Orbital ordering in the geometrically frustrated $\text{MgV}_2\text{O}_4$: Ab initio electronic structure calculation

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I. INTRODUCTION

The orbital degree of freedom is an important entity in the condensed matter physics which plays a crucial role in stabilizing many exotic phases observed in the strongly correlated electron systems. When the degenerate $d$ orbitals of the transition metals are partially filled then occupation of a particular orbital at a particular site is expected to be dictated by the occupation of another orbital at another site, which can lead to various kind of orbital ordering (OO) similar to the spin ordering. For example, in the case of LaMnO$_3$ degenerate $e_g$ orbitals are occupied by only one electron and predicted to show antiferro-orbital ordering (AFOO) in the $xy$ plane in 1955 by Goodenough. The Coulomb correlation is found to play an important role in the orbital physics of transition metal oxides. However, it is still not clear whether it just enhances the effect of lattice distortions or really drives the OO via superexchange. In spite of the ambiguity about the exact mechanism behind the OO, it is almost clear that such OO is often accompanied by reduction in the crystal symmetry. Thus in the geometrically frustrated system OO is expected to relax the frustration leading to the formation of novel magnetic phases earlier forbidden by the frustration.

Spinel vanadates with general formula AV$_2$O$_4$ (A=Cd, Mg, and Zn) is an important geometrically frustrated system which has attracted a great deal of attention for a decade because of OO induced structural transition and formation of fascinating magnetic phases. All the studied compounds show cubic to tetragonal transition at low temperature and paramagnetic (PM) to AFM transition at slightly lower temperature. The consensus is emerging among the researchers regarding the OO in the present work we would like to address these issues for MgV$_2$O$_4$ (MVO). The recent experimental work on this compound has shown quite different results in comparison to the well studied ZnV$_2$O$_4$ (ZVO). In the tetragonal phase space group of MVO is $\bar{I}4/m2$ whereas that of ZVO is $I4_1/amd$. The magnetic moment (MM) of V ion in MVO is $0.47 \mu_B$ which is $0.15 \mu_B$ less than that in ZVO. Such a reduced value of MM in ZVO is due to large but negative contribution from the orbital part of MM. However, experimental data of MVO do not suggest such a large contribution from the orbital part and indicating to a weaker reason for observed small MM. Moreover, the MM is also seen to make an angle of $8^\circ$ with the $z$-axis indicating to a weak SOC in MVO compound.

Here we explore the role played by spin and orbital degrees of freedom in deciding the electronic and magnetic properties of MVO by using ab initio electronic structure calculations. The AFM interaction in the presence of strong Coulomb correlation is found to be crucial in driving the system to insulating ground state. The $d_{xz}$ and $d_{yz}$ orbitals get ordered in the tetragonal phase and OO becomes more robust in the presence of AFM interaction. The spin and orbital part of MM is found to: $1.4 \mu_B$ and $0.2 \mu_B$, respectively. The light of this result and in the presence of large exchange coupling of $58$ meV one can suggest that the geometrical frustration may be responsible for the experimentally observed low AFM transition temperature ($42$ K) and small MM ($0.47 \mu_B$).

II. COMPUTATIONAL DETAILS

The non-magnetic (NM), ferromagnetic (FM), and AFM solutions of MVO are obtained by using state-of-the-art full-potential linearized augmented plane wave (FP-LAPW) method. The lattice parameters and atomic positions used in the calculations are taken from the literature. The muffin-tin sphere radii automatically set in the calculations are 1.5664, 1.7045, and 1.4943 Bohr for Mg, V, and O atoms, respectively. For the ex-
change correlation functional, we have adopted recently
developed generalized gradient approximation (GGA)
form of Perdew et al. The effect of on-site Coulomb in-
teraction is also considered within GGA+U formulation
of the density functional theory. In GGA+U method
the U and J are used as parameters. We varied U from
3-5 eV and fixed J=0.5 eV. We found similar results for
all values of U. The results correspond to U=4 eV are
only discussed in the manuscript. In order to see the role
of orbital degrees of freedom on the electronic and mag-
netic properties of the compound SOC is also considered
in the calculations. The self-consistency was achieved
by demanding the convergence of the total energy to be
smaller than 10^{-4} Hartree/cell.

