Orbital degrees of freedom have been shown to play an important role in understanding the electronic and magnetic properties of transition metal oxides. This is particularly so for frustrated magnets with partially filled orbitals. A well-studied case is vanadium spinels $A_{2}V_{4}O_{12}$ where the $A$-site sublattice is occupied by divalent ions such as $Zn^{2+}$ or $Mn^{2+}$, and the $B$-site magnetic $V^{3+}$ ions form a pyrochlore lattice. It is known that geometrical frustration of classical spins on such a lattice precludes simple Néel ordering and gives rise to a highly degenerate ground state. Orbital ordering in these compounds partially relieves the frustration by creating disparities in nearest-neighbor exchange constant, hence setting the stage for magnetic ordering at lower temperatures.

In this paper, we investigate the physics of frustrated vanadium chains in which the interplay of geometrical frustration, spin-orbital couplings, Jahn-Teller effect, and enhanced quantum fluctuations leads to a rich phase diagram. Our work is partly motivated by an attempt to understand another vanadium compound $CaV_{2}O_{4}$, which at room temperature crystallizes in the orthorhombic calcium-ferrite structure (space group $Pnam$). Contrary to its spinel cousins, $V^{3+}$ ions in $CaV_{2}O_{4}$ are arranged in zigzag chains of edge-sharing $VO_{6}$ octahedra (Fig. 1). Antiferromagnetic interaction on zigzag chains consisting of triangular loops is subject to geometrical frustration as well. The rather weak and frustrated interchain couplings make the vanadium chains quasi-1D systems susceptible to quantum fluctuations. Couplings of vanadium orbitals to spins and phonons add yet another dimension to the intriguing physics of zigzag chains.

In $CaV_{2}O_{4}$, the zigzag geometry results in a spin-1 chain with comparable nearest and next nearest-neighbor interactions. Combined with the observation that $3d^{2}$ configuration of $V^{3+}$ ions tend to have an easy-plane anisotropy the quasi-1D compound $CaV_{2}O_{4}$ has been a favorable candidate for the long-sought chiral spin liquid where a long-range chiral order coexists with algebraically decaying spin correlations. However, as first pointed out by Pieper et al. orbital degeneracy in this compound drastically changes the above picture. Since the $t_{2g}$ levels are split into a singlet and a doublet due to a flattened $VO_{6}$ octahedron, with the low-energy singlet always occupied, a double degeneracy remains for the other electron. The orbital degrees of freedom in $V^{3+}$ ion is thus described by an Ising-like variable.

Recent experimental studies on $CaV_{2}O_{4}$ seem to rule out a possible chiral liquid phase as well. A structural transition at $T_s \approx 141$ K reduces the crystal symmetry to monoclinic $P2_1/n$. It was suggested in Ref. 8 that the simultaneous orbital ordering relieves the magnetic frustration of zigzag chains. As the inter-chain frustration is also lifted by the lattice distortion, a three-dimensional Néel order sets in at $T_N \approx 71$ K. The collinear spins are parallel to the crystal $b$-axis as evidenced by both nuclear magnetic resonance and neutron diffraction measurements.

To make progress toward an understanding of the ground-state structure and the nature of phase transitions in $CaV_{2}O_{4}$, here we study the zero-temperature phase diagram of its building blocks, i.e. zigzag chains with $S = 1$ spins and Ising orbital variables. We propose a theoretical model which includes the superex-
change (SE) interaction, relativistic spin-orbit (SO) coupling, and Jahn-Teller (JT) effect. We find that antiferro-orbital order is favored by an Ising-like orbital exchange is destroyed in the presence of large on-site spin-orbit or Jahn-Teller coupling. Depending on the underlying orbital configuration, magnetic properties of the zigzag chain is equivalent either to those of two weakly coupled $S = 1$ chains, or of an unfrustrated spin-1 ladder. In the limit of large spin-orbit coupling, the zigzag chain can be viewed as a spin-2 chain with anisotropic interaction. Finally, we discuss implications for CaV$_2$O$_4$.

**Model Hamiltonian.** We first define a local reference frame for the two crystallographically inequivalent vanadium chains (referred to as type-I and II chains here) in CaV$_2$O$_4$ such that the $z$-axis is parallel to the tetragonal direction of flattened VO$_6$ octahedron [Fig. 1(a)]. Nearest-neighbor bonds along the chain are parallel to the local [011] and [101] directions alternatively. In the following, we employ a convention in which even-numbered bonds are along the [011] axis.

