Applied Surface Science 458 (2018) 191–197

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Strain and interlayer coupling tailored magnetic properties and valley splitting in layered ferrovalley 2H-VSe_2

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ARTICLE INFO

Keywords:
Ferrovalley
Strain
Layer thickness
Magnetic moment
Magnetocrystalline anisotropy
Valley splitting

ABSTRACT

Geometry structure, band structure, magnetic moment and magnetocrystalline anisotropy energy of layered 2H-VSe_2 are investigated by first-principles calculations. It is found that the VSe_2 is intrinsic ferromagnetic with an in-plane magnetocrystalline anisotropy no matter how the change of the strain and layer thickness is. Additionally, the valley splitting in monolayer VSe_2 can be modulated by strain due to the modulated intrinsic exchange interaction of V 3*d* electrons. Interestingly, the valley splitting decreases and the V magnetic moment monotonously increases as a strain increases, showing that the valley splitting is related to the magnetic moment. Furthermore, the slight effect of interlayer coupling on V magnetic moment appears. The tunable magnetism and valley splitting may provide novel applications in multifunctional nanoelectronics.

1. Introduction

With the discovery of graphene [1,2], the two-dimensional (2D) materials have attracted more and more attention, which provides the practical platforms to exploit the novel properties for nanoelectronics and valleytronics [3,4]. As the valleytronic materials, the monolayer transition metal dichalcogenides (TMDs) with 2H phase are the most promising materials with unique potential candidates for utilizing and manipulating the valley index effectively [5–9]. Owing to breaking the space inversion symmetry with the spin-orbit coupling (SOC) effect from the *d* orbitals of heavy transition metals [10], the strong coupled spin and valley degrees of freedom are established. In the previous results, the valley splitting in monolayer TMDs such as MoS_2, WSe_2 can be modulated by the optical pumping [11,12], external electric field [4] and external magnetic field [13–16], showing that these materials recover to the initial paravalley state once the electric field, magnetic field or optical pumping are removed. Thus, the TMDs monolayers can be used in multifunctional electronic devices modulated by external fields. Recently, the concepts of ferrovalley are proposed as a new member of ferro family, which is defined as a ferromagnetic monolayer with spontaneous valley polarization [17]. A typical ferrovalley material is VSe_2, which has the spontaneous valley polarization and intrinsic magnetic moment from the V-*3d* orbitals. Particularly, intrinsic VSe_2 monolayers are semiconductors with indirect band gaps and ferromagnetic ground states [18,19]. The complicated and versatile electric structure of TMD monolayers inspires us to believe that VSe_2 monolayers deserve specific attention as possible 2D materials with both precise and controllable magnetism. The estimated Curie temperature of 2H-VSe_2 can reach 590 K [20], showing that the 2H-VSe_2 monolayers could be used in the valleytronic devices above room temperature. It is worthy to mention that the ultrathin VSe_2 nanosheet stacked with less than five layers [21] and the 0.4-nm thick VSe_2 monolayer nanosheets [22] have been successfully synthesized, which provide the potential candidates to explore the ferromagnetic characteristics and valley index.

Previous theoretical results on the magnetic and electric characteristics of 2H-VX_2 (X = Se, S) monolayers as the function of external strain have been reported in the past years [18,19]. Whereas, the strained effects on the magnetic characteristics and valley index in VSe_2 monolayers are not systematically understood yet. Additionally, the magnetic characteristics of VSe_2 with different layers are also not reported, so the layered effects on the magnetic properties in VSe_2 are not clear yet. The other important thing in ferromagnets, the magnetocrystalline anisotropy energy (MAE) is an vital characteristic for its practical applications in data storages [23–26]. Thus, the effects of strain and layer thickness on the magnetic moment, MAE and valley splitting of VSe_2 monolayers are investigated by using first-principles calculations in this work. It is found that the VSe_2 is an intrinsic ferromagnet no matter how the strain and layer thickness change. MAE is positive in all the models, suggesting an in-plane magnetocrystalline anisotropy. Additionally, the valley splitting in monolayer VSe_2 can be modulated by strain, where the maximum of 81 meV appears at a strain

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https://doi.org/10.1016/j.apsusc.2018.07.070
Received 4 April 2018; Received in revised form 6 July 2018; Accepted 10 July 2018
Available online 11 July 2018

of −4%. However, the valley splitting disappears as the layer thickness increases from monolayer to five layers. Our results can provide a more significant basis for valleytronic devices.

