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Semiconductor-to-metal Phase Transition in Monolayer ZrS_2: GGA+U Study

Ashok Kumar[1,*], Haiying He[2], Ravindra Pandey[3], P. K. Ahluwalia[4] and K. Tankeshwar[1]

[1]*Physics Department, Panjab University Chandigarh-160014, India*
[2]*Valparaiso University Valparaiso, IN, USA*
[3]*Michigan Technological University Houghton, MI, USA*
[4]*Himachal Pradesh University Shimla-171005, India*
**E-mail: ashok.1777@yahoo.com*

Abstract. We report structural and electronic properties of ZrS_2 monolayer within density functional theory (DFT) by inclusion of Hubbard on-site Coulomb and exchange interactions. The importance of on-site interactions for both ZrS_2 bulk and monolayer has been highlighted that significantly improves the electronic band-gap. It is demonstrated that mechanical strain induces structural phase transition that results in semiconductor-to-metal transition in monolayer ZrS_2. This phenomenon has important implications in technological applications such as flexible, low power and transparent electronic devices.

Keywords: Monolayer, TMDs, Electronic Structure, Strain, DFT, GGA+U.
PACS: 71.15.-m, 71.20.-b, 73.22.-f, 64.60.-i

INTRODUCTION

Transition-metal dichalcogenides (TMDs) monolayers such as MoS_2[1-2] have aroused enormous amount of interest not only because of their novel electronic and catalytic properties but also due to the wide range of tunability of these properties via mechanical strain and external electric field engineering[3-6]. Two-dimensional (2D) TMDs have been found to exist in a wide variety of materials ranging from metal to wide-gap semiconductors with more than one structural phases. It has been shown recently that Mo and W dichalcogenides can exhibit two thermodynamically stable hexagonal (H) and tetragonal (T) structural phases which provides opportunities for flexible, low power and transparent electronic devices[7].

In this paper, we present within state-of-art density functional theory (DFT) with inclusion of Hubbard U on-site Coulomb interactions that ZrS_2 monolayer shows structural phase transition by applying mechanical biaxial strain, that results in semiconductor-to-metal transition.

COMPUTATIONAL DETAILS

DFT calculations are performed using Projector-Augmented Wave (PAW) pseudopotential implementation of Vienna Ab-initio Simulation Package (VASP)[8]. The electrons exchange and correlation effects are described by generalized gradient approximation (GGA) functional of Perdew-Burke-Ernzerhof (PBE). Kohn-Sham wave functions are expanded in a plane-wave basis set with a kinetic energy cutoff of 400 eV on a 20 × 20 ×1 Monkhorst-Pack grid using Gaussian smearing of 100 meV. A 25 Å vacuum region perpendicular to monolayer is used for calculations.

The on-site two-electron integrals are expressed in terms of two parameters U and J, which would appear in Hartree–Fock like treatment,. The Hubbard parameter U gives the strength of on-site Coulomb interactions while the parameter J adjust the strength of exchange interaction. These two parameters in the somewhat simplified, yet rotationally invariant method of Dudarev et al.[9], are combined into a single parameter U_{eff}=U-J, which has been taken as 5 eV in our calculations.

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RESULTS AND DISCUSSIONS

The most stable crystal structure of bulk ZrS_2 exists in tetragonal (T) phase in contrast to the hexagonal (H) phase in MoS_2 and its dichalcogenides family. The atomic configurations of 2D ZrS_2 triatomic monolayers in two phases are shown in Figure 1. The position of S atoms in upper atomic layer is directly above the position of S atoms in lower atomic layer in H-phase [Figure (1d)] while their positions are displaced in T-phase [Figure (1c)].

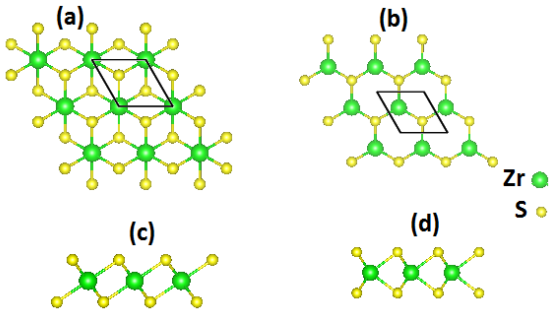

FIGURE 1. ZrS_2 monolayer with T-phase [top view (a) and side view (c)] and H-phase [top view(b) and side view (d)]. Surface unit cell is also shown.

It is well-known that conventional DFT approach has shortcomings when applied to the systems containing partially d or f valance shells to describe electronic properties. The origin of this failure is associated with the inadequate description of the strong coulomb repulsion between the d or f electrons localized on metal ions. The lattice constant of bulk and monolayer ZrS_2 with both conventional DFT i.e. GGA and beyond DFT i.e. GGA+U level of theory remains nearly same as shown in Table 1. The calculated electronic band-gap of bulk ZrS_2 is ~ 55% off than experimental value at GGA+PBE level whereas significant improvement in the band-gap value can be seen by including on-site interactions[Table 1]. Also ~ 45% band-gap opening with GGA+U has been noticed in case of monolayer.

TABLE 1. Lattice constant and electronic band-gap of ZrS_2.

