

Complete description of the magnetic ground state in spinel vanadates

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We explore a source-free local spin density approximation (LSDA)+ U functional within density functional theory for its capabilities in describing noncollinear spin textures; capturing the noncollinear magnetic ground state of the spinel vanadates AV_2O_4 ($A = \text{Mn, Fe, and Co}$) remains an outstanding challenge for state-of-the-art *ab initio* methods. We demonstrate that both the noncollinear spin texture, as well as the magnitude of local moments, are captured, provided the source term (i.e., magnetic monopole term) is removed from the exchange-correlation magnetic field \mathbf{B}_{XC} . This suggests that for treatment of strongly correlated magnetic materials within the LSDA+ U method the subtraction of the unphysical magnetic monopole term from the \mathbf{B}_{XC} is essential.

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The strongly correlated electron systems (SCES) derive their richness from competing and coexisting multiple long-range orders (LROs) such as charge, magnetic, orbital order, etc. [1]. A strong interplay among various degrees of freedom (e.g., charge, spin, orbital, and lattice) in these materials provides a perfect platform for both basic and applied physics questions [2]. The family of spinel vanadates (AV_2O_4) belongs to such a class of materials where strong correlation, complex spin texture, and geometric frustration of the underlying lattice work in tandem [3,4]. This richness of physics in vanadates has attracted a lot of attention of the condensed matter and materials science community [4–9].

Despite a large amount of work done on these materials, the modern day theoretical method of choice for treating strong correlations, namely, density functional theory (DFT) [10,11] with the local spin density approximation (LSDA)+ U exchange correlation (XC) functional, fails to describe spinel vanadates in two crucial ways. First, in experiment the moment on V atoms is much lower (e.g., $1.3\mu_B$ in MnV_2O_4 [5] to $0.65\mu_B$ in ZnV_2O_4 [12]) than the DFT values [6,13–15] with a difference between the two as high as 60%. The reasons behind this large reduction in V moment remains contested with speculations including spin frustration, quantum fluctuations, and spin-orbit interaction effects. Second, the experimentally observed ground-state magnetic structure is a complex spin texture, i.e., a noncollinear arrangement of V spins (with a large angle between the A and V spins), while DFT predicts a collinear ferrimagnetic ground state [6,13–18]. This incorrect DFT ground state entails that the interesting physics of magnetic phase transitions in these materials stays beyond any *ab initio* description.

In the present Rapid Communication, with an example of three spinel vanadates (FeV_2O_4 , MnV_2O_4 , and CoV_2O_4), we probe the reason behind the failure of DFT, which is otherwise

an excellent theory for *ab initio* descriptions of complex magnets. DFT is in principle an exact theory, but in practice requires an approximation for the XC functional. Here, we demonstrate that this approximation lies at the heart of the failure to capture the magnetic structure; local spin density approximation (LSDA)- [19] or generalized gradient approximation (GGA)- [20] like functionals generate magnetic fields, (\mathbf{B}_{XC}), which have a large source term leading to magnetic monopoles (i.e., $\nabla \cdot \mathbf{B}_{\text{XC}} \neq 0$). This unphysical source term gets further enhanced when the on-site Coulomb correlation U is added to treat strong correlations in materials via a LSDA+ U -like approach. The presence of this source term in turn leads to a large discrepancy in calculated magnetic ground-state and experimental data. Removal of this source term, by using a recently developed source-free XC functional [21,22], reproduces the experimentally observed noncollinear magnetic state (both in terms of the canting angle as well as the magnitude of V moments) in all three spinel vanadates, making the LSDA/GGA+ U method highly accurate for the materials under consideration.

