

Electronic correlations in monolayer VS₂

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The layered transition metal dichalcogenide vanadium disulfide (VS₂), which nominally has one electron in the 3*d* shell, is potent for strong-correlation physics and is possibly another realization of an effective one-band model beyond the cuprates. Here monolayer VS₂ in both the trigonal prismatic and the octahedral phases is investigated using density functional theory plus Hubbard *U* (DFT + *U*) calculations. Trigonal prismatic VS₂ has an isolated low-energy band that emerges from a confluence of crystal-field splitting and direct V-V hopping. Within spin density functional theory, ferromagnetism splits the isolated band of the trigonal prismatic structure, leading to a low-band-gap, $S = \frac{1}{2}$, ferromagnetic Stoner insulator; the octahedral phase is higher in energy. Including the on-site interaction *U* increases the band gap, leads to Mott insulating behavior, and, for sufficiently high values, stabilizes the ferromagnetic octahedral phase. The validity of DFT and DFT + *U* for these two-dimensional materials with potential for strong electronic correlations is discussed. A clear benchmark is given by examining the experimentally observed charge density wave in octahedral VS₂, for which DFT grossly overestimates the bond length differences compared to known experiments; the presence of charge density waves is also probed for the trigonal prismatic phase. Finally, we investigate why only the octahedral phase has been observed in experiments and discuss the possibility of realizing the trigonal prismatic phase. Our work suggests that trigonal prismatic VS₂ is a promising candidate for strongly correlated electron physics that, if realized, could be experimentally probed in an unprecedented fashion due to its monolayer nature.

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Transition-metal dichalcogenides (TMDCs), composed of layers of chalcogen-metal-chalcogen units (hereafter called monolayers) that stack and adhere via weak bonding, are a diverse class of materials known to exhibit charge density waves, metal-insulator transitions, superconductivity, and novel optoelectronic properties [1]. Recent breakthroughs in the ability to isolate and manipulate few-layer and monolayer materials, derived from TMDCs like MoS₂ and other layered crystals such as graphite, have enabled new possibilities for device applications as well as fundamental studies of low-dimensional systems [2].

Many TMDCs are nominally d^0 (e.g., TiS₂) or band insulators in which an even number of *d* electrons completely fills the valence band (e.g., MoS₂). Such configurations preclude the possibility of strong electronic correlations and/or magnetism in the ground state. However, there are known examples from experiments of nonoxide layered materials exhibiting magnetism and, in some cases, insulating behavior. Spin- $\frac{3}{2}$ CrXTe₃ is a ferromagnetic (FM) insulator with a Curie temperature of 33 K for $X = \text{Si}$ and 61 K for $X = \text{Ge}$; monolayers in this class of materials have been predicted to be stable with FM exchange as well [3–8]. The spin- $\frac{1}{2}$ insulator CrX₃ is a ferromagnet below 37 K for $X = \text{Br}$ and 61 K for $X = \text{I}$; in CrCl₃ FM layers stack in an antiferromagnetic (AFM) pattern with a Néel temperature of 17 K [9–12]. FM Fe₃GeTe₂, which is metallic, has a substantial Curie temperature of 150 K [13,14]. In-plane antiferromagnetism is also observed; MnPS₃ and MnPSe₃ are spin- $\frac{5}{2}$ antiferromagnets with Néel temperatures of 78 and 74 K, respectively [15,16]. Additionally, there

are numerous antiferromagnets in the family of Fe pnictide superconductors [17].

VS₂ is an interesting candidate among the many possible TMDCs. Here nominal electron counting indicates that V donates two electrons to each S, leaving it in a d^1 (i.e., spin- $\frac{1}{2}$) configuration. Therefore, VS₂ might be potent for strong-electronic-correlation physics, especially since its 3*d* electrons will be significantly more localized than the 4*d* or 5*d* electrons of NbS₂ or TaS₂, respectively. Similarly, the electronic states of the sulfur anion should be more localized than those of selenium or tellurium.

The structure of a monolayer TMDC consists of one metal layer sandwiched between two chalcogen layers, with each layer corresponding to a triangular lattice. This gives rise to two basic types of chalcogen-metal-chalcogen stacking: ABA stacking, in which the metal layer hosts a mirror plane, or ABC stacking. The latter gives rise to approximate octahedral coordination of the transition metal (TM) by chalcogens, which results in the fivefold *d* manifold splitting into a threefold set (T_{2g}) and a twofold set (E_g) of orbitals. More precisely, the octahedral environment experiences a trigonal distortion due to the ability of the chalcogens to relax in the out-of-plane direction. This results in a point-group symmetry lowering $O_h \rightarrow D_{3d}$ and a further splitting of the *d* orbitals $T_{2g} \rightarrow A_{1g} + E'_g$. For convenience, we refer to the distorted octahedral (D_{3d}) phase as the OCT phase in the remainder of this paper.

Alternatively, ABA stacking results in a trigonal prismatic (TP) coordination of the TM by the chalcogens. The TP coordination, which is compared to that of the OCT structure in Fig. 1, splits the *d* manifold into a onefold A'_1 orbital and two types of twofold orbitals (E' and E''). Both OCT and TP coordinations are possible for VS₂, and the TP coordination is particularly intriguing since it could potentially be a physical realization of a one-band model with strong interactions;

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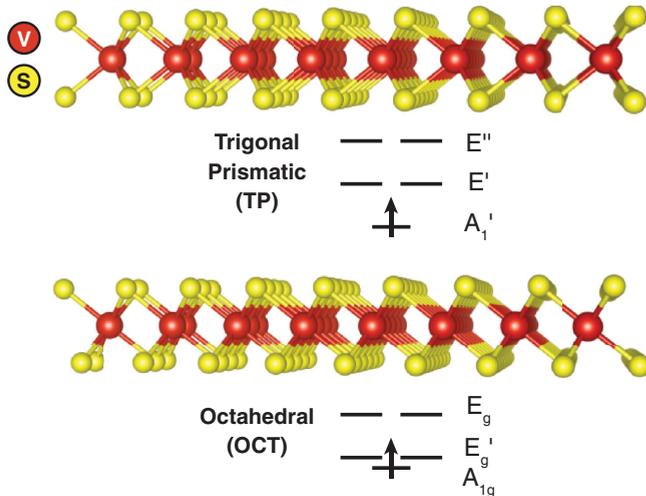


FIG. 1. Side view of crystal structures of trigonal prismatic and octahedral monolayer VS_2 and schematic V $3d$ orbital fillings from crystal-field theory. Red and yellow spheres represent ionic positions of V and S, respectively.

this rare feature is a hallmark of the copper oxide (cuprate) high-temperature superconductors [18].

Experimentally the TP phase has not been realized, but bulk VS_2 was first synthesized in the OCT phase in the 1970s by deintercalating LiVS_2 [19]. It exhibits a charge density wave (CDW) below $T = 305$ K with a wave vector $q \approx \frac{2}{3}K$, where K is the corner of the Brillouin zone [19–21]. In the CDW phase Mulazzi *et al.* found metallic resistivity and no lower Hubbard band in the photoemission spectrum, suggesting rather weak electronic correlations [21]. Only a very small paramagnetic response was observed in the magnetic susceptibility, which it was suggested might stem from V located between neighboring VS_2 monolayers. A more recent high-pressure synthesis by Gauzzi *et al.* found much more appreciable local magnetic moments but no long-range CDW, and it was speculated that “nanometer-size domains” might be responsible [22]. Using phonon calculations, they also showed that the presence of a CDW soft mode is very sensitive to the lattice parameters. Nanosheets, though not a monolayer, of OCT VS_2 have been synthesized and interpreted as showing ferromagnetism [23–26].