Geometrical frustration of the zigzag chain comes from the fact that second-nearest-neighbor bonds parallel to local [110] axis have a length close to that of nearest-neighbor bonds. In fact, the second-nearest-neighbor interaction is the dominant one as $d_{xy}$ ($d_{zx}$) orbital is occupied at every site due to the flattened VO$_6$ octahedra. The remaining orbital degeneracy is described by a pseudospin-$\frac{1}{2}$ with $\sigma^z = \pm 1$ corresponding to the $|yz\rangle$ and $|zx\rangle$ states, respectively.

Having introduced the basic notations, we now discuss a minimal model for the spin-orbital chain. Since orbital interaction with a 90° angle between vanadium-oxygen bonds is governed by direct $d\sigma d\sigma'$ exchange of $t_{2g}$ orbitals, the corresponding spin interaction on a bond depends on whether the relevant orbital is occupied. Essentially, orbitals participate in the superexchange only via orbital projectors $P_{yz/zx}$. Noting that $P_{yz/zx} = (1 \pm \sigma^z)$/2, we first define the antiferro-orbital and ferro-orbital bond operators

$$O_{n,n+1} = \frac{1}{2}(1 - \sigma^z_n \sigma^z_{n+1}), \quad \bar{O}_{n,n+1} = \frac{1}{4}(1 \pm \sigma^z_n)(1 \pm \sigma^z_{n+1})$$

with ± signs for even and odd numbered bonds, respectively. The model Hamiltonian is divided into three parts: $H = H_0 + H_\perp + H_{\text{on-site}}.$ The first $H_0$ term represents decoupled spin and orbital systems

$$H_0 = J_0 \sum_n S_n \cdot S_{n+1} - \sum_n (K \bar{O}_{n,n+1} + K' \bar{O}_{n,n+1}).$$

Since $J_0$ couples every second-nearest neighbors, the spin part can be viewed as two decoupled $S = 1$ Haldane chains, corresponding to the two blue lines in Fig. 1(b). The $K$ and $K'$ terms denote the energy gain of an antiferro-orbital and a ferro-orbital bond, respectively. In general, we have $K > K'$ due to a finite on-site Hund's coupling $J_H$, hence an antiferro-orbital order in the ground state of $H_0$.

The $H_\perp$ term introduces interactions between the two spin-1 chains:

$$H_\perp = \sum_n (J_1 \bar{O}_{n,n+1} - J'_1 \bar{O}_{n,n+1}) S_n \cdot S_{n+1}.$$ (2)

As discussed above interaction between spins depends on orbital occupations: the antiferromagnetic coupling $J_1$ is nonzero only when $d_{xy}$ ($d_{zx}$) orbital is occupied at both sites of an even (odd) bond, whereas the strength of ferromagnetic $J'_1$ term depends on the expectation value of the antiferro-orbital bond operator $\bar{O}_{n,n+1}$.

Explicit expressions relating the exchange constants to microscopic parameters are obtained from the SE Hamiltonian of vanadium spinels where neighboring VO$_6$ octahedra share the same edge as in zigzag chains considered here. Assuming an exact octahedral site-symmetry, we find $K = (1 + 2\eta)\frac{t^2}{U}$, $J_2 = J_1 = K' = (1 - \eta)\frac{t^2}{U}$, and $J'_1 = \eta\frac{t^4}{U}$ to lowest order in Hund’s parameter $\eta \equiv J_H/U$. Here $t$ is the hopping integral, and $U$ is the on-site Coulomb repulsion. The parameters of the model can be estimated from known values of the same parameters in other vanadium compounds. Measurements on cubic vanadates yield $J_H \approx 0.68$ eV, $U \approx 6$ eV, and $t \approx -0.35$ eV, which gives $\eta \approx 0.11$ and $t^2/U \approx 20.4$ meV. The estimate of $\lambda$ is less certain, we find $\lambda \approx 13 - 25$ meV. In the following, we shall measure energy in units of $t^2/U$.

