Investigation of electronic and magnetic ground state of a geometrically frustrated ZnV$_2$O$_4$ compound by using LDA+$U$ calculations

Sohan Lal and Sudhir K. Pandey

School of Engineering, Indian Institute of Technology Mandi,
Kamand 175005, Himachal Pradesh, India

(Dated: November 18, 2014)

Abstract

In the present work we investigate the applicability of LDA+$U$ method in understanding the electronic and magnetic properties of a geometrically frustrated ZnV$_2$O$_4$ compound where delicate balance of electron, lattice, orbital and spin interactions plays an important role in deciding its physical properties. In the ferromagnetic phase only one type of orbital solution is found to exist in all range of $U$ studied here. However, in the antiferromagnetic (AFM) phase two types of orbital solutions, AFM(OS1) and AFM(OS2), exist for $U \geq 4$ eV. If the difference of the electronic occupancy of $d_{xz}$ and $d_{yz}$ orbitals is less than 0.25 then AFM(OS1) solution is stabilized whereas for higher values AFM(OS2) solution is stabilized. The use of unconstrained calculation within the fully localized double counting scheme is unable to predict the AFM ground state for $U \leq 3$ eV. Our results clearly suggest the important of constrained calculations in understanding the electronic and magnetic properties of a compound where various competing interactions are present. In the AFM state the orbital ground state of the compound changes with varying $U$ where AFM(OS1) is found to be the ground state for $U \leq 3$ eV and for higher values of $U$, AFM(OS2) is the ground state. The analysis of the band gap suggests that the AFM(OS2) is the real ground state of the compound.

PACS numbers: 75.25.Dk, 71.20.-b, 71.27.+a
I. INTRODUCTION

Theoretically it has always been a challenging task to know the true ground state of a correlated electron system. The task becomes more daunting when the system possesses various competing interactions. The density functional theory (DFT) has been remain one of the prominent theoretical tool to study the ground state properties of various materials.\textsuperscript{1-4} The ground state properties of the metallic and semiconducting systems are normally described by considering local density approximation (LDA) or generalized gradient approximation (GGA) exchange correlation functional.\textsuperscript{5-7} For strongly correlated systems they are described by adding orbital dependent Hartree-Fock (HF) potential to the LDA/GGA functional which is known as LDA+U/GGA+U approximation.\textsuperscript{8-11} In this approximation one has to deal with the double counting (DC) of the correlated electrons. In this situation the best way is to identify and subtract the mean-field-part of the HF potential. Czyżyk and Sawatzky proposed a scheme that is applicable for the weakly correlated system which is known as around mean field (AMF) DC scheme.\textsuperscript{12} For strongly correlated systems AMF DC scheme may not be valid. In these systems one can prefer the fully localized (FL) DC scheme, where the average effect for localized states is subtracted with integer occupation number.\textsuperscript{9,11} It is also well known that LDA+U calculation often converge to the local minima and hence it may predict the wrong ground state of the system.\textsuperscript{13-16} In order to know the magnetic ground state of a system one has to compare the energy of various spin configurations. If no constraint is applied to the moments of the magnetic ions, it has normally been seen that the magnetic moment (MM) inside the muffin-tin sphere of ferromagnetic (FM) and antiferromagnetic (AFM) solutions are slightly different. In such a situation, a small change in the MM may predict the wrong ground state of the system where several kinds of competing interactions among various degrees of freedom play an important role in deciding its electronic and magnetic properties.

