Sub-room temperature ferromagnetism and its nature in VSe$_2$ monolayer

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Magnetic van der Waals materials provide an ideal platform for exploring two-dimensional magnetism of technological and scientific importance. Among them, 1T-VSe$_2$ has been reported as one of the first room-temperature two-dimensional ferromagnets. However, this conclusion remains elusive both theoretically and experimentally. By using charge self-consistent LDA+DMFT approach, suited for both itinerant and localized characters of electrons in the open-$d$ subshells, we show that the monolayer is ferromagnetically ordered below 250K, implying the possible competition between charge density wave and ferromagnetic order. We predict that its ferromagnetism is vulnerable to interlayer coupling and extra charge dopings. The formation of local moment is attributed to the concerted effect of the quasiparticle pre-localization caused by reduced dimensionality and the electronic correlation. This study provides an important example where the reduced dimensionality is an essential factor to form local moments and subsequent magnetic orderings.

**Introduction.**—Two-dimensional (2D) magnetism has played central roles in numerous scientific and technological advancements including high temperature superconductivity, quantum Hall related phenomena, and the development of new devices [1–17]. In the past couple of years, notable magnetic orders have been observed even in single atomic layers [18–22]. These 2D magnetic van der Waals materials have been expected to open up a wide range of possibilities. The vast phase space with different elements and structures suggests the straightforward tuning of its magnetic properties. Moreover, due to the ease of fabricating 2D heterostructures, magnetic van der Waals materials have a great potential to provide a new unit for multifunctional devices, [23–26].

Among them, one of the fascinating materials is 1T-VSe$_2$ [21, 27–34]. This layered compound is composed of the ABC-stacked Se-V-Se atomic sheets (Figure 1a). Since each V atom is surrounded by six Se, ionically V-$d$ states are split into $t_{2g}$ and $e_g$ manifolds. Due to the trigonal distortion, $t_{2g}$ degeneracy is further lifted to form higher-lying $a_{1g}$ and two-fold degenerate $e_{g \pm \pi}$ states as depicted in Figure 1. Most interestingly, VSe$_2$ monolayer is claimed to be a 2D ferromagnet with Curie temperature ($T_c$) above room temperature [21, 33]. It is particularly interesting because bulk VSe$_2$ remains paramagnetic down to low temperature [27, 28, 30, 34].

However, this conclusion remains elusive both theoretically and experimentally. For example, the reported experimental moments of $\approx 15\mu_B$ [21] or $5\mu_B$ [33] are too large to be compared with the calculated values of about 0.6$\mu_B$ [30, 38]. Furthermore, other experimental studies report the absence of ferromagnetic order for the same material [32, 34], which certainly requires a thorough theoretical investigation. The claim of monolayer ferromagnetism heavily relies on the first-principles calculation result based on DFT-GGA (density functional theory within generalized gradient approximation) which consistently produces the ferromagnetic ground state [35, 37].

An obvious problem is, however, that DFT-GGA predicts the ferromagnetic phase also for the bulk VSe$_2$ being in a sharp contrast to the experimental fact of paramagnetism [27, 28, 30, 35, 37, 39]. In order to perform a reliable investigation, one needs the higher-level theoretical framework suited for both itinerant and localized characters of electrons associated with the open-$d$ shells. First-principles methods in combination with dynamical mean-field theory (DMFT) provide an efficient way to study the dual nature of electrons by mapping a quantum many-body lattice problem onto a multi-orbital quantum impurity problem in an effective electron bath [40]. We hereby adopt the charge self-consistent LDA+DMFT to investigate the magnetic...
properties of VSe$_2$. For the construction of DMFT computations, the on-site Coulomb interaction parameters (Hubbard $U$ and Hund $J_H$) associated with V-d orbitals have been calculated within constrained random phase approximation (cRPA) [41,43], and the nominal double-counting scheme [44] is used for the self-energy correction (see Figure 1b, 1f).

**Methods.** The calculations have been performed by all-electrons DFT code Wien2K [61], EDMFTF [62], and ComDMFT package [63]. GGA functional parameterized by Perdew, Burke, and Ernzerhof [64] was adopted. The k-point grids of 16$\times$16$\times$7 and 26$\times$26$\times$1 were used for bulk and monolayer VSe$_2$, respectively. Crystal structure was determined by internal relaxation within GGA functional with the fixed experimental cell parameters [27, 28, 31, 35, 65, 66] and the force criterion of 0.5 mRyd per Å. For monolayer calculation, the vacuum layer of 30Å has been taken into account. For on-site Coulomb interaction parameters, we used the cRPA technique [41–43] as implemented in ComDMFT package [63]. GGA functional parameterized by FfWMBPT code [60] for LDA-GGA [68]. In order to properly describe the trigonal iron oxide phase, the nominal double-counting scheme has been adopted with 3 electron occupation in the V-d orbitals as predicted by DFT-GGA [65]. In order to properly describe the trigonally distorted local environment around V-d orbitals, we adopted a local basis set that diagonalizes the matrix $\epsilon_{imp} + \text{Re}\Delta(\omega = 0)$ (where, $\epsilon_{imp}$: impurity levels, $\Delta(\omega)$: hybridization function between local impurity and bath) during LDA+DMFT charge self-consistent calculation. Our LDA+DMFT calculations were performed by using Wien2K+EDMFTF. We also double-checked the result of paramagnetic phases using ComDMFT built on top of FlapwMBPT code [69] for ab initio LDA calculations.

