Orbital Ordering in Fe_{1-x}Mn_{x}V_{2}O_{4} : A First Principles Study

Dibyendu Dey,1,* T. Maitra,2 and A. Taraphder1,3

1Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur - 721302, India
2Department of Physics, Indian Institute of Technology Roorkee, Roorkee - 247667, India
3Centre for Theoretical Studies, Indian Institute of Technology Kharagpur, Kharagpur - 721302, India

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Long range orbital order has been investigated in Fe_{1-x}Mn_{x}V_{2}O_{4} as a function of doping (x) using first principles density functional theory calculations including the effects of Coulomb correlation and spin-orbit interaction within GGA+U and GGA+U+SO approximations. Through a detailed analysis of corresponding Wannier orbital projections of the Vanadium d bands, we have clearly established that for x<0.6, the orbital order at V sites consists of a linear superposition of d_{xz} and d_{yz} orbitals of the type d_{xz±d_{yz}}. Within each ab-plane a ferro-orbital ordering of either d_{xz}+d_{yz} or d_{xz}-d_{yz} is observed which alternates in successive ab-planes along the c-direction. On the contrary, for x>0.6, it is the d_{xz} or d_{yz} orbital which orders at V sites in successive ab-planes along c-direction (so called A-type ordering). At Fe sites, we observe an orbital ordering of d_{xz±d_{yz}} orbitals for x<0.6 and d_{xz} orbitals for x>0.6. Effect of spin-orbit interaction on orbital ordering is found to be not significant in the entire range of doping studied.

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I. INTRODUCTION

Correlated and frustrated electronic (spin) systems have recently observed a major surge in research activities due to the inherently rich fundamental physics involved in their understanding as well as their potential for practical applications. Vanadium spinel oxides belong to one such family of systems which, of late, has become the centre of attraction for studying phenomena involving the competition among various degrees of freedom, like spin, orbital and lattice in presence of both Coulomb correlation and geometric frustration.12 These compounds with chemical formula AV_{2}O_{4} can be broadly divided into three categories on the basis of A-site cation properties, namely; (i) A site non-magnetic (i.e. A= Zn, Mg, Cd), (ii) A-site magnetic but orbitally inactive (i.e. A = Mn, Co), (iii) A-site magnetic and orbitally active (i.e. A = Fe). As V ion is both magnetic and orbitally active, the additional magnetic and orbital degrees of freedom of A site ion bring in a very complex and rich physics with competing spin, lattice and orbital interactions (in some cases also spin-orbit interactions) in these systems. The competition among different degrees of freedom then manifests itself in several structural (accompanied often by orbital ordering) and magnetic transitions as observed experimentally in these systems.

FeV_{2}O_{4} is a rare example among the Vanadium spinel oxides where both Fe and V cations are magnetic as well as orbitally active. This system is reported to show three successive structural transitions (cubic→ tetragonal→ orthorhombic→ tetragonal) and two magnetic transitions (paramagnetic (PM) → collinear ferrimagnetic (FIM) → non-collinear ferrimagnetic (NC-FIM)) as the temperature is lowered.3–6 Another example is MnV_{2}O_{4} which has A-site magnetic but not orbitally active. This compound shows one structural (cubic→ tetragonal) and two magnetic ( PM→ FIM→ NC-FIM) transitions.5,7–10. ZnV_{2}O_{4} can be the third example with a nonmagnetic and non-orbitally active A-site ion which undergoes one structural (cubic→ tetragonal) and one magnetic (PM → antiferromagnetic) transition.11,12 Although most of the structural and magnetic transitions (along with the magnetic orders) have been unambiguously established by various experiments, the orbital order which often accompanies the structural transitions are still a matter of intense investigation and continuous debate.3,12–16

The debate is mostly centered around the orbital order of the V sites in these spinels. V ion in its 3+ valence state has two d-electrons in the orbitally degenerate t_{2g} levels. In most of these systems, low temperature structure is tetragonal and VO_{6} octahedra have tetragonal compression accompanied often by a trigonal distortion. Due to the tetragonal compression along z-direction the energy of the d_{yz} orbital is lowered and it is occupied by one d electron. However, the second d electron has a choice: occupy either d_{xz} or d_{yz} orbital or a combination of these two. There are various possible scenarios proposed for the orbital order in these systems based on the symmetry of the tetragonal phase and the type of dominant interactions. Some of the proposed orbital ordering models include ferro-orbital ordering of complex orbitals such as d_{xz±d_{yz}} with dominant spin-orbit interaction,11,12 A-type antiferro-orbital ordering of real orbitals d_{xz} and d_{yz} alternating along c-direction where SO interaction is not considered strong and an orbital ordering of real and complex orbitals for systems with intermediate strength of SO interaction etc. Also, experiments have not yet been able to establish the orbital order unambiguously in these systems as there are measurements reported in the literature supporting each of these models.

