Magnetic doping in two-dimensional transition-metal dichalcogenide zirconium diselenide

Xu Zhao [a], [*], Tianxing Wang [a], Congxin Xia [a], Xianqi Dai [a], [c], Shuyi Wei [a], Lin Yang [b]

[a] College of Physics and Materials Science, Henan Normal University, Xinxiang, Henan 453007, China
[b] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China
[c] Department of Physics, Zhengzhou Normal University, Zhengzhou, Henan 450044, China

ABSTRACT

Zirconium diselenide (ZrSe$_2$) is one of many members of the layer-structured transition-metal dichalcogenide family. We report a systematic study of the magnetic properties of 1T-ZrSe$_2$ doped with 3d transition metals (TM) using the first-principles calculation. The calculations show that the pristine 1T-ZrSe$_2$ is semiconductors with indirect gaps of 0.439eV. The magnetism can be obtained for V, Cr, Mn, and Fe doping. The reduced total magnetic moment is 1.027μ_B, 1.841μ_B, 3.062μ_B, 0.249μ_B, respectively, and mainly comes from the transition metal 3d orbitals. The strong $p-d$ hybridization was found between the 3d orbital of TM and 4p orbital of Se. We further performed DFT + U calculations with U on the TM impurities 6eV to describe the strong electron-electron correlation, we found that the magnetic moment of dopants were been increased to 2.791μ_B, 3.152μ_B, 4.348μ_B, 4.600μ_B, respectively, which indicates a transition from the low to high spin state. The electronic structure analysis reveals that the V−, Cr−, Mn−, and Fe−doped systems turn into magnetic metal. These results can provide useful guidance to engineer the magnetic properties of 1T-ZrSe$_2$ in future experiments.

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1. Introduction

Nowadays, the researches of Two-dimensional (2D) materials have become a hot topic. Among them, transition-metal dichalcogenides (TMDC) has a wide variety of interesting physical properties such as semiconducting, metallic, superconducting, and magnetic behavior and has been extensively studied [1—26]. They are a class of important layered materials, in which transition metal and chalcogen atoms form X-M-X-type sandwich layers by strong chemical bonding and between layers much weaker van der Waals type interactions dominate [14,15]. Hence, and they show easy cleavage planes parallel to the layers to form low dimensional structures [16—18] and ease of insertion of atoms or molecules in the interstitial sites between adjacent layers [14]. Meanwhile, they show highly anisotropic mechanical, optical, and electrical properties [19,20]. The highly anisotropic structure of these materials, in combination with different d orbital occupations in different TM elements, gives rise to a lot of intriguing physical and chemical properties [21], ZrS$_2$ and ZrSe$_2$ are semiconductors with indirect

gaps Meanwhile, ZrX$_2$ et al. layered semiconductors have proven to be important candidates for third-generation solar cells with band gaps falling in the range of visible or infrared light regime [22]. Electronic properties of ZrX$_2$ et al. have been investigated by various experimental techniques, including optical absorption, direct and inverse photo-emission spectroscopy [22—26]. The researchers have found that out of the 14 two-dimensional semiconductors with composition of MX$_2$, where M (= Mo, W, Sn, Hf, Zr and Pt) is the transition metal, and X is S, Se and Te, three compounds, MoTe$_2$, HfSe$_2$ and ZrSe$_2$ are promising regarding to their mobility and band gap. The phonon limited mobility can be above 2500 cm^2 V^{-1}·s^{-1} at room temperature [27]. Developing effective method to manipulate electronic structures, magnetic states of two-dimensional (2D) materials is vital to realize its application in nanoscale devices. Introducing transition metal (TM) in 2D system is an effective route to modulate its magnetic and electronic properties. The enormous amount experimental and theoretical studies have confirmed that the substitution of TM atoms can induce magnetism in nonmagnetic nanomaterials [28—32]. In spite of these intensive experimental efforts, the systematical study of the electronic and novel magnetic characteristics in 1T-ZrSe$_2$ so far is still limited. Therefore, it is expected that the impurities in 1T-

* Corresponding author.
  E-mail address: zhaoxu@htu.cn (X. Zhao).

