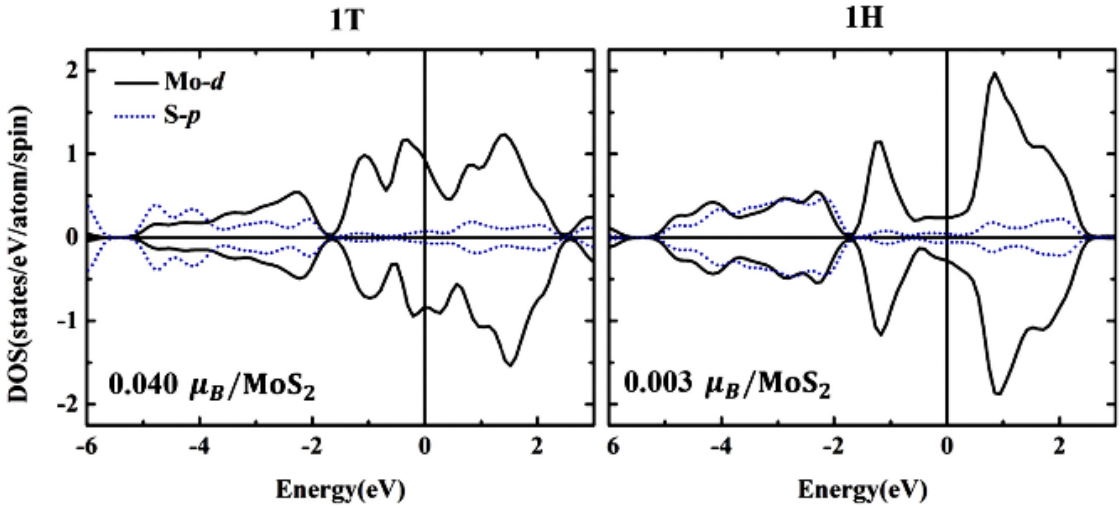

Figure 4. Spin-polarized orbital-projected density of state (DOS) of the local 1T phase MoS_2. Left panel represents the Mo-d and S′-p orbital in 1T and right panel does the Mo-d and S-p orbital in the nearest neighbor 1H to S′.

Further, we also calculated MCA energy through the path path of the 1H $\rightarrow$ (local 1T) phase. On the 1H phase, there is no MCA enegy, however, it sharply increases to 0.14 in coor.5. Then it seems to be saturated.

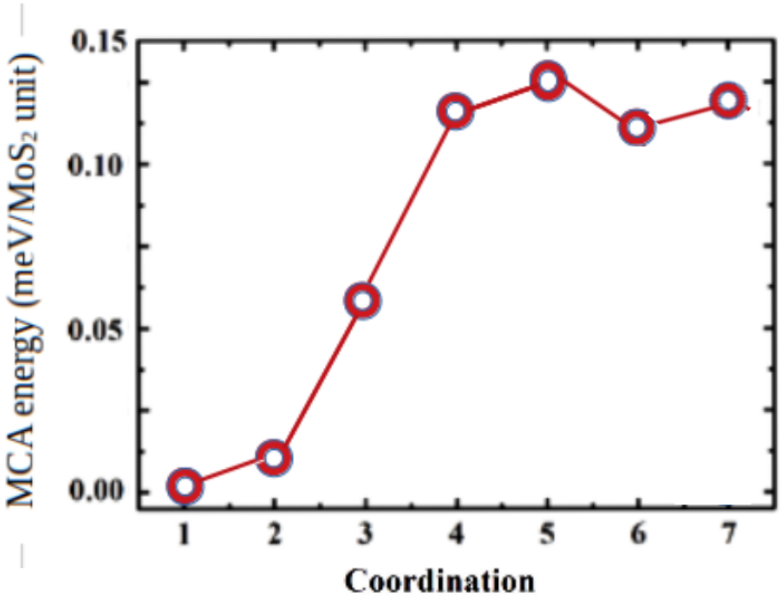

Figure 5. MCA energy on the path of the 1H → (local 1T) phase transition.

The magnetic moment shown in the local 1T phase is consistent with the previous experimental and theoretical results of observation of the magnetic moment in MoS_2 with S defects. As such, the local 1T structure means that a natural magnetic/nonmagnetic boundary can be created, and if used properly, it can be expected to implement MoS_2-based spintronic devices.

4. Conclusion

This paper investigates the electronic structure and magnetism of single-layer MoS_2 when phase transition occurs by using the first principle calculation using VASP. The total energy, band gap, and magnetism especially MCA energy are examined by setting 1H → 1T phase transition and 1H → (local 1T) phase transition. The change in the magnetic moment and MCA energy were calculated. As a result, the barriers of 1H → 1T and 1H (local 1T) were quite high, 1.98 and 2.50eV/MoS_2, respectively. In the 1H phase, the band gap, which was about 1.8 eV, narrowed slightly during the phase transition, indicating that it had a metallic electronic structure at 1H or 1T. However, unlike 1H → 1T, the magnetic moment as well as magnetocrystalline anisotropy energy were observed in the 1H → (local 1T) path, and if the complete local 1T was calculated to have a magnetic moment of about 0.049 μ_B/MoS_2, Form DOS, we can know the most of the magnetic moments appeared to contribute to Mo atoms in the 1T environment. Also, 0,14 meV/MoS_2 MCA energy was obtained in the 1H → (local 1T) path. The topical 1T phase is expected to be used as a spintronic device, demonstrating that it is possible to naturally generate magnetic/nonmagnetic boundaries within a single layer MoS_2.

5. Future works

5.1. How make H → (local 1T) phase transition uniformly in experiment?

5.2. Is it same result with Nudged Elastic Band (NEB) calculations?subsection

5.3. Why MCA energy occurs and saturates?

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