Quantum 120° model on pyrochlore lattice: orbital ordering in MnV$_2$O$_4$

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We present an analytical model of orbital ordering in vanadium spinel MnV$_2$O$_4$. The model is based on recent first-principles calculation indicating a strong trigonal distortion at the vanadium sites of this compound [Phys. Rev. Lett. 102, 216405 (2009)]. At the single-ion level, the trigonal crystal field leaves a doubly degenerate atomic ground state and breaks the approximate rotational symmetry of $t_{2g}$ orbitals. We find that the effective interaction between the low-energy doublets is described by a quantum antiferromagnetic 120° model on the pyrochlore lattice. We obtain the classical ground state and show its stability against quantum fluctuations. The corresponding orbital order consisting of two inequivalent orbital chains is consistent with the experimentally observed tetragonal symmetry. A periodic modulation of electron density function along orbital chains is shown to arise from the staggering of local trigonal axes. In the presence of orbital order, single-ion spin anisotropy arising from relativistic spin-orbit interaction stabilizes the experimentally observed orthogonal magnetic structure.

I. INTRODUCTION

Geometrically frustrated magnets with orbital degeneracy exhibit a variety of complex ground states with unusual magnetic and orbital orders. Not only do these spin-orbital models deepen our understanding of systems with competing degrees of freedom, they also describe the low-energy physics of several transition-metal compounds. Of particular interest is spin-orbital model on three-dimensional pyrochlore lattice where geometrical frustration between nearest-neighbor spins leads to a macroscopic degeneracy in the classical ground state. Experimentally, a signature of strong frustration is the macroscopic degeneracy in the classical ground state.

Interest in antiferro-orbital order is rekindled by a recent experimental characterization of another vanadium spinel MnV$_2$O$_4$ where the A-site Mn$^{3+}$ ion is in a 3$d^5$ high spin configuration ($S = 5/2$). In contrast to other vanadium spinels, MnV$_2$O$_4$ first undergoes a magnetic transition at $T_F = 56$ K into a collinear ferrimagnetic phase with Mn and V moments aligned antiparallel to each other. At a slightly lower temperature $T_S = 53$ K, a structural distortion lowering the crystal symmetry to tetragonal $I4_1/a$ is accompanied by an ordering of the transverse components of V spins. The ground-state orbital configuration is suggested to be the $A$-type antiferro-orbital order. Also contrary to collinear magnetic order in other vanadium spinels, a peculiar non-collinear order with transverse component of vanadium spins forming an orthogonal structure in the $ab$ plane was observed in MnV$_2$O$_4$.

Recently we have demonstrated the stability of orthogonal magnetic structure in the limit of strong relativistic spin-orbit coupling. However, findings from first-principles calculation indicate a significant trigonal distortion at the vanadium sites of MnV$_2$O$_4$ whose effect is yet to be understood. The same authors find an orbital order consisting of two inequivalent orbital chains similar to the $A$-type order. More importantly, they observe an additional modulation of electron density profile within each orbital chain: the orbitals rotate alternatively by about 45° along the chain. This complex orbital pattern

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We find that the effective interaction between the low-energy doublets is described by a quantum antiferromagnetic 120° model on the pyrochlore lattice. We obtain the classical ground state and show its stability against quantum fluctuations. The corresponding orbital order consisting of two inequivalent orbital chains is consistent with the experimentally observed tetragonal symmetry. A periodic modulation of electron density function along orbital chains is shown to arise from the staggering of local trigonal axes. In the presence of orbital order, single-ion spin anisotropy arising from relativistic spin-orbit interaction stabilizes the experimentally observed orthogonal magnetic structure.

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is also supported by a recent NMR measurement.\cite{24}

Based on these observations, we present an analytical model of spinel MnV$_2$O$_4$ assuming that the $t_{2g}$ orbitals is split into a singlet and a doublet by a strong trigonal crystal field. As one electron occupies the low-energy $a_{1g}$ orbital, a double degeneracy remains for the other electron. After introducing a pseudospin-$1/2$ to describe the doubly degenerate atomic ground state, we find that their effective interaction is governed by a highly anisotropic quantum 120° Hamiltonian.\cite{25,26} By treating quantum fluctuations using the semiclassical framework, the classical ground state of the 120° model is shown to be stable against quantum fluctuations. Orbital ordering and lattice distortion derived from the classical ground states are consistent with the experiments. We also shown that an alternatively rotated orbital basis due to the staggered trigonal axes explains the periodic density-modulation observed in \textit{ab initio} calculations. Moreover, since the very presence of trigonal distortion breaks the (approximate) rotational symmetry of $t_{2g}$ orbitals, orthogonal magnetic structure thus comes naturally from spin-orbit interaction and the staggering of trigonal axes.

The rest of the paper is organized as follows. Sec. II discusses the effective orbital 120° model on pyrochlore lattice and its semiclassical ground states. The corresponding orbital order and lattice distortion are discussed in Sec. III. The modulation of electron density function corresponding orbital order and lattice distortion are discussed in Sec. IV. The details of magnetic structure is presented in Sec. V. And finally Sec. VI presents a conclusion.

