Orbital ordering in the geometrically frustrated MgV$_2$O$_4$: *Ab initio* electronic structure calculations

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In the light of recent interesting experimental work on MgV$_2$O$_4$ we employ the density functional theory to investigate the crucial role played by different interaction parameters in deciding its electronic and magnetic properties. The strong Coulomb correlation in presence of antiferromagnetic (AFM) coupling is responsible for the insulating ground state. In the ground state, the d_{xz} and d_{yz} orbitals are ordered and intrachain vanadium ions are antiferromagnetically coupled. The calculation gives small spin-orbit coupling (SOC), which provides a tilt of $\sim 11.3^\circ$ to the magnetic moment from the z axis. In the presence of weak SOC and strong exchange coupling, the experimentally observed small magnetic moment and low AFM transition temperature appear to arise from spin fluctuation due to activeness of geometrical frustration.

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.[1] 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.[2] 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.[3,4] 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) are important geometrically frustrated systems that have attracted a great deal of attention for a decade because of OO induced structural transition and formation of fascinating magnetic phases.[5–15] All the studied compounds show cubic to tetragonal transition at low temperature and paramagnetic (PM) to AFM transition at slightly lower temperature.[5–8,13] The consensus is emerging among the researchers regarding the OO induced structural transition, however, the exact pattern of OO remains a matter of controversy.[9,10,12,14,15] Moreover, the exact role of spin-orbit coupling (SOC) along with its strength in stabilizing the magnetic and orbital ordering is yet to be decided in this series of compounds.[9,10,14] 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).[15] In the tetragonal phase, the space group of MVO is $I\bar{4}m2$ whereas that of ZVO is $I4_1/amd$. The magnetic moment (MM) of V ion in MVO is ~ 0.47 μ_B, which is ~ 0.15 μ_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.[14] However, experimental data of MVO do not suggest such a large contribution from the orbital part and indicate to a deeper reason for the observed small MM. Moreover, the MM is also seen to make an angle of $\sim 8^\circ$ 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 an 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 and -0.2 μ_B, respectively. In 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 μ_B).

II. COMPUTATIONAL DETAILS

The nonmagnetic (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.[16] The lattice parameters and atomic positions used in the calculations are taken from the literature.[15] 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 exchange correlation functional, we have adopted the recently developed generalized gradient approximation (GGA) form of Perdew *et al.*[17] The effect of on-site Coulomb interaction is also considered within GGA + U formulation of the density functional theory.[18] 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. Only results that correspond to $U = 4$ eV are discussed in the manuscript. In order to see the role of orbital degrees of freedom on the electronic and magnetic 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 trigonal 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, respectively. The four nearby V atoms form a regular tetrahedron with an edge of length 2.98 Å. Each tetrahedron is surrounded by four neighboring tetrahedra via corner sharing and formation of chains of V atoms, see Fig. 1(b). In the tetragonal phase, the tetrahedra become distorted with a V-V bond length of 2.971 and 2.980 Å. Such a small distortion would reduce 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 compound we obtained various magnetic solutions using tetragonal structure. The total densities of states (TDOS) that correspond to these solutions are shown in Fig. 2. It is clear from Figs. 2(a)–2(d) that the GGA solutions provide a metallic state as opposed to the experimentally observed insulating 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.[19–22] The NM and FM solutions obtained from GGA + U calculations also provide a metallic state as evident from Figs. 2(e) and 2(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 solution of ZVO within LSDA + U is found to derive insulating ground state of the compound.[14] 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 2(h). It is important to note that the increased value of U enhances the band gap in both cases. Thus the present work clearly establishes that the AFM coupling of V moments in presence of strong on-site Coulomb interaction is
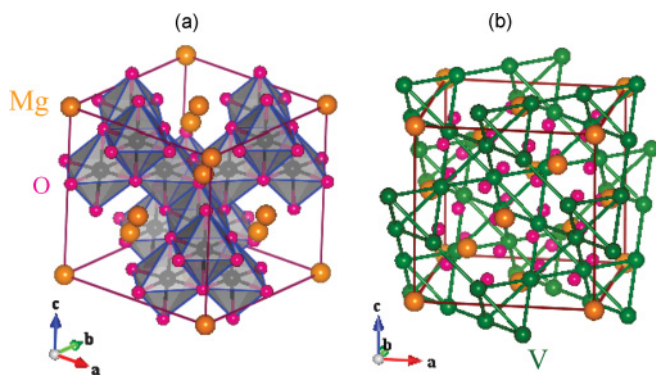

