Confinement effect enhanced Stoner ferromagnetic instability in monolayer 1T-VSe₂

Junyi He, Qing Xie and Gang Xu

Wuhan National High Magnetic Field Center and School of Physics, Huazhong University of Science and Technology, Wuhan 430074, People’s Republic of China

* Authors to whom any correspondence should be addressed.
E-mail: gangxu@hust.edu.cn

Keywords: 2D materials, Van Hove singularity, Stoner theory, saddle point

Abstract

Monolayer 1T-VSe₂ has been reported as a room-temperature ferromagnet. In this work, by using the first-principles calculations, we unveil that the ferromagnetism in monolayer 1T-VSe₂ is originated from its intrinsic huge Stoner instability enhanced by the confinement effect, which can eliminate the interlayer coupling, and lead to a drastic increase of the density of states at the Fermi level due to the presence of Van Hove singularity. Our calculations also demonstrate that the Stoner instability is very sensitive to the interlayer distance. These results provide a useful route to modulate the nonmagnetic to ferromagnetic transition in few-layers or bulk 1T-VSe₂, which also shed light on the enhancement of its Curie temperature by enlarging the interlayer distance.

1. Introduction

Ferromagnetic (FM) order in 2D materials is a highly desirable property that provides a new physical degree of freedom to manipulate spin behaviors in spintronic devices [1, 2]. Previously, magnetism in 2D was mainly realized through depositing films onto magnetic substrates, magnetic atoms adsorption, or doping [3–5]. The shortcomings of these methods are obvious: (1) one does not have an ideal 2D system from depositing and it is impractical to integrate with spintronic devices, and (2) disorder effects make the electronic properties hard to design. Due to these reasons, 2D materials with intrinsic magnetic order have been actively pursued.

The CrI₃ [6] and Cr₂Ge₂Te₆ [7] are the first two experimentally reported 2D materials exhibiting long-range FM order with the Curie temperatures $T_c$ 45 K and 30 K, respectively [6, 7]. These discoveries have stimulated numerous research interests on 2D magnetism. Very recently, several materials with higher $T_c$ have been experimentally and theoretically explored, including MnSe₂ [8], Fe₂GeTe₂ [9], and 1T-VSe₂ [10–14]. Among them, the 1T-VSe₂ is of particular interest since the bulk 1T-VSe₂ has a van der Waals nature, which can be easily exfoliated to few-layers thickness. This gives 1T-VSe₂ the advantage to be tailored and manipulated for nano spintronic devices at low cost.

However, the nature of the ground phase of 1T-VSe₂ is still under hot debate. Two groups have observed CDW ground states and concluded that magnetic order is absent in the monolayer limit due to the CDW suppression [15, 16]. Wong et al claimed that a spin frustrated phase was observed and the FM phase must be attributed to extrinsic factors [17]. Chua et al [18] and Yu et al [12] suggested that the observed FM is not intrinsic, but caused by defects. Wen et al [13], Vinai et al [14] and Feng et al [19] reported that no FM signal was observed in monolayer VSe₂. Nevertheless, Bonilla et al [10] and many others [11, 12] have presented strong experimental evidences for intrinsic 2D magnetism in monolayer 1T-VSe₂. On the contrary, the bulk 1T-VSe₂ was proven to be nonmagnetic (NM) [20], thus an NM to FM phase transition would take place when VSe₂ is exfoliated from bulk to monolayer. This is in contrast with other 2D magnetic materials, where the FM phase is more stable in the bulk system.

In this paper, we study the ground-state properties of 1T-VSe₂ by first-principles calculations. Through a comprehensive study of the density of states (DOS) and band structures of the bulk and few-layers 1T-VSe₂,
we reveal that the monolayer system has the strongest FM instability due to the presence of Von Hove singularity (VHS) originated from saddle points at the Fermi level. We also find that in the few-layers case, the couplings of \(dz^2\) orbitals between interlayer V atoms split the saddle points away from the Fermi level and weaken the FM instability. The strongest FM instability in the monolayer is confirmed by the largest energy difference between the NM and FM phases and also verified by using the phenomenological Stoner theory [21–24]. We thus conclude that the room-temperature FM order in the monolayer 1T-VSe\(_2\) is intrinsic due to its unique electronic structures. Finally, we study the FM instability with respect to the interlayer distance \(d\) (see figure 1(a)) and predict that it is possible to tune the NM to FM phase transition in few-layers 1T-VSe\(_2\) by enlarging the interlayer distance \(d\). Our study provides an explanation to the origin of FM order in monolayer 1T-VSe\(_2\) and also proposes a mechanism to tune the NM to FM phase transition in few-layers 1T-VSe\(_2\).