II. 120° MODEL

The site symmetry of vanadium ions in most vanadates is dominated by a cubic crystal field. Nonetheless, splitting of $t_{2g}$ triplet due to an additional trigonal distortion is known to play an important role in some cases. Most notably, stabilization of the unusual magnetic structure in the insulating phase of V$_2$O$_3$ is only be understood when the trigonal splitting is properly taken into account.\cite{27,28} The effects of trigonal distortions in vanadium spinels vary from one compound to another. For example, the trigonal splitting of $t_{2g}$ levels is essential to the understanding of heavy fermion behavior in metallic LiV$_2$O$_4$.\cite{29} On the other hand, it seems to have a negligible effect in another well-studied spinel ZnV$_2$O$_4$.\cite{30}

Recently, experiment\cite{15} and \textit{ab initio} calculation\cite{24} both indicate a strong trigonal distortion at the vanadium sites of MnV$_2$O$_4$. In order to understand its effects at least qualitatively and in order to make analytical calculations tractable, we consider the limit of a dominating trigonal crystal field in this paper. As discussed in the introduction, the trigonal distortion still leaves a doubly degenerate atomic ground state. The possible long-range order of these localized doublets is investigated using the effective Hamiltonian approach. By studying the ground state of the effective model, we discuss its implications for orbital and magnetic ordering in MnV$_2$O$_4$.

In the presence of a trigonal distortion, the crystal field of reduced site symmetry (from cubic $O_h$ to $D_{3d}$) splits $t_{2g}$ orbitals into a singlet and a doublet separated by an energy gap $\Delta$. The $C_3$ symmetry axis of $D_{3d}$ group is parallel to the local $\{111\}$ direction of the ion (Fig. 1). The $a_{1g}$ singlet is the symmetric linear combination of $t_{2g}$ orbitals under $C_3$ rotation

$$|a_{1g}\rangle = \nu_x |yz\rangle + \nu_y |zx\rangle + \nu_z |xy\rangle,$$

where $\nu = (\nu_x, \nu_y, \nu_z)$ is a unit vector parallel to the local trigonal axis (Fig. 1). We use the following chiral basis for the $e_g$ doublet

$$|e^+_g\rangle = \nu_x e^{-i\omega} |yz\rangle + \nu_y e^{+i\omega} |zx\rangle + \nu_z |xy\rangle,$n

$$|e^-_g\rangle = \nu_x e^{+i\omega} |yz\rangle + \nu_y e^{-i\omega} |zx\rangle + \nu_z |xy\rangle,$$

where $\omega = 2\pi/3$. A complete basis for V$^{3+}$ ion with 3$d^2$ configuration is given by $|a_{1g}e^+_g\rangle$, $|a_{1g}e^-_g\rangle$, and $|e^+_g e^-_g\rangle$. Here the two-electron state is defined as the antisymmetric sum of individual one-electron states, i.e. $|\alpha\beta\rangle \equiv (|\alpha\rangle |\beta\rangle - |\beta\rangle |\alpha\rangle)/\sqrt{2}$. Since the $a_{1g}$ singlet has the lowest energy, the atomic ground state is doubly degenerate. To describe the low-energy doublet manifold, we introduce a pseudospin-$\frac{1}{2}$ operator $\tau$ such that $|\tau_z = \pm 1\rangle$ are identified with $|a_{1g}e^{\pm}_g\rangle$, respectively.

In vanadium spinels, the superexchange (SE) interaction with a 90° angle between vanadium-oxygen bonds
Potts-like orbital interactions which depend only on or-
to the doublet manifold
\[ |\alpha \rangle \]
where
\[ t \]
anticiferro-orbital order consisting of alternating
\[ \hat{\tau} \]
atures are difficult. In this paper, we choose the sim-
nation of the nearest-neighbor bond (Fig. 1). The effective
Hamiltonian has a form of the so-called 120° model, which was first introduced as an effective model for per-
tronic properties of orbital interaction, we first examine
\[ H_{\text{eff}} = \sum_{ij} \left\{ J_2 (1 - S_i \cdot S_j) P_{\alpha,i} P_{\alpha,j} \right\} 
+ \{ J_0 S_i \cdot S_j + J_1 \} \left\{ P_{\alpha,i} (1 - P_{\alpha,j}) + (1 - P_{\alpha,i}) P_{\alpha,j} \right\} \}

The various exchange constants are
\[ J_0 = J \eta/(1 - 3 \eta), \]
\[ J_1 = J(1 - \eta)/(1 - 3 \eta), \]
and
\[ J_2 = J(1 + \eta)/(1 + 2 \eta), \]
where
\[ J = t_{\text{dd}}^2 / U \]
sets the overall energy scale and
\[ \eta = J_0 / J \approx 0.11 \]
denotes the ratio of Hund’s exchange to on-site Coulomb repulsion. The subscript \( \alpha \equiv \alpha \langle i j \rangle \) of the projection operators specifies the type of orbitals in which electron hopping is possible between sites \( i \) and \( j \), e.g., \( \alpha \langle i j \rangle = xy \) for nearest-neighbor bonds on \( (110) \) and \( (110) \) chains (blue bonds in Fig. 1).