FIG. 1. (Color online) Atomic arrangement of the unit cell. The formation of VO6 octahedra and V4 tetrahedra are shown in (a) and (b), respectively.
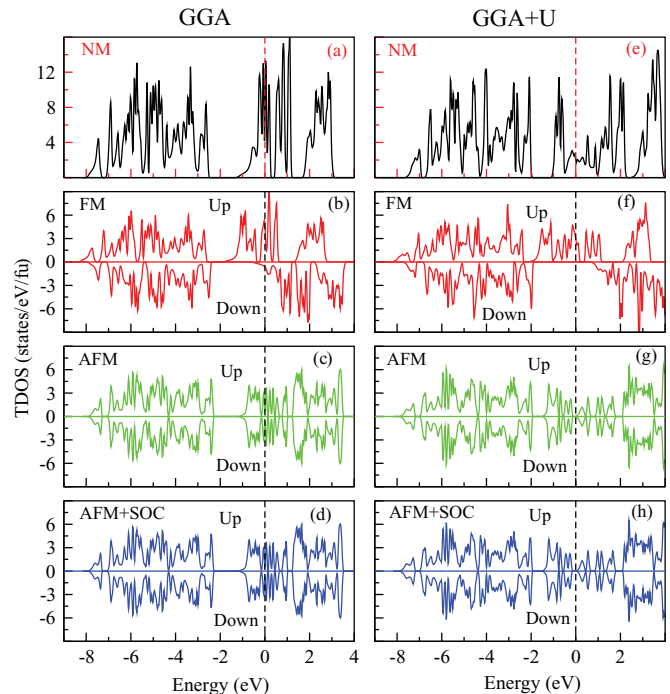

FIG. 2. (Color online) Evolution of total density of states (TDOS) with various interaction parameters. Please see the text for the details.

responsible for the insulating ground state and SOC provides robustness to the insulating property of the compound.

Now we discuss the effect of different interaction parameters on the electronic structure of the compound. First we start with GGA results. In the absence of magnetic interaction there is a large density of states (DOS) at the Fermi level (ϵ_F) with dominating contribution from the V $3d$ states. This may be considered as a signature of magnetic ground state under Stoner theory. The magnetic interaction reduces the DOS at ϵ_F by ~50% due to exchange splitting of the bands contributing at the ϵ_F and providing almost a half-metallic state, see Fig. 2(b). Moreover, the energy of FM solution is found to be ~0.65 eV/fu (fu = formula unit) 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 μ_B. Interestingly, FM interaction induces finite MM (~0.14 μ_B) at the Mg ions occupying $2c$ $(0,1/2,1/4)$ Wyckoff sites. The total MM/fu comes out to be ~3.6 μ_B, which corresponds to $S \approx 1$ 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 the ϵ_F drastically (~4 times less than that of FM). The ϵ_F lies at the minima of DOS, which is a reminiscence of the pseudogap. 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 μ_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 solution. 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 comparing 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 expected to be negligibly small. Our GGA calculation gives the strength of SOC of ∼5 meV for the V $3d$ electrons.

Figures 2(e)–2(h) depict the effect of on-site Coulomb interaction among the V $3d$ electrons on the electronic properties of the compound in the presence of various interaction parameters. On-site Coulomb correlation reduces 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 ϵ_F due to transfer of spectral weight (earlier contributing at ϵ_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 increases 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 than that obtained 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 μ_B. The total MM/fu comes out to be 4 μ_B, 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.[15] 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 I where we have listed the occupancy of $d_{x^2-y^2}$,[23] 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 $d_{x^2-y^2}$ orbitals. The V1 and V2 sites are mainly occupied by d_{xz} orbitals 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 PM phase there is a local MM at the V site and hence magnetic solutions would provide a better representation of the PM state in comparison to NM solution. Table I 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} (d_{xz}) 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

TABLE I. Occupancies of $d_{x^2-y^2}$, d_{xz}, and d_{yz} 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.

	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 (μ_B)	1.43(1.35)	1.43(−1.35)	1.43(−1.35)	1.43(1.35)

correlation in establishing the AFM ground state. The MM of vanadium ions that correspond to FM and AFM solutions are found to be ∼1.43 and 1.35 μ_B, 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 the 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 that are purely electronic and structural in origin.[1,3,4] 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 the LDA + DMFT method.[3,4] It is important to note that the 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 a better 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 II where we have shown the spin (S), orbital (L), and total (J) moments of the V ion corresponding to FM and AFM solutions. The orbital part of MM in the AFM state comes out to be ∼−0.2 μ_B, which is ∼7 times less than the spin part of MM suggesting a weak SOC in MVO with respect to ZVO[14] where a large orbital moment of −0.75 μ_B 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 is tilted at ∼8° from the z axis.[15] However, the above

TABLE II. The expectation value x, y, and z components of spin (S), orbital (L), and total (J) moments of V ion obtained from FM and AFM (in brackets) GGA + U + SOC ($U = 4$ eV) solutions.