The ground-state DFT calculations were carried out within the full potential linearized augmented plane wave (LAPW) method as implemented in the ELK code [23]. All calculations were performed in the presence of a spin-orbit coupling term in the Hamiltonian. A \mathbf{k} -point grid of $8 \times 8 \times 6$ was used. The exchange correlation effect was treated using the local spin density approximation (LSDA) and LSDA+ U functionals. Dudarev formalism of the LSDA+ U method is used [24] in the present work. The on-site Coulomb correlation U was applied to the d orbitals of both V- and A-site atoms. A fully unconstrained minimization was performed; a random magnetic field was applied to break the symmetry and subsequently reduced to zero over a self-consistent cycle. In this way the self-consistent magnetization is not biased by the initial guess of the magnetization density, which is treated as an unconstrained vector field. The experimental structural parameters used in our calculations are taken from Ref. [25]

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for MnV_2O_4 and FeV_2O_4 and from Ref. [26] for CoV_2O_4 . In the case of CoV_2O_4 we have considered a cubic structure with space group $Fd\bar{3}m$ [25] as no evidence of a cubic to tetragonal structural transitional was found in the majority of the studies reported in the literature for this compound [27–29].

Spin texture. In the insulating noncollinear magnetic ground state observed in low-temperature experiments, all three materials [5,26,27,30,31] possess the A -site ($A = \text{Fe}, \text{Co}, \text{Mn}$) spin moments aligned along the c axis, while the V moments significantly cant away from the c axis (by an angle of up to 65° [5]). In FeV_2O_4 and CoV_2O_4 , the V moments form a structure known as a “two-in-two-out” structure in each $V_4\text{O}_4$ cube [28,30], whereas in MnV_2O_4 the observed structure is somewhat more complex [5].

In contradiction to low-temperature experiments, DFT calculations using LSDA show a metallic collinear ground state. Since vanadates are strongly correlated insulators [4,32], adding an on-site Coulomb repulsion by using the LSDA+ U method, as expected, opens a gap. However, the magnetic ground state remains a collinear ferrimagnet [6,13–18], a situation that cannot be improved by changing the functional from LSDA+ U to GGA+ U or meta-GGA. Adding spin-orbit coupling to the Hamiltonian introduces a weak noncollinearity.

In order to understand the reason behind this profound discrepancy between theory and experiments we examine the approximate XC functionals used. It has been shown before that for materials such as Fe pnictides the incorrect magnetic ground state can be attributed to the unphysical source term in the LSDA (and GGA) XC magnetic fields, the removal of which, via the source-free XC functional, results in agreement with experiments [21]. In the present case the problem is more complex in that not only the magnitude (as in the case of Fe pnictides) but also the direction of the local moments obtained using the LSDA+ U functional are very different from low-temperature experimental data. Whether the source term in the LSDA+ U magnetic field is also responsible for this discrepancy in the spin texture remains to be seen.

We employ the source-free LSDA+ U functional [21] (hereafter denoted by LSDA_{SF}+ U) to perform a fully unconstrained optimization of magnetization density (both the direction and magnitude). For the source-free functional a correction is provided to the XC \mathbf{B} field in the following manner: The Helmholtz theorem entails that any analytic function can be divided into a source-free part and a divergence-free part. The idea of the source-free functional is to use this decomposition on $\mathbf{B}_{\text{XC}}(\mathbf{r})$ and retain only the source-free part. Since this correction is applied only to the \mathbf{B}_{XC} (and hence the magnetization density) it does not directly effect the charge density. For these LSDA_{SF}+ U calculations, values of $U = 0.0, 5.0,$ and 4.0 eV were used on A -site d orbitals of MnV_2O_4 , FeV_2O_4 , and CoV_2O_4 , respectively. In agreement with experiments, we find a noncollinear magnetic ground state for all three compounds; both the “two-in-two-out” [28,30] spin arrangements of FeV_2O_4 and CoV_2O_4 [Figs. 1(a) and 1(b)] and the complex spin texture in MnV_2O_4 [28,30] [Fig. 1(c)] are perfectly captured. Since these compounds are isostructural and electronically similar, a wildly different