Here we employ first-principles electronic structure calculations based on DFT to explore the physics of VS_2 . We focus on a single layer of the material since the realization of a strongly correlated monolayer material could enable one to probe Mott physics via gating and strain in an unprecedented way. We find that DFT captures the $q = \frac{2}{3}K$ CDW in OCT VS_2 and explains the lack of correlations observed experimentally, though it substantially overestimates the structural distortion. The addition of an appreciable on-site Hubbard U interaction to the V site leads to antialigned spins in OCT VS_2 and yields V-V distance distortions and metallic behavior in reasonable agreement with known experiments. Unlike the OCT phase, we find that TP VS_2 has an isolated low-energy A_1' band at the level of non-spin-polarized DFT due to the crystal field and direct V-V hopping. The preferred magnetic order is ferromagnetic, as opposed to the AFM ordering found in the cuprates, and

this magnetism opens up a small band gap by splitting the A_1' band. The on-site interaction leads to a low-band-gap, $S = \frac{1}{2}$, FM Mott insulator. For a narrow range of U we find evidence of a CDW in TP VS_2 . Although DFT predicts that FM TP VS_2 is the ground state, for moderate values of U we find that the OCT structure becomes thermodynamically favored.

II. COMPUTATIONAL DETAILS

DFT [27,28] calculations within the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [29] are performed using the Vienna *ab initio* simulation package (VASP) [30–33]. The Kohn-Sham equations are solved using a plane-wave basis set with a kinetic energy cutoff of 500 eV and the projector augmented wave method [34,35]. The out-of-plane lattice vector length is chosen to be 20 Å. To sample the reciprocal space we employ a $24 \times 24 \times 1$ k -point grid for the primitive unit cell and k -point grids with approximately the same k -point density for supercells. We utilize the tetrahedron method with Blöchl corrections [36] for all calculations except for structural relaxations and phonon calculations in metals, for which we employ the first-order Methfessel-Paxton method [37] with a 50-meV smearing. The total energy, ionic forces, and stress tensor components are converged to 10^{-6} eV, 0.01 eV/Å, and 10^{-3} GPa, respectively.

To compute maximally localized Wannier functions (MLWFs) we employ the WANNIER90 code [38]. The rotationally invariant DFT + U approach with fully localized limit double-counting [39] is used to explore the impact of an on-site Hubbard U on V $3d$ electrons. Values of on-site Coulomb repulsion U are computed from first principles via the linear response approach of Cococcioni and de Gironcoli [40]. We do not employ an on-site exchange interaction J since this effect is present within spin density functional theory [41]. We use the direct (supercell) approach in PHONOPY [42] to compute phonon dispersion relations. For these calculations we employ a $5 \times 5 \times 1$ supercell for smaller U and a larger $6 \times 6 \times 1$ supercell for $U > 3$ eV, which we find is needed to capture the presence of soft mode instabilities. Phonons at select q points are obtained using the frozen phonon method to assess supercell convergence of direct calculations. Images of crystal structures are generated with VESTA [43].

III. RESULTS AND DISCUSSION

A. CDW in OCT VS_2 within DFT

Given that a collection of experiments exists for the bulk OCT phase, we begin by addressing the physics of the OCT monolayer. Since bulk OCT VS_2 is known to undergo a CDW transition below $T = 305$ K [19–21], we explore the presence of such a CDW in the monolayer OCT structure. We compute the phonon frequencies using the frozen phonon method for $q = \frac{2}{3}K$, the experimental CDW wave vector from electron microscopy, and verify the soft mode in the non-spin-polarized (NSP) bulk OCT phase as found in a previous study [22]. We find that the frequency is $\omega = 60i$ cm^{-1} . For the monolayer, at this wave vector we find the same soft mode in the NSP state, now with a slightly softer frequency, $\omega = 80i$ cm^{-1} . Given the in-plane experimental CDW wave vector and the similarity

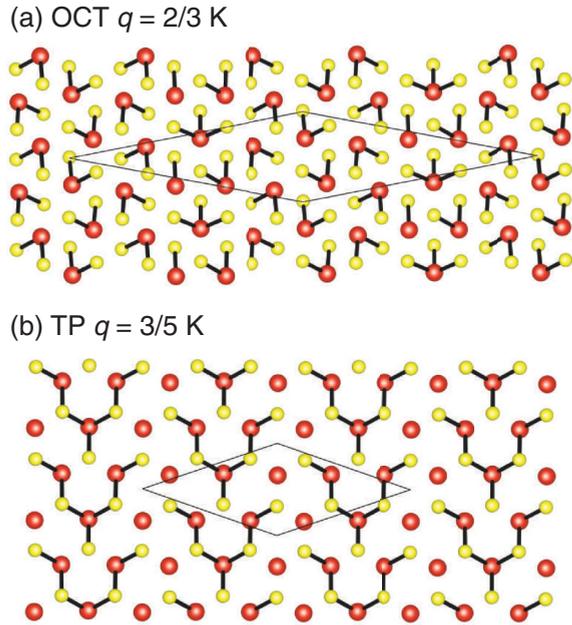


FIG. 2. Orthographic projection along the out-of-plane axis of the (a) FM, $U = 0$, $q = \frac{2}{3}K$, OCT and (b) FM, $U = 3.8$ eV $q = \frac{3}{5}K$, TP relaxed structures. Vanadium (sulfur) ions are indicated by red (yellow) spheres and thick black lines show the shortest V-S bonds. The unit cell is indicated by thin black lines.

of the soft mode for the bulk and the monolayer, we expect the monolayer CDW to be representative of that of the bulk. Additionally, at the slightly different wave vector of $q = \frac{3}{5}K$ we find a soft mode of smaller magnitude, $\omega = 48i$ cm⁻¹, in the monolayer.

Without any CDW the lowest-energy state of monolayer OCT VS₂ is an FM metal with a V magnetic moment of $0.5\mu_B$, which is 13 meV lower in energy than the NSP state. The relaxed NSP $q = 2/3 K$ OCT CDW state is 12 meV lower in energy than the pristine (without-CDW) FM state. Although we find no soft mode for the pristine OCT FM structure, performing a further structural relaxation of the NSP, $q = \frac{2}{3}K$, OCT CDW structure with FM initialization leads to an additional small (<1 -meV) energy lowering (see Fig. 5). In this structure, depicted in Fig. 2(a), distinct V sites have one, two, or three nearest-neighbor (NN) S atoms instead of the six of the pristine OCT structure. The CDW has substantially suppressed the V magnetic moments, to $0.0 - 0.2\mu_B$, which is consistent with the weak correlations observed by Mulazzi *et al.* However, the V-S and V-V distances exhibit massive variations, 2.2–2.6 and 3.0–3.7 Å, respectively. Sun *et al.* found that x-ray absorption fine spectroscopy (XAFS) data within the CDW phase was better interpreted by assuming two distinct V-V distances (as opposed to one); a difference in V-V distance of 0.19 Å was found [44]. Therefore, DFT is severely overestimating the structural deformation in the CDW state and beyond-DFT approaches will be necessary to describe the OCT CDW phase; we address this point in detail using DFT + U in Sec. III D. Also, additional experimental studies would be helpful to understand the lack of long-range CDW found using high-pressure synthesis.

B. Non-spin-polarized DFT electronic structure

The NSP band structure and density of states for TP VS₂ are shown in Fig. 3. We do find an isolated low-energy band as in the crystal-field picture shown in the top panel in Fig. 1, but there is a major difference from the simple schematic. The projected density of states shows that this isolated band is mainly of d character, while the unoccupied manifold above it has a slightly less predominant d character (i.e., stronger hybridization with S p); the manifold below is predominantly S p , with some hybridization with V d . However, projecting the V d density of states onto just the A'_1 orbital ($d_{3z^2-r^2}$) reveals the main discrepancy with the simple schematic: the isolated band is only roughly half A'_1 character and the remaining half is E' character. This puzzle was first noted by Kertesz and Hoffman in the context of TMDCs several decades ago [45].