III. RESULTS AND DISCUSSIONS

The atomic arrangements in the unit cell are shown in
Fig. 1. It is evident from Fig. 1(a) that each V atom
is surrounded by six O atoms forming an octahedron.
The octahedra are edge shared to each other. The small
drional distortion splits six V-O bonds of an octahedron
in two groups containing three bonds each with bond
length of 2.016 and 2.033 Å. The four nearby V atoms
form a regular tetrahedron with an edge of length 2.98 Å.
Each of the tetrahedron is surrounded by four neighbor-
ing tetrahedra via corner sharing and forming the chains
of V atoms, see Fig. 1(b). In the tetragonal phase the
tetrahedra become distorted with the V-V bond length
of 2.971 and 2.980 Å. Such a small distortion would re-
duce the geometrical frustration and is expected to give
rise to novel electronic and magnetic phases.

In order to know the exact ground state of the com-
ound we obtained various magnetic solutions using
tetragonal structure. The total density of states (TDOS)
correspond to these solutions are shown in Fig. 2. It is
clear from Figs. 2(a)-(d) that the GGA solutions provide
metallic state as opposed experimentally observed insu-
lating behavior. This result is not surprising as the GGA
underestimates the Coulomb correlation among the 3d
electrons which is often found to be responsible for
insulating ground state of the transition metal oxides.
The NM and FM solutions obtained from GGA+U cal-
culations also provide metallic state as evident from Figs.
2(e) and (f). This indicates that there may be a deeper
reason for the insulating ground state of the system. At
this juncture, it is important to note that the FM solu-
tion of ZVO within LSDA+U is found to derive insulating
ground state of the compound in order to know
the exact cause for insulating ground state of MVO we
performed AFM calculations. The AFM solution creates
a soft gap and in presence of SOC it provides a hard gap
of ~0.16 eV, see Figs. 2(g) and (h). It is important to
note that the increased value of U enhances the band
gap in both the cases. Thus present work clearly estab-
lishes that the AFM coupling of V moments in presence
of strong on-site Coulomb interaction is responsible for
insulating ground state and SOC provides robustness to
the insulating property of the compound.

Now we discuss the effect of different interaction pa-
rameters on the electronic structure of the compound.
First we start with GGA results. In the absence of mag-
netic interaction there are large density of states (DOS)
at the Fermi level (\(\epsilon_F\)) with dominating contribution
from the V 3d states. This may be considered as a signa-
ture of magnetic ground state under Stoner theory. The
magnetic interaction reduces the DOS at \(\epsilon_F\) by ~50% due
to exchange splitting of the bands contributing at the \(\epsilon_F\)
and providing almost half-metallic state, see Fig. 2(b).
Moreover, the energy of FM solution is found to be ~0.65
eV/fu less than that of NM solution indicating the magnetic ground state. The energy difference
between the band edge of the up and down spins
may be considered as a measure of exchange interaction
which is found to be ~0.4 eV. The MM of V is found to
be ~1.25 \(\mu_B\). Interestingly, FM interaction induces finite
MM (~0.14 \(\mu_B\)) at the Mg ions occupying \(2c\) (01/2,1/4)
Wyckoff sites. The total MM/fu comes out to be ~3.6
\(\mu_B\), which corresponds to \(S\approx\pm 1\) state of the \(V^{3+}\) ion. It is
evident from Fig. 2(c) that the AFM interaction among
the V moments reduces the DOS at \(\epsilon_F\) drastically
(~4 times less than that of FM). The \(\epsilon_F\) lies at the min-
ima of DOS which is a reminiscence of the pseudo-gap.
The AFM interaction reduces the band width (BW) of
the system and the BW of the deeper bands decreases by
~0.3 eV. Further, it decreases the MM of V by ~0.1 \(\mu_B\)
and does not create any MM at Mg sites. The energy/fu
of the AFM solution is ~0.16 eV less than that of FM so-
lution. This is a clear evidence of the AFM ground state
whose spin ordering will be discussed in the later part of
the manuscript. The inclusion of SOC at this stage does
not have any significant effect on the electronic structure
of the compound as evident from Fig. 2(d). By com-
paring the energy of the AFM and AFM+SOC solutions
one can get the rough estimate of SOC strength of V 3d
electron as the contribution from Mg and O atoms is ex-
pected to be negligibly small. Our GGA calculation gives
the strength of SOC of ~5 meV for the V 3d electrons.

