

Magnetostructural correlations and spin model of $(\text{VO})_2\text{P}_2\text{O}_7$

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We report a theoretical density functional analysis of the exchange interactions in $(\text{VO})_2\text{P}_2\text{O}_7$ using molecular fragments. The calculations confirm that the magnetic structure must be described on the basis of linear dimer chains. The strongest exchange interaction is found through O-P-O bridges. The magnitude of the exchange parameters is governed not only by V-V distance but also by the whole structure along the superexchange pathway. The two chains present in the structure of $(\text{VO})_2\text{P}_2\text{O}_7$ are magnetically inequivalent. For the monoclinic phase of $(\text{VO})_2\text{P}_2\text{O}_7$, important variations in the calculated parameters for dimers with identical bridges are observed within one chain. The magnetic structure of this chain should be described not by two but by three or even four coupling constants.

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I. INTRODUCTION

The vanadium pyrophosphate compound $(\text{VO})_2\text{P}_2\text{O}_7$ (VPO) is a low-dimensional $S=1/2$ Heisenberg system whose magnetic interaction scheme, described by a spin Hamiltonian \mathcal{H} which may be written as

$$\mathcal{H} = \sum_{i < j} J_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j), \quad (1)$$

has been under discussion for more than ten years.¹⁻¹⁷ The crystal structure reveals patterns which are indicative either of a spin ladder system, or of an alternating dimer chain system. Thus, in the structure of the VPO compound¹⁸ shown in Fig. 1, infinite two-leg spin ladders are formed along the **a** direction by stacked vanadium dimers D_{O} , lying along the **b** axis and characterized by di- μ -oxo bridges. The privileged exchange paths in the spin ladder model correspond to the shortest V-V distances. The dimer chains, located along the **b** axis, result from the alternation of exchange interactions within D_{O} dimers and those through the O-P-O bridges of dimers D_{OPO} .

The spin ladder model, visually more natural than the dimer chain model, has first prevailed in the analysis of the VPO magnetic properties.¹⁻⁶ However, it was shown as early as 1987 that the magnetic susceptibility data of VPO can also be accurately fitted by the alternating antiferromagnetic Heisenberg chain model.¹ Although the two models, both described by two exchange parameters, clearly correspond to different schemes of exchange interactions, it is only recently when experimental studies such as inelastic neutron scattering (INS),^{7,9} ESR,¹¹ ³¹P NMR and high-field magnetization measurements^{12,13} demonstrated that VPO is a dimer chain system. Nevertheless, the most intriguing feature of the VPO compound remained unexplained: the existence revealed by INS experiments of two excitation gaps with the energies $\Delta_1=36$ K and $\Delta_2=67$ K.^{7,9} The energy spectrum of an alternating antiferromagnetic chain should have just one gap. This result was confirmed by magnetization and NMR studies, and the existence of two gaps were attributed to the

inequivalence of the two types of dimer chains coexisting in VPO.^{12,13} It has been proposed that the slight differences in the V-V distances between the two chains result in different exchange parameters¹³ (see Table I). Recently, it was suggested that VPO can crystallize in two different crystal structures of monoclinic¹⁸ and orthorhombic¹⁵ symmetries. Two inequivalent dimer chains are present in both structures.

However, the small differences in the V-V distances do not allow us to assign unambiguously the exchange parameters to the different chains. Moreover, it is well known that the exchange coupling parameters between magnetic sites linked by indirect exchange interactions depend, not only on the distances between the sites, but also on several fine details of the local surrounding. Thus, for a series of hydroxo- and alkoxo-bridged Cu(II) dimers with planar Cu_2O_2 cores, quantum chemical calculations based on the density functional theory (DFT) clearly demonstrated the strong dependence of the magnetic coupling constant on the Cu-O-Cu bond angle as well as on the out-of-plane shift of the atom