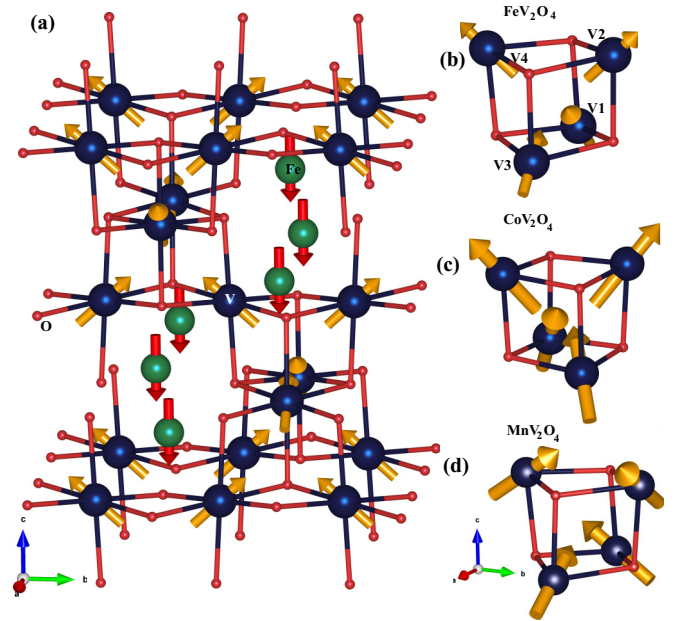


FIG. 1. The noncollinear magnetic structure obtained using LSDA_{SF}+ U with $U = 2.7$ eV shown (a) within the unit cell for FeV_2O_4 , and within the $V_4\text{O}_4$ cube for (b) FeV_2O_4 , (c) CoV_2O_4 , and (d) MnV_2O_4 .

value of U on the V site to describe them is not expected. Indeed, we find that, in the absence of the source term, we require the same value of $U = 2.7$ eV acting on the V atoms to reproduce the experimentally observed diverse noncollinear magnetic ground state of these three materials.

As for the value of the angle between the V - and A -site spins, consistent with the experimental observations, our results show that the A -site moment is collinear with the c axis in the presence or absence of the source term in the functional. On the other hand, the canting angle of the V spins is highly functional, dependent in that the LSDA+ U functional, in the presence of spin-orbit coupling, leads to a small canting angle of 19° for all three materials. These results are unlike experiments which show that the canting angle is much smaller in CoV_2O_4 than in MnV_2O_4 or FeV_2O_4 . Removal of the source term from this functional has a dramatic effect on the canting angle (see Fig. 2); for MnV_2O_4 and FeV_2O_4 the agreement with experiments is excellent, but for CoV_2O_4 the results overshoot slightly. However, consistent with the experimental trend [5,27,30,33,34], we find that the canting angle is smaller in CoV_2O_4 than in MnV_2O_4 or FeV_2O_4 .

Magnitude of the moment. As discussed in the Introduction, experimental measurements via neutron diffraction [5,28,30] and x-ray magnetic circular dichroism (XMCD) [35] on spinel vanadates report a small moment on the V atoms in all these compounds: $1.3\mu_B$ in MnV_2O_4 , $0.85\mu_B$ in FeV_2O_4 , and $0.9\mu_B$ in CoV_2O_4 . This moment is much smaller than $2\mu_B$, the expected value for a V^{3+} state. Furthermore, XMCD measurements performed on MnV_2O_4 and FeV_2O_4 reveal a very small value of the orbital moment [36], indicating the V moment is primarily spin in character [37], and so the cancellation of the spin moment by the orbital moment cannot be the reason behind this reduction in the moment. As far as

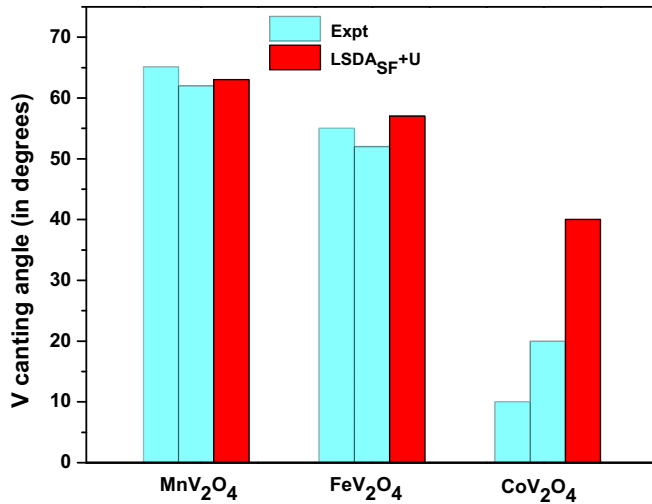


FIG. 2. Canting angle of V moments with respect to the c axis calculated with source-free LSDA+ U (red) and compared with the corresponding experimental values [5,26,27,30,33,34] (cyan) for MnV₂O₄, FeV₂O₄, and CoV₂O₄. The on-site Coulomb repulsion $U = 2.7$ eV on V atoms is used for all materials (for values of U on A-site atoms, see Table I). Note that employment of the standard LSDA functional results in a grossly wrong value of the canting angle of 0° which increases to 19° upon inclusion of the spin-orbit coupling term.

the moment on the A site is concerned, all experiments report a large moment [5,30,35,36].