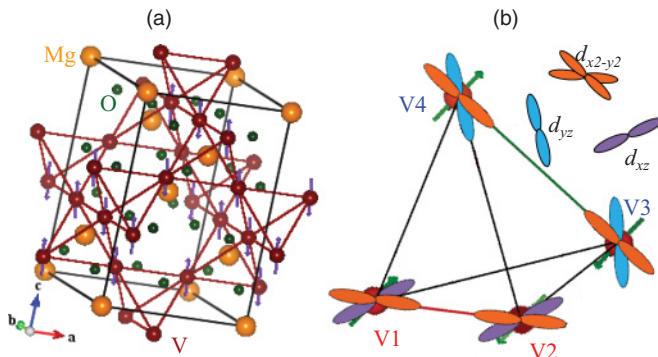|	x	y	z
S	∼0 (∼0)	∼0 (∼0)	0.71(0.67)
L	−0.02 (−0.1)	∼0 (∼0)	−0.07 (−0.17)
J	−0.02 (−0.1)	∼0 (∼0)	0.64(0.5)

FIG. 3. (Color online) (a) Intrachain antiferromagnetic ordering along the x and y directions. (b) Spin and orbital arrangements at the tetrahedron level.

calculated values of spin and orbital moments cannot account for the experimentally observed magnetic moment of 0.47 μ_B. At this point it is important to note that the experimentally estimated magnetic moment of 0.63 μ_B for ZVO is well accounted by taking into account the calculated large but negative orbital moment of -0.75 μ_B.[14] 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 $La_{1-x}Ca_xMnO_3$ and predicted different OO that correspond to different spin arrangements.[2] According to this scheme, the length of FM bond should be greater than that of AFM bond. However, we have observed the opposite behavior as the AFM bond is 0.03 Å larger than the FM bonds.

As mentioned above, the calculated small orbital moment of -0.2 μ_B for MVO cannot account for the experimentally observed value of total MM $\sim$0.47 μ_B, whereas the calculated large orbital moment of -0.75 μ_B for ZVO provides a good description of its experimentally observed total MM of 0.63 μ_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 fluctuations at low temperature. Such spin fluctuations are expected to reduce the MM drastically. The level of frustration in magnetic systems is defined by the frustration index $f \equiv |\theta_{CW}|/T^*$, where θ_{CW} is the Curie-Weiss temperature and T^* is the critical temperature at which the system ultimately develops long-range spin order.[24] The higher the value of f the 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 θ_{CW} depends. The rough estimate of it can be found by mapping the energies of FM and AFM solutions to the Heisenberg Hamiltonian.[25] 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 θ_{CW}.[26] 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 issues 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_2O_4 by using *ab initio* electronic structure calculations. This compound is a Mott insulator and its insulating ground state is arising due to the combined effect of strong Coulomb correlation and AFM interaction. The d_{xz} 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° 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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[1] D. I. Khomskii, Phys. Scr. **72**, CC8 (2005), and references therein.

[2] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).

[3] E. Pavarini, E. Koch, and A. I. Lichtenstein, Phys. Rev. Lett. **101**, 266405 (2008).

[4] E. Pavarini and E. Koch, Phys. Rev. Lett. **104**, 086402 (2010).

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

[6] N. Nishiguchi and M. Onoda, J. Phys. Condens. Matter **14**, L551 (2002).

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

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

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

[10] O. Tchernyshyov, Phys. Rev. Lett. **93**, 157206 (2004).

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

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

[13]P. G Radaelli, New J. Phys. **7**, 53 (2005).

[14]T. Maitra and R. Valentí, Phys. Rev. Lett. **99**, 126401 (2007).

[15]E. M. Wheeler, B. Lake, A. T. M. Nazmul Islam, M. Reehuis, P. Steffens, T. Guidi, and A. H. Hill, Phys. Rev. B **82**, 140406(R) (2010).

[16][http://elk.sourceforge.net].

[17]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).

[18]F. Bultmark, F. Cricchio, O. Grånäs, and L. Nordström, Phys. Rev. B **80**, 035121 (2009).

[19]V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys. Condens. Matter **9**, 767 (1997).

[20]S. K. Pandey, A. Kumar, S. Patil, V. R. R. Medicherla, R. S. Singh, K. Maiti, D. Prabhakaran, A. T. Boothroyd, and A. V. Pimpale, Phys. Rev. B **77**, 045123 (2008).

[21]S. K. Pandey and K. Maiti, Phys. Rev. B **78**, 045120 (2008).

[22]S. K. Pandey, Phys. Rev. B **81**, 035114 (2010).

[23]$d_{x^2-y^2}$ orbial in the body-centered tetragonal coordinate system is same as the d_{xy} orbital in the face-centered cubic coordinate system.

[24]J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, Rev. Mod. Phys. **82**, 53 (2010).

[25]S. K. Pandey and K. Maiti, Europhys. Lett. **88**, 27002 (2009).

[26]H. Mamiya and M. Onoda, Solid State Commun. **95**, 217 (1995).