Charge and Orbital Orderings, and Frustration in Quasi-one-dimensional Ferrimagnetic Insulator $\beta$-V$_2$O(PO$_4$)

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Using ab initio calculations based on the correlated band theory, we have investigated the quasi-one-dimensional chain system $\beta$-V$_2$O(PO$_4$), showing both charge and spin orderings. Even in the uncorrelated region, the pure transition from the tetragonal to the monoclinic structure leads to a sizable charge difference between the two types of V ions, regardless of magnetic orders. In the ferrimagnetic phase, inclusion of the on-site Coulomb repulsion $U$ leads to a full orbital-polarization of V1 ($t_{2g}^3$, $S = \frac{3}{2}$) and V2 ($a_{1g}^{14}e_{g}^{3}$, $S = 1$) above $U_{\text{eff}} \approx 3.5$ eV, leading to local spin moments of 2.30 and $-1.54$ $\mu_B$, respectively, with small orbital moments of several hundredth $\mu_B$. So, the net moment is nearly 1 $\mu_B$ per formula unit, which is about 2–3 times larger than the experimental value. Our results show significant variations, strongly depending on the strength of $U_{\text{eff}}$, in energy differences between various magnetic states as well as a small magnetic anisotropy. These results suggest that the substantial difference between the calculated and experimental moments is attributed to quantum fluctuation of the pyrochlore-like weakly linked V$_4$ tetrahedral structure. Our findings are expected to provide a good platform to investigate the interplay among the charge-, spin-, and lattice-degrees of freedom, and geometrical frustration.

I. INTRODUCTION

In condensed matters, the interplay among the charge-, spin-, orbital-, and lattice-degrees of freedom leads to abundant interesting phenomena. Over the past several decades, low-dimensional spin systems have been intensively investigated due to their exotic phenomena such as spin-Peierls (or dimers),[1] spinon confinement,[2] and even high Tc superconductivity.[3] In particular, quasi-one-dimensional (1D) chains with (weakly) frustrated structures have been attracted significant interest owing to various characteristic quantum magnetic states driven by the competition between the low dimensionality and frustration.[4] Most studies have been carried out on 1D chains with weakly linked triangular lattices, e.g., Ca$_3$Co$_2$O$_6$,[6] $\beta$-TeVO$_4$,[8] and Sr$_2$Rh$_4$O$_{12}$-family.[10] Another example is the trans-1,4-cyclohexanedicarboxylate of alternating Fe$^{2+}$ and Fe$^{3+}$ with a 1D chain and spin ladder structure.[11]

Many vanadium oxides exhibit metal-insulator transition (MIT), charge ordering ([CO], and even orbital ordering, but their mechanisms have been debated over the past several decades. For example, the binary and perovskite-type ternary vanadium oxides such as VO$_2$ (with V$^{4+}$ d$^1$) and V$_2$O$_3$ (with V$^{3+}$ d$^2$)[12–17] have been intensively investigated owing to their peculiar MITs and possible applications to information technology and, electronic and photonic devices.[18] In the quasi-1D para-magnetic VO$_2$, MIT is induced by the dimerization of V ions.[10] On the other hand, for the antiferromagnetic monoclinic V$_2$O$_3$ it is not clear whether MIT accompanies orbital-ordering.[12–14][17] In addition, V$_4$O$_7$ consisting of two independent cation chains exhibits an unconventional MIT involved in dimerized spin-singlet V$^{4+}$ ions and magnetically ordered V$^{3+}$.[19]

In this paper, we provide a promising candidate of a distinct low-dimensional and frustrated system showing a quasi-1D ferrimagnetic Heisenberg spin chain structure with a weak pyrochlore-like tetrahedral link of vanadium ions in the $\beta$-V$_2$O(PO$_4$) vanadium phosphate. In the formal charge concept of (PO$_4$)$^{3-}$ and O$^{2-}$, V$_2$O(PO$_4$) is a mixed valent system with two V$^{2.5+}$ ions in average. As will be addressed below, this system shows charge and spin orderings intertwined with the lattice degree of freedom. Therefore, below the spin ordering temperature, there are chains of alternating V$^{2+}$ ($d^3$, $S = \frac{3}{2}$) and V$^{3+}$ ($d^2$, $S = 1$) ions. The chain structure exists more rarely than in a V$^{4+}$ system.