An interesting feature of Hamiltonian (3) is the static
Potts-like orbital interactions which depend only on or-
\[ P_{\alpha} = \frac{2}{3} \hat{\tau} \cdot n_\alpha, \]
where the three unit vectors are (Fig. 2):
\[ n_{yz} = \frac{1}{2} \hat{x} - \frac{\sqrt{3}}{2} \hat{y}, \]
\[ n_{zx} = \frac{1}{2} \hat{x} + \frac{\sqrt{3}}{2} \hat{y}, \]
\[ \hat{n}_{xy} = -\hat{x}. \]

A remark is now in order: the restricted Hilbert space
\[ |\pm \rangle \]
already precludes descriptions of, e.g. the A-type antiferro-orbital order consisting of alternating \( |xy, yz \rangle \) and \( |xy, zx \rangle \) states. A more general approach is to intro-
\[ H_{\text{eff}} = J_2 \sum_{\langle ij \rangle} (\tau_i \cdot n_\alpha)(\tau_j \cdot n_\alpha), \]
where
\[ J_2 = \frac{1}{3} 2 J_1 - J_2 + (S_i \cdot S_j)(J_2 + 2 J_0) > 0 \]
and
\[ \alpha = \alpha \langle i j \rangle = yz, zx, \]
and \( xy \) depending on the orientation of the nearest-neighbor bond (Fig. 1).

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The effective Hamiltonian
\[ H_{\text{eff}} \]
$zz$ bonds, while interaction of pseudospin $i \in C$ with its neighbor $j \notin C$ is of the $xy$ type exclusively. It could be easily checked that such a subset cannot be found in pyrochlore lattice. However, orbital interactions are still frustrated simply due to geometry: antiferromagnetic pseudospin interaction cannot be satisfied on all nearest-neighbor bonds simultaneously$^{38}$.

Despite being geometrically frustrated, the strong anisotropy of $120^\circ$ interaction significantly reduces the number of degenerate ground states. To see this, we note that the energy of a single bond is minimized classically by a pair of pseudospins pointing toward $\pm \hat{n}_i$, respectively, where $\hat{n}_i$ is the unit vector characterizing the anisotropic interaction of the bond. However, such absolute minimum cannot be attained at every nearest-neighbor bonds due to geometrical frustration. Even worse, pseudospin correlation on some bonds is frustrated, i.e. $\tau_i \cdot \tau_j > 0$. In order to minimize the energy cost, frustrated pseudospins thus tend to align themselves perpendicular to $\hat{n}_i$. Through both analytical calculation and Monte-Carlo simulations, we find that collinear states with pseudospins perpendicular to either one of the three $\hat{n}_i$ are the classical ground states (Fig. 3). The total degeneracy is six due to an additional $C_2$-rotation about $\tau_z$ axis. This is in stark contrast to the macroscopic ground-state degeneracy of classical Heisenberg spins on the pyrochlore lattice.$^2$

The three inequivalent ground states shown in Fig. 3 are characterized by the locations of frustrated bonds. More specifically, we introduce three staggered order parameters$^{39}$

\begin{align}
I_{yz} &= (\tau_0 + \tau_1 - \tau_2 - \tau_3)/4, \\
I_{xx} &= (\tau_0 - \tau_1 + \tau_2 - \tau_3)/4, \\
I_{xy} &= (\tau_0 - \tau_1 - \tau_2 + \tau_3)/4 \\
\end{align}

(7)

to describe the orbital order. Here $\tau_i$ denotes pseudospin average on $i$th sublattice. These order parameters measure the difference of orbital configuration on bonds of the same type. For example, a nonzero $I_{xy}$ indicates an antiferro-orbital order across the two $xy$ bonds of a tetrahedron [see Fig. 3(c)]. The nonzero order parameter characterizing the collinear states of Fig. 3 are: (a) $I_{yz} = -\frac{\sqrt{3}}{2}\hat{x} - \frac{1}{2}\hat{y}$, (b) $I_{xx} = -\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}$, and (c) $I_{xy} = \hat{y}$.

This should be contrasted with the continuously degenerate collinear ground states in Heisenberg model, i.e. $I_{ss} = \hat{e}$ with $\hat{e}$ being an arbitrary unit vector.$^{29}$

The stability of classical ground states in the presence of quantum fluctuations is investigated using the semiclassical Holstein-Primakoff transformation. We find that the anisotropy of the orbital exchange leads to a gapped quasiparticle spectrum in the whole Brillouin zone. At the harmonic level, quantum fluctuations around collinear ground states are shown to give a negligible correction to the sublattice ‘magnetization’ ($\tau_i$) (about 4%), indicating the stability of the classical ground states. A detailed account of the semiclassical calculation is presented in Appendix A.

III. ORBITAL ORDER AND LATTICE DISTORTION

Before closing this section, we remark that phonon-mediated orbital exchange in spinels also has the form of $120^\circ$ interaction with an effective exchange $J_r \propto g^2/k_{F_{1g}}$, where $g$ is a Jahn-Teller coupling constant and $k_{F_{1g}}$ is the elastic constant of $F_{1g}$ phonons.$^{21}$ Detailed derivation is presented in Appendix A. In fact, noting that $(\tau_x, \tau_y)$ forms a doublet irreducible representation of $D_{3d}$ group, the $120^\circ$ type interaction in Eq. (5) is the only anisotropic pseudospin interaction allowed by lattice symmetry. In this perspective, we shall regard $J_r$ as an effective model parameter in the following discussion.