In order to resolve this anomaly and to gain further insight into the electronic structure of the TP phase, we compute MLWFs for the full p - d manifold of TP VS₂, which results in atom-centered V d -like and S p -like orbitals. The Hamiltonian is represented in the MLWF basis, and we explore the impact of removing various matrix elements in the Hamiltonian corresponding to V-S and V-V hoppings; S-S hoppings are always retained. A similar analysis is performed for the OCT phase for comparison.

Figures 4(a) and 4(c) show the density of states from the MLWF Hamiltonian for NSP TP and OCT VS₂ (black curves), respectively, which are identical to those of DFT by construction. The OCT structure, unlike the TP structure, does not have an isolated low-energy band since the crystal-field splitting of the T_{2g} into A_{1g} and E'_g is relatively weak, as is also typical for oxides in this structure. Now we examine the tight-binding approximation in which we remove all V-S and V-V matrix elements beyond NN (thick red lines). In both phases, we qualitatively reproduce all of the gaps and other prominent features of the spectra. For both structures, we find V-V hopping beyond NN is negligible, and therefore all of the

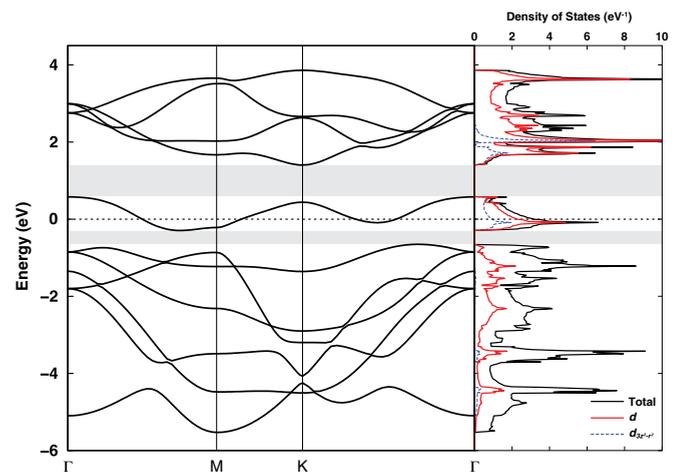


FIG. 3. NSP electronic band structure and total (solid black line), d (solid red line), and $d_{3z^2-r^2}$ (dashed blue line) density of states for TP VS₂ within DFT. The dotted black line indicates the Fermi energy and the shaded areas illustrate the gaps around the isolated low-energy band. The k -point labels Γ , M , and K correspond to the center, edge midpoint, and corner of the Brillouin zone, respectively.

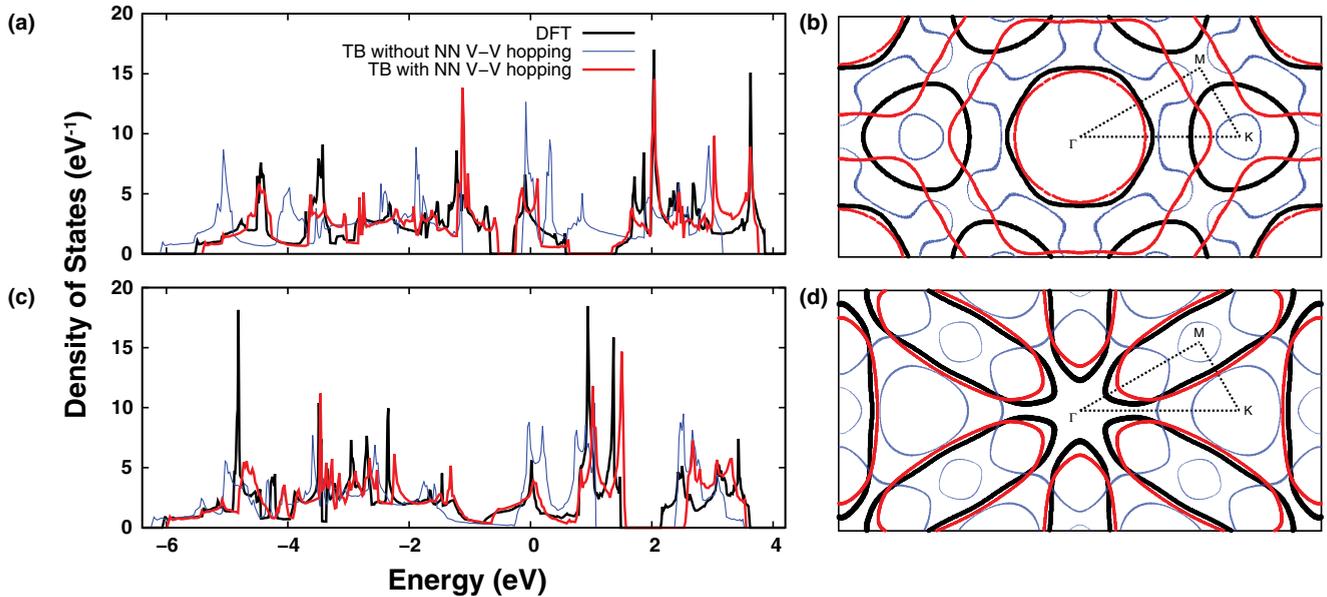


FIG. 4. (a) Density of states and (b) Fermi surface for NSP TP VS₂. Thick black lines correspond to DFT, while thick red (thin blue) lines indicate tight-binding results with (without) V-V hopping matrix elements. Dotted lines show the irreducible Brillouin zone. (c, d) Corresponding plots for OCT VS₂.

quantitative deviation between the black and the red curves is due to V-S hopping beyond NN.

If we only include NN V-S hoppings and no NN V-V hoppings (thin blue lines), we still capture the qualitative features of the spectra for the OCT structure, though there are now large quantitative differences. However, for the TP phase there is a qualitative change: there is no longer a gap between the isolated *d* band and the higher-energy *d* bands. Therefore, V-V hopping plays a strong role in splitting off the isolated band. Furthermore, it addresses the observation presented by Kertesz and Hoffman. The fact that NN V-V hoppings have a strong interorbital component explains why *A*₁' only contributes half the character of the isolated band. Interestingly, we also find that the rapid decay of these direct TM-TM hoppings with strain explains the semiconductor-to-semimetal transition in the isostructural *d*² material MoS₂ under strain [46].

Figures 4(b) and 4(d) illustrate the Fermi surfaces of the TP phase and OCT phase, respectively. In DFT, the Fermi surface of the TP structure has hole pockets centered at Γ and *K*, while that of the OCT structure has a single cigar-shaped electron pocket centered at *M*. For the OCT structure the tight-binding approximation is sufficient to properly capture the Fermi surface topology, but for the TP structure this is not the case and longer-range V-S hopping is needed.

At this level of theory we predict an isolated low-energy band in the TP phase, but as discussed in the next section there is an FM instability once spin polarization is included even at the DFT level. This strongly suggests that electronic correlations will be important in the TP phase of this material, which therefore is our focus for the remainder of the paper.