The remaining single-ion interactions are included in the Hamiltonian

$$H_{\text{on-site}} = -\lambda \sum_n \sigma^x_n \sigma^z_n - \delta \sum_n \sigma^z_n.$$ (3)

The first term originates from relativistic SO coupling $\lambda (\mathbf{L} \cdot \mathbf{S})$. Since $d_{xy}$ orbital is always occupied, the $x$ and $y$ components of the orbital angular momentum are quenched; the remaining $L^z = -\sigma^z$ in the pseudospin representation. A similar situation has been studied in cubic vanadates. The effect of the monoclinic structural transition at $T_s$ is modeled by the second term with $2\delta$ denoting the level splitting due to the induced orthorhombic distortion of VO$_6$ octahedra. Note that the orthorhombic distortion is different on type-I and II chains.

**Orbital orders.** We first consider a simpler case of the model Hamiltonian by assuming the presence of a collinear Néel order on the zigzag chain. This is a plausible assumption as the SO term $\lambda \sigma^z_n S^x_n$ breaks the spin SU(2) symmetry and, as will be discussed later, closes the energy gap of longitudinal magnons at large enough $\lambda$, hence signaling a transition to the Néel state with $S^x_n$ parallel to $\pm z$. Even with this simplification, the competition between inter-site exchange and various on-site interactions still poses a rather nontrivial problem. This study also sheds light on orbital orders in the ground state of CaV$_2$O$_4$, where spins develop a three-dimensional collinear antiferromagnetic order at $T_N \approx 71$ K.

Due to the strong second-nearest-neighbor exchange $J_2$, collinear orders on a zigzag chain consisting of repeated $++--$ spins have a quadrupole unit cell. There
are a total of four degenerate Néel states related to each other by lattice translations and time reversal [Figs. 2(a) and (b)]. After applying a \( \pi \)-rotation about \( z \)-axis to pseudospins at \( S_z < 0 \) sites, we obtain an effective orbital Hamiltonian:

\[
H_{orb} = \sum_n [J \pm (-1)^n K] \sigma_n^x \sigma_{n+1}^x - \sum_n (h_z \sigma_n^z + h_x \sigma_n^x) .
\]

This model is equivalent to an Ising chain with alternating nearest-neighbor couplings in a skewed magnetic field. The effective exchange constants are \( J = (2K - K')/4 \) and \( K = \nu^2(2J'_1 + J_1)/4 \). Here we have assumed \( \langle S_n \cdot S_{n+1} \rangle = \mp \nu^2 \) on even and odd bonds, respectively. The longitudinal and transverse fields are given by \( h_z = \delta + \nu^2 J_1/2 \) and \( h_x = \lambda \), respectively. The parameter \( \nu < 1 \) characterizes the magnitude of the Néel order. Its value can only be determined with a proper treatment of the SO coupling term. For simplicity, we set \( \nu = 1 \) in the following calculation. Hamiltonian (4) without the staggered exchange \( K \) is one of the simplest models exhibiting nontrivial quantum critical point\(^\text{18}\) numerical calculation shows an order-disorder transition belonging to 2D Ising universality class. The staggered exchange \( K \) involves higher-order spatial derivatives in the continuum limit and thus represents an irrelevant perturbation in the RG sense.

A schematic phase diagram of model (4) is shown in Fig. 3(a), where an antiferro-orbital phase is separated from the orbital paramagnet by an Ising transition line. Along the \( \delta \)-axis (\( \lambda = 0 \)), the antiferro-orbital phase coexists with ferro-orbitally ordered phase, shown in Figs. 2(c) and (d) respectively, at the multicritical point \( \delta_c = (2K - K' - 2J) / 2 \). On the other hand, in the large \( \lambda \) limit, the pseudospins are polarized by the transverse field \( h_x \) such that spins \( S^z = \pm 1 \) are accompanied by complex orbitals \( \frac{1}{2}(d_{yz} \pm id_{xz}) \), respectively, resulting in a uniform orbital occupation \( n_{yz} = n_{xz} = 1/2 \) at all sites [Fig. 2(e)]. Using the infinite-system DMRG method with periodic boundary condition\(^\text{19}\) we obtain a critical \( \lambda_c \) at \( \delta = 0 \), taking into account the effect of staggered \( \mathcal{K} \). The Ising transition line is bounded by the critical points \( (\delta_c, 0) \) and \( (0, \lambda_c) \). Fig. 3(b) shows \( \delta_c \) and \( \lambda_c \) as a function of parameter \( \eta = J_H / U \). As expected, the antiferro-orbital phase shrinks with decreasing Hund’s coupling \( J_H \). In a full quantum treatment of the zigzag chain, we expect a similar critical line characterized by massless orbital excitations (Fig. 1).