Figs. 2(e)-(h) depict the effect of on-site Coulomb in-
teraction among the V 3d electrons on the electronic
properties of the compound in the presence of various
interaction parameters. On-site Coulomb correlation re-
duces the BW as it localizes the electrons. In the case of
NM and FM solutions there is a drastic decrease in the
V 3d DOS at the \(\epsilon_F\) due to transfer of spectral weight
(earlier contributing at \(\epsilon_F\)) away from it. Moreover, FM
interaction gives rise to a perfectly half-metallic state
with a band gap of ~2.5 eV in the down-spin channel.
In the presence of AFM interaction among the V spins
the system becomes insulating due to formation of upper
and lower Hubbard bands. Further, inclusion of SOC in-
creases the separation between upper and lower Hubbard
bands. The exchange interaction estimated from the FM
solution is ~0.5 eV which is 0.1 eV more that that ob-
tained from simple GGA calculation. This enhancement
is attributed to increased Hund’s coupling strength due to increased spatial localization of V 3d electrons, which also enhances the MM at V sites by ∼0.2 μB. The total MM/fu comes out to be 4 μB, which corresponds to S=1 state of the V^{3+} ion. Such a large value of magnetic moment at V site is in sharp contradiction with the experimentally observed small magnetic moment.\(^\text{12}\) This clearly indicates that some other parameters are playing important role in deciding the magnetic properties of the compound. On comparing the energy of various solutions we find that the AFM state is the true ground state of the system as energy of NM>FM>AFM.

In order to study the role of orbital degrees of freedom we have performed FM GGA+U calculations in both cubic and tetragonal phases. In the cubic phase the occupancies of \(d_{xz}\) and \(d_{yz}\) orbitals are same at every V sites, whereas for the tetragonal phase the occupancies of these orbitals are found to be different at different site which is a direct evidence of OO taking place in the tetragonal structure. Moreover, the OO pattern does not depend on the nature of magnetic interaction as evident from Table 1 where we have listed the occupancy of \(d_{x^2-y^2}\), \(d_{xz}\), and \(d_{yz}\) orbitals of four V atoms forming the tetrahedron and obtained from FM and AFM solutions. It is evident from the table that each site is occupied by \(d_{x^2-y^2}\) orbital. The V1 and V2 sites are mainly occupied by \(d_{xz}\) orbital and that of V3 and V4 sites by \(d_{yz}\). At this juncture it is important to note that OO is observed in the PM phase of the spinel vanadates and in the FM phase there is a local MM at the V site and hence magnetic solutions would provide the better representation of the PM state in comparison to NM solution. Table 1 also indicates the AFM coupling between V1 and V2 (V3 and V4) and FM coupling between V1 and V4 (V2 and V3). Interestingly, AFM interaction appears to provide more stability to the OO as the occupancy of \(d_{yz}\) orbital at V1 and V2 (V3 and V4) sites is found to decrease by ∼0.08. Moreover the energy/fu of AFM solution is also ∼0.24 eV less than that of FM solution suggesting the AFM ground state. This energy difference between AFM and FM solutions is ∼80 meV less than that obtained from GGA solution. This highlights the importance of Coulomb correlation in establishing the AFM ground state. The MM of vanadium ions corresponds to FM and AFM solutions are found to be ∼1.43 and 1.35 μB, respectively.