From above discussions it is clear that the normal LDA+U calculations are prone to predict the wrong ground state of the complex systems where various competing interactions are present. Spinel vanadates having general formula AV$_2$O$_4$ (A=Zn, Cd and Mg) are one such complex system which has attracted a great deal of attention for last 12 years.\textsuperscript{17-31} At room temperature magnetic V ions of these compounds form a geometrically frustrated pyrochlore lattice due to corner sharing tetrahedral network.\textsuperscript{17,18} The magnetically active V$^{3+}$
ions have two $3d$ electrons in $t_{2g}$ orbitals and form $S=1$ state, which are antiferromagnetically coupled to each other. These compounds undergo the structural and magnetic transitions from cubic to tetragonal and paramagnetic to antiferromagnetic, respectively at two different temperatures and show qualitatively similar structural and magnetic behavior\cite{18,21,26}. These structural and magnetic transitions observed in these compounds were intriguing for a long time as compounds with geometrically frustrated pyrochlore lattice normally do not show any structural and magnetic transitions. Because of the presence of 2 electrons in the $t_{2g}$ orbitals, V ions become Jahn-Teller active and hence one expects its effect on the structure. Many groups proposed that the orbital ordering is the key factor responsible for low temperature structural transitions observed in these compounds\cite{22,24,26,33}. Due to this structural transition geometrical frustration gets relaxed and hence these compounds show magnetic transitions. However, the non-coincidence of the structural and magnetic transitions also suggests the presence of certain degree of geometrical frustration in these compounds. The experimentally observed values of the magnetic moments in these compounds are found to be much smaller than the expected value of $2\mu_B$, which has been attributed either to the presence of large but negative value of orbital momentum or to the activeness of geometrical frustration\cite{21,27,30}. These discussions clearly show that the structural, electronic and magnetic properties of these compounds are decided by the complex interplay of the electronic, lattice, spin and orbital degrees of freedom.

Most of the theoretical studied carried out on these compounds are based on model calculations which are fully parameter dependent. There are very few LDA+$U$ based first principles studies available in the literature. In spite of the wide applicability of this method in studying the ground state properties of correlated electron system, there is no systematic studies available in the literature which show applicability of the LDA+$U$ in predicting the experimentally observed ground state of these complex oxides. In this work we have made such an attempt on ZnV$_2$O$_4$ which is the most studied compound among the spinel vanadates. The experimentally observed magnetic structure of ZnV$_2$O$_4$ is AFM. The crystal structure of the compound consists of edge sharing octahedra both along the $a$ and $b$-axes. Along these directions spins are antiferromagnetically aligned having sequences $\uparrow\downarrow\uparrow\downarrow$, whereas they are ferromagnetically aligned along $c$-axis\cite{21,26}. ZnV$_2$O$_4$ compound has insulating ground state with the band gap $\sim 0.32$ eV\cite{34}. It shows structural and magnetic transitions at $\sim 50$ and $40$ K, respectively\cite{17}. The experimentally observed magnetic moment
per V atom is found to be $\sim 0.63 \mu_B^{21}$. This is the most frustrated compound among the spinel vanadates with the frustration index of $\sim 21^{20}$.

Here we report the applicability of LDA+$U$ method in understanding the electronic and magnetic properties of ZnV$_2$O$_4$ compound. This work clearly suggests the inadequacy of the unconstrained LDA+$U$ calculations in predicting the AFM ground state for a wide range of $U$. The constrained LDA+$U$ calculations provide correct AFM ground state of the compound in all range of $U$ studied here. The FM calculations show only one type of orbital solution (OS1). In the AFM phase two types of orbital solutions, AFM(OS1) and AFM(OS2), exist for $U \geq 4$ eV and only AFM(OS1) is found to exist for $U \leq 3$ eV. The ground state of the compound with varying $U$ is found to depend on the values of the electronic occupancy difference of $d_{xz}$ and $d_{yz}$ orbitals ($|d_{xz}-d_{yz}|$). For $|d_{xz}-d_{yz}| < 0.25$, AFM(OS1) is the ground state and for higher values of $|d_{xz}-d_{yz}|$, AFM(OS2) becomes the ground state of the system. The comparison of the experimental band gap with the calculated one suggests that the AFM(OS2) is the true ground state of the compound.