We now discuss the orbital order and lattice distortions corresponding to the semiclassical ground states. Specifically, we shall focus on the collinear state characterized by $I_{xy} = +\hat{y}$ [Fig. 3(c)]. Since $P_{yz} + P_{xx} + P_{xy} = 2$, orbital orders are essentially described by linear combinations

\begin{align}
P_1 &= P_{yz} + P_{xx} - 2P_{xy} = -\tau_x, \\
P_2 &= \sqrt{3}(P_{xx} - P_{yz}) = -\tau_y, \\
P_3 &= 0,
\end{align}

(8)

which transform as a doublet irreducible representation under symmetry group $D_{3d}$. Since pseudospins pointing along $\pm y$ directions are sitting on $[110]$ and $[101]$ chains, respectively, the ground state shown in Fig. 3(c) consists of two distinct orbital chains characterized by $P_1 = 0$, $P_2 = \mp 1$, respectively. The staggered part $P_2$ of the orbital order comes from the occupation difference between $yz$ and $zx$ orbitals. The uniform part given by $P_{yz} = P_{xx} = P_{xy} = 2/3$ indicates that the three orbitals are equally occupied on average.

Due to Jahn-Teller effect, a long-range orbital order also implies a lattice distortion in the ground state, which is indeed observed in MnV$_2$O$_4$ below $T_S = 53$ K. On symmetry ground, the coupling between orbital doublet
where \( \delta_1, \delta_2 \) are coordinates of normal modes transforming as an \( e_g \) representation of group \( D_{4h} \). The two symmetry-breaking modes can be thought of as analogous to the tetragonal and orthorhombic distortions in a cubic VO\(_6\) octahedron. The energy cost associated with the distortion is \( \frac{k}{2}(\delta_1^2 + \delta_2^2) \), where \( k \) is an effective elastic constant. For orbital order characterized by \( I_{xy} = +\hat{y} \), minimization with respect to phonons yields distortions described by \( \delta_1 = 0 \) and \( \delta_2 = \pm g/k \) on the two inequivalent orbital chains: octahedra on [110] and [110] chains are elongated along the \( x \) and \( y \) axes, respectively. The overall distortion preserves the tetragonal symmetry (lattice constants \( a = b > c \)) and is consistent with the observed space group \( I\overline{4}d/a \).

It is interesting to note that the staggered orthorhombic distortions of VO\(_6\) octahedra actually correspond to a softened \( q = 0 \) lattice phonons with \( F_{1g} \) symmetry\( \Delta \). This is consistent with the fact that, by integrating out \( F_{1g} \) phonons, orbital Jahn-Teller coupling gives the same 120° pseudospin interaction (Appendix A). In this respect, orbital ordering and structural transition in MnV\(_2\)O\(_4\) can also be viewed as softening of \( F_{1g} \) phonons due to cooperative Jahn-Teller effect.

Despite the similarities between the antiferro-orbital order of 120° model and the \( A \)-type order proposed in Ref. 16, inclusion of spin-orbit interaction illustrates an important difference between the two cases. As we shall discuss later, spin-orbit coupling gives rise to an orthogonal magnetic order in 120° model, which is in stark contrast to collinear spins in the case of \( A \)-type orbital order.

### IV. MODULATION OF ELECTRON DENSITY FUNCTION

The staggering of trigonal axes along orbital chains also results in a periodic variation of electron density distributions, despite the orbital occupation numbers are invariant within the chain. This is because the actual orbital wavefunction corresponding to \( \tau = \pm \hat{y} \) also depends on the local \( C_3 \) axis:

\[
\begin{align*}
|\tau_y = +1\rangle &= \sqrt{2}(\nu_x \cos \xi |X\rangle + \nu_y \sin \xi |Y\rangle) + \nu_z |Z\rangle, \\
|\tau_y = -1\rangle &= \sqrt{2}(\nu_x \sin \xi |X\rangle + \nu_y \cos \xi |Y\rangle) + \nu_z |Z\rangle.
\end{align*}
\]

Here the angle \( \xi \) is defined by \( \tan \xi = (1 - \sqrt{3})/(1 + \sqrt{3}) \), and \( |X\rangle = |zx, xy\rangle, \ |Y\rangle = |xy, yz\rangle \) and \( |Z\rangle = |yz, zx\rangle \) are the two-electron basis introduced in Ref. 17. Note that since \( \tau_y \) is diagonal in the chiral basis \( |\pm\rangle \), eigenstates of \( \tau_y \) are composed of real orbitals.

We now consider orbital chains running along [110] direction, in which the local \( C_3 \) axis alternates between \( \nu_0 \) and \( \nu_3 \) [Fig. 4(c)]. Along the chain, the electrons are in the \( |\tau_y = +1\rangle \) state whose electron density can be readily computed

\[
\rho(r) = \frac{1}{2} \sum_{i=1,2} \int \delta(r - r_i)|\langle r_1, r_2|\tau_y = +1\rangle|^2 d^3r_1 d^3r_2 = \rho_0(r) \pm \delta\rho(r),
\]

where the + and − signs refer to sites with \( \nu_0 \) and \( \nu_3 \) trigonal axes, respectively. Introducing basis functions, e.g. \( \psi_{xy}(r) = f(r) xy \), where \( f(r) \) is a spherically symmetric function, the uniform and staggered parts of electron density are given by

\[
\rho_0(r) = \frac{1}{3} \psi_{xy}^2(r) - \frac{2}{3} \cos \xi \sin \xi \psi_{yz}(r) \psi_{xz}(r) \\
+ \left( \frac{1}{2} - \frac{1}{3} \cos^2 \xi \right) \psi_{yz}^2(r) + \left( \frac{1}{2} \psi_{xy}(r) \right) \psi_{xz}^2(r),
\]

\[\delta\rho(r) = -\frac{1}{3\sqrt{2}} \psi_{xy}(r) \left( \sin \xi \psi_{yz}(r) + \cos \xi \psi_{xz}(r) \right).\]

The resulting density functions are plotted in Fig. 4. A similar density modulation, in which orbitals rotate alternatively by about 45° along the orbital chain, is also observed in first-principle density functional calculations\( \Delta \).