Very recently, the doped variants of FeV_{2}O_{4} and MnV_{2}O_{4} (i.e. Fe_{1−x}Mn_{x}V_{2}O_{4} (0 ≤ x ≤ 1)) have been studied experimentally by Kawaguchi et al.19 and D.
Choudhuri et al.\textsuperscript{20} where a detail magnetic and structural phase diagram has been obtained. Kawaguchi et al. have also analyzed the orbital ordering at Fe and V sites in $\text{Fe}_{1-x}\text{Mn}_x\text{V}_2\text{O}_4$ for different doping (x) on the basis of local Jahn-Teller distortions of $\text{FeO}_4$ tetrahedra and $\text{VO}_6$ octahedra respectively. From their analysis, the authors have predicted that in the range $0 \leq x \leq 0.6$, the $d_{x^2-y^2}$ orbital should order at all Fe sites and at V sites a long range ferro-orbital ordering of complex orbitals of the type $d_{x^2} \pm i d_{y^2}$ should be present. On the other hand, for the range $0.6 < x \leq 1$, it is the $d_{xz}$ orbital that orders at Fe sites and an A-type antiferro-orbital order should exist at V sites where within each ab-plane it is ferro-orbital order of either $d_{xz}$ or $d_{yz}$ but along c-direction it is antiferro (i.e. alternate arrangement of $d_{xz}$ and $d_{yz}$ orbital). However, a very recent XMCD measurements reveal that though there is a difference in the occupied orbital state in $\text{Fe}_2\text{V}_2\text{O}_4$ and $\text{Mn}_2\text{V}_2\text{O}_4$, the orbitals that order (at V sites) in $\text{Fe}_2\text{V}_2\text{O}_4$ as well as in $\text{Mn}_2\text{V}_2\text{O}_4$ are not complex but real orbitals\textsuperscript{21}. Even though the observation of orbital order consisting of real orbitals rather than complex ones corroborates the previous theoretical predictions reported in the literature on these two systems\textsuperscript{15,16}, the exact nature of orbital ordering proposed from theory and experiments differ significantly. In view of these disagreements regarding the orbital state of parent compounds and also to study the effect of doping, we have decided to investigate the issue of orbital order in the whole range of x in $\text{Fe}_{1-x}\text{Mn}_x\text{V}_2\text{O}_4$ from a theoretical perspective using ab-initio density functional theory calculations.