As mentioned in the introduction that the OO is normally considered as a cause for the structural transition in the PM phase of spinel vanadates. However, based on present work it is difficult to say whether OO is the cause of structural transition or it is just an effect of it. In order to understand the cause of OO seen in different transition metal oxides mainly two mechanism exist in the literature which are purely electronic and structural in origin.\(^\text{12,13}\) To separate out these two contributions to the OO, Pavarini et al. have carried out beautiful work on two canonical OO systems viz. KCuF\(_3\) and LaMnO\(_3\), where they have used LDA+DMFT method.\(^\text{14}\) It is important to note that GGA+U method used in the present work is a static mean-field theory whereas LDA+DMFT used in the work of Pavarini et al. is a dynamical mean-field theory and hence better in approximation. Thus in order to know the exact cause of OO in the MVO compound work in line with Pavarini et al. is desirable.

Now we study the effect of SOC on the magnetic state of the compound. The GGA+U+SOC solutions also give AFM ground state as the energy/fu of AFM solution is found to be ∼0.18 eV less than that of FM solution. As mention above the AFM interaction provides more stability to the OO which further enhances the orbital moment as evident from Table 2 where we have shown the spin (\(S\)), orbital (\(L\)) and total (\(J\)) moment of the V ion corresponds to FM and AFM solutions. The orbital part of MM in the AFM state comes out to be ∼0.2 μB which is ∼7 times less than the spin part of MM suggesting the weak SOC in MVO with respect to ZVO where large orbital moment of -0.75 μB has been reported. The direction of total MM is found to be ∼11.3° away from the z-axis. The small value of orbital moment and the direction of total magnetic moment are in consonance with the experimental findings where neutron scattering studies have revealed the small orbital moment and MM tilted at ∼8° from the z-axis.\(^\text{15}\) However, the above calculated values of spin and orbital moments cannot account for the experimentally observed magnetic moment of 0.47 μB. At this point it is important to note that the experimentally estimated magnetic moment of 0.63 μB for ZVO is well accounted by taking into account the calculated large but negative orbital moment of -0.75 μB.\(^\text{16}\) This indicates that the orbital sector of the MVO is not as influential as found in the ZVO in deciding the magnetic state of the V ions. Thus there may be a deeper reason for the experimentally observed small magnetic moment in the MVO which will be discussed in the next paragraph. The final spin and orbital ordering patterns obtained from the calculations are shown in Fig. 3. The spins are forming AFM chains in the \(x\) and \(y\) directions and nearest neighbor AFM chains are connected by lines with FM ordering. The AFM chains are accompanied by ferro-orbital ordering (FOO) where \(d_{xz}\) and \(d_{yz}\) orbitals are occupied along the \(x\) and \(y\) directions, respectively. The AFOO supports the formation of FM chains where neighboring sites are alternatively occupied by \(d_{xz}\) and \(d_{yz}\) orbitals. These spin and orbital ordering patterns are in accordance with the Goodenough-Kanamori schemes. Here it is important to note that historically Goodenough has given the semi-covalent scheme for explaining the experimentally observed complex magnetic structures in La\(_{1-x}\)Ca\(_x\)MnO\(_3\) and predicted different OO corresponds to different spin arrangements.\(^\text{2}\) According to this scheme length of FM bond should be greater than that of AFM bond. However, we have observed opposite behavior as AFM bond is 0.03 Å larger than the FM bonds.

