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Electronic and magnetic properties of structural defects in pristine $ZrSe_2$ monolayer

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ABSTRACT

In the present study, we research the electronic and magnetic properties of structural defects in pristine $ZrSe_2$ by using the first-principles methods based on density functional theory. Twelve cases of vacancy defects are considered by removing Zr, Se or Zr+Se atoms in pristine monolayer $ZrSe_2$. In selecting vacancy defects, we consider the order of ascending defect concentration of Zr and Se, and also calculate the different relative positions of Se atoms with the same defect concentration of Se, compare the electronic and magnetic properties with them. The results show that vacancy defects in pristine $ZrSe_2$ monolayer, which all induce to the increase of the total magnetic moment except V_{1Se}. In addition, we find the total magnetic moment increases as the number of defective atoms increases in case of Se atoms vacancy defects, and the largest total magnetic moment appears on the case of V_{6Se}. Moreover, we also found that almost all the vacancy defects in monolayer $ZrSe_2$ show metallic property and ferromagnetism and total energies can be increased with the increasing of the number of vacant atoms in $ZrSe_2$ monolayer. In particular, when the relative position of the defective atom changes, the total magnetic moment changes dramatically. In three cases of Zr atoms vacancy defects the lowest total energy is V_{1Zr}, the most stable case is V_{1Se} in the case of twelve vacancy defects we considered. Its vacancy-defect formation energy is 2.287 eV. These results have a few guiding significance for relevant experiments based on $ZrSe_2$.

1. Introduction

In recent years, the layered transition-metal dichalcogenides (TMCDs) has attracted great interest because of its potential applications in areas such as electronics, optoelectronic, catalytic properties and photovoltaic devices [1–6]. Transition-metal dichalcogenides (TMCDs) were believed as important candidates for use as an absorber layer in low cost thin film solar cells and to study the electronic structure of low dimensional systems [7,8]. In particular, TMCDs have already been applied in many fields, such as lithium batteries [9,10], photoemitting devices [11], photovoltaics [12], catalysis [13,14], and lubricants [15]. And the magnetic properties of transition-metal dichalcogenides (TMCDs) for the nanoscale spintronic applications have been attracted extensively attention. A number of experimental and theoretical research have confirmed that TMCDs display lots of excellent physical properties, such as semiconducting, metallic, superconducting, and magnetic behavior [16,17]. Because of the restrictions on the two-dimensional direction movement of this system, it will show some unique properties of physicomechanical properties, thermal properties, electrical properties and optical properties, which will making it become hot topics in the study of physics, chemistry, biology and other fields, and in energy conversion in the next few years or ten years, biocatalysis, flexible electronic devices, sensors and other fields with the application of infinite possibility. Recent studies have shown that we can engineer the band gap of TMCDs by building TMCDs hetero-structures [18–21] or thinning them down to monolayer [22–24].

Zirconium diselenide ($ZrSe_2$) is one of many members of the layer-structured transition-metal dichalcogenide family, which have in a simple 1T-CdI_2 like structure with space group P $\bar{3}$m1 [25]. Bulk $ZrSe_2$, the Zr atoms are located at the center, between two selenium atomic layers, hence the structure consists of X–M–X trilayer atomic units, strong covalent bonds within the layer and weak van der Waal's bonded to interlayer [26]. These semiconductors materials are considered to be potential materials for solar energy applications [27,28], by reason of its band gaps within the infra red and the visible range of the spectrum. Some authors have already studied the electrical and magnetic properties of bulk systems by theoretically and experimentally [27–30]. At the same time, there is a lack of information on the electronic