C. DFT energy level diagram

The total energy of different structures and magnetic configurations of monolayer VS₂ within DFT is shown in

Fig. 5. For NSP states, the TP structure is lower in energy than the OCT structure by 15 meV. For both structures, the formation of an FM state results in a significant energy lowering compared to the NSP state. The magnitude of the energy decrease is 13 meV for the OCT and 49 meV for the TP structure. In the FM state, V in the TP structure is fully spin polarized with a magnetic moment of $1.0\mu_B$, whereas for the OCT structure the moment is only $0.5\mu_B$,

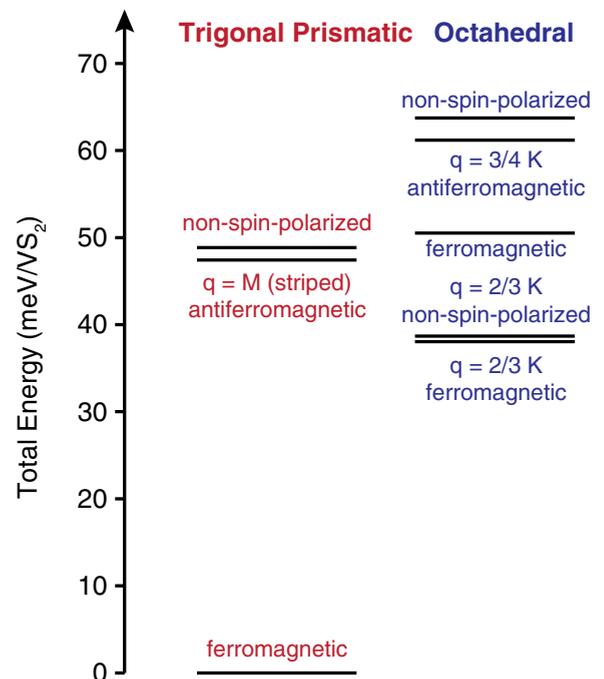


FIG. 5. Energy level diagram for TP (left; in red) and OCT (right; in blue) VS₂ within DFT. The energy of the FM TP state is used as the reference energy.

indicating that the TP phase exhibits stronger signatures of electronic correlations. For the OCT phase one must also consider the CDW phase, which lowers the OCT energy by 12 meV compared to the FM state and greatly weakens the magnetism, giving moments of only $0.0 - 0.2\mu_B$. Ultimately, the TP FM state is the ground state since it is still far lower in energy (38 meV) than the OCT FM CDW phase. The only remaining task is to provide evidence that there are no other magnetic or phonon instabilities.

To confirm that the exchange is FM in VS₂, we also investigate $q = M$ and $q = \frac{3}{4}K$ AFM configurations. For the TP phase, only the striped ($q = M$) AFM configuration is found to converge. This metastable state is metallic with small V magnetic moments of $\pm 0.2\mu_B$ and is only 1.4 meV lower in energy than the NSP state. Therefore, TP VS₂ strongly prefers ferromagnetism and we interpret it as a “Stoner insulator” rather than a Mott insulator at the level of spin-dependent DFT, given that a gap does not persist for an arbitrary magnetic ordering. For the OCT structure a metastable $q = \frac{3}{4}K$ AFM configuration is found only 2.4 meV lower in energy than the NSP state, and it, similarly, is metallic with small V moments of $\pm 0.4\mu_B$. The FM nature of the exchange in this system is not unexpected since the V-S-V angle is $84 - 85^\circ$, close to the 90° ferromagnetism given by the Goodenough-Kanamori rules [47–49].

We compute the phonon dispersion and density of states of FM TP VS₂, shown in Fig. 6, to assess the dynamic stability of this phase. The out-of-plane acoustic (ZA) branch has the $\omega \sim q^2$ form near Γ , characteristic of two-dimensional materials. There is no frequency gap between the acoustic and the optical branches. The out-of-plane optical (ZO) branches are the highest-frequency phonons. Since there are no modes with imaginary frequency, this phase is stable at the level of DFT.

The above analysis of the magnetism and the phonons allows us to conclude that the FM TP phase is the ground state within DFT. One would not interpret this as a Mott insulator

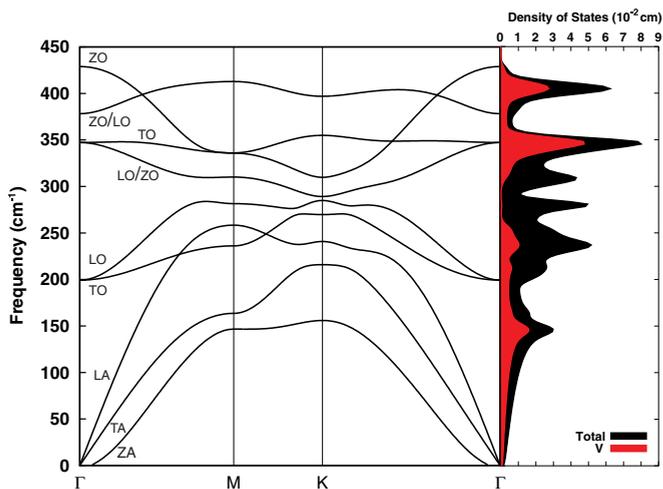


FIG. 6. Phonon dispersion relation and total (black region) and V-projected (red region) phonon density of states for FM TP VS₂ within DFT. Band labels identify the mode character near the Γ point. Branches: Z, out-of-plane; T, transverse; L, longitudinal; A, acoustic; O, optical.

within DFT given that the band gap does not persist for all spin configurations.

D. Impact of on-site Hubbard U

We use the linear response approach [40] to estimate the correlation strength U for V in VS₂. Computing screened interactions for use in beyond-DFT methods is still an active area of research, but the linear response approach is useful to set a baseline for the expected value of U . For FM states, we obtain $U = 3.84$ eV for the TP phase and $U = 3.99$ eV for the OCT phase. For the TP phase, we also compute U for the NSP state and obtain 4.14 eV. These values are generally smaller than those for oxides of vanadium [50] and larger than those for sulfides of titanium and tantalum [51,52]. Ultimately, one still needs to carefully investigate the effect of U on the physical observables, given the methodological uncertainties.

Another useful benchmark that could provide a bound for U is the CDW in the OCT phase. We performed structural relaxations to check whether the CDW is still captured for finite U . The total energy lowering ΔE , V-S bond length range, and V magnetic moment range for the relaxed structures are listed in Table I for NSP and FM OCT VS₂ for $q = \frac{3}{5}K$ and $q = \frac{2}{3}K$. For NSP states the energy lowering from the CDW increases substantially with U and is 60 meV for $U = 3$ eV. For FM states, the CDW persists for moderate values of U but it is substantially dampened once U reaches 3 eV, with a total energy lowering of only 1 meV. However, at $U = 3$ we find evidence of a new $q = \frac{2}{3}K$ CDW ground state with AFM-like correlations. This system is a ferrimagnetic metal with two V moments of $1.3\mu_B$, three V moments of $1.4\mu_B$, and four

TABLE I. Total energy change per formula unit with respect to the pristine structure of the same magnetic state, V-S bond length range, and V magnetic moment range for the non-spin-polarized and ferromagnetic states of octahedral VS₂ with $q = \frac{3}{5}K$ and $q = \frac{2}{3}K$ relaxed structures.

	U (eV)	ΔE (meV)	V-S bond length range (\AA)	V magnetic moment range (μ_B)
Non-spin-polarized				
$q = \frac{3}{5}K$	0	-17	2.22–2.52	—
	1	-20	2.23–2.51	—
	2	-33	2.24–2.51	—
$q = \frac{2}{3}K$	0	-25	2.18–2.57	—
	1	-27	2.20–2.56	—
	2	-34	2.21–2.55	—
Ferromagnetic				
$q = \frac{3}{5}K$	0	-7	2.21–2.53	0.03–0.38
	1	-2	2.30–2.42	1.17–1.19
	2	-14	2.26–2.51	1.21–1.39
$q = \frac{2}{3}K$	3	-1	2.37–2.42	1.30–1.40
	0	-12	2.18–2.57	-0.02–0.18
	1	-12	2.26–2.47	1.14–1.20
	2	-10	2.27–2.49	1.27–1.32
	3	-1	2.39–2.40	1.28–1.33

V moments of $-1.2\mu_B$. We refer to it as an AFM state for simplicity since the total magnetization is only $0.21\mu_B$ per formula unit.

Further evidence of this tendency of AFM correlations in OCT VS₂ for larger U comes from calculations of the $q = M$ and $q = \frac{3}{4}K$ AFM states. For $U = 3$ eV the $q = M$ and $q = \frac{3}{4}K$ AFM states are also lower in energy than the pristine FM state, by 29 and 19 meV, respectively. The $q = \frac{2}{3}K$ AFM CDW state is even lower in energy, 39 meV lower than the pristine FM state, and therefore is the ground state. For $U = 4$ eV this trend persists, as the $q = M$ and $q = \frac{3}{4}K$ phases with antialigned magnetic moments are lower in energy than the pristine FM phase, by 35 and 29 meV, respectively. It should be emphasized that these antialigned magnetic states are strongly coupled to the structural distortions; performing an unrelaxed $U = 3$ eV calculation based on the FM $U = 0$ or $U = 3$ eV relaxed structure of the primitive unit cell (i.e., without any CDW) demonstrates that the FM spin ordering persists as the ground state.