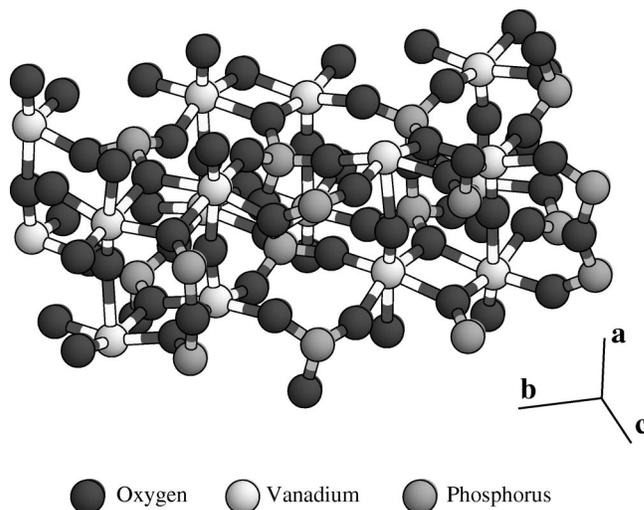


FIG. 1. Unit cell of the $(\text{VO})_2\text{P}_2\text{O}_7$ compound (Ref. 18). The space group is the monoclinic P_{21} one, with $a=7.28$ Å, $b=16.59$ Å, $c=9.58$ Å, and $\beta=89.98^\circ$.

TABLE I. Spin gaps (Ref. 9), exchange parameters (Ref. 13), and V-V distances in VPO. The exchange parameters J_O and J_{OPO} , respectively, characterize exchange interactions in D_O and D_{OPO} dimers. $(V-V)_O$ and $(V-V)_{OPO}$ correspond to the distances within the D_O and D_{OPO} dimers, respectively. The distances are from the monoclinic structure of Nguyen *et al.* (Ref. 18), the ones in parenthesis correspond to the structure of the orthorhombic form recently evidenced by Hiroi *et al.* (Ref. 15).

Spin gap (K)	J_{OPO} (K) ^a	J_O (K) ^a	$(V-V)_O$ (Å)	$(V-V)_{OPO}$ (Å)
36	119	101	3.21 (3.18)	5.16 (5.18)
67	130	90	3.23 (3.26)	5.15 (5.13)

^aIt should be stressed here that the values of the coupling parameters J_O and J_{OPO} given in this table are the *reverse* of the ones proposed in Ref. 13. To designate the dimers' exchange parameters, the authors (misleadingly) used the same symbols as in the INS studies of Garrett *et al.* (Ref. 9); however, attention was not paid to the fact that the parameters were not associated to the same types of dimers. Hence, the values given here take into account this inversion that does not affect the physical significance of the results reported in Ref. 13.

bounded to the bridging oxygen.¹⁹ Small differences of a few degrees in the Cu-O-Cu angle and in the out-of-plane shift can drastically change the exchange parameter values, and in some cases even change its sign. Similar effects were recently illustrated in the spin-Peierls compound CuGeO_3 .²⁰ Considering the VPO monoclinic phase structure,¹⁸ noticeable differences in the angular parameters characterizing the exchange pathways of D_O and D_{OPO} dimers can be found not only between its two structurally inequivalent chains, we note *A* and *B*, but also within each chain. Therefore, if one wants to amply consider magnetostructural correlations in VPO, two questions immediately arise: (1) How are the exchange parameters influenced by small structural differences in D_O or D_{OPO} dimers for two chains or within one chain? (2) Can two spin gaps originate from a single chain if, due to small internal differences, it is described by more than two coupling parameters? In this paper, we will try to quantitatively answer both questions on the basis of DFT quantum chemical calculations of exchange parameters. Recently, a qualitative analysis of the exchange interactions in VPO has been reported.¹⁶ However, it is based on the comparison of monoenergetic energy gaps obtained with the extended Hückel formalism and does not give access to the exchange parameters.

II. THEORETICAL MODEL

In this paper, we consider in details the monoclinic structure of VPO described in Ref. 18. The elementary cell contains two $D_O(D_O^{X\{1,2\}})$ and $D_{OPO}(D_{OPO}^{X\{1,2\}})$ dimers for each dimer chain *X* (*X*=*A* or *B*), as shown in Fig. 2(a).