**Results.** To resolve the key issue in this material, namely, the possible monolayer ferromagnetism, we calculated the ferromagnetic order parameter $m = \mu_B\langle(\sigma^z)\rangle$ (where $\mu_B$ is Bohr magneton and $\langle(\sigma^z)\rangle$ is the up(down)-spin electron occupation in the V-d sub-shell) as a function of temperature; see Figure 3b. The magenta squares and the blue triangles represent the LDA+DMFT results for monolayer and bulk VSe$_2$, respectively. The first thing to be noted is the absence of ferromagnetic order for the bulk phase as known from experiments. Note that GGA predicts the ferromagnetic order even for bulk, which significantly undermines its predictability for the magnetic ground state of monolayer VSe$_2$ [36, 37, 39].

For monolayer, our LDA+DMFT calculation clearly shows that ferromagnetic order is developed. In this regard, our result is seemingly in better agreement with the previous experimental reports of monolayer ferromagnetism [21, 33] rather than paramagnetism [22, 34]. As for the critical temperature and the moment size, however, the calculated $T_c$ $\approx$ 250K and $\mu = 0.365\mu_B$ are markedly lower and smaller than the experimental value of $T_c \geq 300K$ and $\mu = 5–15\mu_B$, respectively [21, 33]. These differences might reflect the presence of charge density wave (CDW) phase whose temperature range varies from 120K to 360K depending on experiments [21, 33, 34, 45]. Or, there can be certain types of extrinsic effects in experimental situations such as defects and/or the interaction with substrate. Considering all these issues, in the below we pursue the deeper understanding of magnetism in VSe$_2$.

Figure 3 presents the temperature dependent local spin susceptibility $\chi_m = \int_{0}^{\pi} d\tau\langle m(\tau)m(0)\rangle$ (where $\tau$ is an imaginary time) which clearly shows the localized moments formed in the monolayer. Magenta squares and blue circles are the result of monolayer ($\chi_m^{\text{mono}}$) and bulk ($\chi_m^{\text{bulk}}$) susceptibility, respectively. For the latter, Pauli-like temperature-independent behavior demonstrates the electron delocalization in bulk VSe$_2$, being consistent with experimental report [35]. For the former, on the other hand, $\chi_m^{\text{mono}}$ exhibits the weak but clear inverse-temperature dependence, indicative of the electron localization (see the inset). This local nature is another important new aspect that LDA+DMFT reveals for VSe$_2$ magnetism. We also found that the localized moment is formed mainly in the V-$e_{g\pm}$ and V-$a_{1g}$ orbitals.

In the following paragraphs, we argue that this local behavior in the monolayer VSe$_2$ is attributed to the concerted effect of reduced dimensionality and electronic correlation. Figure 3b shows the calculated non-interacting spin susceptibilities ($\chi_m^{\text{non}} U=0$) in monolayer (magenta squares) and bulk (blue circles) in their paramagnetic phases. Note that the bulk susceptibility ($\chi_m^{\text{bulk}}$) exhibits the Pauli-like behavior whereas the inverse-temperature dependence is clearly identified for the monolayer susceptibility ($\chi_m^{\text{mono}}$, see the inset). Note that this behavior of $\chi_m^{\text{mono}}$ is solely attributed to the band structure (without interaction effect), particularly to the van Hove singularity near the Fermi level [16, 54]. As shown in Figure 2a, van Hove singularity is strongly enhanced in the monolayer VSe$_2$, implying the vanishing electron velocity; compare the dispersions along K–G and H–A–L in Fig. 2a to 2b. This electronic behavior naturally leads to the saddle-point formation [67] and the divergence in DOS. For the bulk, on the other hand, the inter-layer coupling is noticeable; for example, compare the dispersion along the M–K–G path to that along H–A–L (Figure 2a and 2b). It naturally weakens the van Hove singularity leading to the broader DOS near the Fermi energy as shown in Figure 2 to 2e. This characteristic band feature of monolayer VSe$_2$ is the effect of reduced dimensionality.
The local dynamical correlation plays a crucial role on top of the pre-localization of electrons caused by two dimensionality. We found that the correlation enhances the electron localization in two distinctive ways. First, the local dynamical correlation renormalizes the electronic structure, especially the bands with the critical point. The orbital character of these bands are mainly V-\(e_g\) and V-\(a_{1g}\) as shown in Figure 2 and 3. Their \(Z^{-1}\) values greater than two demonstrate the strong enhancement of electron localization caused by the band structure renormalization. It can further be confirmed by comparing \(\chi^{\text{non}}_m\) to the spin susceptibility within bubble approximation: \(\chi^\text{bubble}_m = 2\mu_B^2 \sum_{i,j} \int_0^\beta d\tau G_{i,j}(\tau)G_{j,i}(-\tau)\) (where \(G_{i,j}\) is a LDA-DMFT local Green’s function). As shown in Figure 3a and 3b, \(\chi^\text{bubble}_m\) is more than two times greater than \(\chi^{\text{non}}_m\). It is consistent with the \(Z^{-1}\) value of V-\(e_{g}^{\pm}\) and V-\(a_{1g}\) orbitals, demonstrating that this enhancement originates from the band renormalization. Second, in addition to the quasiparticle bandstructure effect, the dynamical correlation facilitates the electron localization in the two-particle level. Compared to \(\chi^\text{bubble}_m\), the spin susceptibility, \(\chi_m\), is strongly enhanced; compare the magenta line in Figure 3b with that in Figure 3a. Its temperature dependence is also more pronounced than \(\chi^\text{bubble}_m\), indicative of the important contribution coming from vertex correction to the spin susceptibility of vanadium.