In contradiction to these experiments, and in agreement with previous *ab initio* work [6,18], we find that DFT calculations performed using the LSDA and LSDA+ U functionals show a large moment on V atoms with a percentage deviation of up to 40% from experiment [see Fig. 3(a)]. Interestingly, there does not exist a value of U for which the correct moment on the V atoms can be obtained [see Fig. 3(b)]. Use of LSDA_{SF} and LSDA_{SF}+ U with $U = 2.7$ eV on the V atom d orbitals, the value of U that gives the correct spin texture, remarkably, also leads to the value of the V moment, in close agreement with experiments with the worst error being only a 2% deviation [see Fig. 3(a)]. The moment on the A site is well described by both the LSDA/LSDA+ U and their source-free counterparts (see Table I for the values of U on the A site). Thus the source-free LSDA+ U functional provides a complete description of the ground state of all three spinel vanadates with a single value of U for the V site in all three compounds.

A study of the magnitude of the V moment as a function of U on the V site, while keeping the U in the A site fixed, leads to a striking observation; an increase of U within LSDA+ U functional generates, as expected, an increased

on-site localization of charge and an increased local moment on the V atoms [see Fig. 3(b)]. A consequence of this is that there does not exist a value of U for which the correct value of the V moment is obtained. However, the V moment calculated by excluding the source term from the LSDA+ U functional shows exactly the opposite trend: The V moment *decreases* with U [see Fig. 3(c)]. This is a counterintuitive yet explainable trend—as the value of U increases, the source term in the XC magnetic field also increases. The removal of this source term then has a significant effect on the magnetization density, leading to an increase in the noncollinearity in the magnetization vector field. This highly noncollinear vector field, when integrated around an atomic site, leads to a decrease in the V moment as a function of increasing U . This suggests that in treating the magnetic ground state of strongly correlated materials within the LSDA+ U framework by varying U can alter the unphysical source term in \mathbf{B}_{XC} in an uncontrolled manner. These results indicate that the removal of the source term for the XC functional is crucial for treating strongly correlated materials.

Orbital ordering. Spinel vanadates are known to possess highly coupled spin and orbital degrees of freedom where the noncollinear magnetic state at low temperatures is often accompanied with orbital ordering [5,37]. Among the three materials studied in this work, two (MnV₂O₄ and FeV₂O₄) show orbital ordering at low temperatures, while one (CoV₂O₄) of them exhibits no structural transition or orbital ordering [27,28,38] with the orbital moment quenched [28,37] in all three. The question then arises if the source-free functional can capture this difference between the three studied materials. To investigate this we look at the V-atom projected partial density of states (DOS) (see Fig. 4) for all three materials. From these results it is clear that in the case of MnV₂O₄ and FeV₂O₄ there is an orbital order—the d_{xz} orbital is predominantly occupied at the V1 and V3 sites whereas the d_{yz} orbital is predominantly occupied at the V2 and V4 sites. In the case of CoV₂O₄, however, we see that all three t_{2g} orbitals are almost equally occupied, as expected in a cubic structure. So there is no orbital order in this case. The values of the calculated orbital moments at the V site are found to be small in all three materials, which is consistent with XMCD measurements [35,37] as well as previous DFT calculations [6,18]. In Table II we provide the calculated orbital moments at A sites. Thus the source-free LSDA+ U functional reproduces not only the low-temperature experimental spin texture but also the correct orbital moment and ordering.