II. COMPUTATIONAL DETAIL

The FM and AFM calculations of ZnV$_2$O$_4$ have been carried out by using the state-of-the-art full-potential linearized augmented plane wave (FP-LAPW) method.\cite{35} The calculations are carried out in the tetragonal phase. The lattice parameters and atomic positions are taken from the literature.\cite{21} Perdew -Wang/Ceperley -Alder exchange correlation functional is used in the calculation.\cite{7} The effect of on-site Coulomb interaction among V 3$d$ electrons is considered within LDA+$U$ formulation of the density functional theory.\cite{11} FL and AMF DC schemes have been considered in both FM and AFM calculations.\cite{9,12} In this method $U$ is used as a parameter. To explain the electronic and magnetic properties of the compound, we have varied $U$ from 0-6 eV. The muffin-tin sphere radii used in the calculations are 2.0, 2.0 and 1.54 Bohr for Zn, V and O, respectively. (6,6,6) k-point mesh size is used. Convergence target of total energy was achieved below $10^{-4}$ Hartrees/cell.
III. RESULT AND DISCUSSION

First of all we study the applicability of unconstrained LDA+U calculations in predicting the experimentally observed ground state of ZnV$_2$O$_4$ compound for a wide parameter range. The FM and AFM solutions corresponding to both DC schemes were obtained by varying $U$ from 0 to 6 eV where $U=0$ provides simple LDA solution. For both the DC schemes and for all values of $U$, only one type of orbital solution (OS) exists in the FM state of the compound. For $U \leq 3$ eV only one OS exists in the AFM state, which is similar to that observed in FM state. However, for $U \geq 4$ eV two type of OS exist which are denoted by OS1 and OS2. Here, OS1 is similar to that obtained in the FM state. From here onward AFM structure with two orbital solutions OS1 and OS2 are denoted by AFM(OS1) and AFM(OS2), respectively. The nature of both the orbital solutions is explained later in the manuscript. The unit cell of ZnV$_2$O$_4$ contains eight V atoms which are structurally equivalent as shown in the Fig. 1. However, all the eight V atoms are not orbitally equivalent. According to the orbital occupancy, these V atoms can be divided into two groups containing (V1,V2,V5,V6) and (V3,V4,V7,V8) atoms, and mainly occupying the $d_{xz}$ and $d_{yz}$ orbitals, respectively. In order to know the magnetic ground state of the compound we have compared the total energy of FM and AFM solutions for all values of $U$ studied here. The energy difference $\Delta E = E_{AFM} - E_{FM}$ corresponds to both the DC schemes with varying $U$ is plotted in Fig. 2, where $\Delta E_1 = E_{AFM(OS1)} - E_{FM}$ and $\Delta E_2 = E_{AFM(OS2)} - E_{FM}$.

It is evident from Fig. 2(a) that the ground state predicted by both the DC schemes is not consistent for $U=1-3$ eV as FL and AMF DC schemes give FM and AFM(OS1) ground state, respectively. Above $U=3$ eV both the DC schemes show FM ground state. Interestingly both the DC schemes provide AFM(OS2) ground state for $U \geq 4$ eV as evident from Fig. 2(b). Thus AFM(OS2) appears to be the true ground state of the compound for $U \geq 4$ eV. However, for $U=1-3$ eV FL DC scheme fails to provide correct magnetic ground state. Keeping the earlier report about the strength of on-site Coulomb interaction in mind one may come to the conclusion that FL DC scheme is not suitable for predicting the correct ground state of the compound. However, the careful analysis of the data suggests that the cause of this discrepancy lies in the unconstrained nature of the calculations which is clear from the following discussion. The MM per V atom of FM ($M_{FM}$) and AFM(OS1) ($M_{AFM(OS1)}$) solutions for FL DC scheme is shown in Table I for $U=1-6$ eV. It is clear from
the table that the values of \( M_{FM} \) and \( M_{AFM(OS1)} \) are different because of the unconstrained nature of the calculations. The difference between these two moments \( \Delta M_1 \) decreases from 0.178 to 0.06 \( \mu_B \) when \( U \) is increased from 1 to 6 eV. The value of \( \Delta M \) is \( >0.13 \mu_B \) for \( U \leq 3 \) eV. At this stage one may conjecture that the observed extra MM per V atom in FM solution as compared to AFM solution appears to responsible for making the total energy of the FM solution less than that of AFM for \( U=1-3 \) eV. At this point it is important to note that AMF DC scheme also provides similar values of \( \Delta M \) with varying \( U \). However, in spite of this discrepancy AMF DC scheme is able to predict the correct AFM ground state of the compound.