II. METHODOLOGY

We have performed ab-initio density functional theory calculations within various approximations such as GGA, GGA+U and GGA+U+SO for $\text{Fe}_{1-x}\text{Mn}_x\text{V}_2\text{O}_4$ with $x=0$, 0.25, 0.5, 0.75 and 1. The experimental structures of parent and doped compounds have been taken from experiments\textsuperscript{3,19,20}. In case of $x=0.25$ and $x=0.75$ we have taken the available experimental structural data for $x=0.2$ and $x=0.8$ and optimized the structure as described below. The optimization (volume, c/a ratio and oxygen positions) has been done by using Perdew-Burke-Ernzerof Generalized Gradient Approximation (PBE-GGA) exchange-correlation functional\textsuperscript{22}, within the full potential linearized augmented plane-wave (FP-LAPW) method as implemented in the WIEN2k code\textsuperscript{23}. We have used the package 2DROptimize available within WIEN2k package for the optimization of volume and c/a ratio. For this purpose we have considered nine different volumes around the experimental volume and for each volume nine c/a ratios were considered. During the optimization involving these 81 structures, the free internal parameters (here oxygen positions) were also optimized. Final optimized structural parameters were obtained by the analysis of the following data; (i) Energy vs. c/a for each volume, (ii) energy vs. volume (with optimized c/a) and (iii) c/a vs. volume. Each curve was then fit to 3rd, 4th and 5th order of polynomial and the lattice constants a and c were calculated from the best fit. We have listed some optimized structural parameters for $x=0$, 0.5 and 0.75 in Table I which we have used for our calculations reported here. We have considered the muffin-tin radii of 2.00, 1.95, 1.65 a.u for Fe(Mn), V and O respectively. The plane wave cutoff $R_{\text{K}\text{max}}$ was set to 8.0 for all calculations and the number of k points in the irreducible wedge of the Brillouin zone (BZ) were taken to be 60 for $x=0$, 0.25, 0.5 and 72 for $x=0.75$, 1. The expansion of the radial wavefunction in spherical harmonics was considered up to angular momentum quantum number $l=10$. We also performed calculations including the correlation effects arising from the d electrons of Fe/Mn and V. For this, we have used a self-interaction corrected (SIC) GGA+U\textsuperscript{24} approximation which takes into account the on-site Coulomb interaction U and removes the self-Coulomb and self exchange correlation energy. Spin-orbit (SO) coupling is included by the second variational method\textsuperscript{25} with scalar relativistic wavefunctions. All the calculations were performed for the collinear ferrimagnetic spin arrangement of Fe/Mn and V ions. WANNIER90\textsuperscript{26} and WIEN2WANNIER\textsuperscript{27} (the interface program between WIEN2k and WANNIER90) were used to fit the bands around Fermi level by localized Wannier orbitals and to analyze the band characters in terms of these orbitals.

III. RESULTS AND DISCUSSION

On the basis of symmetry of the crystal structure and observed orbital ordering in our calculations, we divide these compounds into two groups (i) $x=0$, 0.25, 0.5 which we refer to as $x \leq 0.6$ case as crystal symmetry remains same in the range $0 \leq x \leq 0.6$, (ii) $x=0.75$, 1 which we refer to as $x > 0.6$ case where symmetry is different from the former one.

A. $\text{Fe}_{1-x}\text{Mn}_x\text{V}_2\text{O}_4$ ; $x=0$, 0.25, 0.5

In the low temperature tetragonal phase, the crystal structures of $\text{Fe}_{1-x}\text{Mn}_x\text{V}_2\text{O}_4$ at $x=0$, 0.25, 0.5 have the $I4_1/\text{amd}$ symmetry as observed experimentally\textsuperscript{3,19,20}. Our optimized structures also have the same symmetry although the local trigonal and tetragonal distortions as well as the c/a ratios differ slightly. In Table I we compared the structural parameters of experiment and optimized one for $x=0.5$ case. We clearly observe from Table I that the local trigonal and tetragonal distortions at $\text{FeO}_4$ tetrahedron and $\text{VO}_6$ octahedron as well as the c/a ratio of the optimized structure are comparable and more importantly have the same signs (i.e. compression or elongation along a particular direction) as the experimental one. Therefore, we discuss below the results ob-
FIG. 1. (Colour online) Spin polarized DOS are shown for x=0.5. (a) Total DOS, (b) partial DOS of Fe in minority spin channel (c) partial DOS of V in majority spin channel.

FIG. 2. (Colour online) Orientation VO$_6$ octahedron is shown in (a) with respect to reference frame of the tetragonal unit cell (abc) and also shown is the xyz frame in which Wannier orbitals are defined. The d$_{xy}$, d$_{xz}$ and d$_{yz}$ Wannier orbitals are shown in (b), (c) and (d) respectively.

GGA+U Results: As both parent compounds (FeV$_2$O$_4$ and MnV$_2$O$_4$) as well as the doped ones are known to be Mott insulators, we have included in our calculations the Coulomb correlation within GGA+U approximation. The calculations have been performed for various values of U$_{eff}$ (= U – J, where U is on-site Coulomb interaction and J is the Hund’s exchange interaction strength) ranging from 3eV to 5eV at Fe, Mn