V$_2$O(PO$_4$) was initially reported to be tetragonal at room temperature.[20] Based on the assumption of a ferromagnetic (FM) state in the tetragonal structure, through theoretical investigations, Jin et al. proposed that this system is a magnetic Weyl semimetal.[21] However, recently, Pachoud et al.[22] revealed a tetragonal-to-monoclinic structure transition at $T_s \approx 600$ K, leading to two distinct V sites. At $T_s$, a transition of negative to positive thermal expansion simultaneously occurs. Through a resistivity measurement demonstrating the semiconducting behaviors in both phases and analysis of the temperature-dependent bond valence sums, they concluded that CO occurred in the 1D V-V chain at $T_s (= T_{C\text{CO}}$). This suggested that the very rare negative thermal expansion in the high-temperature (tetragonal) phase was driven by loss of CO. In the low-temperature (monoclinic) phase, a ferrimagnetic (FI) spin ordering is observed at the Curie temperature of $T_C = 164$ K. Isothermal magnetization measurements indicated the FI order between nearest neighbor (NN) V ions, which was
confirmed by a neutron powder diffraction measurement. Xing et al. confirmed most of these results with a single crystalline sample, but observed a lower $T_C = 128$ K than that of the polycrystalline sample. The magnetic susceptibility above $T_C$ provides a high Curie-Weiss temperature of $\Theta_C = -900$ K and effective moment of 3.7 $\mu_B$ per V ion. The effective moment is closer to the value of the $V^{2.5+}$ ion than to that of the $V^{2+}$ ion, implying a complex magnetic interaction. The total moment, incompletely saturated even at 6 T, is $0.27 – 0.31 \mu_B$, comparable to the value of $0.6 \mu_B$ obtained by Pachoud et al. The magnitudes of the local moments are approximately $1.2 – 1.5 \mu_B$ for $V^{2+}$ and $1.4 – 1.8 \mu_B$ for $V^{2.5+}$, which are substantially reduced from the nominal values of $S = 1$ and $\frac{2}{3}$, respectively. From the resistivity data, the energy gap of 0.48 eV could be estimated. 

As mentioned above, this vanadium phosphate shows various peculiar properties. In addition to the negative thermal expansion in the high T phase, which will not be discussed here, this system exhibits several interesting properties in the low T phase: (i) 1D mixed spin chain with a promising frustrated structure, (ii) CO FI insulator, and (iii) magnetic moments substantially reduced from the nominal values of $S = 1$ and $\frac{2}{3}$, respectively. Through ab initio calculations, including correlation effects, we have investigated the electronic and magnetic structures of the low T monoclinic phase, which has not been previously reported in detail.

### II. CRYSTAL STRUCTURE AND CALCULATION METHODS

Our calculations were carried out for the monoclinic $V_2O_5$ component, containing two formula units, displayed in Fig. 1(a), with the experimental lattice parameters of $a = 7.5552$ Å, $b = 7.5979$ Å, $c = 7.2110$ Å, and the angle $\beta = 121.2^{\circ}$. As shown in the structure (space group: No. 15, $C2/c$), V1 and V2 atoms occupy at $4c (\frac{1}{2}, \frac{1}{2}, 0)$ and $4b (0, \frac{1}{2}, 0)$ sites, respectively. O1 and O2 lie at $4f (x, y, \frac{1}{2})$ sites. O3 and P atoms reside at $4e (0, y, \frac{1}{4})$ sites. O1 and O2 are shared by VO6 octahedra and PO4 tetrahedra, whereas O3 atoms are vertically connected only to the VO6 octahedra. We used the internal parameters experimentally obtained at 10 K. As summarized in Table I, the V1-O6 octahedron has an approximately 3% (in average) longer V-O bond length than that in the V2-O6 octahedron. The octahedron of V2 is more irregular than that of V1, indicating a substantial trigonal distortion in the V2-O6 octahedra. These lead to the charge and orbital orderings, as will be shown below.