In addition to the differences in the V-V distances, the D_O and D_{OPO} dimers differ by bond angles characterizing their exchange pathways, shown in the diagrams of Fig. 2(b). The V-V distances and values of selected bond angles are given

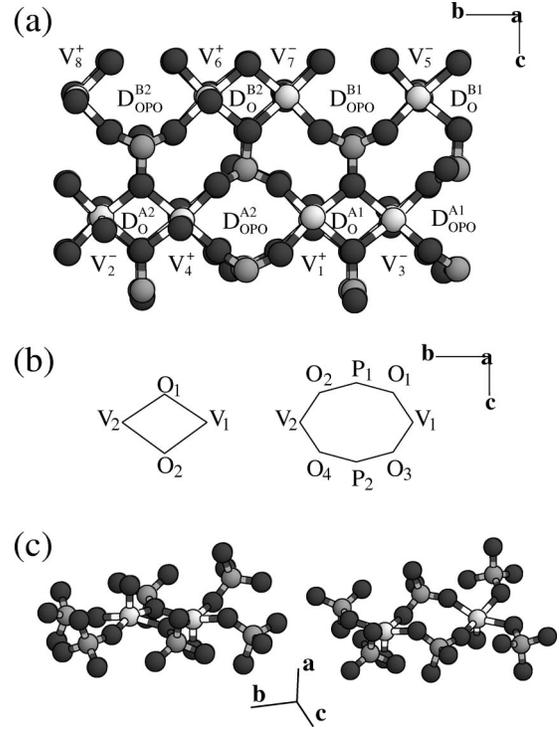


FIG. 2. (a) The dimers $D_O^{A\{1,2\}}$ and $D_{OPO}^{A\{1,2\}}$ ($D_O^{B\{1,2\}}$ and $D_{OPO}^{B\{1,2\}}$) define the dimer chain *A* (*B*). The symbol V^+ (V^-) identifies the vanadyl groups pointing at the $+a$ ($-a$) direction. (b) Diagrams of the exchange pathways in D_O (left) and D_{OPO} (right) dimers. (c) D_O (left) and D_{OPO} (right) type fragments used for our calculations. The peripheral H atoms are not shown.

in Tables II and III for the D_O and D_{OPO} dimers, respectively.

We readily see that D_O or D_{OPO} dimers belonging to different chains, and even to the same chain, are inequivalent. Concerning the D_O dimers, their V_2O_2 cores are nearly planar (see caption, Table II), and the changes in the bond angles are less than 2° . Actually, the most important variations in the selected angles are observed within the D_{OPO}^B dimers set. One can expect that eight exchange parameters are needed to describe the exchange interaction in the two chains.

Given the local character of the exchange interaction, the calculations were performed on molecular fragments made of each dimer's vanadyl VO groups and the PO_4^{3-} tetrahedra in their closest vicinity. The oxygen valence in PO_4^{3-}

TABLE II. V-V distances (Å) and selected bond angles ($^\circ$) characterizing the exchange pathways of the D_O dimers. Their V_2O_2 cores are nearly planar, the dihedral angles being 0.8° , 0.1° , 0.8° , and 1.4° for D_O^{A1} , D_O^{A2} , D_O^{B1} and D_O^{B2} , respectively.

	$d(V-V)$	$V_1-O_1-V_2$	$V_1-O_2-V_2$
D_O^{A1}	3.23	102.6	102.3
D_O^{A2}	3.23	102.1	102.4
D_O^{B1}	3.21	100.9	102.6
D_O^{B2}	3.21	101.2	101.8

TABLE III. V-V distances (\AA) and selected bond angles ($^\circ$) characterizing the exchange pathways of the D_{OPO} dimers.