The periodic modulation of the electron density functions along orbital chains is a natural consequence of the staggering of local symmetry axes. In contrast, such density-modulation is absent in other orbital orders proposed for vanadium spinels. In \( A \)-type order, the two orbital chains are characterized by occupied two-electron states \( |X\rangle \) and \( |Y\rangle \), respectively. Along a given chain, e.g. \( |X\rangle \) chain, the electron density \( \rho(r) = \frac{1}{2} \psi_{xy}^2(r) + \frac{1}{2} \psi_{yz}^2(r) \) is invariant. In the ferro-orbital order proposed as the ground state of ZnV\(_2\)O\(_4\) there is only one type of orbital chain, along which the two electrons occupy states \( \frac{1}{\sqrt{2}}(|X\rangle \pm i|Y\rangle) \) alternatively, giving rise to a staggered orbital angular momentum \( \mathbf{L} = \pm \hat{z} \).

Despite the \( \pi \)-phase modulation, the electron density \( \rho(r) = \frac{1}{2} \psi_{xy}^2(r) + \frac{1}{2} (\psi_{xy}(r) + \psi_{yz}^2(r)) \) is the same at all sites.
is more efficient in relieving the magnetic frustration. It long-range antiferromagnetic spin correlation first develops. Consequently, upon decreasing the temperature, chain couplings.

magnetic order is not realized due to frustrated inter-
ops along orbital chains. However, three-dimensional
FIG. 5: Magnetic orders of vanadium spinels. The ◯ and ◦ symbols denote ±Sz components, respectively. In the limit ∆ ≫ λ ≫ Jr, the spin anisotropy is dominated by Eq. (15), and the in-plane spins point along diagonal directions ⃗Sx ± Sỹ. The corresponding magnetic orders are shown in (a) and (b) for the case of non-magnetic and magnetic A-site ions, respectively. In the opposite limit Jr ≫ ∆ ≫ λ, spin anisotropy is governed by Eq. (17), the resulting magnetic orders are shown in (c) and (d) for the respective case of non-magnetic and magnetic A-site ions.

V. MAGNETIC ORDER

In the absence of orbital order, interaction between vanadium spins is governed by an isotropic Heisenberg model, which is known to exhibit strong geometrical frustration on pyrochlore lattice. The energy minimum of the model is attained by a macroscopically large number of states in which the total spin of every tetrahedron is zero Sx = 0. The magnetic frustration is partially relieved below T_F ≈ 56 K as the antiferromagnetic Mn-V exchange induces a ferrimagnetic order with antialigned Mn and V spins pointing along the crystal c axis. The transverse components of V spins remain disordered.

The residual frustration is relieved by anisotropic spin exchange as well as single-ion anisotropy in the presence of long-range orbital order. The anisotropic spin exchange comes from the dependence of magnetic interaction on the underlying orbital configurations, as indicated by SE Hamiltonian (9). For example, orbital order corresponding to Lxy = ±y gives rise to an anisotropic exchange constant such that J[110] ≈ ±J2 for bonds along [110] and [110] directions, i.e., directions of orbital chains, and J[011] = J[010] ≈ ±J2 for bonds along other directions. Consequently, upon decreasing the temperature, long-range antiferromagnetic spin correlation first develops along orbital chains. However, three-dimensional magnetic order is not realized due to frustrated inter-chain couplings.

On the other hand, single-ion anisotropy resulting from the relativistic spin-orbit (SO) interaction V′_LS = λ(⃗L ⋅ ⃗S) is more efficient in relieving the magnetic frustration. It is interesting to note that the chiral basis |e_x±⟩ introduced in Eq. (2) are simultaneous eigenstates of angular momentum operator projected onto the local trigonal axis:

\[(\vec{L} \cdot \vec{\nu})|e_x^\pm⟩ = ±|e_y^\pm⟩.\]  (14)

Restricted to the doublet subspace ±⟩, the angular momentum operator is given by \(\vec{L} = \vec{\nu} \tau_z\), and the effective SO interaction becomes

\[V_{LS} = \lambda(\vec{S} \cdot \vec{\nu}) \tau_z.\]  (15)

We first consider limit ∆ ≫ λ ≫ Jr, where the single-ion physics dominates the Hamiltonian. The atomic ground state is a non-Kramers doublet (λ > 0 in V^3+ ion)

\[|↑⟩ = |τ_z = +1⟩ \otimes |S \cdot \vec{\nu} = -1⟩, \]

\[|↓⟩ = |τ_z = -1⟩ \otimes |S \cdot \vec{\nu} = +1⟩,\]  (16)

Long-range ordering of spins and orbitals depends further on the relative strength of antiferromagnetic Mn-V and V-V exchanges.