In conclusion, we have explored the source-free LSDA+ U functional within DFT, with which we investigate the magnetic ground state for spinel vanadates AV_2O_4 ($A = \text{Mn, Fe, and Co}$). In doing so, we find that the well-known failure of

TABLE I. Magnetic moments (in μ_B) per A-site atom obtained using LSDA, LSDA+ U , and their source-free counterparts. The values of U used for the A site are given (in eV) in the parentheses and a $U = 2.7$ eV was applied to the d orbitals of the V atom.

Vanadate	Expt.	LSDA	LSDA _{SF}	LSDA+ U	LSDA _{SF} + U
MnV ₂ O ₄	4.2 [5], 4.11 [36]	4.02	3.98	4.11 ($U = 0$)	4.10 ($U = 0$)
FeV ₂ O ₄	4 [30]	3.22	3.15	3.42 ($U = 5$)	3.44 ($U = 5$)
CoV ₂ O ₄	2.46 [35]	2	2.08	2.45 ($U = 4$)	2.41 ($U = 4$)

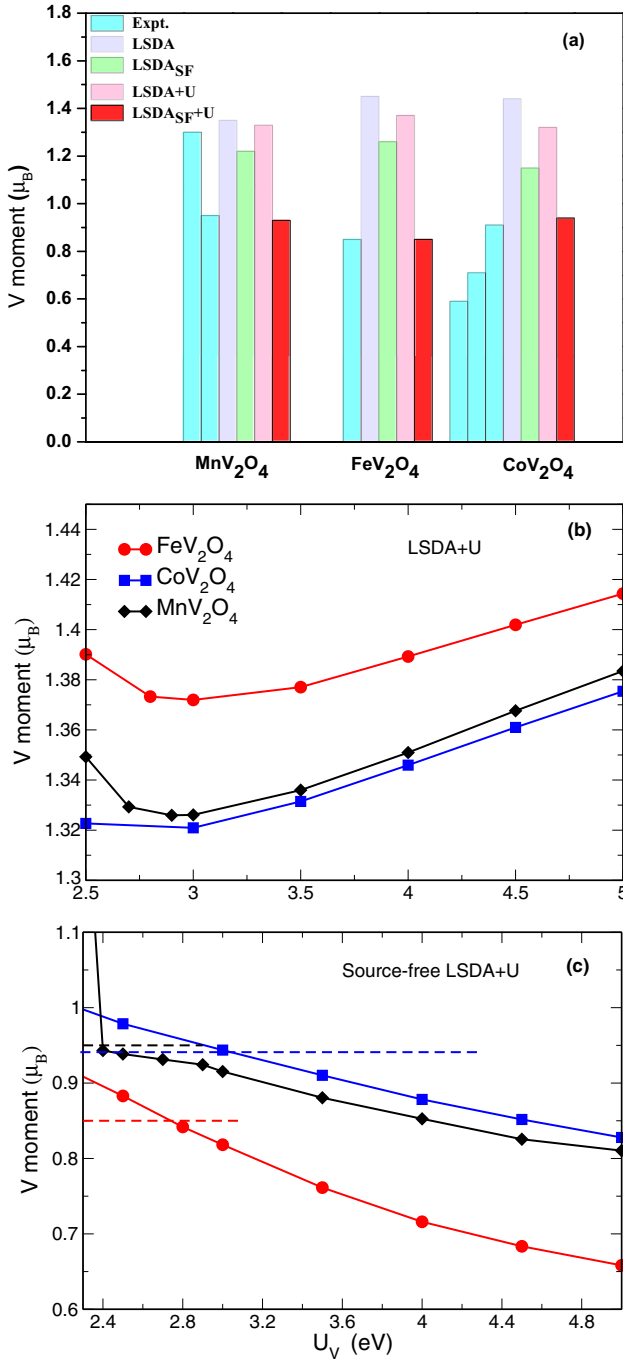


FIG. 3. (a) V magnetic moment calculated using LSDA (light blue), LSDA_{SF} (green), $\text{LSDA}+U$ (pink), and $\text{LSDA}+U_{\text{SF}}$ (red) compared with the corresponding experimental (cyan) values [5,26–28,30,35] for MnV_2O_4 , FeV_2O_4 , and CoV_2O_4 . The on-site Hubbard U parameter on V d orbitals is set equal to 2.7 eV and the value of U for A -site d orbitals is set equal to 0.0, 5.0, and 4.0 eV for Mn, Fe, and Co, respectively. Variation of total spin magnetic moment of V as a function of this on-site Hubbard U on V d orbitals using (b) $\text{LSDA}+U$ and (c) the source-free $\text{LSDA}+U$ functional. Horizontal dotted lines are the experimental data taken from Refs. [25,26,28]. The discontinuity in the moment as a function of U in the case of MnV_2O_4 is due to this metal-insulator transition at $U = 2.4$ eV.