In order to verify the above conjecture, we have performed the constrained calculations where the magnitude of the MM of each V atoms is kept fixed for every type of solutions. The comparison of energy obtained from these calculations are shown in Fig. 3 where \( \Delta E_1= E_{AFM(OS1)}-E_{FM} \) and \( \Delta E_2= E_{AFM(OS2)}-E_{FM} \). It is clear from Fig. 3(a) that AMF DC scheme provides correct AFM ground state for all values of \( U \) studied here whereas FL DC scheme predicts AFM(OS1) ground state for \( U \leq 4 \) eV. Above \( U=4 \) eV, FL DC scheme gives FM ground state which is not as per experimental results. Interestingly, both the DC schemes predicts AFM(OS2) as a ground state which is evident from Fig. 3(b). These results clearly show the drastic improvement in predicting the AFM ground state of the compound when constraint on the magnetic moments of V atoms is invoked.

As mentioned above, for \( U \geq 4 \) eV, two orbital solutions OS1 and OS2 exit in the AFM phase of the compound. In order to know the true ground state of the compound for \( U \geq 4 \) eV we have calculated \( \Delta E=E_{AFM(OS2)}-E_{AFM(OS1)} \). The \( \Delta E \) vs \( U \) plot for both the DC schemes are shown in Fig. 4. This graph clearly shows that the AFM(OS2) is the true ground state of the compound as we got large but negative values of \( \Delta E \) for \( U \geq 4 \) eV. Moreover, \( \Delta E \) decreases continuously with increase in \( U \) from 4-6 eV. The decrease in the \( \Delta E \) with increasing \( U \) gives rise to more stability to the OS2 as compared to OS1. Thus present work clearly shows the capability of both the DC schemes in predicting the experimentally observed AFM ground state on invoking the constraint calculations. This work also suggests that for \( U \leq 3 \) eV AFM(OS1) is the ground state whereas for \( U \geq 4 \) eV AFM(OS2) is the true ground state of the system.

In order to know the nature of two orbital solutions OS1 and OS2 found in the AFM phase of the compound we have plotted the electron occupancy of \( d_{xz} \) and \( d_{yz} \) orbitals of
the orbitally equivalent V atoms (i.e. V1,V2,V5,V6) in Fig. 5 for both the DC schemes.

It is clear from the figure that in OS1 solution the occupancy of \(d_{xz}\) orbital is larger than that of \(d_{yz}\), whereas in OS2 solution the opposite behaviour is observed. Both the DC schemes provide almost the same value of orbital occupancy in OS1 solution. However, in OS2 solution FL DC scheme gives higher occupancy for \(d_{yz}\) orbital in comparison to AMF DC scheme. The occupancy of \(d_{xz}\) orbital is almost the same in both the DC schemes. The absolute value of electron occupancy difference between \(d_{xz}\) and \(d_{yz}\) orbitals (\(|d_{xz}-d_{yz}|\)) is also plotted in Fig. 5. In the OS1 solution the \(|d_{xz}-d_{yz}|\) shows non-monotonic behaviour for both the DC schemes where it first increases from \(\sim 0.19\) to \(\sim 0.23\) for \(U=1-3\) eV and then decreases at \(U=4\) eV. Above \(U=4\) eV, \(|d_{xz}-d_{yz}|\) again started increasing. In the case of OS2 solution, \(|d_{xz}-d_{yz}|\) increases monotonically. In FL (AMF) DC scheme, it increases from \(\sim 0.35\) (0.28) to \(\sim 0.39\) (0.39) for \(U=4-6\) eV. These results clearly show the discontinuous change in the value of \(|d_{xz}-d_{yz}|\) at \(U=4\) eV where the ground state of the system changes from AFM(OS1) to AFM(OS2) with varying \(U\). This point has been made more clear in Fig. 6 where we have shown \(|d_{xz}-d_{yz}|\) with varying \(U\). This figure suggests the stabilization of AFM(OS1) ground state for \(|d_{xz}-d_{yz}|<0.25\) and for higher values AFM(OS2) ground state is stabilized.