	$d(\text{V-V})$	$\text{O}_1\text{-P}_1\text{-O}_2$	$\text{O}_3\text{-P}_2\text{-O}_4$	$\text{V}_1\text{-O}_1\text{-P}_1$	$\text{P}_1\text{-O}_2\text{-V}_2$	$\text{V}_1\text{-O}_3\text{-P}_2$	$\text{P}_2\text{-O}_4\text{-V}_2$
D_{OPO}^{A1}	5.14	116.4	115.1	154.9	142.8	156.4	132.8
D_{OPO}^{A2}	5.14	115.9	115.0	157.7	145.1	155.8	130.9
D_{OPO}^{B1}	5.16	116.3	113.8	149.8	154.4	136.4	139.5
D_{OPO}^{B2}	5.16	113.0	115.3	147.5	150.9	139.6	140.9

groups was saturated with protons. D_{O} and D_{OPO} type fragments are shown in Fig. 2(c). It must be stressed here that the relative positions of the V, P, and O atoms within each fragment remain the same as in the crystal. This allows us to entirely preserve the local environment of the magnetic V sites and the one of the O and P atoms involved in the superexchange paths. Keeping in mind the d^1 electronic configuration of V^{4+} , two low-lying singlet and triplet electronic states can be expected for each dimer. Following the notation used in Eq. (1), the exchange parameter J of a dimer is given by its singlet-triplet excitation energy $J = E_T - E_S$. It has been estimated by means of a combined DFT broken-symmetry (BS) approach for which it reads:²¹ $J = E_T - E_{\text{BS}}$, where E_{BS} is the energy of the calculated single-determinant BS state which is taken as an estimate of the singlet state. Actually, in the BS method originally developed by Noodleman and Norman,²² spin contamination by the triplet state is taken into account, and the coupling parameter reads after spin projection: $J = 2(E_T - E_{\text{BS}})$. However, the use of spin projection methods in DFT remains a delicate issue as it can lead to an overcorrection.²³ By taking the BS state as a raw estimate of the real singlet state, we do not take into account contamination arising from the triplet state. Despite the apparent alogism of such a choice,²⁴ Ruiz *et al.*,¹⁹⁻²¹ have shown that the nonspin-projected equation $J = E_T - E_{\text{BS}}$ leads to a better agreement with the experimental data than the spin projected equation does. Concerning the use of BS methods, one can refer to recent methodological works^{21,23-25} for an overview of the current state of the art.

Four calculations I-IV were done using the ADF package.²⁶⁻²⁸ We used for I-III the density functional consisting of the Vosko-Wilk-Nusair local density approximation (LDA) functional,²⁹ the Becke generalized gradient approximation (GGA) exchange correction,³⁰ and the Perdew GGA correlation correction.³¹ For IV, the pure-exchange LDA functional with GGA corrections made of the Becke exchange³⁰ and the Lee-Yang-Parr correlation³² parts. Slater-type basis sets were used. I is characterized by double- ζ basis sets extended with a polarization function for O and P, and for V, by a double- ζ basis set and a triple- ζ basis set for the $3d$ shell. II-IV are characterized by triple- ζ basis sets for O, P, and V, plus a polarization function for P and O. The mesh used for the evaluation of electron repulsion integrals is finer in the III case than in the others (accint 5.0 vs 4.0, with reference to the ADF program manual). In all calculations, we employed for H a double- ζ basis set, and the core shells were frozen up to the $1s$ level for O and up to the $2p$ level for P and V.

III. RESULTS AND DISCUSSION

The calculated J values are given in Table IV. We have also calculated the exchange parameters in the **a** direction, i.e., the ladder direction. Despite the relatively short V-V distances, exchange through O bridges is quite small (a few Kelvins). We stress the fact, that although the coupling along the ladder direction appears negligible in comparison of the one along the chain direction (this work and also Ref. 9), interchain coupling may not be neglected. Indeed, recent studies performed on $(\text{VO})_2\text{P}_2\text{O}_7$ (Ref. 10) and spin-Peierls systems³³ indicated that the two-dimensional character resulting from very weak interchain coupling is likely to play a significant role in the understanding of the properties of these systems. Their positive values indicate that the dimer chains are antiferromagnetic.