2. Computational details

VSe\(_2\) usually adopts the 2H and 1T structures. While the 2H-VSe\(_2\) shows semiconducting behavior, the 1T-VSe\(_2\) is a metal [25–27] and shows strong experimental evidence for FM ordering in the few-layers limit [10]. Different from the triangular prismatic crystal field in the 2H structure, 1T-VSe\(_2\) has an octahedral crystal structure and belongs to \(P\bar{3}m1\) space group, where V atoms form a triangular lattice and each V atom occupies the center of the octahedron surrounded by six Se atoms, as shown in figures 1(a)–(c). As a result, each layer of VSe\(_2\) is stoichiometric [28]. The bulk crystal is composed of an AA stacking of VSe\(_2\) sandwiches.

First-principles calculations based on density functional theory are carried out by using the Vienna \textit{ab initio} simulation package [29]. The Perdew–Burke–Ernzerhof functional [30] is employed to treat the exchange–correlation interactions. The cutoff energy for wave function expansion is set to 500 eV. We use \(19 \times 19 \times 9\) and \(21 \times 21 \times 1\) \(\Gamma\)-centered \(k\) meshes to sample the BZ in the bulk and slab calculations, respectively. Structures are optimized until the force on each atom is less than 0.001 eV Å\(^{-1}\). A vacuum layer of 15 Å is set to minimize artificial interactions between layers in the slab calculations. For the bulk calculations, the lattice constants \(a = b = 3.356\) Å, and \(c = 6.105\) Å are used [31].

3. Results and discussion

We first calculate and plot the total and projected DOS of the NM bulk 1T-VSe\(_2\) in figure 2(a), which are in good agreement with previous results [19, 32–34]. The density at the Fermi level is about 2.9 states eV\(^{-1}\), confirming its metallic nature. The projected DOS demonstrates that the states between \(-0.9\) eV and \(3.5\) eV are mainly contributed by the V 3d orbitals. In an octahedral crystal field, the five 3d orbitals split into the lower \(t_2\) and the upper \(e\) manifolds, which mainly contribute to the DOS around \(-0.9–1.4\) eV and \(1.9–3.5\) eV, respectively. Furthermore, due to the presence of a triangular field, the \(t_2\) manifold splits into the lower \(a_1\) (\(dz^2\)) and upper \(e'\) (\(d_{xy}\) and \(d_{x^2−y^2}\)) orbitals. This picture is also verified from the projected band structures in figure 2(b), in which the \(dz^2\) is the lowest 3d orbital that crosses the Fermi level and dominates the low-energy physics of the bulk 1T-VSe\(_2\).

We further plot the total and projected DOS of the NM monolayer 1T-VSe\(_2\) in figure 2(c). Compared with the bulk DOS in figure 2(a), we notice that these two DOS plots share many similarities. For instance, they both have high densities around 1 eV and they both possess energy gaps at \(\sim 1.4\) eV. This is reasonable...
Figure 2. Results of the bulk and monolayer 1T-VSe2 in the NM phase. (a) The total and projected DOS of bulk 1T-VSe2 in the NM phase. (b) NM band structures of bulk VSe2 with V-3d orbitals projections. (c) The total DOS and projected DOS of the 3d orbitals of V in the monolayer case. (d) The corresponding band structures along the high symmetry k-path. (e) Three-dimensional plot of the dz^2 band in the first Brillouin zone (BZ). (f) Zoom-in band dispersion near the saddle point S.

due to that 1T-VSe2 is a layered vdW material. The interlayer coupling does not significantly alter the electronic structures. Nevertheless, a sharp peak appears at the Fermi level E_F in the monolayer case as shown in figure 2(c). The DOS at E_F is about N(E_F) ≈ 6.4 state eV⁻¹, much higher than the bulk value. Such high DOS suggests the presence of VHS on the band structures. We thus plot the band structures along high symmetry k-path in figure 2(d) and observe that only the d_z^2 band crosses the Fermi level. On the Γ – M path there is a maximum at Γ and on the Γ – K path a minimum at S appears. These characteristics indicate the presence of a saddle point. To show more details, we plot this band on the whole BZ in figure 2(e), where there are six saddle points on the Γ – K and Γ – K’ paths. Figure 2(f) zooms in the band structures around the saddle point S. The red and blue solid lines are the band dispersions along Γ – K and its orthogonal directions, which represent hole-like and electron-like dispersions, respectively. These dispersions evidently show the topology of a saddle point [35, 36]. Therefore, we have demonstrated that the high DOS and its divergent behavior are due to the presence of saddle-points VHS on the band structures.