Now we discuss the possible reason for the existence of two orbital solutions for \(U \geq 4\) eV in AFM phase of the compound. The electron occupancies of \(d\), \(d_{\uparrow}\), and \(d_{\downarrow}\) orbitals along with the MM of the V atoms are shown in Table II. First of all we consider OS1 solution. It is evident from the table that the total number of \(d\) electrons show small \(U\) dependence within FL DC scheme as its value decreases from 2.48 to 2.42 with increasing \(U\) whereas AMF DC scheme do not provide any \(U\) dependence to the total number of \(d\) electrons. Within FL DC scheme, the number of \(d_{\uparrow}\) (\(d_{\downarrow}\)) increases (decreases) from 1.94 to 2.02 (0.54 to 0.40) for \(U=1\) to 6 eV. Hence MM increases from 1.40 to 1.62 \(\mu_B\) when \(U\) increases from 1 to 6 eV. However, \(d_{\uparrow}\) and \(d_{\downarrow}\) electrons do not show much \(U\) dependence within the AMF DC scheme and hence MM remains almost the same, which is \(\sim 1.37\) \(\mu_B\). In OS2 solution, the FL DC scheme shows a slight \(U\) dependence to the total number of \(d\), \(d_{\uparrow}\), and \(d_{\downarrow}\) electrons, which leads to the increment of MM from 1.61 to 1.66 \(\mu_B\) when \(U\) increases from 4 to 6 eV. The AMF DC scheme does not show any \(U\) dependence to the total number of \(d\) electrons. However, the number of \(d_{\uparrow}\) and \(d_{\downarrow}\) electrons show small \(U\) dependence and leading to the increment of MM from 1.44 to 1.51 \(\mu_B\) as \(U\) increases from 4 to 6 eV. On comparing the
MM of both the solutions on can find that the MM of OS2 solution is always more than that of the OS1 solution. As mentioned earlier in the manuscript, such a small difference in the MM of two solutions may lead to difference in their energy. Thus at this stage one may attribute the negative value of $\Delta E$ in Fig. 4 to the higher value of MM for the OS2 solution, who may further raise the doubt about AFM(OS2) as a true ground state of the compound at higher $U$. In order to address this doubt we have carried out the constrained calculations where the magnitude of MM of V atoms is kept the same in both the cases. The results thus obtained show that the energy of AFM(OS2) is always less than that of AFM(OS1) for all values of $U$ and for both the DC schemes. Thus this work clearly suggests that the AFM(OS2) is the true ground state of the compound for $U \geq 4$ eV. These results also suggest that the reason for the existence of two orbital solutions at higher $U$ appears to be due to the existence of two orbital states with respect to the AFM ordering as explained above.

Finally we discuss the dependence of ground state insulating gap on various parameters studied here. Both the DC schemes shows similar $U$ dependence gap in AFM(OS1) ground state. At $U=1$ eV, the compound shows metallic gap. At $U=2$ eV a small gap of $\sim 0.06$ eV is opened up, which increases to $\sim 0.09$ eV at $U=3$ eV. It is important to note that the experimentally observed insulating gap of the compound is $\sim 0.32$ eV, which is much larger than the highest gap obtained in AFM(OS1) solution. Thus AFM(OS1) does not appear to be the ground state of the compound as the value of $U$ required to open up the experimental band gap will be higher than 3 eV. In the AFM(OS2) ground state, both the DC schemes show different $U$ dependence band gap. At $U=4$ eV, FL DC scheme shows a band gap of $\sim 0.36$ eV whereas AMF DC schemes fails to create any hard gap. At $U=5$ eV, AMF DC scheme creates a hard gap of $\sim 0.51$ eV, which increases to 0.93 eV at $U=6$ eV. The value of band gap within FL DC scheme increases from $\sim 0.96$ to 1.5 eV when the value of $U$ changes from 5 to 6 eV. On comparing the calculated band gap with the experimental one we can conclude that the AFM(OS2) is the real ground state of the compound and the value of $U$ for this compound is expected to be $\sim 4$ eV. This value of $U$ appears to make sense in the light of the work of Canosa et al. where $d$ electrons of ZnV$_2$O$_4$ compound is put in the intermediate localization range.
IV. CONCLUSIONS