One observes that for the best quality triple- ζ basis sets (calculations II-IV) the results are not very sensitive to either the exchange-correlation functionals used or the numerical accuracy employed for evaluating the repulsions integrals. One also notes that the calculated values remain about twice the experimental values given in Table I. It is well known that the LDA approach can lead to an overestimation of the relative stabilization of the singlet state in comparison with the triplet state and that this stabilization can be more or less compensated according to the GGA corrections used.²⁴ However, we believe the calculated parameters correctly reflect the magnetostructural correlations for the different exchange interactions in both chains. Indeed the differences between the calculated J_{O} or J_{OPO} parameters are independent of the approach we used. So, the following general conclusions can be drawn up.

(1) For both chains, despite the shortest V-V distances in D_{O} dimers, we find the inequality

$$J_{\text{O}} < J_{\text{OPO}}, \quad (2)$$

is fulfilled. This result is in agreement with the experimental one obtained by the INS study of $\text{VODPO}_4 \cdot \frac{1}{2}\text{D}_2\text{O}$, a precursor of VPO with an alternating $D_{\text{O}}\text{-}D_{\text{OPO}}$ chain.⁸ It is also in agreement with the values reported in Table I for both

TABLE IV. Evaluated exchange parameters (in K).

	J_{O}^{A1}	J_{O}^{A2}	J_{O}^{B1}	J_{O}^{B2}	J_{OPO}^{A1}	J_{OPO}^{A2}	J_{OPO}^{B1}	J_{OPO}^{B2}
I	224	224	259	273	272	280	324	349
II	217	217	252	265	250	257	302	324
III	217	217	252	265	248	257	301	324
IV	212	212	245	257	257	263	308	331

chains. By using the average values of the J_O and J_{OPO} parameters for a given chain ($[J_O^{X1} + J_O^{X2}]/2$ and $[J_{OPO}^{X1} + J_{OPO}^{X2}]/2$ with $X=A$ or B), we obtain that the J_O/J_{OPO} ratio for calculations II-IV is in the range 0.78~0.82 for chain A and 0.81~0.85 for chain B. These ranges are in relatively good agreement with the values of 0.69 and 0.85 that can be deduced from the experimental values of Table I. As in the experimental work,¹² we find a smaller alternation value for chain A. However, in our case, the most important J_{OPO} values are obtained for chain B.

(2) Comparing the exchange parameters in the two chains for similar bridges, we note that there is no unambiguous correlation between the parameter value and the V-V distance. If for D_O pathway, the longest V-V distances (chain A) correspond to smallest J_O exchange parameters, for D_{OPO} , the most important J_{OPO} exchange parameters are found for chain B with V-V distances 0.02 Å longer than in chain A. Clearly, other structural details such as angular variations also influence the values of the exchange parameters. Considering the V_2O_2 core of D_O dimers belonging to the two chains, the changes in the V-V distances, bond, and dihedral angles are relatively weak (Table II) to explain the difference of about 20% between J_O^A and J_O^B parameters. Thus, one would have to consider the shifts of the P atoms bounded to the bridging oxygens out of the median V_2O_2 plane. Indeed it has been shown for hydroxo and alkoxo-bridged Cu(II) dimers that the out-of-plane shift of the atom bounded to the bridging oxygen plays a fundamental role in the magnetic coupling.¹⁹ For the studied system, all out-of-plane shifts of the bound P atoms differ significantly as the O-O-P angles made by the bridging O atoms and the considered P atoms vary between 174°–178° in chain A and between 163°–165° in chain B. For the D_{OPO} dimers, further studies are required to determine the relevant structural parameters influencing the O-P-O pathway.

(3) In the monoclinic phase of VPO, the elementary cell contains eight V atoms with four atoms belonging to each chain, A and B. As a result, each chain contains two dimers of D_O type and two dimers of D_{OPO} type. Our results show that within chain A, the structural differences between the D_O dimers do not lead to noticeable differences between the J_O parameters and the variations of the J_{OPO} parameters are quite small. Conversely, the variations of the exchange parameters are quite important within chain B, especially for the D_{OPO} dimers. For the moment, it is difficult to attribute the variation in one-type exchange parameters to a given structural feature. As in (2), the nearest surrounding not only of V centers but also of all bridging atoms can influence the indirect exchange interactions. The important thing is that the difference in J_{OPO} parameters is of the same order as the difference between J_{OPO} and J_O . These important results question the description of $(VO)_2P_2O_7$ magnetic structure in terms of simple alternating antiferromagnetic chain. It appears that at least one chain, chain B, might be characterized not by two, but by three or even four parameters.