Basically, the crystal consists of substantially distorted VO6 octahedra and nearly regular PO4 tetrahedra, as shown in Fig. 1(a). The PO4 tetrahedra, at layers of $b = 1/4$ and 3/4, are corner- and edge-shared with four oxygen ions of the octahedra. At the $b = 1/2$ layer, the V-V chains are stretched in the direction perpendicular to the V-V chains at the $b = 0$ layer. Here, the chain is on the ac-plane. The face-sharing VO6 octahedra form a quasi-1D chain with a notably short intrachain V-V distance of 2.68 Å. The interchain V-V ionic distances are 5.35 Å (in-plane) and 3.60–3.63 Å (interlayer). Remarkably, due to the relatively short interlayer interchain V-V distance, the network of V ions leads to a pyrochlore-like tetrahedral link, as displayed in Fig. 1(b).

The calculations were based on the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, implemented in the accurate all-electron full-potential WIEN2k code. The correlation effects are treated by the GGA+U approach. The strength of the effective on-site Coulomb repulsion $U_{eff} = U - J$ is varied in the range of $2 – 5$ eV, where $J$ is the Hund’s rule coupling. We also obtained results with a separate $U$ and $J$ scheme, but both results were very close to each other. So, only the results obtained from the $U_{eff}$ scheme are

### TABLE I: Nearest neighbor interatomic distances in the PO4 tetrahedra and VO6 octahedra (in units of Å).

| Distance     | Value          |
|--------------|----------------|
| V1-O         | 2×2.100, 2×2.096, 2×2.084 |
| V2-O         | 2×1.989, 2×2.032, 2×2.059 |
| P-O          | 4×~1.53        |

FIG. 1: (a) Side view of the monoclinic structure of $V_2O_5$ (PO4), consisting of PO4 tetrahedra and VO6 octahedra. The V ions form a quasi-1D chain. (b) Network of the corner-sharing V4 tetrahedra. As shown in the Inset, the interchain V-V distances along the vertical direction are approximately 1.3 longer than the intrachain value. (For details, see text.) (c) Conventional Brillouin zone and high symmetry points of the body-centered tetragonal structure, as given in Ref. [21].
Brillouin zone was sampled with a $(1.96 \text{ a.u. for V, 1.28 \text{ a.u. for O, and 1.61 \text{ a.u. for P}})$. The energy $E_F$, which is denoted by the vertical dashed line set at zero, lies just below the sharp peak, leading to a large total DOS $N(E_F) = 8.72$ states per eV per f.u. per spin at $E_F$. Both are similar, but some clear distinctions are visible above $E_F$, indicating the CO.

III. UNDERLYING ELECTRONIC STRUCTURE

Before considering the complications of spin order and correlation effects, we consider the nonmagnetic state within the GGA level to understand the basic underlying features of the electronic structure.

Figure 2 shows the nonmagnetic total and atom-projected densities of states (DOSs), indicating a $(V_2)^5^+$ configuration, as expected from the formal charge. The V $d$ orbitals in the range of $-2$ to $3.2$ eV are separated with a large hybridization gap of $2.2$ eV from the O $p$ orbitals, which are spread in the range of $-8$ to $-4.2$ eV. The VO$_6$ octahedral structure leads to a crystal field splitting of triplet $t_{2g}$ and doublet $e_g$ manifolds. The crystal field splitting measured from the center of each manifold is about $2.5$ eV. In this system, the triplet $t_{2g}$ manifold splits into the doublet $e_g'$ (or $e_g''$) and singlet $a_{1g}$ orbitals due to the sizable trigonal distortion in the octahedra. Setting the z-axis along the V-V chain, the $a_{1g}$ orbital has a $d_{2z}$-like shape, thus leading to a strong V-V direct interaction along the chain. The $e_g'$ orbitals can be represented by[12]

$$e_{g,1}' = \frac{1}{\sqrt{3}} (d_{xz} - \sqrt{2} d_{x^2-y^2}).$$

A small monoclinic distortion, as that in this system, leads to a small splitting of the $e_g'$ orbitals.