In summary, we have studied the applicability of LDA+$U$ method in understanding the electronic and magnetic properties of a complex system, where several types of competing interactions among electron, spin, orbital and lattice degrees of freedom exist, by considering ZnV$_2$O$_4$ compound as a case study. Our work clearly suggests that the unconstrained LDA+$U$ calculations are not the correct methods for predicting the exact electronic and magnetic ground states of such systems. It is suggested that the constrained LDA+$U$ calculations should be preferred if one wants to predict the real magnetic ground state of an unknown complex system as small change in the magnetic moments of magnetic atoms in various spin configurations may lead to the prediction of wrong ground state of the compound. The present study on ZnV$_2$O$_4$ compound shows the existence of only one type of orbital solution in ferromagnetic phase. However, in the antiferromagnetic phase two kinds of orbital solutions, AFM(OS1) and AFM(OS2), exist for $U\geq 4$ eV and only AFM(OS1) is found to exist for $U \leq 3$ eV. The ground state of the compound changes from AFM(OS1) to AFM(OS2) with varying $U$, which is related to the discontinuous change in the electronic occupancy difference of $d_{xz}$ and $d_{yz}$ orbitals ($|d_{xz}-d_{yz}|$). Such change in the ground state occurs around $U=3$ eV. The detailed analysis of the $U$ dependent band gaps suggests that the AFM(OS2) is the true ground state of the compound.

ACKNOWLEDGMENTS

S.L. is thankful to UGC, India, for financial support.

* Electronic mail:goluthakur2007@gmail.com
† Electronic mail:sudhir@iitmandi.ac.in

1 Theory of the Inhomogeneous Electron Gas, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

2 G. D. Mahan and K. R. Subbaswamy, Local Density Theory of Polarizability (Plenum, New York, 1990).
3 R. M. Martin, *Electronic Structure Basic Theory and Practical Methods* (Cambridge University Press, 2004).

4 D. J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials, and the LAPW Method* (Springer, 2006).

5 J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 23 (1992).

6 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. **77**, 18 (1996).

7 J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O.A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, Phys. Rev. Lett. **100**, 136406 (2008).

8 V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyżyk and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).

9 A. I. Liechtenstein, V. I. Anisimov and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).

10 I. V. Solovyev, A. I. Liechtenstein and K. Terakura, Phys. Rev. Lett. **80**, 5758 (1998).

11 F. Bultmark, F. Cricchio, O. Gränäs and L. Nordstrom, Phys. Rev. B **80**, 035121 (2009).

12 M. T. Czyżyk and G. A. Sawatzky, Phys. Rev. B **49**, 14211 (1994).

13 M. A. Korotin, S. Yu. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomskii and G. A. Sawatzky, Phys. Rev. B **54**, 5309 (1996).

14 K. Knížek, Z. Jiráek, J. Hejtmánek and P. Novák, J. Phys.: Condens. Matter **18**, 3285 (2006).

15 B. Dorado, B. Amadon, M. Freyss, and M. Bertolus, Phys. Rev. B **79**, 235125 (2009).

16 S. K. Pandey, Phys. Rev. B **81**, 035114 (2010).

17 S. -H. Lee, D. Louca, H. Ueda, S. Park, T. J. Sato, M. Isobe, Y. Ueda, S. Rosenkranz, P. Zschack, J. Íñiguez, Y. Qiu and R. Osborn, Phys. Rev. Lett. **93**, 156407 (2004).