Can an antiferromagnetic chain described by more than two exchange parameters result in a two spin-gap spectrum? Unfortunately, to our knowledge there is no data in the lit-

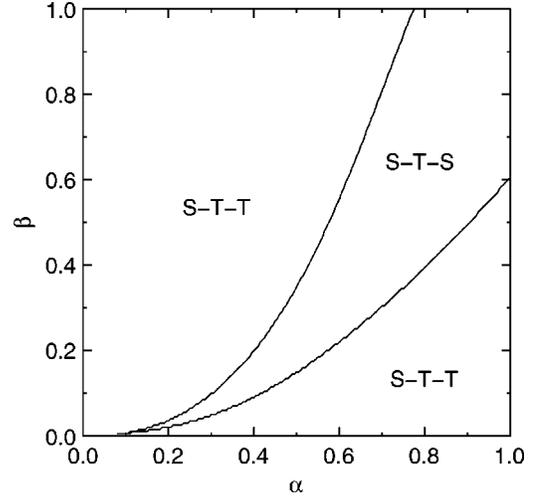


FIG. 3. Dependence of the nature of the lowest excited states on α and β parameters.

erature on three or four parameters magnetic chains. Intuitively, one can expect that two gaps may originate from the unpairing of neighboring spins linked by interactions of different strength. In order to address the spin gap issue, we consider a simpler spin model characterized by three coupling parameters J_O , J_{OPO}^1 , and J_{OPO}^2 . We thus constrain the parameters $J_O^{\{1,2\}}$ to be equal. We used a finite cluster made of 12 $S=1/2$ magnetic sites with periodic conditions. It was shown earlier that clusters of this size give a quite satisfactory description of the linear alternating antiferromagnet.^{4,34} We successfully used such a cluster for the analysis of VPO ^{31}P NMR data.¹⁷ Of course, the results of numerical calculations for small finite systems cannot be transferred automatically to infinite systems. However, one can hope to get a preliminary insight in three-parameter alternating antiferromagnetic chain. The spin Hamiltonian has been diagonalized within the $S=0,1$ subspaces for different values of $\alpha = J_O/J_{OPO}^1$ and $\beta = J_{OPO}^2/J_{OPO}^1$.

The two-gap energy spectrum of infinite system must be reflected in our approach by two lowest excited triplet (T) states following the ground singlet (S) level. We find in our calculations that the lowest levels of three-parameter alternating antiferromagnetic chain correspond to $S-T-T$ or $S-T-S$ successions. The phase diagram of these two possibilities in the α - β space is presented in Fig. 3.

As it follows from our results, in order to get two low-lying $S-T$ gaps in one chain, we need at least one of α and β parameters to be rather different from one. However, our J calculations suggest that both α and β should be close to 1. Thus, the existence of two gaps generated by one chain can be excluded.

IV. CONCLUSION

In this paper, we presented the first, to our knowledge, quantum chemical calculations of exchange interactions in $(VO)_2P_2O_7$. The values of exchange parameters depend not only on the nature of bridging atoms and V-V distances, but also on critical structural details, such as bond angles char-

acterizing the exchange pathways. The transfer of exchange parameters between different phases of vanadium-phosphorus oxides must be done with great care by taking into account their high sensibility to fine structural details. Our results show that the description of $(VO)_2P_2O_7$ magnetic structure in terms of two-parameter alternating dimer chains has serious limitations. At least, one of the chains must be described not by two but by three parameters. Fur-

ther theoretical studies are needed to provide more accurate information on the excitation spectrum of such complicated magnetic system.

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