$ZrSe_2$ will induce more important physical properties.

In this work, we present a systematic investigation of the electronic and magnetic properties of 1T-$ZrSe_2$ doped with 3d transition metal (TM) using the density functional theory. The paper is organized as follows. In Sec. 2 we give the theoretical methods used in the work. In Sec. 3 we investigate systematically the electronic and magnetic properties of the 1T-$ZrSe_2$ using the first-principle calculation. Section 4 summarizes the work.

2. Theoretical models and methods

1T-$ZrSe_2$ consists of a layer of Zr atoms sandwiched between two layers of Se atoms. The Zr atom is octahedrally coordinated with the chalcogen atoms. $ZrSe_2$ adopts the CdI_2 structure (1T structure) with the space group $P\bar{3}m1$ (see Fig. 1). The lattice parameters a and c are optimized in the self-consistent calculation for trigonal crystal structure (a = 3.773 Å, c = 6.133 Å [33]). In terms of Wykoff sites, (M = Zr or Hf) occupies the 1c site (0, 0, 0), and X occupies the 2s sites (1/3, 2/3, ±u). The only internal structural parameter u is often close to 1/4 in equilibrium [15].

Our calculations were performed with first-principles Vienna ab initio simulation package (VASP) [34] in which projector augmented wave (PAW) method [35] is implemented. During our calculation, the generalized gradient approximation (GGA), electron exchange and correlation, Perdew–Burke–Ernzerhof (PBE) parametrization [36] is used. In all calculations, all structural parameters including the lattice constants (a and c) and the internal coordinate (u) were fully relaxed. An energy cutoff of 400 eV for the plane-wave expansion of the wavefunctions was used. A 5 × 5 1T-$ZrSe_2$ supercell with one substituted TM atom was used to model the doped $ZrSe_2$ structure, which is large enough to avoid interactions of TM atoms between the supercell. Ten different 3d TM (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) atoms were considered to substitute the Zr atom. The Brillouin-zone integrations are performed by using the special k-point sampling of the Monhkorst–Pack scheme. The k-points 9 × 9 × 1 are used for the two-dimensional 1T-$ZrSe_2$ supercell. In order to avoid any artificial interaction between neighboring images, the vacuum layer along z-direction is at least 15 Å for the $ZrSe_2$ supercell. All the structures are fully relaxed to minimize the total energy of the systems until a precision of 10^{-5} is reached. Both the atomic positions and cell parameters are optimized until the residual forces fall below 0.01 eV/Å.

To account for the electron correlations of d electrons in the transition metal dopants, we further performed DFT + U scheme [37] with U = 6eV on the TM impurities and the onsite exchange interaction is J = 0.87eV, similar to a previous study of transition metal-doped Se-based layered material [38].

3. Results and discussion

Firstly, we investigate the structural and electronic properties of doped 1T-$ZrSe_2$ supercell. The numerical results show that the optimized bulk lattice parameters a = 3.796 Å and c = 6.465 Å are in good agreement with experimental [33]. The calculated Se-TM binding length, d_{Se-TM}, and magnetic moment, M_{tot} and M_{TM}, and total energy of doped system, E_{tot} and the formation energy in different experimental conditions, E_{form} are listed in Table 1. It can be seen that the d_{Se-TM}, except for d_{Se-Sc}, d_{Se-Mn}, d_{Se-Cu}, and d_{Se-Zn}, is less than 2.707 Å, The covalent-bond interaction between TM and Se atoms is enhanced. As the decrease of atomic size, the d_{Se-TM} decreases from Sc to Ni, except for Mn, and then increases from Ni to Zn. The shortest d_{Se-TM} of 2.485 Å was found for a Ni impurity. To probe the stability of the TM-doped 1T-$ZrSe_2$, the formation energy E_{form} can be calculated according to the following formula [39–42].