As mentioned above that the calculated small orbital moment of -0.2 μB for MVO cannot account for the experimentally observed value of total MM ∼0.47 μB,
whereas calculated large orbital moment of -0.75 $\mu_B$ for ZVO provides a good description of its experimentally observed total MM of 0.63 $\mu_B$. These results appear to suggest that the geometrical frustration is still active in the tetragonal phase of MVO which can give rise to spin fluctuation at low temperature. Such spin fluctuation is expected to reduce the MM drastically. The level of frustration in magnetic systems is defined by frustration index $f \equiv |\theta_{CW}|/T^*$, where $\theta_{CW}$ is the Curie-Weiss temperature and $T^*$ is the critical temperature at which the system ultimately develops long-range spin order. Higher the value of $f$ more will be the level of frustration. Thus the above conjecture about the activeness of frustration can further be tested by estimating the Heisenberg exchange interaction strength ($J_H$) between V moments on which $\theta_{CW}$ depends. The rough estimate of it can be found by mapping the energies of FM and AFM solutions to the Heisenberg Hamiltonian. Our calculation gives $J_H \approx 58$ meV. Using this value of $J_H$ we have estimated the AFM transition temperature based on mean-field theory and it comes out to be $\sim 925$ K, which is closer to the experimental value of $\theta_{CW}$.

Using experimental $T^*\approx 42$ K we have estimated the value of $f \approx 22$. Such a large value of $f$ further strengthens the conjecture about the activeness of frustration in MVO compound.

Here it is important to note that the GGA+$U$ formulation of density functional theory is a mean-field theory, which is not capable of addressing issue related with spin fluctuations directly. Thus, to address this one needs to go beyond the mean-field theory.

IV. CONCLUSIONS

In conclusion, we have investigated the electronic and magnetic properties of a geometrically frustrated MgV$_2$O$_4$ by using ab initio electronic structure calculations. This compound is a Mott-insulator and its insulating ground state is arising due to combined effect of strong Coulomb correlation and AFM interaction. The $d_{x^2}$ and $d_{yz}$ orbitals are found to be ordered in the tetragonal phase. The spins are forming AFM ordered chains along the $x$ and $y$ directions and making an angle $\sim 11.3^0$ with the $z$-axis. The SOC is weak and geometrical frustration appears to be active in deciding the magnetic state of the system.

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FIG. 1. (Color online) Atomic arrangement of the unit cell. The formation of VO6 octahedra and V4 tetrahedra are shown in (a) and (b), respectively.

FIG. 2. (Color online) Evolution of total density of states (TDOS) with various interaction parameters. Please see the text for the details.

FIG. 3. (Color online) (a) Intra-chain antiferromagnetic ordering along the $x$ and $y$ directions. (b) spin and orbital arrangements at the tetrahedron level.

Table 1: Occupancies of $d_{x^2}$, $d_{y^2}$, and $d_{z^2}$ orbitals and magnetic moments of four V atoms (viz. V1, V2, V3, and V4 forming the tetrahedron, see Fig. 3(b)) corresponding to FM and AFM (in brackets) solutions obtained from GGA+$U$ ($U=4$ eV) calculations.
Table 2: The expectation value $x$, $y$ and $z$ components of spin ($S$), orbital ($L$) and total ($J$) moment of V ion obtained from FM and AFM (in brackets) GGA+$U$+SOC ($U=4$ eV) solutions.

|        | V1    | V2    | V3    | V4    |
|--------|-------|-------|-------|-------|
| $d_{x^2-y^2}$ | 0.62(0.65) | 0.62(0.65) | 62(0.65) | 62(0.65) |
| $d_{xz}$        | 0.64(0.66) | 0.64(0.66) | 0.18(0.1) | 0.18(0.1) |
| $d_{yz}$        | 0.18(0.1)  | 0.18(0.1)  | 0.64(0.66) | 0.64(0.66) |
| MM ($\mu_B$)    | 1.43(1.35) | 1.43(1.35) | 1.43(-1.35) | 1.43(1.35) |

|        | $x$    | $y$    | $z$    |
|--------|--------|--------|--------|
| $S$    | ∼0[ ∼0] | ∼0[ ∼0] | 0.71(0.67) |
| $L$    | -0.02(-0.1) | ∼0[ ∼0] | -0.07(-0.17) |
| $J$    | -0.02(-0.1) | ∼0[ ∼0] | 0.64(0.5) |