We suggest that the VHS in monolayer 1T-VSe2 may cause FM instability according to the phenomenological Stoner theory [21], which states that the FM phase is favored when the Stoner criteria N(ϵ_f) · I > 1 is satisfied. Here N(ϵ_f) is the DOS at the Fermi level in the NM state, and I is the Stoner parameter that measures the strength of the magnetic exchange interaction, which is related to the energy splitting between the spin-up and spin-down states in the FM phase via the following formulas [37]

\begin{align*}
E_\uparrow(k) &= E_0(k) - I \frac{n_\uparrow}{n}, \\
E_\downarrow(k) &= E_0(k) + I \frac{n_\downarrow}{n}.
\end{align*}

Here E_0(k) is the energy of the NM phase, E_σ(k) and n_σ are the energy and number of electrons with spin σ (σ = ↑, ↓) in the FM phase, respectively. The total number of electrons is n = n_↑ + n_↓. Since only the d_z^2 band is responsible for the Stoner instability in monolayer 1T-VSe2, n_↑ and n_↓ can be estimated as 1. Therefore we have n = 2. Finally, the Stoner parameter I can be estimated as E_↓(k) - E_↑(k).

Figure 3(a) presents the DOS of the spin-up and spin-down states in the FM phase of the monolayer 1T-VSe2. By comparing with the NM results in figure 2(c), we observe that the sharp VHS peak splits into two peaks, which is a typical signature of the FM exchange interaction. We assume the exchange interaction
Such splitting is larger than that in the typical vdW materials [38–40]. This is because that the VHS peak in 1T-VSe$_2$ is mainly contributed by the orbitals of the two V atoms in the bilayer unit cell. The upper and lower I bands display an NM property [10–12]. To study this transition, we show the evolution of the Stoner criterion $N(E_F) \cdot I$ with respect to the number of layers $N$. (d) The energy difference $\Delta E = E_{FM} - E_{NM}$ as a function of $N$. 

Figure 3. Results of the monolayer 1T-VSe$_2$ in the FM phase. (a) The spin polarized DOS, $\tilde{E}_i$ and $\tilde{E}_d$ denote the energy shift of the VHS peaks, which are used to evaluate the energy difference between the spin-up and spin-down states. (b) The evolution of the Stoner criterion with respect to the number of layers $N$. (c) The evolutions of DOS at the Fermi level $N(E_F)$ and the Stoner parameter $I$ with respect to $N$. (d) The energy difference $\Delta E = E_{FM} - E_{NM}$ as a function of $N$. 

is $k$-independent and use the energy difference of the VHS peaks to evaluate its average magnitude [37], which gives $I = 0.68$ eV. Together with $N(E_F) = 6.4$ state eV$^{-1}$ in the NM phase, we obtain a Stoner criterion $N(E_F) \cdot I = 4.3$. This large value indicates a strong FM instability in the monolayer 1T-VSe$_2$.

Recent experiments have shown that the monolayer 1T-VSe$_2$ exhibits FM order, while the bulk 1T-VSe$_2$ displays an NM property [10–12]. To study this transition, we show the evolution of the Stoner criterion $N(E_F) \cdot I$ with respect to the number of layers $N$ in figure 3(b), from which a drastic decrease of $N(E_F) \cdot I$ from the mono- to the bilayer is observed, indicating the decrease of FM instability in the bilayer 1T-VSe$_2$. We further plot the evolutions of $N(E_F)$ and $I$ with respect to $N$ in figure 3(c), which clearly shows that the drastic decrease is due to the decrease of $N(E_F)$ since $I$ is insensitive to $N$ (see the red curve in figure 3(c)). We notice that when $N \geq 2$, the Stoner criterion $N(E_F) \cdot I$, density $N(E_F)$, and Stoner parameter $I$ fluctuate slightly around their saturated values. These results prove that when the system transforms from the monolayer to bulk, only the monolayer exhibits a strong FM instability. Our result well explains the recent experiment by Bonilla et al, where a strong FM signal has been detected in the monolayer while the bilayer has a significantly weak FM signal comparable with the bulk [10]. This trend is also manifested by the energy difference $\Delta E = E_{FM} - E_{NM}$ between the FM and NM phases as depicted in figure 3(d), from which we observe that the maximal energy difference occurs in the monolayer case, and a drastic decrease of $\Delta E$ takes place from the monolayer to the bilayer.