$$E_{form} = E_{(doped)} - E_{(pure)} + n(\mu_{Zr} - \mu_{TM})$$

Where $E_{(doped)}$ and $E_{(pure)}$ are the total energies of the 1T-$ZrSe_2$ with and without the TM dopants. μ_{Zr} and μ_{TM} are the chemical potential for Zr host and TM dopant atoms, respectively, which depends on the material growth conditions and satisfies the boundary conditions. n is the number of Zr atoms replaced by TM dopants. We use the energy per atom of TM metal as μ_{TM}. μ_{Zr} is defined within a range of values corresponding to Zr-rich or Se-rich growth conditions. For a Zr-rich condition, μ_{Zr} is taken as the energy of isolated Zr atom, while for an Se-rich condition, μ_{Zr} is determined from the difference in energy between a diatomic Se_2 molecule and one formula unit of stoichiometric 2D $ZrSe_2$ [43].

We can see from Table 1 that for the TM-doped 1T-$ZrSe_2$, the formation energy is lower under Se-rich conditions, which indicates that it is energy favorable and relatively easier to incorporate TM atom into 1T-$ZrSe_2$ under Se-rich experimental conditions. The smallest E_{form} of −3.967eV was found for a Sc substitution, the largest E_{form} of 1.463eV was found for a Cu substitution, which
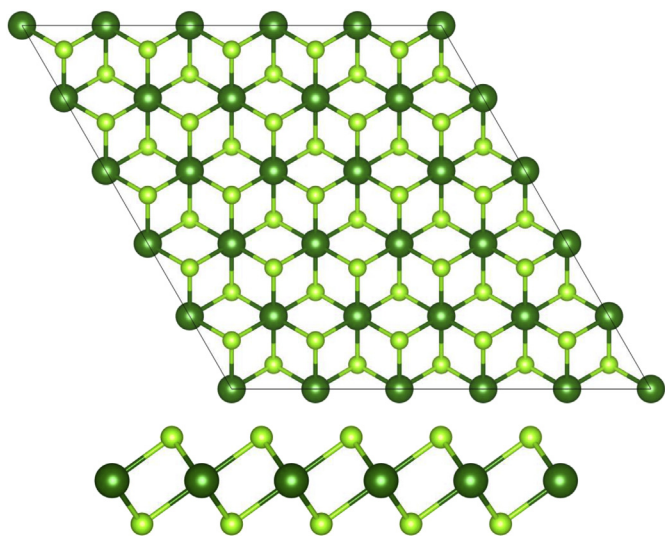

Fig. 1. Schematic structure of 1T-$ZrSe_2$ and the top and side vies of layered forms are shown. The green and light green balls represent Zr and Se atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
The calculated Se-TM binding length, d_{Se-TM}, and magnetic moment, M_{tot}, and total energy of doped system, E_{tot} and the formation energy in different experimental conditions, E_{form} in TM-doped 1T- $ZrSe_2$.

System	d_{Se-TM}(Å)	M_{tot} (M_{TM}) (μ_B)	E_{tot}(eV)	E_{form}(eV)	
				Zr-rich	Se-rich
Sc	2.723	0.00	−484.731	0.057	−3.967
Ti	2.600	0.00	−485.272	0.941	−3.083
V	2.569	1.027(1.224)	−484.662	2.726	−1.298
Cr	2.599	1.841(1.599)	−484.840	3.081	−0.943
Mn	2.707	3.062(3.432)	−484.325	3.04	−0.984
Fe	2.518	0.249(0.048)	−482.376	4.396	0.372
Co	2.502	0.00	−481.073	4.473	0.449
Ni	2.485	0.00	−479.559	4.457	0.433
Cu	2.707	0.00	−476.727	5.487	1.463
Zn	2.727	0.00	−475.229	4.526	0.502
pure	2.707	0.00	−486.926		