2. Computational details

Density functional theory (DFT) calculations are performed by Vienna *ab* Initio Simulation Package [27,28] with the generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof (PBE) [29,30]. As is known to all, the GGA/PBE functional always underestimate the band gaps. Nevertheless, we mainly focus on the electronic structures and the corresponding variation trends around Fermi level, which are no significant effect on our results and conclusions. Kohn-Sham single-particle wave-functions are expanded in the plane wave basis set with a kinetic energy cutoff of 500 eV. The Brillouin zone is sampled using a set of 13 × 13 × 1 Gamma-Centered *k*-mesh for the structure optimizations and electronic structure calculations. A 15-Å thick vacuum layer is adopted for monolayers and 20-Å is adopted for multilayers to prevent artificial couplings between adjacent periodic images. The energy and force convergence criteria are 10^{-5} eV and 0.01 eV/Å, respectively. DFT-D2 method is used to describe van der Waals interactions for all layered models [31]. Spin-orbit coupling (SOC) interaction is considered in all the calculations. For the Hubbard-*U* term, it has a negligible effect on lattice constant, magnetic moment and MAE in 2H-VSe_2, which is reported by Marco et al. [32]. Thus, we leave out of Hubbard-*U* term in this work. In the calculation of DOS, the parameter of SIMGA is 0.05 in order to ensure the DOS is precise and slinky.

The strain ranging from −6% to 6% is applied on the unit cell of 1×1×1 VSe_2 with an interval of 2%, which is defined as $\varepsilon = [(a - a_0)/a_0] \times 100\%$, where a and a_0 present the lattice constants of strained and original monolayers, respectively. The strained effects on VSe_2 monolayers are the change of lattice constants, bond lengths and angles, so the calculation is launched by setting larger/smaller lattice constants. The optimized lattice constants, bond lengths and angles of VSe_2 monolayers with different strains are shown in Table 1. The MAE is defined as MAE = $E(\perp)$-$E(||)$, where $E(\perp)$ and $E(||)$ represent the total energies of the perpendicular and parallel magnetization directions, respectively. Here, we chose that the perpendicular direction is [0 0 1] and the parallel direction is [1 0 0]. Correspondingly, the negative (positive) MAE indicates that the easy magnetization axis is perpendicular (parallel) to VSe_2, respectively.

3. Results and discussions

Fig. 1(a)–(c) show the lattice geometry structures of 2H-VSe_2. It can be seen that the bulk structure of 2H-VSe_2 is trigonal prismatic geometry (D_{3h} group), which has a hexagonal lattice. In order to confirm the arrangement of magnetic moment in VSe_2 monolayer, the difference between the ferromagnetic and anti-ferromagnetic states is calculated as a function of strain. A 2 × 2 × 1 supercell structure is chosen since the number and position of V atoms are appropriate to show the magnetic arrangement. Fig. 1(d) and (e) show the arrangement of magnetic moment in VSe_2 monolayers with the ferromagnetic and anti-ferromagnetic ground states, respectively. By GGA/PBE calculations, the energy difference between the anti-ferromagnetic and ferromagnetic ground states is always positive, suggesting that the ferromagnetic ground state is more stable in 2H-VSe_2 monolayer. Concretely, the energy difference increases monotonously with the increase of strain from −6% to 6%, as shown in Fig. 1(f). Based on the mean field theory and Heisenberg model with long-range interaction, the Curie temperature (T_C) can be estimated from [33].