In the V $d$-orbital region, the blowup band structure with the $a_{1g}$ fatband is given in the left panel of Fig. 3. Interestingly, the partially filled $e_g'$ orbital is relatively well localized with a width of $0.7$ eV, leading to a sharp peak at $0.1$ eV in the DOS. The bonding and antibonding $a_{1g}$ orbitals below and above the $e_g'$ orbital have an approximately twice larger bandwidth than that of the $e_g'$ orbital due to the strong $dd\sigma$ interaction. This is illustrated in the orbital-projected DOSs of the singlet $a_{1g}$, doublet $e_g'$, and doublet $e_g$ manifolds, in the right panel of Fig. 3.

As given in the Inset of Fig. 3, the atom-projected DOSs of V1 and V2 already show some distinction, leading to a sizable charge difference of $0.08$ e between them obtained from the Bader charge decomposition. This value is almost independent of the magnetic states studied here. This is consistent with the experimental observations,[22, 23] in which the pure tetragonal-monoclinic structure transition leads to the CO.

IV. FERRIMAGNETIC STATE

We have considered a few possible spin-ordered states including two different FI orders. The FI1 state has the antiferromagnetic intrachain and ferromagnetic interchain configuration, whereas the FI2 state involves both intra- and inter-chain antiferromagnetic interactions. So in the FI2 state, the spins of the NN same-type V ions
in the interlayer chain along the $\hat{b}$ direction, which is vertical to the ferrimagnetic V1-V2 chain, are also antialigned. The magnitudes of the V local moments in FI1 and FI2 are almost identical, but the net moment of FI2 is precisely compensated. In the GGA, as shown in Fig. 4(a), FI1 is energetically favored over the nonmagnetic (by 1.5 eV/f.u.), FM (by 0.1 eV/f.u.), and FI2 (by 12 meV/f.u.) states, consistent with the experimental results.\cite{22, 23} Such a large magnetization energy is induced by the large spin moments of the V ions of 1.5–2.3 $\mu_B$. For comparison, the energy gain due to a simple Stoner instability $IM^2/4$ leads to a similar value, where the Stoner parameter $I \lesssim 1$eV can be roughly estimated by the exchange splitting $\Delta_{ex} \approx IM \approx 2.3$ eV (see below). Remarkably, the energetic preference among the spin–ordered states substantially depends on strength of $U_{eff}$, suggesting a delicate magnetic character. This issue will be further considered in the Discussion section. In this section, we will focus on the FI1 state, which has been suggested from the experiments.\cite{22, 23}

A. Uncorrelated regime: GGA level

In the FI1 state, the V local moments are 1.94 (V1) and –1.71 (V2) $\mu_B$, leading to a net moment of 0.64 $\mu_B$/f.u. The net moment is close to the value obtained in the polycrystalline sample,\cite{22} but about twice that of the single crystalline sample.\cite{23} Considering the interstitial moment, these values are consistent with that of V$^{2.5+}$, which is reflected in the DOS, presented in Fig. 5(a).

Figure 5(a) shows the orbital-projected DOSs of the V1 and V2 ions in the FI1 state. $E_F$ is just above the peaks at $\sim 50$ meV (–100 meV) for the up (down) channel. The exchange splitting of the $t_{2g}$ manifold is about 2.3 eV in both V ions, while the hybridization gap between the $O\rho$ orbital and this manifold is 2.5 eV, yielding the well-isolated $t_{2g}$ manifolds with a bandwidth of 2.5 eV around $E_F$. The partially filled $t_{2g}$ manifolds in the up and down channels are the V1 and V2 character, respectively. In each majority $t_{2g}$ manifold, the centers of the completely filled $a_{1g}$ orbitals are approximately 1 eV lower than those of the $e_g'$ orbitals. Besides, the V2 $e_g'$ orbital in the down channel has a center higher by 50 meV and significantly longer unfilled tails than those of V1, which is in the up channel and is almost filled. This feature leads to a sizable charge difference of 0.08e between the V1 and V2 ions. Additionally, upon the application of $U$ to the V ions, the almost filled V1 $e_g'$ manifold is simply pushed down, and a Mott transition occurs in the effectively half-filled $e_g'$ manifold of V2 in the down channel (see below).