| Lattice Constants | O-Fe-O | V-O | O-V-O |
|-------------------|--------|-----|--------|
| Optimized; x=0    | a=5.9630, c=8.4485, c/a=1.004 | 107.078$^\circ$ (along-c) | 1.9933 Å (along-c) | 85.597$^\circ$ |
|                   | c=8.4485, c/a=1.004 | 110.681$^\circ$ | 2.0351 Å | 94.403$^\circ$ |
| Experimental; x=0.5 | a=5.9863, c=8.4994, c/a=1.004 | 108.004$^\circ$ (along-c) | 2.0079Å (along-c) | 84.493$^\circ$ |
|                   | c=8.4994, c/a=1.004 | 110.210$^\circ$ | 2.0283Å | 95.507$^\circ$ |
| Optimized; x=0.5  | a=5.9497, c=8.4497, c/a=1.004 | 108.649$^\circ$ (along-c) | 2.0318Å (along-c) | 85.612$^\circ$ |
|                   | c=8.4497, c/a=1.004 | 109.884$^\circ$ | 2.0361Å | 94.388$^\circ$ |
| Optimized; x=0.75 | a=6.0502, c=8.40, c/a=0.982 | 111.984$^\circ$ (along-c) | 2.033Å (along-c) | 83.715$^\circ$ |
|                   | c=8.40, c/a=0.982 | 109.884$^\circ$ | 2.032Å | 96.285$^\circ$ |

TABLE I. Structural parameters and various distortions observed in the optimized structures for x=0, x=0.5 and x=0.75 are listed. Corresponding experimental data is also given in case of x=0.5 case for comparison.
ground state orbital order in these systems. As men-

opposite to Fe (Mn) spin moments).

Fe (Mn) and V spins (i.e. V spin moments are aligned
have considered collinear ferrimagnetic order among the
Fe/Mn (V) sites. In addition, in all our calculations we
the results obtained for the \( U_{\text{eff}} \)
values of

and V sites. We note that conclusions drawn from our
calculations do not change when we vary the values of
\( U_{\text{eff}} \) in the above range. Therefore, we present below
the results obtained for the \( U_{\text{eff}} \) value of 4eV (3eV) at
Fe/Mn (V) sites. In addition, in all our calculations we
have considered collinear ferrimagnetic order among the
Fe (Mn) and V spins (i.e. V spin moments are aligned
opposite to Fe (Mn) spin moments).

Our primary goal here is to ascertain the type of
ground state orbital order in these systems. As men-
tioned above we observed qualitatively similar behaviour
as far as the orbital order is concerned for \( x=0, 0.25 \) and
0.5. Therefore, we present the case of \( x = 0.5 \) in detail
below. In Fig. 1(a) we show the total density of states (DOS) of Fe, Mn, V and O in both the spin channels
within GGA+U approximation. Consistent with the
experimental observation the insulating ground state with a
gap of about 0.2eV is obtained. Furthermore, we see that
due to the tetrahedral crystal field, the Fe d- states are
split into \( t_{2g} \) and \( e_g \) with \( e_g \) states having lower energy.
The valence state of Fe is 2+ as the spin up (majority)
states are fully filled by 5 d electrons and spin down (mi-
nority) \( e_g \) states are partially filled by one electron. Par-
tial filling of the minority \( e_g \) states causes Jahn-Teller
effect which in turn further splits these states to lower
energy \( d_{x^2−y^2} \) and higher energy \( d_{z^2} \) state. This energy
level splitting can be understood by looking at the lo-
cal distortions of FeO\(_4\) tetrahedron presented in Table I.
In the high temperature cubic phase, all six interior O-
Fe-O bond angles are degenerate having a value 109.4°.
Whereas, in the low temperature tetragonal phase FeO\(_4\)
tetrahedron is elongated along c-direction making \( d_{x^2−y^2} \)
the ground state orbital. Therefore, the minority spin
electron occupies \( d_{x^2−y^2} \) orbital as we can see in the par-
tial DOS of Fe d-states in the minority spin channel pre-
sented in Fig 1(b).