To assess which regime of U best agrees with experiments on the CDW phase, we compare the V-V and V-S distances of our calculated structures with those of known experiments in Fig. 7. For the V-V distance the high-temperature value of Sun *et al.* agrees well with that of Murphy *et al.*, which may be reasonable since the temperature is approaching the CDW transition at 305 K. Gauzzi *et al.*, who do not find a long-range CDW, observe a slightly larger V-V distance at low temperatures. The work of Sun *et al.* is the only work that presents atomic distances at low temperatures well within the CDW phase; they report a V-V distance difference of 0.19 Å.

Applying DFT + U while not allowing spontaneously broken translational symmetry, the V-V and V-S distances of the pristine FM state increase roughly linearly with U . For this state, within DFT ($U = 0$) PBE predicts larger bond

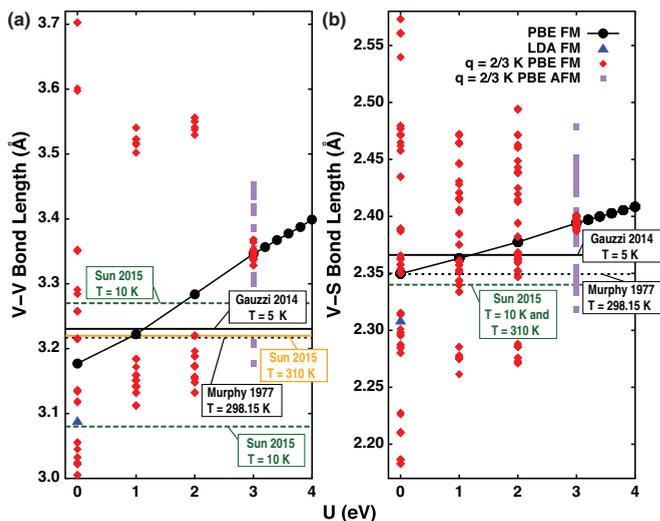


FIG. 7. (a) V-V and (b) V-S distances for OCT VS₂ in the pristine FM phase, $q = \frac{2}{3}K$ FM CDW phase, and $q = \frac{2}{3}K$ AFM CDW phase as a function of U . The two dashed green lines for the low-temperature experiment by Sun *et al.* in (a) correspond to the two measured V-V distances. For comparison, the $U = 0$ value for the pristine FM phase is also shown within the local density approximation (LDA).

lengths than the local density approximation, as is typical. As discussed in Sec. III A, for $U = 0$ the range of V-V distances of the $q = \frac{2}{3}K$ FM CDW phase (0.70 Å) is over 3.5 times the low-temperature XAFS measurement by Sun *et al.* For $U = 1$ and 2 eV the range we compute is smaller but still over twice the experimental value, while the range collapses to only 0.04 Å for $U = 3$ eV. Alternatively, reasonable agreement with experiment occurs for the $U = 3$ eV $q = \frac{2}{3}K$ AFM CDW phase. This phase still contains an appreciable CDW distortion, unlike the corresponding FM phase, and the range of V-V distances, 0.28 Å, is comparable to that in experiments. Furthermore, the metallic nature of this phase (unlike the gapped FM CDW phase) is qualitatively consistent with the experimental resistivity [19,21,44]. Therefore, an appreciable U value of around 3 eV may be most reasonable for OCT VS₂, and we find evidence of AFM correlations in this regime. The V-S bond lengths show a similar trend: the $q = \frac{2}{3}K$ FM CDW phase exhibits a massive range of values for $U = 0$ that is dampened for $U = 1$ and 2 eV and nearly disappears for $U = 3$ eV. We note that Sun *et al.* report only a single temperature-independent V-S bond length, however. A detailed structural refinement from experiment would be instrumental for a more stringent evaluation of available first-principles methodologies.

DFT + U corresponds to a Hartree-Fock (mean-field) solution to the quantum impurity problem of dynamical mean-field theory [53,54]. Given the manner in which the Hartree-Fock approximation tends to overemphasize the effects of interactions, it would not be surprising to require a smaller value of U relative to that of the linear response approach to provide a proper description. Especially given that there are currently no experiments for the TP phase, the above analysis indicates the need to explore a range of U values in what follows.

We explore the effect of U on the electronic spectrum of FM TP VS₂ using DFT + U . As shown in Fig. 8(a), for $U = 0$ already there is a small band gap of 30 meV generated by the exchange splitting of the A'_1 state. With increasing U the spin-down A'_1 state is shifted up in energy, which increases the band gap to 0.6 eV; the band gap saturates once the spin-up E' levels become the lowest unoccupied states. This value is somewhat smaller than the 1.1-eV band gap obtained via hybrid functional calculations, which is presumably due to the nonlocality of the potential in the hybrid functional [55]. For small U , the U -induced energy shift of the correlated orbital $|d_\alpha\rangle$ with occupancy n_α takes the form $U(1/2 - n_\alpha)$ within DFT + U , so one expects an occupied state ($n_\alpha = 1$) to shift down in energy by $U/2$ and an unoccupied state ($n_\alpha = 0$) to shift up in energy by $U/2$. In this case, however, the spin-up d levels are significantly hybridized such that their occupancies are very close to 1/2 (i.e., 0.45–0.48) within DFT. This necessitates that the spin-up d manifold is essentially fixed in energy for small U . The trend happens to persist over the full range of U shown, which is responsible for the band-gap saturation observed here as well as in a previous study [55]. For comparison, the impact of U on the density of states of FM OCT VS₂ is shown in Fig. 8(b).

For U of 2 and 4 eV the metastable striped $q = M$ AFM configuration is 115 and 66 meV higher in energy than the FM state, with band gaps of 0.1 and 0.7 eV and V

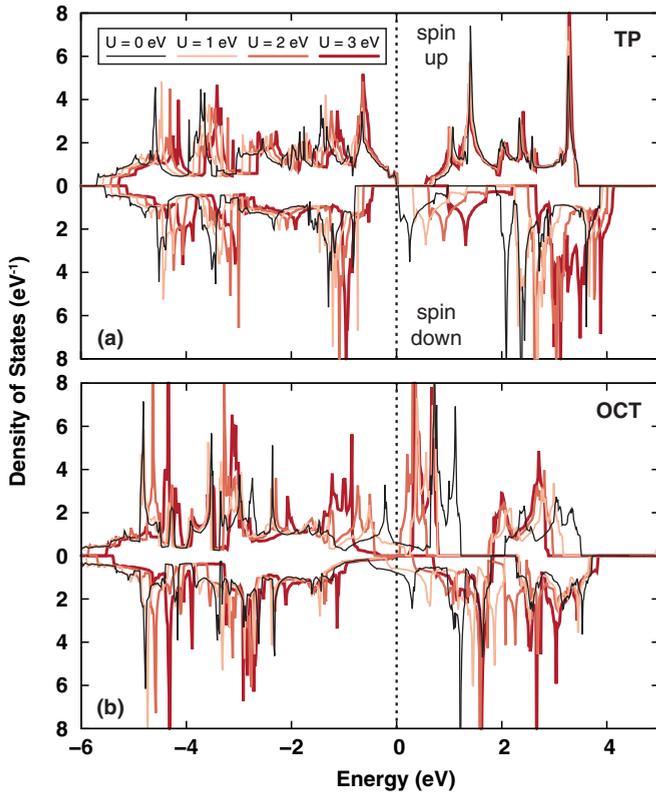


FIG. 8. Electronic density of states for FM VS₂ in the (a) TP and (b) OCT phases for different values of U . The dotted black line indicates the Fermi level.

magnetic moments of $\pm 0.6\mu_B$ and $\pm 1.3\mu_B$, respectively. The insulating behavior for this higher-energy magnetic configuration indicates that the system has been driven into a regime of Mott physics, as crudely interpreted from DFT + U ; this is in contrast to the DFT description in terms of a Stoner instability.