18 H. Mamiya, M. Onoda, T. Furubayashi, J. Tang, and I. Nakatani, J. Appl. Phys. **81**, 5289 (1997).

19 N. Nishiguchi and M. Onoda, J. Phys: Condens. Matter **14**, L551 (2002).

20 M. Onoda and J. Hasegawa, J. Phys. Condens. Matter **15**, L95 (2003).

21 M. Reehuis, A. Krimmel, N. Büttgen, A. Loidl and A. Prokofiev, Eur. Phys. J. B **35**, 311 (2003).

22 H. Tsunetsugu and Y. Motome, Phys. Rev. B **68**, 060405(R) (2003).

23 Y. Motome and H. Tsunetsugu, Phys. Rev. B **70**, 184427 (2004).

24 O. Tchernyshyov, Phys. Rev. Lett. **93**, 157206 (2004).

25 S. Di Matteo, G. Jackeli, and N. B. Perkins, Phys. Rev. B **72**, 020408(R) (2005).

26 P. G. Radaelli, New J. Phys. **7**, 53 (2005).
27 T. Maitra and R. Valentí, Phys. Rev. Lett. 99, 126401 (2007).

28 E. M. Wheeler, B. Lake, A. T. M. N. Islam, M. Reehuis, P. Steffens, T. Guidi, and A. H. Hill, Phys. Rev. B 82, 140406(R) (2010).

29 S. K. Pandey, Phys. Rev. B 84, 094407 (2011).

30 S. K. Pandey, Phys. Rev. B 86, 085103 (2012).

31 S. Lal and S. K. Pandey, Eur. Phys. J. B 87, 197 (2014).

32 T. Suzuki, M. Katsumura, K. Taniguchi, T. Arima and T. Katsufuji, Phys. Rev. Lett. 98, 127203 (2007).

33 Y. Huang, L. Pi, S. Tan, Z. Yang and Y. Zhang, J. Phys: Condens. Matter 24, 056001 (2012).

34 D. B. Rogers, R. J. Arnott, A. Wold and J. B. Goodenough, J. Phys. Chem. Solids 24, 347 (1963).

35 http://elk.sourceforge.net.

36 S. B. Canosa, F. Rivadulla, V. Pardo, D. Baldomir, J. -S. Zhou, M. G -Hernández, M. A. L. -Quintela, J. Rivas and J. B. Goodenough, Phys. Rev. Lett. 99, 187201 (2007).
TABLE I. The magnetic moment per vanadium atom of ferromagnetic ($M_{FM}$) and antiferromagnetic OS1 ($M_{AFM(OS1)}$) solutions along with the change in magnetic moment ($\Delta M_1$) of both solutions for fully localized double counting scheme within unconstrained LDA+$U$ calculations for $U=1$-6 eV.

| $U$ (eV) | $M_{FM}(\mu_B)$ | $M_{AFM(OS1)}(\mu_B)$ | $\Delta M_1(\mu_B)$ |
|---------|-----------------|------------------------|---------------------|
| 1       | 1.589           | 1.411                  | 0.178               |
| 2       | 1.641           | 1.475                  | 0.166               |
| 3       | 1.659           | 1.527                  | 0.132               |
| 4       | 1.678           | 1.575                  | 0.103               |
| 5       | 1.690           | 1.609                  | 0.081               |
| 6       | 1.699           | 1.639                  | 0.060               |

TABLE II. Total number of $d$, $d_{\uparrow}$ and $d_{\downarrow}$ electrons along with the magnetic moment per V atom of orbitally equivalent V atoms (i.e. V1,V2,V5,V6) for AFM(OS1) and AFM(OS2) solutions with varying $U$ for fully localized and around mean field (in brackets) double counting schemes.