In the case of a non-magnetic A-site ion, the ground state consists of a uniform occupation of either |↑⟩ or |↓⟩ states. It is easy to check that the resulting non-collinear spin configuration (\(S_z = +\vec{\nu}\) or \(S_z = -\vec{\nu}\)) also minimizes the V-V exchange. The corresponding ferro-orbital order is characterized by order parameter \(m_z \equiv \frac{1}{2}(\tau_0 + \tau_1 + \tau_2 + \tau_3) = ±\hat{z}\). On the other hand, the Mn-V exchange is minimized by a staggering of occupied |↑⟩ and |↓⟩ states such that the Sz component at every site is opposite to Mn spins (whose effect can be thought of as an external magnetic field). The ground state can then be viewed as a collection of two inequivalent spin-orbital chains running along [110] and [110] directions [Fig. 5(b)]. The corresponding orbital configuration is described by order parameter Lxy = ±z.

When Jr is comparable or larger than λ, the competition between SO interaction and orbital-exchange gives rise to a \(\tau_z \propto \lambda/J_r\). The perturbation (15) thus is essentially of order \(\lambda^2\). To be consistent, we should take into account the second-order perturbations of SO interaction simultaneously. A straightforward calculation yields

\[V'_{LS} = \frac{\lambda^2}{3\Delta} \tau_z(S^2_x + S^2_y - 2S^2_z) + \frac{\lambda^2}{\sqrt{3}\Delta} \tau_y(S^2_x - S^2_y).\]  (17)

This expression can be thought of as an invariant product of two irreducible \(eg\) representations of \(D_{3d}\). Now consider ground state characterized by Lxy = +y in which pseudospins \(\tau_i = ±y\) along [110] and [110] orbital chains, respectively. The second term in Eq. (17) thus introduces a staggered spin anisotropy with easy axis parallel to y or x axes depending on \(\tau_y = +1\) or +1, respectively.

To determine the equilibrium spin configuration, we note that the two competing anisotropies Eqs. (16) and (17) have a magnitude of order \(\lambda^2/J_r\) and \(\lambda^2/\Delta\), respectively. Consequently, when orbital exchange (including phonon-mediated exchange) dominates the trigonal splitting \(J_r \gg \Delta\), the anisotropy \(±(S^2_x - S^2_y)/\Delta\) wins and aligns
spins to either \( x \) or \( y \) directions along the respective orbital chains. The resulting magnetic orders are shown in Figs. (c) and (d) for the case of non-magnetic and magnetic \( A \)-site ions, respectively. In particular, the one shown in Fig. (d) is consistent with the proposed magnetic ground state for \( \text{MnV}_2\text{O}_4 \) in Ref. 14.

In order to understand in more detail the transition between these two limiting cases, we performed an explicit calculation of the magnetic structure using Eqs. (6), (15), and (17). Since a detailed knowledge of Mn-Mn and Mn-V exchanges is required in order to compute the ferromagnetically ordered \( S_z \) component, we set \( S_z = 1/\sqrt{3} \) to simplify the calculation. As Fig. 6 shows, below a critical \( J_\tau \approx 0.18 \lambda \), pseudospins \( \tau \) are polarized along \( z \) direction, while the transverse spin components pointing along the diagonal directions form the orthogonal structure shown in Fig. 6(b). Above the critical \( J_\tau \), the transverse spins rotate uniformly (the rotation is described by angle \( \phi \)) while maintaining the orthogonal structure. At the same time, pseudospins develop a finite antiferro-orbital order along \( \tau_y \) which is characterized by angle \( \psi \). The calculation shows that at \( J_\tau \gtrsim 10 \lambda \), the spin anisotropy is already dominated by Eq. (17) as the angle \( \phi \approx 0 \) and the in-plane spins essentially point along either \( x \) or \( y \) axis.

VI. CONCLUSIONS

To summarize, we have proposed and studied a spin-orbital model for vanadium spinel \( \text{MnV}_2\text{O}_4 \) taking into account a large trigonal distortion at the vanadium sites. Instead of conventional \( t_{2g} \) triplet, our starting point is the doubly degenerate \( e_g \) eigenstates of the trigonal crystal field. By introducing a pseudospin-1/2 for the low-energy doublet, we have shown that the effective orbital interaction resulting from both the superexchange and cooperative Jahn-Teller effect is described by a quantum 120° Hamiltonian on pyrochlore lattice. From both analytical and numerical calculations, we have found six classical ground states with collinear pseudospins perpendicular to either one of the three unit vectors characterizing the anisotropic interactions. The classical ground state is further shown to be stable against quantum fluctuations.

The ground-state structure obtained from our model is consistent with main experimental observations and \textit{ab initio} calculation of \( \text{MnV}_2\text{O}_4 \), namely, an antiferro-orbital order with tetragonal \( 14_1/a \) space group, a density-modulation along orbital chains, and an orthogonal magnetic structure. The orbital order corresponding to the semiclassical ground states consists of two inequivalent orbital chains running along \( \langle 110 \rangle \) and \( \langle 110 \rangle \) directions, similar to the so-called \( A \)-type antiferro-orbital order. However, the staggering of trigonal axes along orbital chains gives rise to a periodic variation of the electron density function, which is absent in the \( A \)-type order. Moreover, since the trigonal distortion breaks the approximate rotational symmetry of \( t_{2g} \) orbitals, orthogonal magnetic structure is shown to be stabilized by the staggering of the single-ion spin anisotropies.