We also examine the impact of U on the phonon dispersion relation of the FM TP state to assess the dynamical stability of VS₂. Figure 9 illustrates the main result. For $U = 3.0$ eV the phonons are all still stable, as in the DFT case. For $U = 3.2$ eV one can observe the formation of a small dip in the TA branch between Γ and K . Once U is equal to 3.4 eV, a soft mode is formed. There is an additional soft mode at $q = K$ whose eigenvalue is smaller in magnitude.

To corroborate and refine our finding of U -induced soft modes in the TP phase, we performed frozen phonon calculations at several q points. The frozen phonon method removes the possibility of image interactions, which can cause errors in the supercell approach. For $U = 3.4$ eV we find a $130i$ cm⁻¹ soft mode at the K point, a $100i$ cm⁻¹ soft mode at $q = \frac{1}{2}K$, and a $188i$ cm⁻¹ soft mode at $q = \frac{3}{5}K$; this reveals that the supercell approach is qualitatively correct but with substantial quantitative errors.

We performed structural relaxations for the two wave vectors with the softest phonon modes, $q = K$ and $q = \frac{3}{5}K$, using supercells commensurate with these wave vectors. The total energy lowering ΔE , V-S bond length range, and V magnetic moment range for the relaxed structures are listed in Table II. For $U = 3.2$ eV no structural distortion is found

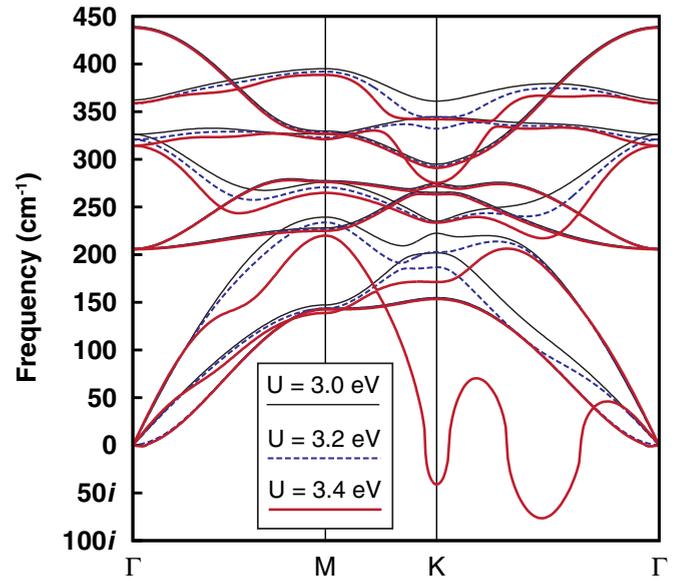


FIG. 9. Phonon dispersion relation for FM TP VS₂ for $U = 3.0$ eV (thin solid black lines), $U = 3.2$ eV (thin dashed blue lines), and $U = 3.4$ eV (thick solid red line).

for either wave vector. With larger U values, the relaxed structures exhibit a lower total energy and modulation of V-S bond lengths and V magnetic moments. For $q = \frac{3}{5}K$ the magnitude of ΔE increases monotonically from 1 to 45 meV as U increases, corresponding to an enhanced CDW. The V-S bond lengths vary by as much as 0.09 Å and the V magnetic moments differ by as much as $0.8\mu_B$ at a given U . For $3.4 \text{ eV} \leq U \leq 3.8 \text{ eV}$ the $q = K$ soft mode also shows an appreciable but smaller energy lowering ($|\Delta E| \leq 10$ meV), with significantly smaller magnitudes of the differences in V-S bond length (0.03 Å) and V magnetic moment ($0.01\mu_B$); for $U > 3.8$ eV this CDW state becomes higher in energy than the undistorted FM state. For $U = 5$ eV we do not find a stable (or even metastable) $q = \frac{3}{5}K$ or $q = K$ CDW state, indicating

TABLE II. Total energy change per formula unit, V-S bond length range, and V magnetic moment range for ferromagnetic, trigonal prismatic $q = K$ and $q = \frac{3}{5}K$ relaxed structures for several U values.

U (eV)	ΔE (meV)	V-S bond length range (Å)	V magnetic moment range (μ_B)
$q = K$			
3.4	-0.1	2.38–2.40	1.38–1.39
3.6	-3	2.38–2.40	1.41–1.41
3.8	-10	2.38–2.41	1.44–1.44
4.0	+9	2.38–2.43	1.32–1.50
4.2	+16	2.38–2.44	1.33–1.52
$q = \frac{3}{5}K$			
3.4	-1	2.37–2.42	1.17–1.56
3.6	-7	2.37–2.44	1.16–1.71
3.8	-19	2.36–2.45	1.18–1.82
4.0	-34	2.36–2.46	1.19–1.90
4.2	-45	2.36–2.47	1.20–1.97

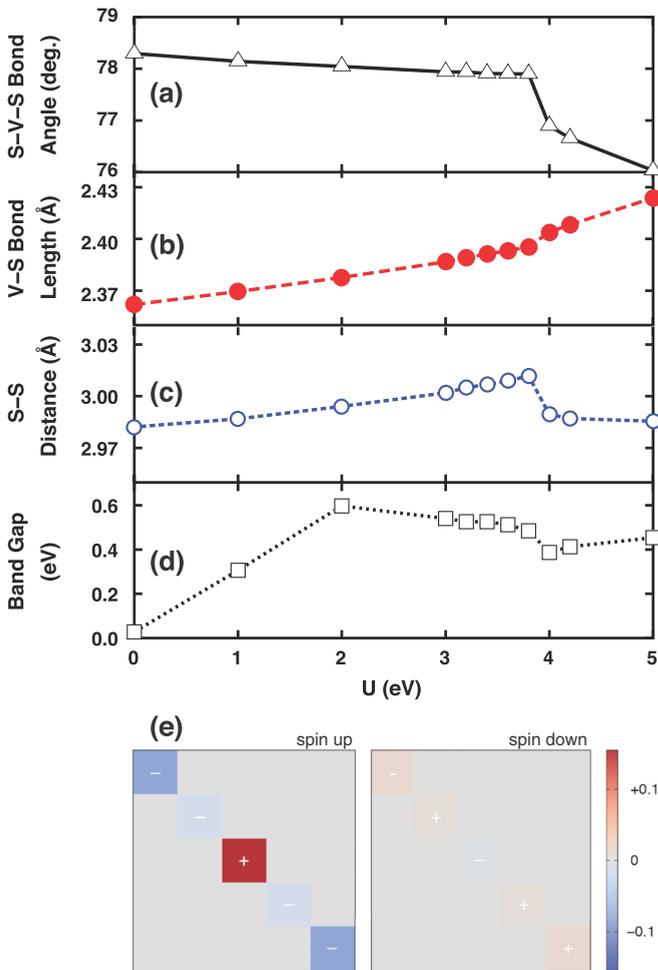


FIG. 10. (a) S-V-S bond angle, (b) V-S bond length, (c) out-of-plane S-S distance, and (d) electronic band gap as a function of U for FM TP VS_2 . (e) Density matrix difference for $U = 4$ eV (ground state minus metastable state) for spin-up (left) and spin-down (right) electrons. Matrix rows (columns) correspond to the d_{xy} , d_{yz} , $d_{3z^2-r^2}$, d_{xz} , and $d_{x^2-y^2}$ states from top to bottom (left to right).

that the prediction of a CDW state for TP VS_2 only exists within a narrow window of U values.