**Spin liquid phases.** We now discuss the original Hamiltonian (1)–(3) in small \( \lambda \) limit without assuming the existence of a magnetic order. It is important to note that the spin part of the Hamiltonian in this limit preserves a continuous \( SU(2) \) symmetry, which can not be broken in one dimension. One thus expects stable spin-liquid phases whose properties depend critically on orbital configurations. Furthermore, the absence of \( \sigma^z \) term at \( \lambda = 0 \) indicates that the orbital part is described by a classical Ising-like Hamiltonian. Consequently, the search of ground states reduces to first enumerate over all possible Ising configurations \( \{ \sigma_n^z \} \), and then compare their energies taking into account contribution from spins. As antiferro-orbital and ferro-orbital orders are favored by SE and JT interactions, respectively, it is natural to consider these two configurations first.

In the case of antiferro-orbital order [Fig. 2(c)] where bond operators \( \langle O_{n,n+1} \rangle = 0 \) and \( \langle O_{n,n+1} \rangle = 1 \), the zigzag chain behaves as two spin-1 chains weakly coupled by a frustrated ferromagnetic \( J'_1 \). The corresponding spin liquid phase (SL1 phase in Fig. 2) has an energy gap at an incommensurate wavevector\(^\text{20}\). On the other hand, the frustrated \( J'_1 \) coupling is quenched by the ferro-orbital
order shown in Fig. 2(d). Depending on the sign of ferro-
Ising order $\langle \sigma^z_n \rangle = \pm 1$, the $J_1$ term is nonzero only on
even or odd bonds, but not both. The spin Hamiltonian
is equivalent to that of a spin-1 ladder with rung cou-
pling $J_1$. The magnetic ground state is again disordered
(SL2 phase in Fig. 1). The magnetic energy of spin-1
ladder with arbitrary rung coupling has been calculated
using quantum Monte Carlo method in Ref. 21. Com-
paring the energy of the two phases, including both spin
and orbital contributions, yields a boundary $\delta_c$ surpris-
ingly close to the one obtained assuming a preexisting
Néel order.

Although the SU(2) symmetry is broken in the pres-
ence of SO coupling, both spin liquids persist up to fi-
nite $\lambda$. For SL2 phase stable at $\delta > \delta_c$, SO coupling
provides an easy-axis anisotropy $D S^2_z$ with $D \approx -\lambda^2 / 2 \delta$.
The spin-1 ladder undergoes an Ising transition to a Néel
phase (N2 phase in Fig. 4) with increasing $\lambda$. At large $\delta$,
the condition $D = D_0$ gives rise to a critical $\lambda_c \propto \sqrt{\delta}$. On
the other hand, Néel transition at small $\delta$ can be under-
stood by considering the $\lambda$ dependence of the spin gap in
SL1 phase. The singlet ground state of weakly coupled
Haldane chains has triply degenerate magnon excitations
with dispersion $\omega_k = \sqrt{\Delta_0 + \nu^2 (k - k_0)^2}$. In the limit of
vanishing $J'_1$, the system reduces to two decoupled Hal-
dane chains with $k_0 = \pi / 2$, $\Delta = 0.410 J_2$ (Haldane gap for
spin-1), and $\nu = 2.49 J_2 \frac{\lambda}{\lambda_1}$ A simple second-order pertur-
bation calculation adds a correction to the spin gap

$$\Delta = \Delta_0 - \frac{\lambda^2 |\langle 0 | S^z_n | k \rangle|^2}{\Delta_\sigma - \Delta_0},$$

(5)

where $\Delta_\sigma \approx 2 (\delta_c - \delta)$ is the energy of a domain-wall
pair (a flipped pseudospin in the antiferro-orbital state), $|0\rangle$ is the singlet ground state, and $| k \rangle$ denotes one-
magnon excitation with wavevector $k$. The matrix el-
ment $\langle 0 | S^z_n | k \rangle = \sqrt{Z} e^{i k n}$, with $Z \approx 1 \frac{\lambda^2}{\lambda_1}$. For $\Delta_\sigma > \Delta_0$,
the spin gap decreases with increasing $\lambda$ and eventually
reaches zero at $\lambda_{c2} \propto \sqrt{2 (\delta_c - \delta) - \Delta_0}$, signaling a tran-
sition into magnetically ordered phase (N1 phase).