B. Correlated regime: fully charge-ordered state

The effects of correlations were considered with the GGA+U approach to obtain the observed insulating phase. Figure 4(b) shows a plot of $U_{eff}$ vs. energy gap $E_g$. A gap opens at $U_{eff} \approx 3.5 (4.0)$ eV for the FI1 (FM) state, similar to that of VO$_2$.\cite{16} Interestingly, with the increase in $U_{eff}$ in the FM state, a transition from metal...
to half-semimetal with linearly crossing bands near $E_F$ (not shown here) occurs at $U_{\text{eff}} \approx 1$ eV, and then the energy gap is completely open at $U_{\text{eff}} \approx 4$ eV. Therefore, in the range of $U_{\text{eff}} \approx 1$–4 eV, a magnetic Weyl semimetal phase appears, as suggested for the presumed tetragonal FM V$_2$OPO$_4$.[21] On the other hand, in the FI2 state, $U_{\text{eff}} \approx 1.5$ eV is sufficient to open a gap, similar to the value of the antiferromagnetic V$_2$O$_3$.[15]

Further, we focus on the FI1 insulating state at $U_{\text{eff}} = 4$ eV, where a gap is clearly visible. The band structure and total DOS in the region of the V $d$-orbitals are given in Fig. 6. The corresponding orbital-projected DOSs are shown in Fig. 6(b). In the down channel, the V2 $a_{1g}$ and one of the V2 $e_{g}'$ orbitals around $-2$ eV are completely filled, whereas the V1 $t_{2g}$ manifold is fully filled in the up channel. The upper Hubbard band, i.e., the other unfilled $e_{g}'$ orbital, below 1 eV, has the $e_{g}'$ character, as shown in the Inset of Fig. 6. Thus, the application of $U$ leads to an orbital ordering of $a_{1g}^{1}e_{g}^{1}$ in V2 (3d$^2$), in contrast to the $e_{g}^2$ configuration in the antiferromagnetic V$_2$O$_3$. This leads to a spin-asymmetric gap of 0.25 eV between the spin-up V1 $t_{2g}$ and -down V2 $e_{g}'$ bands. In the state, the local moments are $2.30\ \mu_B$ (V1) and $-1.54\ \mu_B$ (V2), consistent with $S = 3/2$ and 1, respectively. Considering the interstitial moment and small contributions from the other ions, the total spin moment is $1\ \mu_B$/f.u., which is about three times larger than the experimentally observed value in the single crystalline sample.[23] This issue is further discussed below.

The CO can be analyzed with a few different approaches.[28] Our calculated Bader charges $Q_B$ are $Q_B$(V1) = +1.58, $Q_B$(V2) = +1.94, $Q_B$(PO$_4$) = −2.23, and $Q_B$(O3) = −1.30, leading to a large charge difference of 0.36e between the V ions. Compared with the formal values of +2, +3, −3, and −2, respectively, in the CO state, this charge difference seems to be significantly smaller. However, this value is significantly larger than the value of 0.2e observed in the charge disproportionated Na$_{1/2}$Co$_2$ with Co$^{3+}$ and Co$^{4+}$ ions.[27] The summation of the occupation matrix gives 2.64 (2.38) for V1 (V2), indicating the charge difference of 0.26e between the two V ions, consistent with the Bader charges. Another approach is to analyze the radial charge densities $4\pi r^2\rho(r)$, as suggested by Quan, Pardo, and Pickett,[28, 29] which have a clear difference in their tails in a CO state. Figure 7(a) shows the densities of the two V ions, obtained from WIEN2K. Below approximately 0.5 a.u., the charge densities insignificantly differ, while a difference is observed above this value. This distinction is more clearly observed in the spin-resolved charge densities in Fig. 7(b), particularly in the majority densities.