Parameter	Bulk	Monolayer(T)	Monolayer (H)
Lattice constant (Å)	3.69[a] 3.73[b] 3.66[c]	3.70[a] 3.75[b]	3.58[a] 3.65[b]
Band-gap (eV)	0.77[a] 1.30[b] 1.68[c]	1.10[a] 1.60[b]	0.80[a] 1.15[b]

[a] GGA+PBE; [b] GGA+PBE+U; [c] Exp.[10]

The mechanical strain has proved to an useful tool to alter the electronic properties of materials in the past [4-5]. The applied strain (e) is represented by $\Delta a/a_0$, where a_0 is unstrained lattice constant and Δa is change in the lattice constant after deforming the lattice. The strained cell is modeled by varying the lattice value 'a' with homogeneous biaxial strain (e) as 'a'→ 'ae'.

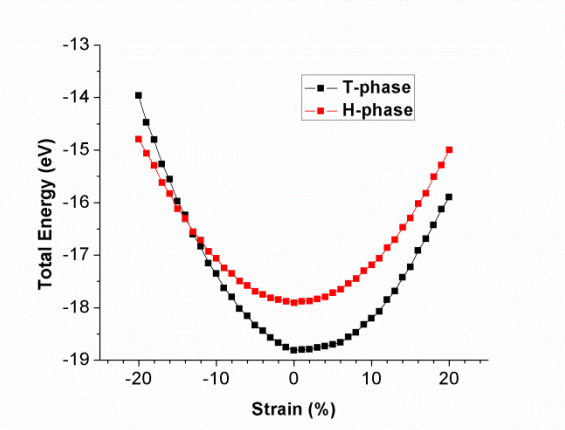

FIGURE 2.Total energy versus biaxial strain curve for the tetragonal (T) and hexagonal (H) phase of monolayer ZrS_2.

It has been demonstrated in Figure 2 that crossover occurs for two curves i.e. T-phase and H-phase, at -13% strain which indicates the structural phase transition in monolayer ZrS_2. Contrary to MoS_2 and its family[7], the structural phase transition in ZrS_2 monolayer happen at compression strain. To see this structural phase transition effects on the electronic

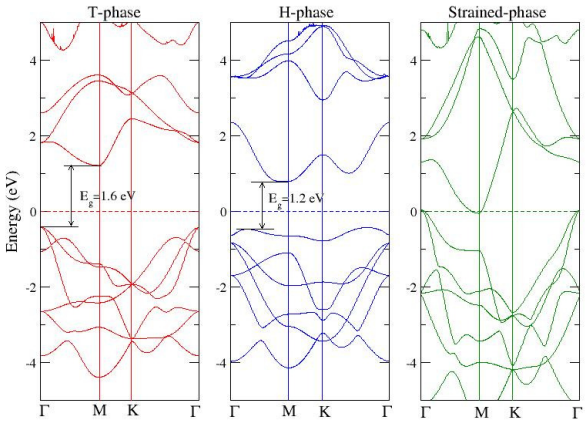

FIGURE 3. Electronic band structures of monolayer ZrS_2 in tetragonal (T) phase, hexagonal (H) phase and under 13% biaxial compression strain at GGA+PBE+U level of theory.

properties, we now look at the electronic band structure.

The electronic band structures of monolayer in T-phase, H-phase and the strained phase, where phase transition occur, are shown in Figure 3. In both T and H-phase, ZrS_2 monolayer is an indirect band-gap semiconductor with band-gap of 1.6 eV and 1.2 eV respectively.

By applying strain, semiconductor-to-metal transition has been found to happen at the critical value of strain where structural phase transition has been observed. This phenomenon may have important technological applications and must be experimentally verified.

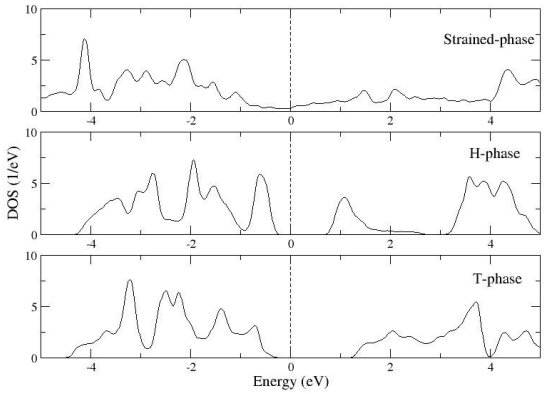

FIGURE 4. Electronic density of states (DOS) of monolayer ZrS_2 in tetragonal (T) phase, hexagonal (H) phase and 13% biaxial compression strain.

Furthermore, it is evident from density of states (DOS) shown in Figure 4 that T-phase has wider gap at Fermi level as compared to H-phase whereas finite DOS at Fermi level in strained phase indicates metallic behavior in ZrS_2 monolayer.

CONCLUSIONS

In conclusions, DFT+GGA+U calculations have been performed to investigate structural phase transition and consequent electronic properties in monolayer ZrS_2. Inclusion of on-site Coulomb interaction significantly improve the band-gap of bulk ZrS_2. Also approximately 45 % band-gap opening has been observed for monolayers. Structural phase transition occurs at 13 % compression strain that results in semiconductor-to-metal transition in monolayer ZrS_2 which may have technological importance.

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