Similarly, Vanadium d-states are split into \( t_{2g} \) and \( e_g \)
with \( t_{2g} \) states having the lower energy due to octahe-
dral crystal field. Majority (here spin down due to ferri-
magnetic ordering) \( t_{2g} \) states are partially filled by two d
electrons. Unlike FeO\(_4\) tetrahedron (where all Fe-O bond
lengths are equal), VO\(_6\) octahedron has both tetragonal
and trigonal distortions in the low temperature tetra-
gonal phase (see Table I). There is a compression of V-
O bonds along c-direction compared to four equal V-O
bonds in the ab-plane. In addition, there also exists a
trigonal distortion (i.e. O-V-O bond angles deviating
from 90°) in the ab-plane as well as out of ab-plane.
Because of the presence of tetragonal compression along c(z)
direction the degeneracy of the \( t_{2g} \) states is further lifted
and \( d_{xy} \) band moves to a lower energy below Fermi level
(FL) and gets fully occupied by one electron. One can
clearly observe this from the partial DOS of Fe d-states
(in majority spin channel) presented in Fig 1(c). We also
observe from Fig 1(c) that there is a further splitting of the
remaining two \( t_{2g} \) states to accommodate the second
electron giving rise to the insulating gap at the FL. The
later splitting of \( t_{2g} \) states happens due to the orbital
ordering. In order to find out the orbital character of
the second highest occupied state , we have calculated
the projections of three Wannier orbitals as shown in Fig
2 of the Vanadium d-bands around the FL. The corre-
responding projections are shown in Fig 3(a), (b) and (c)
for \( d_{xy}, d_{xz} \) and \( d_{yz} \) orbitals respectively. From these fig-
ures we can clearly establish that \( d_{xy} \) orbital character
is the most dominant one among the lower energy bands
and it’s peak has a lower energy than the other two. It
appears only below FL and hence fully occupied which is

![FIG. 3. (Colour online) Projections of V \( t_{2g} \) bands on to
d\(_{xy}, d_{xz} \) and \( d_{yz} \) Wannier orbitals are shown for x=0.5 in (a),
(b) and (c) respectively. It is seen that \( d_{xy} \) has the lowest
energy and it is fully occupied while \( d_{xz} \) and \( d_{yz} \) are occupied
with equal weight.](image-url)
expected because of the compression of V-O bonds along c(z)-direction. Interestingly we further observed that the $d_{xz}$ and $d_{yz}$ characters of exactly equal proportions are present in higher energy bands (i.e. close to FL) and these are partially filled. This implies that $d_{xy}$ orbital has the lowest energy and it is filled by one electron but the 2nd electron occupies equally $d_{xz}$ and $d_{yz}$ orbitals (i.e. a linear superposition of $d_{xz}$ and $d_{yz}$ orbitals).

In order to find out the type of long range orbital order that exists in these systems and the exact composition of the orbitals that order we calculated the 3D electron density in real space and presented it in Fig. 4(a) (for $x=0.5$). As expected we can now clearly see that there is an ordering of $d_{x^2-y^2}$ orbitals at all Fe sites. The V orbitals ordering however is more complicated. In each ab-plane V orbitals are ferro-orbitally ordered with the second electron occupying either $\frac{1}{\sqrt{2}}(d_{x^2}+d_{yz})$ or $\frac{1}{\sqrt{2}}(d_{xz}-d_{yz})$ at all V sites. As we move along c-direction, in successive ab-planes we observe $\frac{1}{\sqrt{2}}(d_{x^2}+d_{yz})$ or $\frac{1}{\sqrt{2}}(d_{xz}-d_{yz})$ alternately ordered. To depict this clearly we have also plotted the corresponding hole densities (i.e. for V states just above FL) of V chains in adjacent ab-planes (see Fig 4(b)). The staggered orbital order along c-direction can be clearly seen here. We observe from Fig. 4 that the electron orbitals point towards each other along a V chain whereas hole orbital point away from each other which could be understood on the basis of kinetic energy gain due to more overlap between the neighbouring V orbitals.

**GGA+U+SO Results**: As it is established from various experimental and theoretical studies that some of these Vanadium spinel oxides also show dominant spin-orbit (SO) interaction effect which then leads to the orbital ordering of complex orbitals rather than real ones, we have included SO interaction in our calculations through GGA+U+SO approximation. However, in the entire series of compounds studied, the effect of SO interaction was not found to be significant either on the electronic structure or on the orbital ordering. Orbital moments also observed to be quite small compared to, for example, ZnV$_2$O$_4$ where it is found to be large. We list the calculated orbital moments for Fe and V for different doping in Table II. Interesting, in a recent XMCD measurement, Nii et al. also observed negligible orbital moment in both FeV$_2$O$_4$ and MnV$_2$O$_4$. Therefore, we conclude that the long range orbital order that is present at V and Fe sites as discussed above involves only real orbitals not the complex ones such as $d_{x^2}\pm id_{yz}$ which was observed in case of ZnV$_2$O$_4$.