Figure 8 shows the charge density isosurface in GGA+U at $U_{\text{eff}} = 4$ eV. The V1 ion has the shape of the equally occupied $t_{2g}$ orbital, i.e., $e_{g}^{3\uparrow}$. On the other hand, the shape of the V2 ion indicates a combination of the $a_{1g}$ and $e_{g}'$ orbitals. So, the lower Hubbard band at $-2$ eV in the spin down is the $e_{g}'$ orbital. Consequently, the V2 ions show the $a_{1g}^{1}e_{g}^{1}$ orbital order. However, this order leads to only a small orbital moment, since the occupation matrix of V2 is nearly symmetric. Our GGA+U+spin-orbit coupling (SOC) calculations show that the orbital moment is about 0.04 $\mu_B$ in each V ion, opposite to each spin moment. This indicates that this order cannot be attributed to the significantly reduced net moment in the experiments.[22, 23] It is worth noting that the O3 ion has a small moment, but exhibits
of the existing candidates of 1D chain and frustrated but the length is relatively short, compared with those. The long sides are longer by 1/3 than the short sides, dra with two sides of 2.67 ˚

t FIG. 8: Charge density plot with the isosurface at 0.025 e/Å³ in the insulating FI1, showing the orbital order. These shapes indicate an equally occupied t₂g orbital for V1 and a₁g plus e′,g orbitals for V2. The O3 ions show an obvious p₃ character, indicating a sizable pdπ interaction along the vertical direction. The densities of the other O ions are invisible.

This implies a considerable pdπ interaction, which would lead to the next nearest neighbor (NNN) superexchange pattern with an angle of 130° along the b direction.

V. DISCUSSION ON QUANTUM FLUCTUATION

As mentioned above, the experimentally observed moments in the system are approximately 1/3 of our calculated values. These discrepancies are significant, although the theoretically calculated moment should not be expected to be identical to the experimentally observed value, considering the theoretical specifications (and some spin in the interstitial region) in the theoretical approach. Below, we discuss a possible mechanism of such a large reduction.

A. Experimental indications

There are several experimental indications of complex unusual magnetic properties of this system. The magnetization exhibits a small magnetic anisotropy, and the magnetic entropy is considerably smaller than those of V²⁺ and V³⁺. The observed Curie-Weiss and ordering temperatures lead to a sizable frustration parameter of |θCW|/Tc ≈ 7.03, comparable with the typical values of frustrated systems. As mentioned above, the V ions form a pyrochlore-like link consisting of the V₄ tetrahedra with two sides of 2.67 Å and four sides of ~3.62 Å. The long sides are longer by 1/3 than the short sides, but the length is relatively short, compared with those of the existing candidates of 1D chain and frustrated structure. For example, the NNN distance is 4.40 – 4.92 Å in β-TeVO₄ of the NN 3.64 Å. In Ca₃Co₂O₆ and Sr₂RhO₄, the NN distances are twice longer than the NN distances of ~2.6 Å. Additionally, this system shows a small coercivity of the order of mT, which implies an easily variable magnetization direction by an external magnetic field or magnetic impurity. It may be expected that the complex behavior originates from strong quantum fluctuations or frustration.

B. Evaluation of the magnetic ground state

We considered three magnetic states, FM, FI1, and FI2. Figure 4(a) shows the evaluation of differences in energy between these three states, as varying the strength of Ueff. Remarkably, with the increase in Ueff, the difference in energy between FM and FI1 is reduced and becomes negative around Ueff ≈ 2.6 eV, indicating that FM is favored over FI1 in this regime. Above this value, the energy difference increases again, leading to an energetically favored FI1 state. Comparing FI1 with FI2, the FI2 state is energetically favored over the FI1 state in the range of Ueff=1.5 to 4.7 eV. Even at Ueff = 5 eV, the energy difference between FI1 and FI2 is just a few meV. This indicates that the NNN superexchange interaction is also crucial in this system. Since this behavior is observed in the reasonable range of Ueff for this vanadium oxide, our results suggest that frustration would be a reliable scenario in this system.