For $U \geq 4$ eV, both the $q = \frac{3}{5}K$ and the $q = K$ soft modes disappear (not pictured). Frozen phonon calculations indicate that the lowest phonon frequency at $U = 4$ eV is 126 cm^{-1} for $q = K$, 97 cm^{-1} for $q = \frac{3}{5}K$, and 79 cm^{-1} for $q = \frac{1}{2}K$. In this regime of $4 \text{ eV} \leq U < 5 \text{ eV}$ we find that the $q = \frac{3}{5}K$ CDW phase is a separate lower-energy state that exists in addition to the metastable undistorted FM state.

The disappearance of the soft modes at $U \geq 4$ eV appears to be related to a separate electronic and structural phase transition that occurs within the primitive cell of FM TP VS_2 . To describe the phase transition, we plot in Fig. 10 several structural parameters (out-of-plane S-V-S bond angle, V-S bond length, and out-of-plane S-S distance) and the band gap as a function of U for FM TP VS_2 . There is a sharp discontinuity in the structural parameters at $U = 4$ eV that most noticeably leads to decreases in the S-V-S bond angle and out-of-plane S-S distance. The band gap shows a discontinuity and begins

to decrease at $U = 2$ eV when the A'_1 level is no longer the lowest unoccupied state. At $U = 4$ eV there is a slight drop in the band gap due to the phase transition, after which it begins to increase roughly linearly. Using the relaxed crystal structure from $U = 4$ eV, we are able to converge a $U = 4$ eV DFT + U calculation to a metastable state 6 meV higher in energy whose electronic properties (e.g., density of states and local density matrix) resemble those of lower U (i.e., $U < 4$ eV) as opposed to this new ground state. This, along with the presence of discontinuities in the structural and electronic properties, indicates that the phase transition is of first order.

To better understand the electronic aspect of the phase transition, in Fig. 10(e) we plot the difference in the V on-site density matrices (ground state minus metastable state) obtained using the same crystal structure. The most significant changes occur in the spin-up channel. Compared to the metastable state, in this spin channel the ground state has 0.16 additional occupancy of the A'_1 ($d_{3z^2-r^2}$) state and 0.16 less total occupancy of the E' ($d_{x^2-y^2}$ and d_{xy}) states.

Given the crude nature of DFT + U , one must view these results with caution. More advanced calculations using DFT + DMFT, in addition to experiments, would be needed to judge the veracity of this predicted CDW. A smaller value of U might be more relevant in VS_2 to compensate for errors associated with Hartree-Fock treatment of the impurity problem.

E. DFT + U relative phase stability

To explore the impact of U on the relative energetics of the TP and OCT phases, in Fig. 11 we show the total energy of the NSP and FM states for TP and OCT VS_2 referenced to the TP FM-state energy. Here we do not focus on the CDWs since they are a small perturbation on the energetics.

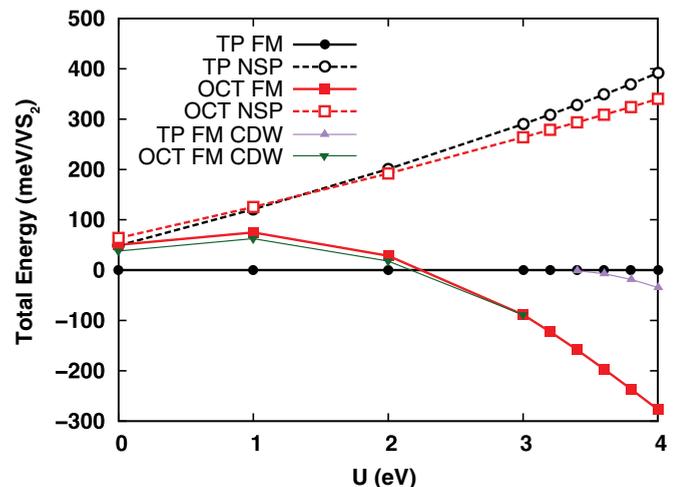


FIG. 11. Total energy of the NSP TP (black dashed line and open circles), NSP OCT (red dashed line and open squares), and FM OCT (red solid line and filled squares) states referenced to the FM TP (black solid line and filled circles) state energy as a function of U . The FM CDW states for the TP phase (purple filled triangles) and OCT phase (green inverted triangles) are a small perturbation on the energetics.

For $U = 0$ the TP FM state is the ground state, with the TP NSP, OCT FM, and OCT NSP states 49, 50, and 64 meV higher in energy, respectively. As U increases the NSP states are each monotonically destabilized by several hundreds of meV compared to the TP FM state as expected. The OCT FM phase has a more complicated nonmonotonic behavior, initially slightly increasing its relative energy with U and then decreasing its relative energy for $U > 1$ eV. For U values larger than 1 eV the OCT FM state becomes an insulator with the A_{1g} state fully polarized (V magnetic moment of $1\mu_B$) and is energetically stabilized; for $U = 3$ eV it is lower in energy by 88 meV than the TP FM state, and the energy stabilization increases upon further increases in U .

To gain further insight into the stabilization of FM OCT over FM TP VS₂ with U , we introduce a new spectral decomposition of the DFT + U energy functional into contributions from DFT (E_{DFT}), filling of V d orbitals (E_{fill}), and ordering of V d orbitals (E_{ord}),

$$E_{\text{DFT}+U} = E_{\text{DFT}} + E_{\text{fill}} + E_{\text{ord}},$$

$$E_{\text{fill}} = U(2l + 1)\mu(1 - \mu), \quad E_{\text{ord}} = -U(2l + 1)\sigma^2,$$

where l is the angular momentum ($l = 2$ for d electrons) and μ and σ are the mean and standard deviation of the eigenvalues of the local d density matrix. The filling and ordering terms added together give the standard interaction and double-counting terms in DFT + U for J set to 0. This decomposition provides a convenient way to isolate and quantify the contributions of the average filling of the d shell and the spin and orbital ordering of the d shell to the interaction and double-counting energetics. The former elucidates the energetics associated with moving charge into or out of the correlated subspace, while the latter is the means by which the Hartree-Fock approximation captures the energetics of electronic correlations.

As shown in Fig. 12(a), for $U = 1$ eV E_{DFT} (black circles) and E_{ord} (blue diamonds) are responsible for the further stabilization of the TP phase compared to $U = 0$. For larger U , the E_{fill} term (green triangles) increasingly favors the OCT phase by as much as 101 meV as U increases. The total $E(\text{OCT}) - E(\text{TP})$ (red squares) decreases with U more rapidly by a factor of 3 to 4 than E_{fill} . E_{DFT} and E_{ord} tend to oppose each other, but overall the negative E_{ord} term is dominant and this contributes significantly to the overall stabilization of the OCT phase. The E_{ord} and E_{DFT} terms increase in magnitude significantly more rapidly once the OCT phase becomes an insulator at $U = 2$ eV. We find the same qualitative behavior when we freeze the ions at the $U = 0$ structures, indicating that this is not an effect of structural relaxation.

The filling factor $\mu(1 - \mu)$ and the ordering factor σ^2 are plotted for both phases in Fig. 12(b) and Fig. 12(c), respectively. Interestingly, the TP and OCT phases have an almost-identical filling of the V d shell with $\mu(1 - \mu) = 0.229$ at $U = 0$. On the other hand, the σ^2 terms are substantially different at $U = 0$: σ^2 is 0.0167 in the TP phase, as opposed to only 0.0083 in the OCT phase. This stems from the complete spin polarization of the A'_1 state in the TP phase, as opposed to the partial spin polarization in the OCT phase. The preceding statement can be supported by investigating the NSP state for both the TP and the OCT phases for $U = 0$, which yields much more similar σ^2 values of 0.0037 and 0.0047, respectively.