To understand the drastic decrease of $N(E_F)$ from the mono to the bilayer, we plot the NM total DOS of bilayer 1T-VSe$_2$ in figure 4(a). Due to the vdW nature, the bilayer DOS is very similar with that of the monolayer, except that two peaks emerge near the Fermi level at $E_F = -0.03$ and $E_F = 0.08$ eV (see the inset in figure 4(a)). These two peaks also originate from the saddle points on the band structures as shown in figure 4(b). We notice that two bands are crossing the Fermi level. They are contributed by the $d_{z^2}$ orbitals of the two V atoms in the bilayer unit cell. The upper and lower $d_{z^2}$ bands are anti-bonding and bonding states, respectively. The energy difference of these two $d_{z^2}$ bands at the $\Gamma$ is about $0.44$ eV, which gives an estimation of the interlayer coupling strength. The VHS splitting at the $S$ point is determined by the two minimum on the $\Gamma-K$ path, which is about $0.11$ eV, consistent with the two peaks on the DOS in figure 4(a). Such splitting is larger than that in the typical vdW materials [38–40]. This is because that the VHS peak in 1T-VSe$_2$ is mainly contributed by the $d_{z^2}$ orbitals, whose lobes from interlayer V atoms are head-to-head aligned along the $z$-direction and form the relatively strong $dd\sigma$ bonds. As a result, the VHSs no longer present at the Fermi level, and the $N(E_F)$ is significantly reduced. Finally, the Stoner criterion $N(E_F) \cdot I$ decreases severely, and the FM instability is weakened. Similar results have been reported in other paper [41]. The vulnerability to extra charge doping claimed by Kim et al is also an evidence that the ferromagnetism is originated from the Stoner instability. The doping would push the Fermi level far away from the saddle points, and thus reduce the Stoner instability.
To summarize, the transition from the bulk NM phase to the monolayer FM phase in 1T-VSe$_2$ can be understood as follows. In the bulk system, the coupling of $d_{z^2}$ orbital between interlayer V atoms splits the VHSs away from the Fermi level. Especially from the bilayer to the monolayer, the enhanced confinement effect eliminates the interlayer $d_{z^2}$ coupling. Thus the VHSs are pushed to the Fermi level, which leads to a drastic enhancement of the $N(E_F)$ and the Stoner criterion $N(E_F) \cdot I$. Eventually, this enhanced $N(E_F)$ causes a strong FM instability in the monolayer. In other words, the confinement effect in the monolayer 1T-VSe$_2$ prevents the interlayer coupling between the $d_{z^2}$ orbitals of V atom and pushes the saddle-point VHS at the Fermi level, which results in a large Stoner criterion and leads to a stable FM ground state.

Our numerical results can well explain the recent observations of the ferromagnetism in monolayer and multilayer VSe$_2$ [10–12]. It can also provide an understanding why no FM ordering exist in the other experiments. Since the lobes of $d_{z^2}$ orbital are perpendicular to the substrate, the distance between VSe$_2$ and substrate, as well as the coupling between the $d_{z^2}$ electrons and the electrons in substrate, could greatly affect the FM properties of monolayer VSe$_2$ on different substrates. If the distance is very short, or the coupling is strong enough, e.g. on Co, Fe, the VHS will be pushed away from the Fermi level. Thus the FM instability is eliminated finally [13, 14, 19].

Based on this understanding, we expect that the magnetic property of a few-layers 1T-VSe$_2$ can be tuned by the interlayer distance $d$ [42, 43] (see figure 1(a)). The evolution of the VHS splitting $\Delta E_d = E_2 - E_1$ between the two peaks in the bilayer 1T-VSe$_2$ with the ratio $\varepsilon = (d - d_0)/d_0$ is shown in figure 4(c). Here $d_0 = 3.067$ Å is the interlayer distance of the bulk. The corresponding evolution of $N(E_F)$ with $\varepsilon$ is also shown in this figure. We observe that $\Delta E_d$ monotonically decreases with the increase of $d$. This means the $dd\sigma$ bond is weakened when the lobes of $d_{z^2}$ orbitals in adjacent layers are moving apart. During this process, the $N(E_F)$ monotonically goes up, reflecting an enhanced Stoner FM instability.

The enhancement of the Stoner instability is also confirmed by the energy differences $\Delta E$ between the FM and NM phases in figure 4(d). We find that $\Delta E$ also monotonically decreases with $\varepsilon$, which indicates that the FM phase becomes more and more stable when $d$ increases. This effect provides a useful route to control the NM to FM transition in few-layers 1T-VSe$_2$ through enlarging the interlayer distance $d$. It also sheds light on tuning the Curie temperature of 1T-VSe$_2$ through nanoengineering. Further experimental studies are highly desirable to verify these conjectures.

**Acknowledgments**

This work is supported by the Ministry of Science and Technology of China (No. 2018YFA0307000) and the National Natural Science Foundation of China (No. 11874022).
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest

The authors declare no competing interests.

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