| $U$ (eV) | AFM(OS1) | AFM(OS2) |
|----------|----------|----------|
| 1        | $d=2.48(2.49)$ | $d_{\uparrow}=1.94(1.92)$ | $d_{\downarrow}=0.54(0.57)$ | $M(\mu_B)=1.40(1.35)$ | $d_{\uparrow}$ | $d_{\downarrow}$ | $M(\mu_B)$ |
| 2        | $d=2.47(2.49)$ | $d_{\uparrow}=1.97(1.92)$ | $d_{\downarrow}=0.50(0.56)$ | $M(\mu_B)=1.47(1.36)$ | $d_{\uparrow}$ | $d_{\downarrow}$ | $M(\mu_B)$ |
| 3        | $d=2.46(2.49)$ | $d_{\uparrow}=1.99(1.93)$ | $d_{\downarrow}=0.47(0.56)$ | $M(\mu_B)=1.52(1.37)$ | $d_{\uparrow}$ | $d_{\downarrow}$ | $M(\mu_B)$ |
| 4        | $d=2.45(2.49)$ | $d_{\uparrow}=2.00(1.93)$ | $d_{\downarrow}=0.44(0.56)$ | $M(\mu_B)=1.56(1.37)$ | $d_{\uparrow}=2.46(2.50)$ | $d_{\downarrow}=2.03(1.97)$ | $M(\mu_B)=0.42(0.53)$ |
| 5        | $d=2.44(2.49)$ | $d_{\uparrow}=2.02(1.93)$ | $d_{\downarrow}=0.42(0.56)$ | $M(\mu_B)=1.60(1.37)$ | $d_{\uparrow}=2.44(2.50)$ | $d_{\downarrow}=2.04(2.00)$ | $M(\mu_B)=0.40(0.50)$ |
| 6        | $d=2.42(2.49)$ | $d_{\uparrow}=2.02(1.93)$ | $d_{\downarrow}=0.40(0.56)$ | $M(\mu_B)=1.62(1.37)$ | $d_{\uparrow}=2.43(2.50)$ | $d_{\downarrow}=2.04(2.00)$ | $M(\mu_B)=0.38(0.49)$ |

VI. FIGURES
FIG. 1. Atomic arrangement of structurally equivalent eight V atoms in the unit cell. The orbitally equivalent atoms (V1,V2,V5,V6) and (V3,V4,V7,V8) are mainly occupied by $d_{xz}$ and $d_{yz}$ orbitals, respectively.
FIG. 2. The total energy difference between antiferromagnetic and ferromagnetic ($\Delta E = E_{\text{AFM}} - E_{\text{FM}}$) solutions per formula unit corresponding to fully localized (FL) and around mean field (AMF) double counting (DC) schemes as a function of $U$ within unconstrained LDA+$U$ calculations for both orbital solutions AFM(OS1) and AFM(OS2) denoted as (a) $\Delta E_1 = E_{\text{AFM(OS1)}} - E_{\text{FM}}$ (b) $\Delta E_2 = E_{\text{AFM(OS2)}} - E_{\text{FM}}$. 
FIG. 3. The total energy difference between antiferromagnetic and ferromagnetic ($\Delta E=E_{AFM}-E_{FM}$) solutions per formula unit corresponding to fully localized (FL) and around mean field (AMF) double counting (DC) schemes as a function of $U$ within constrained LDA+$U$ calculations for both orbital solutions AFM(OS1) and AFM(OS2) denoted as (a) $\Delta E_1=E_{AFM(OS1)}-E_{FM}$ (b) $\Delta E_2=E_{AFM(OS2)}-E_{FM}$. 
FIG. 4. The total energy difference between solutions AFM(OS2) and AFM(OS1) 
($\Delta E = E_{AFM(OS2)} - E_{AFM(OS1)}$) for fully localized (FL) and around mean field (AFM) double counting (DC) schemes within constrained LDA+$U$ calculations for $U \geq 4$ eV.
FIG. 5. The electron occupancy of $d_{xz}$ and $d_{yz}$ orbitals of the orbitally equivalent V atoms (i.e. V1, V2, V5, V6) for solutions AFM(OS1) and AFM(OS2) as a function of $U$ within constrained LDA+$U$ calculations. Figures (a, b) and (c, d) corresponding to fully localized (FL) and around mean field (AMF) double counting (DC) schemes, respectively.
FIG. 6. The difference of the electronic occupancy of $d_{xz}$ and $d_{yz}$ orbitals ($|d_{xz}-d_{yz}|$) of the orbitally equivalent V atoms (i.e. V1, V2, V5, V6) for AFM(OS1) and AFM(OS2) solutions with varying $U$ for fully localized (FL) and around mean field (AMF) double counting (DC) schemes.