The two Néel phases in Fig. 4 are distinguished by
the underlying orbital orders, the phase boundary $\lambda_{c1}$
separating N1 from N2 phases is thus analogous to the
Ising transition line of the orbital only model [Fig. 3(b)].
Since the upper critical $\lambda_{c1} \propto J_H$, at small Hund’s cou-
pling the zigzag chain could bypass the N1 phase and en-
ter the orbital paramagnetic phase simultaneously with a
magnetic ordering. A conjectured phase diagram of the
zigzag chain is shown in Fig. 4.

Anisotropic $J = 2$ spin chain. In the limit of large SO
coupling, the appropriate degrees of freedom are effective
spins of length $J = 2$, where $J = L' + S$ and $L' = 1$ is
the angular momentum of the unoccupied $t_{2g}$ hole. The
system thus behaves as a spin-2 chain with anisotropic ex-
change interaction. Furthermore, JT coupling adds an
anisotropy $D J_z^2 + E (J_x^2 - J_y^2)$, where $D < 0$ and $E \propto \delta$
are proportional to the tetragonal and orthorhombic
distortions of VO$_6$ octahedron, respectively. Assuming A
dominating easy-axis anisotropy $|D| \gg E$, the N2 phase
can also be viewed as Néel ordering of the effective spins
$J_z = \pm 2$ in such a way that spins of a given direction
$S_z = \pm 1$ is coupled to orbital angular momenta $L'_z = \pm 1$,
respectively. The corresponding ferro-orbital order with
complex orbitals $d_{\mu \mp} \pm i d_{\pm z}$ is shown in Fig. 2(e). The
$V^{3+}$ ions have a reduced magnetic moment $\mu = (2S - L') \mu_B = 1 \mu_B$.

Discussion. We have presented and analyzed a min-
imal model of frustrated vanadium chains, pertinent to
quasi-1D compound CaV$_2$O$_4$. A conjectured phase di-
gram (Fig. 4) is obtained based on analytical arguments and
numerical calculations. The observed $P2_1/n$ crys-
tal symmetry of CaV$_2$O$_4$ at low temperatures indicates
that only two inequivalent vanadium sites exist as in the
high temperature phase. The absence of doubled unit
cell resulting from the antiferro-orbital order thus implies
that both vanadium chains are in the orbital paramag-
netic phase. This is a plausible conclusion noting that a
rather small $\lambda_{c1} \approx 0.22 (t^2 / U) \approx 4.5$ meV is estimated
from Fig. 3 assuming $\eta \approx 0.11$. However, the monoclinic
distortion below $T_s$ places the two types of vanadium
chain at rather distinct regions of the phase diagram.

The type-I chain acquires a small $\delta$ in addition to
the dominating tetragonal crystal field and behaves as
a spin-2 chain subject to an easy-axis anisotropy. This
Ising anisotropy is important to the stabilization of three-
dimensional Néel order in CaV$_2$O$_4$, as the collinear spins
are found to point along the easy axis of type-I chains.

The measured V moment $1.06 \mu_B$ is also consistent with
the picture of an anisotropic spin-2 chain. On the other
hand, a strong orthorhombic distortion $\delta$ at type-II ions
completely removes the orbital degeneracy and makes the
vanadium chains effectively spin-1 ladders. In fact, the
well separated $t_{2g}$ levels at type-II ions lead to a pos-
sible easy-plane spin anisotropy. Consequently, induced
collinear order on type-II chains follows the spin direction
of type-I vanadium ions, as indeed observed in CaV$_2$O$_4$.\hfill\hfill

FIG. 4: (Color online) Schematic phase diagram of the zigzag
vanadium chain. The various phases are characterized by the
magnetic properties. SL and N represent spin liquid phase
and Néel order, respectively. The SL1 and N1 phases are
accompanied by an antiferro-orbital order, while in the N2
and SL2 phases the orbitals behave as an orbital paramagnet.
The first-order transition along the dashed line is an extension
of the multicritical point $(\delta_c, 0)$ in the phase diagram Fig. 3.
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