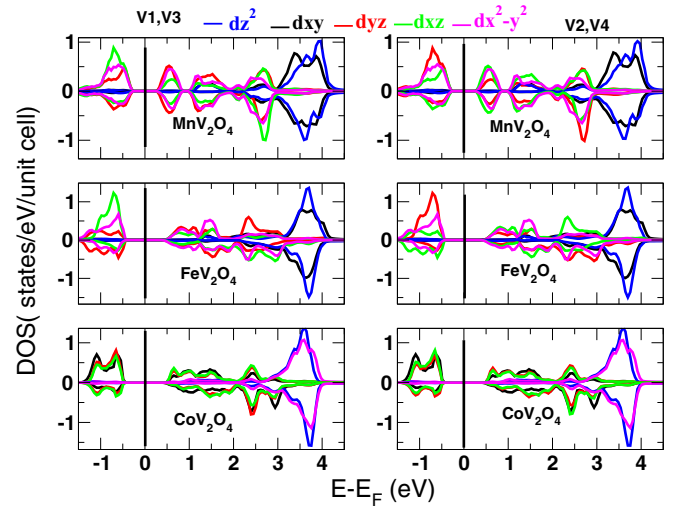


FIG. 4. The partial V-atom projected d density of states in MnV_2O_4 , FeV_2O_4 , and CoV_2O_4 calculated using source-free $\text{LSDA}_{\text{SF}}+U$ with $U = 2.7$ eV at the V site and $U = 0.0, 4.0,$ and 5.0 eV for Mn, Fe, and Co d orbitals, respectively. The left panel shows d DOS for V1 and V3 whereas the right panel for V2 and V4 atoms [see Fig. 1(b)]. Note that in the case of FeV_2O_4 and MnV_2O_4 , the crystallographic a and b axes are rotated by 45° with respect to the planar V-O bonds of VO_6 octahedra, making the set $[d_{x^2-y^2}, d_{xz}, \text{ and } d_{yz}]$ form d_{2g} rather than the conventionally used $[d_{xy}, d_{xz}, \text{ and } d_{yz}]$.

all traditional XC functionals (LSDA, GGA, $\text{LSDA}+U$, meta-GGA) to reproduce the experimentally observed magnitude of local moments and noncollinear spin texture arises from the presence of a large source term in the magnetic field generated by these functionals. Most strikingly, we find that this source term increases on increasing the value of U . We find by removing this unphysical source term from the $\text{LSDA}+U$ functional results in a perfect description of the ground-state magnetism of these materials. Most importantly, we find that for all three materials, for a fixed value of U on the A site, we needed the same value of U on the V site for this correct description, which is highly desirable as these materials are isostructural and electronically similar. This is a great improvement over the traditional $\text{LSDA}+U$ approach where there does not exist a value of U which gives the correct ground state for these materials. These results suggest that in treating strongly correlated magnetic materials within the $\text{LSDA}+U$ formalism, subtraction of the unphysical magnetic monopole term from the exchange correlation magnetic field is essential.

TABLE II. Orbital moments (in μ_B) per A -site atom obtained using $\text{LSDA}+U$ and $\text{LSDA}_{\text{SF}}+U$. The values of U applied to the A site are given (in eV) in the parentheses. $U = 2.7$ eV was used for the d orbitals on the V atom.

Vanadate	FeV_2O_4	MnV_2O_4	CoV_2O_4
$\text{LSDA}+U$	0.0175 ($U = 5$)	0.0032 ($U = 0$)	0.3032 ($U = 4$)
$\text{LSDA}_{\text{SF}}+U$	0.2396 ($U = 5$)	0.0053 ($U = 0$)	0.2877 ($U = 4$)

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