### B. Fe$_{1-x}$Mn$_x$V$_2$O$_4 : x=0.75, 1$

In experiments it has been observed that in $x>0.6$ regime, Fe$_{1-x}$Mn$_x$V$_2$O$_4$ has $I_4'/a$ symmetry in the tetragonal phase at low temperature and $c/a$ ratio is less than 1 unlike $x\leq0.6$ case where it has $I_4/amd$ symmetry and $c/a$ ratio above 1. Therefore, the local distortions at FeO$_4$ tetrahedra and VO$_6$ octahedra are very different from that observed in $x<0.6$ cases discussed in the previous section (refer to $x=0.75$ case in Table I). We observe that in these cases both FeO$_4$ tetrahedra as well as VO$_6$ octahedra are compressed along c-direction. In addition, in the VO$_6$ octahedra four V-O bonds of the ab-plane are split into two short and two long bonds as opposed to the cases below $x=0.6$ where all four V-O bonds in the ab-plane had equal magnitude. These long/short bonds alternately point along x or y-direction (refer to the Fig 2(a)) in successive ab-planes as one moves along c(z)-direction. Trigonal distortions are also present as listed in Table I.

We performed electronic structure calculations for Fe$_{1-x}$Mn$_x$V$_2$O$_4$ at $x=0.75$ and 1 within GGA+U and GGA+U+SO approximations as we discuss below. As the electronic structure and the orbital order (at V sites) are found to be similar in nature for $x=0.75$ and $x=1$ we present the results for $x=0.75$ case.

**GGA+U Results**: In Fig.5 we show the partial DOS for Fe and V d-states in minority and majority spin channels respectively within GGA+U with $U_{e/f}=4eV$ and 3eV at Fe(Mn) and V sites. By looking at the partial DOS of minority Fe d-states we see that JT distortion in this case makes $d_{z^2}$ the ground state. This is consistent with the compression of FeO$_4$ tetrahedra along c(z)-direction. However, the Vanadium d-states undergo a complicated splitting with all $t_{2g}$ orbital (i.e. $d_{xy}$, $d_{xz}$, $d_{yz}$) characters being present above and below FL. This is understandable as VO$_6$ octahedra undergo local and co-
operative JT distortions (both tetragonal and trigonal) leading to orbital ordering. Similar to the previous cases of $x \leq 0.6$, we have analysed the orbital characters by calculating the corresponding Wannier orbital projections of the V $t_{2g}$-bands above and below FL. We show these projections in Fig. 6. Consistent with the JT compression along c-direction, the lowest bands have high contribution from d$_{xy}$ orbital. However, in a significant deviation from the earlier case (i.e. $x \leq 0.6$), here we observe that d$_{xz}$ and d$_{yz}$ are not equally populated. The filled states below FL have dominant contribution from d$_{yz}$ orbital (about 80% or so) whereas d$_{xz}$’s presence is very small (about 20% or so). This implies that the lowest occupied orbital is predominantly d$_{yz}$ in nature whereas the next higher occupied orbital is d$_{yz}$ in nature as also observed in case of MnV$_2$O$_4$\textsuperscript{15}. The polarization of the second highest occupied orbital (i.e. lifting of the degeneracy of d$_{xz}$ and d$_{yz}$) is consistent with the JT distortion which causes the splitting of V-O bonds in the ab-plane into two short and two long ones as mentioned above. Interestingly, we further observed by plotting the corresponding Wannier orbitals in real space that the polarization (ordering) character of the second highest occupied state alternate in successive ab-planes along c-direction. If in one ab-plane it is the d$_{yz}$ which gets polarized (ordered), then in the next ab-plane it is the d$_{xz}$ that becomes the second most populated orbital. This keeps repeating so that the second d-electron of V$^{3+}$ occupies alternately d$_{xz}$ and d$_{yz}$ as we move along c-direction. Note that d$_{xy}$ remains the most populated orbital at all V sites. This is often referred to as A-type orbital ordering in the literature\textsuperscript{8,19,20}. The staggered ordering of d$_{xz}$ and d$_{yz}$

FIG. 5. Spin polarized DOS are shown for x=0.75. (a) Partial DOS of Fe in minority spin channel (b) partial DOS of V in majority spin channel.