The overall orientation of the orthogonal structure actually depends on the relative strength of effective orbital exchange \( J_\tau \) and spin-orbit coupling \( \lambda \). The experimentally proposed orthogonal structure\(^{14,15,17} \) with transverse vanadium spins pointing along either \( x \) or \( y \) axes is stabilized when \( J_\tau > \lambda \). Using the large-\( J \) approach which assumes a dominant \( \lambda \) over superexchange energy scale, we have recently shown that the same orthogonal spin structure is stabilized when the predominant lattice distortion is of \( F_{1g} \) symmetry. In fact, without any Jahn-Teller distortion, the large-\( J \) ground state has a collinear antiferromagnetic order similar to the one proposed in Ref. 17. Noting that \( J_\tau \) also includes contributions from \( F_{1g} \) phonons, results from the two complementary approaches (large trigonal field vs large-\( J \)) are actually consistent: stabilization of the experimentally proposed orthogonal structure requires a dominant \( F_{1g} \) distortion as well as a smaller spin-orbit coupling. This conclusion is also supported by recent \textit{ab initio} calculation which shows that inclusion of spin-orbit coupling does not significantly change the spin-orbital order (a finite \( LS \) coupling, however, is still required to provide the spin anisotropies). Detailed analysis of Jahn-Teller phonons from first-principles calculation might help clarify the role of \( F_{1g} \) phonons.

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phonons with wavevector translational symmetry. We thus restrict our analysis to structural distortion in vanadium spinels preserves the lattice torsion, we notice that all experimentally observed structural modes correspond to the tetragonal and orthorhombic remaining modes, we find that the doublet parity oxygen modes cancels identically). Among the remaining modes, we focus on oxygen phonons with odd parity (coupling to even-parity oxygen modes cancels identically). Among the remaining modes, we find that the doublet $E_g$ and triplet $F_{1g}$ phonons are most effective in JT coupling. The $E_g$ modes correspond to the tetragonal and orthorhombic distortions of the oxygen tetrahedra, whereas the triply degenerate $F_{1g}$ modes represent rigid rotations of oxygen tetrahedra about the three cubic axes (Fig. 7).40

As discussed in Sec. III the orbital doublet $(\tau_x, \tau_y)$ of trigonal crystal field couples to the $E_g$ distortion of VO$_6$ octahedron [Eq. (9)]. To obtain the effective orbital interaction mediated by the above-mentioned lattice phonons, we first express the coordinates $(\delta_1, \delta_2)$ describing the distortion of a local VO$_6$ octahedron in terms of coordinates of lattice $E_g$ and $F_{1g}$ phonons. The energy costs associated with the two modes are characterized by effective elastic constants $k_{E_g}$ and $k_{F_{1g}}$, respectively. After integrating out the phonons, we obtain

$$H_{JT} = -K_1 \sum_{\langle ij \rangle} \tau_i \cdot \tau_j + K_2 \sum_{\langle ij \rangle} (\tau_i \cdot \hat{n}_x)(\tau_j \cdot \hat{n}_y),$$  \(\text{(A1)}\)

with the following effective exchange constants

$$K_1 = 2g^2/k_{E_g} + g^2/k_{F_{1g}}, \quad K_2 = 3g^2/k_{F_{1g}}.$$  \(\text{(A2)}\)

The effective Hamiltonian (A1) contains two competing interactions: the $K_1$ term denotes an isotropic Heisenberg exchange, whereas the $K_2$ term represents the anisotropic 120° interaction introduced in Sec. II. A classical phase diagram of the above model is summarized in Fig. 8, where a ferro-orbital order is separated from the collinear antiferro-orbital ground state of the 120° model discussed previously. Note that the Heisenberg term has a ferromagnetic sign, hence favoring a ferro-orbital ordering. The ferro-orbital state is doubly degenerate with all pseudospins pointing along either $+\hat{z}$ or $-\hat{z}$ directions. On the other hand, pseudospins in the antiferro-orbital phase are in a collinear up-up-down-down configuration. As discussed in Sec. III there are totally six degenerate antiferro-orbital states; the one shown in Fig. 8(b) is characterized by a nonzero order parameter $I_{xy} = +\hat{y}$. By comparing the energies, we find a phase boundary at $r_c = (K_2/K_1)_c = 8/3$.

Appendix B: Semiclassical approach to 120° model

Here we examine quantum corrections to the classical ground state of orbital 120° model on pyrochlore lattice. Our approach is based on a semiclassical Holstein-Primakoff expansion around the collinear state described by order parameter $I_{xy} = +\hat{y}$ [Fig. 3(c)]. To this end, we first generalize the 120° model to pseudospins $T$ of arbitrary length $|T| = \sqrt{T(T + 1)}$:

$$H_{120°} = J_T \sum_{\langle ij \rangle} (T_i \cdot \hat{n}_a)(T_j \cdot \hat{n}_a),$$  \(\text{(B1)}\)
where $J_T$ is an effective coupling constant. We then expand the Hamiltonian in powers of $1/T$ around the classical ground state using Holstein-Primakoff transformation. To simplify the calculation, we rotate the pseudospins around $T_x$ axis such that