Additionally, as expected from the tiny orbital moment, this system shows a little magnetic anisotropy, obtained from GGA+SOC calculations. We considered two quantized directions parallel and perpendicular to the chain. The anisotropy energy is less than a few tenths meV/f.u., which indicates that the application of a small magnetic field can vary the spin direction. This also supports the proposed scenario.

C. Fixed spin moment studies

In order to affirm the delicate magnetic behavior, fixed spin moment (FSM) calculations were performed varying the strength of Ueff. In these calculations, two states, FI1 and FM, were considered by choosing a proper initial condition. Figure 4(b) shows the energy difference ∆E(M) plotted against the total moment M, with respect to the energy at M = 0 for each Ueff, where the net moment is completely canceled by the antialigned V1 and V2. These results are consistent with our self-consistent results, given in Fig. 4(a).

Interestingly, two minima appear, regardless of the value of Ueff. One of them is in the range of 0.5 – 1 µB for the FI1 state, while the other is in the range of 4.5 – 5 µB for the FM state. In the GGA (Ueff = 0), a large range of magnetic field ∆B = ∆E/∆M is required for the magnetic phase transition from FI1 to FM. However,
as increasing $U_{\text{eff}}$, the energy difference $\Delta E$ between the two states decreases and becomes close to zero around $U_{\text{eff}} = 2.5$ eV. So, only a small magnetic field is required for the phase transition around this value of $U_{\text{eff}}$. Above this value, $\Delta E$ monotonously increases reaching 37 meV at $U_{\text{eff}} = 4$ eV, where both states are insulating. Thus, these results also suggest that this system is close to a quantum fluctuation.

Note that the $\Delta E(M)$ curves are discontinuous and both FI1 and FM states appear coincidentally in the range of $M = 2.5 - 3 \mu_B$ in the GGA+U cases, leading to hysteresis. This has been observed in the density functional theory plus $U$ approach, which often leads to multisolutions in a critical region.[27, 32]

VI. SUMMARY

Through ab initio calculations including correlation effects, we have investigated the insulating $\beta$-$\nu_2$OPO$_4$ with a quasi-1D ferrimagnetic Heisenberg spin chain structure, exhibiting the charge and spin orderings at $T_{CO} \approx 600$ K and $T_{SO} \approx 125$ K, respectively. Remarkably, this system has a weak pyrochlore-like tetrahedral link of V ions due to the relatively short interlayer (NNN) distance along the vertical direction.

Consistent with the experimental observation,[22] our calculations indicate that the charge order of alternating $V^{3+}$ and $V^{2+}$ along the chain occurs coincidentally with the structure transition from tetragonal to monoclinic. In the experimentally suggested FI1 state, where the spins of the NN V ions are antialigned along the chain, inclusion of correlation effects leads to a full orbital polarization of V1 ($t_{2g}^{5/2}$, $S = 5/2$) and V2 ($t_{2g}^{11/2}$, $S = 3$), above the critical value of $U_{\text{eff}} = 3.5$ eV for the metal-insulator transition. This yields the net moment of about 1 $\mu_B$ (including the small orbital moments) which is 2–3 times larger than the experimentally observed value. Besides, the energy differences between the few spin-ordered states show the strong $U$-dependence, which is also supported by the FSM calculations. This implies that a magnetic phase transition is feasible and that the NNN superexchange interaction through the $p_d$-$t_{\pi}$ hybridization is sizable. In addition to the several experimental indications mentioned above, the significant variations in energy differences, and our calculated tiny orbital moments of several hundredth $\mu_B$, the substantially quenched moment suggests that quantum fluctuation (frustration) occurs in the pyrochlore-like tetrahedral structure.

Our results suggest that this system is a promising candidate to show the vital interplay among the charge-, spin-, and lattice-degrees of freedom, and geometrical frustration. Further experimental and theoretical researches are required to elucidate the complex magnetic properties.

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