Here we stress that the reduced dimensionality is essential for the local moment formation as demonstrated by the fact that the bulk susceptibility, \(\chi_{m,\text{bulk}}\), remains temperature-independent; see Figure 3a. Namely, the electronic correlation alone cannot induce the moment formation even if the \(\chi_{m,\text{bulk}}\) is significantly greater than \(\chi^{\text{non}}_{m,\text{bulk}}\) in the entire temperature range. As the origin of local moment formation, the combined effect of dimension reduction and electron correlation is not just physically interesting but also possibly important to understand experiments. For example, it implies that the local moment can be suppressed by the inter-layer hoppings or the monolayer-substrate interactions.

In order to explore other possible reasons for the contradictory experimental reports on the monolayer ferromagnetism [21, 32–34], one can consider both cation and anion defects as often observed in this type of chalco-
genide systems [30, 34, 51, 59]. In fact, our calculation shows that the ferromagnetic order is vulnerable to the extra effective charges introduced. Figure 3 presents the calculated ferromagnetic moment \( m \) as a function of varying system charges. In Figure 4, we simulate the effect of both hole-like (negative values) and electron-like (positive values) extra charges by tuning the system charge at the DFT level while, in Figure 5, both DFT system charge and DMFT nominal double-counting value are simultaneously controlled. The results demonstrate that introducing the extra charges through, for example, V or Se defects, can easily suppress the ferromagnetic order. The number of extra charges (i.e., \(-0.3 \leq e \leq +0.3\)) seems to be reasonable to simulate the possible defect concentrations considering the reported values of related systems such as VTe\(_2\), Fe\(_3\)GeTe\(_2\) and FeTe [54, 58, 60]. This result hopefully provides useful information to understand the previous experimental reports and to stimulate the further investigations.

Finally, an important factor that has not been directly addressed in the current study is the cooperation or competition of ferromagnetism with CDW order. It is known that the monolayer VSe\(_2\) also hosts the CDW order while the CDW vector can be different from its bulk counterpart [21, 52, 54, 55]. It is noted however that the formation of CDW phase likely suppresses the ferromagnetic order rather than enhances as noted in a recent study [58]. Also, experiments unequivocally report that ferromagnetic order sets in well above the CDW temperature [21, 53]. Therefore our conclusion of \( T_c \approx 250 K \) ferromagnetism remains valid as an intrinsic property of monolayer VSe\(_2\) irrespective of the presence of CDW phase.

Conclusion.- To conclude, we investigated the magnetic properties of bulk and monolayer VSe\(_2\) by using charge self-consistent LDA+DMFT approach. Our results show that VSe\(_2\) monolayer is a ferromagnetically-ordered material below 250K whereas its bulk phase is paramagnetic. The electron localization and subsequent local moment formation in the monolayer originate from the quasiparticle pre-localization enabled by the reduced dimensionality and its enhancement by local dynamical correlation. This study provides an important example where the reduced dimensionality is an essential factor to form local moments and subsequent magnetic orderings. Our work will be useful in the understanding and design of possible magnetic devices based on 2D heterostructures.

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The van Hove singularity of monolayer VSe$_2$ is in the G–K and A–H line along which the near-Fermi-level band makes a minimum while it does a maximum along the orthogonal direction to those lines, forming a saddle point. See also the experimental report by Cao et al. which shows that the valance electron number in VSe$_2$ is closer to the vanadium metal ($d^3$) rather than that of VO$_2$ ($d^1$).