FIG. 6. (Colour online) Projections of V $t_{2g}$ bands on to d$_{xy}$, d$_{yz}$, and d$_{xz}$ Wannier orbitals are shown for x=0.75 in (a), (b) and (c) respectively.
FIG. 7. 3D electron density is shown in real space lattice for x=0.75 case in (a). Corresponding hole densities are shown in (b) to depict the nature of unoccupied orbitals.

|   | Fe (\(\mu_B\)) | V (\(\mu_B\)) |
|---|----------------|---------------|
| x=0.5 | 0.11          | 0.22          |
| x=0.75 | 0.00          | 0.07          |

TABLE II. Calculated orbital moments of Fe and V ions in doped systems.

The orbital along c(z)-direction can be understood if we look at the JT distortion which is also also staggered along the same direction as described above. If two longer V-O bonds are pointed along x-direction (refer to Fig. 2(a)) then the second highest occupied orbital has dominant d_{xz} character and if two longer V-O bonds are pointed along y-direction then the second highest occupied orbital has dominant d_{yz} character.

In Fig. 7 we present the 3D electron density in real space for Fe_{1-x}Mn_xV_2O_4 with x = 0, 0.25, 0.5, 0.75 and 1 where experimental measurements related to orbital ordering have recently been reported. We investigated in detail the orbital ordering of Fe and V d-orbitals in these systems from our calculations under various approximations such GGA, GGA+U and GGA+U+SO. We have also performed a detail analysis of long range orbital order by calculating the Wannier orbital projections of the occupied d-bands and plotting those orbitals in real space lattice. On the basis of the observed orbital order from our calculations we divide these systems into two classes; one which includes the compounds x=0, 0.25 and 0.5 and the other includes x=0.75 and 1. In the former, we observe d_{x^2-y^2} orbital order at Fe sites while in the later it is d_{z^2} orbital ordering. As far as V sites are concerned, in the former case, d_{xy} orbital is found to be present at all V sites as expected and the second orbital that is ordered has equal contribution from d_{xz} and d_{yz} (i.e. a linear superposition of the type d_{xz}+d_{yz} or d_{xz}-d_{yz}). In successive ab-planes along c-direction the composition of this orbital alternates between d_{xz}+d_{yz} and d_{xz}-d_{yz}.

We further observe that real orbitals, not complex ones as had been claimed in some reports earlier, are involved in the orbital ordering process. This observation is consistent with the recent XMCD measurements on the parent compounds\cite{21}. For x=0.75 and 1, we observe, apart from d_{xy} orbital being present at all V sites, the second electron occupies preferentially either d_{xz} or d_{yz} in successive ab-planes as one moves along c-direction which is often referred to as A-type orbital ordering in the literature.

IV. CONCLUSIONS

We have performed first principles density functional theory calculations in a series of compounds Fe_{1-x}Mn_xV_2O_4 with x = 0, 0.25, 0.5, 0.75 and 1 where experimental measurements related to orbital ordering have recently been reported. We investigated in detail the orbital ordering of Fe and V d-orbitals in these systems from our calculations under various approximations such GGA, GGA+U and GGA+U+SO. We have also performed a detail analysis of long range orbital order by calculating the Wannier orbital projections of the occupied d-bands and plotting those orbitals in real space lattice. On the basis of the observed orbital order from our calculations we divide these systems into two classes; one which includes the compounds x=0, 0.25 and 0.5 and the other includes x=0.75 and 1. In the former, we observe d_{x^2-y^2} orbital order at Fe sites while in the later it is d_{z^2} orbital ordering. As far as V sites are concerned, in the former case, d_{xy} orbital is found to be present at all V sites as expected and the second orbital that is ordered has equal contribution from d_{xz} and d_{yz} (i.e. a linear superposition of the type d_{xz}+d_{yz} or d_{xz}-d_{yz}). In successive ab-planes along c-direction the composition of this orbital alternates between d_{xz}+d_{yz} and d_{xz}-d_{yz}.

We further observe that real orbitals, not complex ones as had been claimed in some reports earlier, are involved in the orbital ordering process. This observation is consistent with the recent XMCD measurements on the parent compounds\cite{21}. For x=0.75 and 1, we observe, apart from d_{xy} orbital being present at all V sites, the second electron occupies preferentially either d_{xz} or d_{yz} in successive ab-planes as one moves along c-direction which is often referred to as A-type orbital ordering in the literature.

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