$$T_x = \tilde{T}_x, \quad T_y = \pm \tilde{T}_z, \quad T_z = \mp \tilde{T}_y,$$

where $+$ and $-$ signs refer to pseudospins along [110] and [110] chains, respectively. The classical ground state in terms of rotated pseudospins is simply $\tilde{T}_i = +T \tilde{z}$. We then apply the standard Holstein-Primakoff transformation:

$$\tilde{T}_x = T - a^\dagger a, \quad \tilde{T}_y = \sqrt{2T} - a^\dagger a a \approx \sqrt{2T} a,$$

where $a$ and $a^\dagger$ satisfy the canonical boson commutation relations. Substituting Eq. (B3) into $120^\circ$ Hamiltonian, we obtain $H_{120^\circ} = -6N_i J_T T^2 + H_2 + \cdots$, where $N_i$ is the number of unit cells, $H_2$ of order $O(T)$ is the quadratic magnon Hamiltonian, and the omitted terms are of higher orders in $1/T$. We note that the linear term $H_1 \sim O(T^{3/2})$ vanishes identically as expected for expansion around a classical ground state.

After Fourier transformation, the quadratic Hamiltonian reads

$$H_2 = \sum_k \tilde{a}_k^\dagger \left( \frac{3\pi}{2} I + M_k \right) \tilde{a}_k,$$

where $\tilde{a}_k = [a_0(k), \cdots, a_3(k), a_0^\dagger(-k), \cdots, a_3^\dagger(-k)]^T$ is an 8-component column vector, $I$ is a $4 \times 4$ identity matrix, and

$$M_k = \frac{T}{8} \begin{pmatrix} 0 & c_{yz} & c_{zx} & 4c_{xy} \\ c_{yz} & 0 & 4\tilde{c}_{xy} & c_{zx} \\ c_{zx} & 4\tilde{c}_{xy} & 0 & \tilde{c}_{yz} \\ 4c_{xy} & c_{zx} & \tilde{c}_{yz} & 0 \end{pmatrix}. \quad (B5)$$

For convenience, we have defined $c_{\alpha \beta} = \cos((k_\alpha + k_\beta)/4)$ and $\tilde{c}_{\alpha \beta} = \cos((k_\alpha - k_\beta)/4)$ (the lattice constant is set to 1). To diagonalize $H_2$, we consider equation of motion for boson operator $\tilde{a}_k$:

$$\frac{i}{\hbar} \frac{\partial \tilde{a}_k}{\partial t} = \begin{pmatrix} \frac{3\pi}{2} I + M_k & M_k \\ -M_k & -\frac{3\pi}{2} I - M_k \end{pmatrix} \tilde{a}_k \equiv \mathcal{L}_k \tilde{a}_k. \quad (B6)$$

From eigenvectors of matrix $\mathcal{L}_k$, one can construct a canonical transformation $\tilde{T}_k = \tilde{\mathcal{T}}_k \tilde{c}_k$, where matrix $\tilde{\mathcal{T}}_k$ satisfies

$$\tilde{\mathcal{T}}_k^\dagger \eta \tilde{\mathcal{T}}_k = \eta, \quad \tilde{\mathcal{T}}_k^{-1} \mathcal{L}_k \tilde{\mathcal{T}}_k = \eta \Lambda_k. \quad (B7)$$

Here the diagonal matrices $\eta = \text{diag}(I, -I)$ and $\Lambda_k = \text{diag}(\varepsilon_\alpha(k), \cdots, \varepsilon_3(k), \varepsilon_0(-k), \cdots, \varepsilon_3(-k))$. Using Eq. (B7), the diagonalized Hamiltonian becomes

$$H_2 = \frac{1}{2} \sum_k c_k^\dagger \Lambda_k c_k = \sum_m \varepsilon_m(k) c_m^\dagger(k) c_m(k). \quad (B8)$$

By setting $T$ to its physical value $1/2$, the numerically obtained dispersion $\varepsilon_m(k)$ along various symmetry directions of the Brillouin zone is shown in Fig. 9. The spectrum is fully gapped with an energy gap of order $J_T$, implying a small quantum correction. To confirm this, we also compute the harmonic correction to the sublattice ‘magnetization’ $\langle \tilde{T}_z \rangle = 1/2 - \langle a_0^\dagger a_0 \rangle$. Using the explicit expression of the canonical transformation $\tilde{\mathcal{T}}_k$:

$$a_0(k) = u_{s, m}(k) c_m(k) + v_{s, m}(k) c_m^\dagger(-k), \quad (B9)$$

the average quasiparticle number can be computed: $\langle a_0^\dagger a_0 \rangle = (1/N_i) \sum_k (a_0^\dagger(k) a_0(k)) = \sum_m \sum_k v_{s, m}^2$. The numerically obtained sublattice ‘magnetization’ is given by $\langle \tilde{T}_z \rangle \approx 1/2 - 0.02154$. The collinear ground states shown in Fig. 8 thus are stable against quantum fluctuations, at least at the harmonic order.

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The $e_g$ system discussed in Refs. 31,32 refers to the degenerate orbitals $d_{3z^2-r^2}$ and $d_{2x^2-y^2}$ in ions with, e.g. $d^9$ configuration. It should not be confused with the $e_g$ doublet derived from the $t_{2g}$ orbitals.

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It should be noted that, contrary to the case of bipartite cubic lattice, antiferromagnetic and ferromagnetic $120^\circ$-models on pyrochlore lattice are inequivalent.

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