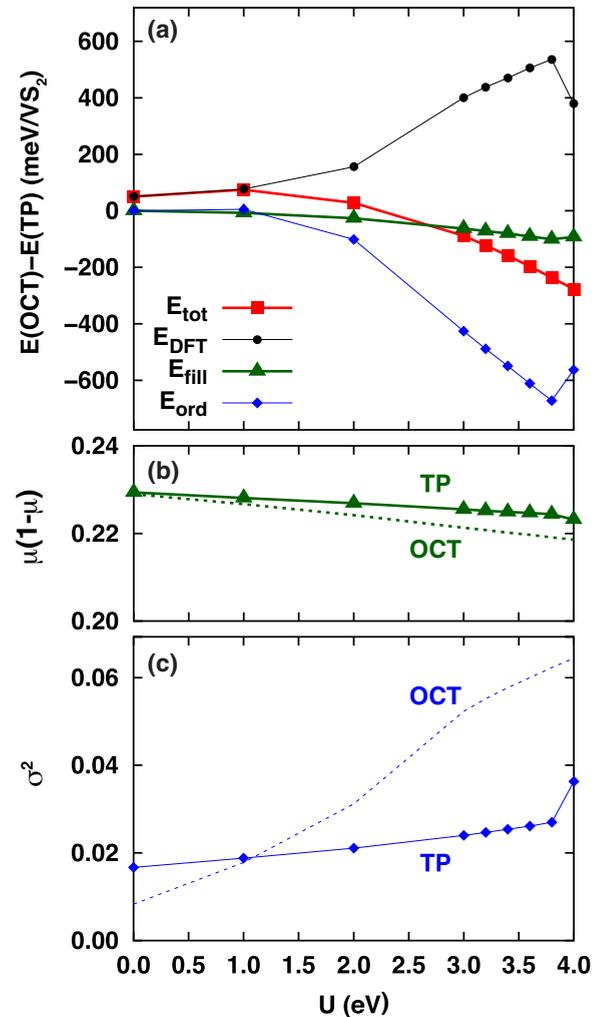


FIG. 12. (a) DFT + U total energy of the FM OCT phase minus that of the FM TP phase (red squares) and decomposition into the DFT (black circles), filling (fill; green triangles), and ordering (ord; blue diamonds) contributions as a function of U . (b) $\mu(1 - \mu)$ and (c) σ^2 as a function of U . (b, c) Solid lines with symbols correspond to the TP phase; dashed lines without symbols, the OCT phase.

Therefore, the pure crystal fields in each respective case result in a similar and small σ^2 , while the differing degrees of spin polarization are responsible for the large initial difference at $U = 0$. This enhanced spin ordering in the TP phase leads to the enhanced stabilization of the TP phase in the limit of small U since $\partial E_{\text{ord}}/\partial U \sim -\sigma^2$ and because the initial fillings are nearly identical. However, this trend is only guaranteed for small U , and as pointed out above the trend reverses for $U > 1$ eV. We therefore proceed to examine each contribution as a function of U . In terms of the filling contribution, the OCT-phase filling factor decreases with U twice as rapidly as it does for the TP phase for $U \leq 3.8$ eV. The σ^2 for the OCT phase increases 5.2 times more rapidly than that of the TP phase for $U \leq 3.8$ eV, since both the A_{1g} and the E'_g states are polarizable, and for $U = 3.8$ eV it has an ordering factor 2.3 times as large. Therefore, both the decreased filling and the increased ordering of the d orbitals of the OCT phase contribute to its stabilization for larger U .

E. Possibility of realizing TP VS₂

Only the OCT phase of VS₂ has been observed experimentally, in bulk and nanosheet forms [19,22–24,26]. DFT predicts that the TP phase is the thermodynamic ground state, while DFT + U predicts that the OCT phase becomes the ground state when U surpasses a moderate value of approximately 2.3 eV. More advanced calculations, including DFT + DMFT and, possibly, cluster extensions of DMFT, will be needed to definitively settle this issue from a theoretical standpoint. Given that TP may in fact be the ground state, or possibly a metastable state sufficiently low in energy to be achieved experimentally, we explore possible reasons why it has not been observed in experiments.

The initial synthetic route to VS₂ was delithiation from LiVS₂ [19]. This lithiated compound has a layered octahedral structure [56]. Therefore, one possibility is that VS₂ is stuck in a metastable OCT state. Within DFT, we compute an energy barrier of 0.69 eV per formula unit based on a linear interpolation between the TP and the OCT monolayer structures allowing only out-of-plane ionic relaxation. This value is in agreement with nudged elastic band calculations that found a barrier of 0.66 eV [57]. The large barrier supports the possibility that it could be very challenging to change phases. Another high-temperature synthesis technique did not use LiVS₂ but still resulted in the OCT phase [58,59]. One possibility is that a finite temperature plays a role in destabilizing the TP phase since there is evidence that the phonon entropy is greater for the OCT phase [57].

A more recent high-pressure synthesis of VS₂ also yielded the OCT phase [22]. We performed spin-polarized DFT (i.e., $U = 0$) calculations of bulk VS₂ under pressure and found that for sufficiently high pressures the OCT phase becomes the ground state, so this could be the reason why the TP phase is not observed. In these calculations we considered 2H_c (MoS₂-like) stacking [60] for the TP phase and O1 (CoO₂-like) and O3 (LiCoO₂-like) stackings [61] for the OCT phase. At 5 GPa the TP phase is still the ground state, but only 15 meV lower in energy compared to the 50 meV for 0 GPa. At 10 GPa the TP phase becomes 26 meV higher in energy than the OCT phase. Based on these observations, if the TP phase is the ground state we predict that synthesis under ambient pressure, under low temperature, and not involving a LiVS₂ precursor will be most effective in attempting to realize TP VS₂.

IV. CONCLUSIONS

We have demonstrated that monolayer TP VS₂ has an isolated low-energy band at the level of NSP DFT, which arises due to a combination of the TP crystal field and the NN V-V hopping. Including spin polarization reveals that the exchange is ferromagnetic and yields an FM insulator

with a small band gap. Other spin configurations result in metallic states substantially higher in energy, indicating that spin-dependent DFT is not putting VS₂ in the Mott regime. While TP VS₂ has not been observed in experiments in any form, spin-polarized DFT does predict that it is lower in energy than the OCT phase. DFT captures the known CDW in the OCT phase, which strongly diminishes the magnetism relative to the undistorted phase. However, DFT appears to grossly overestimate the CDW amplitude in this phase. Specifically, the V-V distance differences from DFT are far larger than those in the existing XAFS study [44].

Accounting for local correlations via DFT + U produces an $S = \frac{1}{2}$ FM insulating state in the TP phase, which is in the Mott regime for moderate values of U . For a small regime of finite U , we find a CDW in the TP phase at $q = \frac{3}{5}K$. For the OCT phase, increasing U diminishes the amplitude of the CDW. For the FM CDW state, the amplitude decreases slowly before rapidly collapsing near $U = 3$ eV. However, for this regime of U , magnetism with antialigned spins becomes energetically favored over ferromagnetism. In this magnetic configuration we find metallic behavior as in experiments and the V-V distance differences in the CDW phase are within reasonable comparison to XAFS experiments.

Regarding the relative phase stability, above a reasonably small U (approx. 2.3 eV) the energy ordering of the TP and OCT phases reverses, with the OCT phase becoming the ground state. More advanced calculations, including DFT + DMFT and, possibly, cluster extensions of DMFT, will be needed to settle which is the ground-state structure and determine whether the CDW in the TP phase is physical.

If the TP phase can be realized, it has the potential for novel physics: it would be a rare example of an $S = \frac{1}{2}$ Mott insulator on a triangular lattice with strong FM correlations. Its monolayer nature might enable doping via gating, allowing one to probe the doped Mott insulator in a precise fashion without simultaneously introducing disorder.

Note added in proof. Recently, we became aware of a related work by H. L. Zhuang and R. G. Hennig [62]. To the extent that this work overlaps with ours, we generally find agreement.

ACKNOWLEDGMENTS

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