$$3k_B T_C = 2\Delta E_{\mathrm{AFM-FM}} \quad (1)$$

According to the calculated energy difference in strained 2H-VSe_2 monolayers, it is clear that the Curie temperature monotonously increases with the increase of the strain from −6% to 6%, the maximum of which reaches 812 K at a strain of 6%. The high Curie temperature is important to the practical applications in the room-temperature spintronic and valleytronic devices. The increased T_c means that the energy difference between AFM and FM states is increasing. In other words, the increased AFM energy or decreased FM energy can make a valid effect on the increased T_c. In detail, the individual magnetic moments of V and Se atoms in strained 2H-VSe_2 monolayers are shown in Fig. (g). As the strain increases from −6% to 6%, the calculated magnetic moment of V atom is 0.77, 0.91, 1.03, 1.08, 1.11, 1.14 and 1.18 μ_B, Meanwhile, the calculated magnetic moment of Se atom is −0.04, −0.06, −0.07, −0.08, −0.09, −0.10 and −0.15 μ_B, respectively. It is worthy to mention that the magnetic moments of V and Se atoms aligned antiparallelly, suggesting that Se atoms play an important role in the way of magnetic couplings between V atoms.

In order to reveal the tunable mechanism of magnetic moments, the density of states (DOS) and electric density diagrams of VSe_2 monolayers at a strain from −6% to 6% with considering SOC are shown in Fig. 2. As the strain increases from −6% to 6%, it can be found that the orbital overlap between occupied d_z^2 orbitals of V atoms and p_z orbitals of Se atoms is increasing, resulting in the enhancement of spin-polarized electrons and large magnetic moments due to the extended ionic bond strength of V-Se which are recorded in Table. 1. Additionally, at compressive strains, we can notice that the direct interaction between the nearest V and V atoms is dominant because of the short distance. As the strain increases, the distance between the nearest V and V atoms and the angle of V-Se-V atoms are both increasing, which reveals that the interaction of V atoms has to be passed through Se atoms. The change of the interaction should be the reason for the change of T_c.

It is worthy to deeply investigate MAE of VSe_2 for exploring the effect of strain on magnetization direction. Therefore, MAEs are calculated and plotted with different strains in Table. 1 and Fig. 3(i), respectively. It can be seen that MAE is increasing as the strain increases from −6% to −2%, then gradually deceasing to 0.279 meV as the strain increases from −2% to 6%. The maximum of MAE appears at a strain of −2%. In this work, MAE of 0.594 meV per unit cell at zero strain is consistent with the result reported by Fuh et al. [34]. These positive MAEs indicate the in-plane magnetocrystalline anisotropy in

Table 1
Some calculative physical parameters are tabulated for monolayer 2H-VSe_2 with different strain. Lattice constant a (Å), Bond length of V-Se atom(Å) and V-V atom (Å), Bond angle of V-Se-V(°), Band gap E_g, Valley splitting V_{spl} with SOC, Magnetic moment (μ_B) of the 1 × 1 unit cell, and MAE (meV) analysis are provided.

Strain (%)	Lattice constant (Å)	Bond length and angle			E_g (meV)	V_{spl} (meV)	MAG (μ_B)		MAE (meV)
		V-Se (Å)	V-V (Å)	V-Se-V(°)			V	Se	
−6%	3.134	2.456	3.134	79.3	–	80	0.77	−0.01	0.017
−4%	3.201	2.469	3.201	80.8	–	81	0.91	−0.04	0.361
−2%	3.268	2.485	3.268	82.2	71	80	1.03	−0.06	0.746
0%	3.334	2.502	3.334	83.5	227	78	1.07	−0.07	0.594
2%	3.401	2.521	3.401	84.8	280	75	1.11	−0.08	0.476
4%	3.468	2.541	3.468	86.1	282	72	1.14	−0.09	0.375
6%	3.534	2.563	3.534	87.2	120	68	1.18	−0.10	0.279