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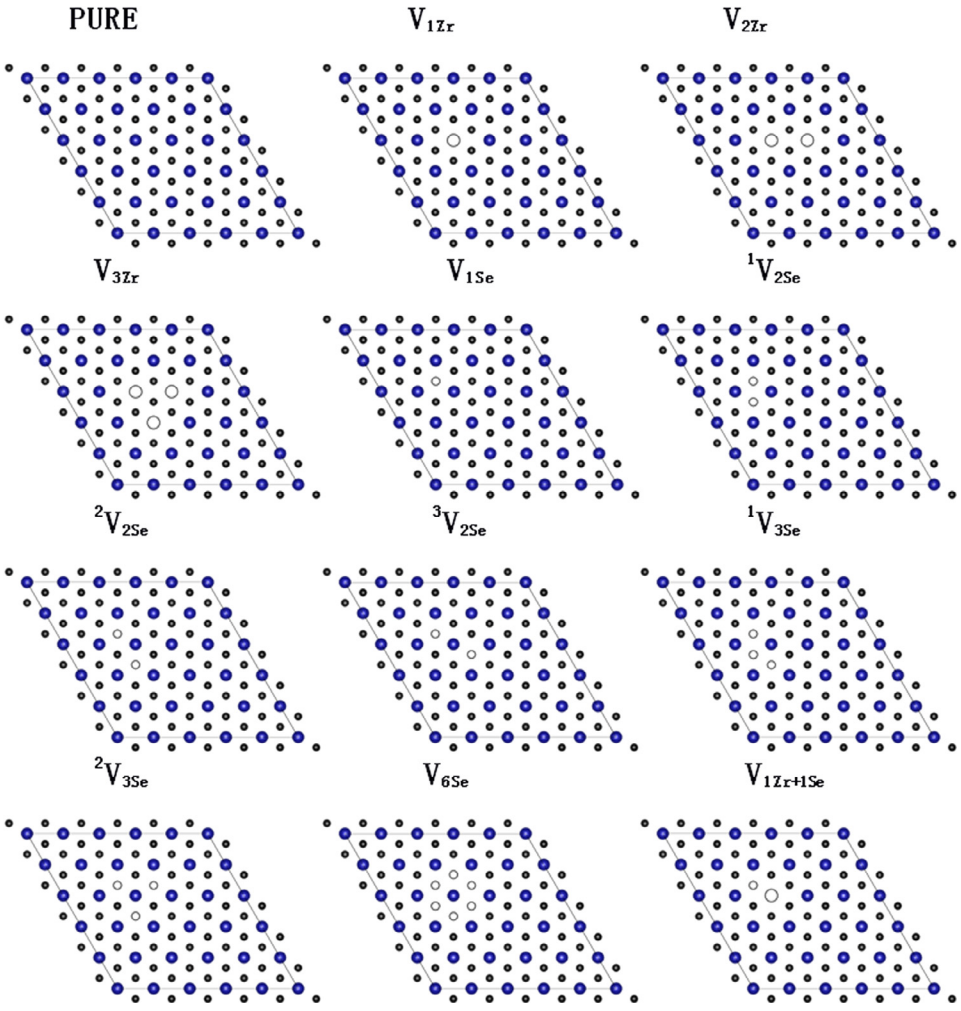

Fig. 1. Top views of twelve possible vacancy defects (PURE, V_{1Zr}, V_{2Zr}, V_{3Zr}, V_{1Se}, $1V_{2Se}$, $2V_{2Se}$, $3V_{2Se}$, $1V_{3Se}$, $2V_{3Se}$, V_{6Se}, $V_{1Zr+1Se}$) types by removing Zr or Se atoms at monolayer $ZrSe_2$ models. Blue and black balls stand for Zr and Se atoms, respectively.

properties and magnetic properties of the structural defects in pristine $ZrSe_2$ monolayer systems.

Structural defects can profoundly affect the structural, thermal, and electronic properties of such materials. We know structural defects and impurities are very common, which is crucial to electronic and magnetic properties of materials. In particular, various studies have revealed that the vacancy defects can modify the electronic properties of nanomaterials [31–33]. Cai et al.'s research shows that the structural defects have a great influence on the mechanical, thermal, electrical and optical properties of materials [34,35]. And structural defects can provide unexpected opportunities to tune the local properties creating new functionalities [35,36].

So in the paper, in order to understand the effect of structural defects on the electronic and magnetic properties of $ZrSe_2$, use the first-principles methods to investigate electronic and magnetic properties of pristine and vacancy defects in $ZrSe_2$ monolayer by analyzing the band structures, total and partial densities of stats (TDOS & PDOS).

2. Theoretical models and calculation details

In their layered $ZrSe_2$, the Zr atoms are located at the center, hence the structure consists of Se–Zr–Se trilayer atomic units, which is strong bonded to the form of a covalent bond within the layer and bonded to each other by weak van der Waal's interlayer forces. This structure determines one can cleave the material down to a single layer thickness by micromechanical cleavage technique [37]. Bulk $ZrSe_2$ is an direct band gap semiconductor, with a gap of 1.20 eV [38], while the single layer $ZrSe_2$ is a indirect band gap and the band gap becomes 0.439 eV [25]. In this work we adopted 5×5 supercell models for $ZrSe_2$ monolayer, removed one or two nearest zirconium atoms (V_{1Zr}, V_{2Zr}), two, three, six selenium atoms (V_{2Se}, V_{3Se}, V_{6Se}), and 1Zr + 1Se atoms, respectively. Due to the spatial symmetry of $ZrSe_2$, there are three cases of the two Se atomic vacancy defects, nearest, next-nearest and outermost site. When three Se atoms moved, we discussed two conditions, three nearest Se atoms vacancy defects and three nearest Se atoms vacancy defects surrounding center Zr atom. All of these systems are illustrated in Fig. 1.

Based on density functional theory (DFT), our calculations were performed with first-principles Vienna abinitio simulation package (VASP) [39] in which projector augmented wave (PAW) method [40] is implemented. Electron exchange and correlation effects were described within the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) parametrization [41]. In the work, supercell of size $5 \times 5 \times 1$ of the $ZrSe_2$ primitive cell was used with a separation of 15 Å between two layers. We use an energy cutoff of 400 eV for the plane-wave expansion of the